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# Dwindling Population of a Scincid Lizard *Mabuya Carinata* (SCHNEIDER, 1801) in Nellore District of Andhra Pradesh, South India

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**Abstract:** ***Mabuya carinata (Schneider, 1801) is the keeled grass skink, commonly observed in our surroundings. This scincid lizard is of least concern according to the Wild Life (Protection) Act, 1972. But it is alarming that population of this species is fast dwindling in different parts of the country. Mabuya is an efficient bio-indicator and plays an important role in food web of terrestrial ecosystems. The present study aims at assessment of population dynamics of this precious animal in Nellore district of Andhra Pradesh. Line transect and direct counting methods were adopted. Statistical analysis was done by using MS Office Excel 2007. The results show that there is drastic decline in the population of Mabuya from 2011 to 2015 at an alarming rate. Threats for the conservation of this animal are examined and remedial measure suggested.***

**Keywords:** *Mabuya*, Bio-indicator, Scinicds

## 1. Introduction

As on 4th November 2017, there are 6263 species of lizards inhabiting different habitats across the globe. Of these, 1634 species belong to the family Scincidae of infraorder Scincomorpha, belonging to order Squamata. The mabuyid skinks include only 201 species belonging to 26 genera [1]. These are highly diverse, worldwide in distribution, Though less in number (3619) of species described so far [1], ophidians received greater attention of wildlife biologists, conservationists, ecologists, and molecular biologists, lizards could not attract much of their attention, though they play an important role in ecosystem dynamics. PubMed database displays 38535 research articles related to reptiles, out of which 11511 can be accessed as abstract or full text article from a public network. 15285 articles are published on snakes, out of which 4444 can be accessed as abstract or full text. 10854 articles are related to lizards as a whole, 3530 can be accessed. While agamids are represented by 169 articles, only 65 can be accessed. 259 articles were published about skinks, only 145 can be accessed. The genus *Mabuya* is poorly represented in literature, only by 111 articles, while only 24 can be accessed [2].

| Sl. No | Subject of Research | Total number of papers published | Total number of papers which can be accessed from a public network |
|---|---|---|---|
| 1 | Reptiles (general) | 38535 | 11511 |
| 2 | Snakes | 15282 | 4444 |
| 3 | Lizards | 10854 | 3530 |
| 4 | Agamids | 169 | 65 |
| 5 | Skinks | 259 | 145 |
| 6 | Mabuya | 111 | 24 |

Skinks are highly diverse and known to be present worldwide. The diversity of mabuyine lizards was earlier attributed to only one genus *Mabuya*, but four new monophyletic genera which have well-defined geographical distribution are proposed [3]. These genera include the African and Madagascan species *Trachylepis*, the Asian species *Eutropis*, the Cape Verde island species Chioninia and the new world skink *Mabuya*. The systemic position of mabuyid skinks is debated [4,5,6].

The genus *Mabuya* is circumtropical in distribution. It consists of about 30 described species. The generic rearrangement of this genus assigning the members of *Mabuya* to Eutropis [7,8] has been much debated. Phylogenetic studies based on the sequences of nuclear and mitochondrial genes [9] confirm the monophyly of the tropical Asian Eutropis. An endemic Indian radiation of members of the genus *Mabuya* was revealed by the nuclear and mitochondrial trees. An initial dispersal of Eutropis around 5.5-17 million years ago, from South East Asia into India was also suggested by these studies. This was followed by two back dispersals from India. These events are thought to give rise to the extant members of the genus *Mabuya*, which include 8 species endemic to India [10].

Members of genus *Mabuya* from Africa and Asia are interesting for researchers of biogeography of Peninsular India. About 200 million years ago (mya), the Peninsular Indian plate was geologically part of the Gondwanaland. It is established that around 160 mya, the Peninsular India plate, together with Madagascar and Seychelles got separated from Africa. Subsequent events led to separation of Madagascar about 80mya, which later drifted across the Indian Ocean and finally collided with the Eurasian plate about 55-42 mya [11]. Then the Peninsular India plate merged with Eurasian plate, with the concurrent exchange of organisms between the two land masses [12]. With this possibility, Gondwanan fauna got scattered out of India [13]. Simultaneously, fauna of Asia and Africa entered the Indian land [14,15]. It is suggested that origin of *Mabuya* took place in the Asian mainland and it dispersed to other parts of the globe [16].

In the light of these facts, we started exploring the biogeography of the common Indian skink *Mabuya carinata*


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(Schneider, 1801). An extensive survey was undertaken in Andhra Pradesh, South India.

## 2. Materials and Methods

SPS Nellore district is selected for this study, because of the fact that it hosts a variety of habitat- rupicolous, forest, grass land and marine. This is selected because species of *Mabuya* are known to exist in all these ecosystems. But we focussed on *Mabuya carinata* only.

Nellore District is the Southernmost Coastal District of Andhra Pradesh. Located between between 13-30' and 15-6' of the Northern latitude and 70-5' and 80-15' of the Eastern Longitudes, the district has occupied a crucial place in the economy of Andhra Pradesh state. It is bound on the north by Prakasam District, on the East by Bay of Bengal, on the South by Chittoor District and Tiruvallur District of Tamilanadu and on the West by Velikonda Hills which separate it from Kadapa District. The eastern half of the District which lice adjacent the coast is fairly fertile and the western half of the district has low elevation towards west with large track of low shrub jungles diversified with rocky, will stony plains. The district has a coastal line of 169 km (Image 1). The maximum temperature is 36 to 46 °C (97 to 115 °F) during summer and the minimum temperature is 23 to 25 °C (73 to 77 °F) during winter. The rainfall ranges from 700 to 1,000 mm (28 to 39 in) through South West and North East Monsoons. Nellore is subject both to droughts and to floods based on the seasons. It is also one of the hottest cities in India with at least 35 super hot days in a year.

Direct counting method was used to arrive at population count of *Mabuya carinata* in the areas surveyed. Conventional distance sampling method was adopted for this survey.

Opportunistic searches comprised of slow walking among the habitat suitable for existence of *Mabuya carinata*. These were carried out over a vast area.

Line transect method was used, where *Mabuya* population is presumed to be high. Transect lines were marked during day time with fishing line for every 5 metres, prior to each attempt. When required, survey was held at dusk, using power full head mounted 6 v spotlights and hand torches. Every potential habitat was searched for the presence of skinks and number of skinks observed was noted down. A noose was used to catch the gecko live. Gecko was released after taking morphometric details as given by Daniel *et.al* [17]. Population analysis was carried out by direct counting. Habitat analysis was done, as described by Kotwal [18]. Sympatric reptiles were identified using the key provided by Smith [19], and Boulinger[20]. No invasive method was used. No animal was either harmed or killed while doing morphometric analysis in the field and no sample was collected for any other purpose. Statistical analysis was done by using Microsoft Office Xcel 2007.

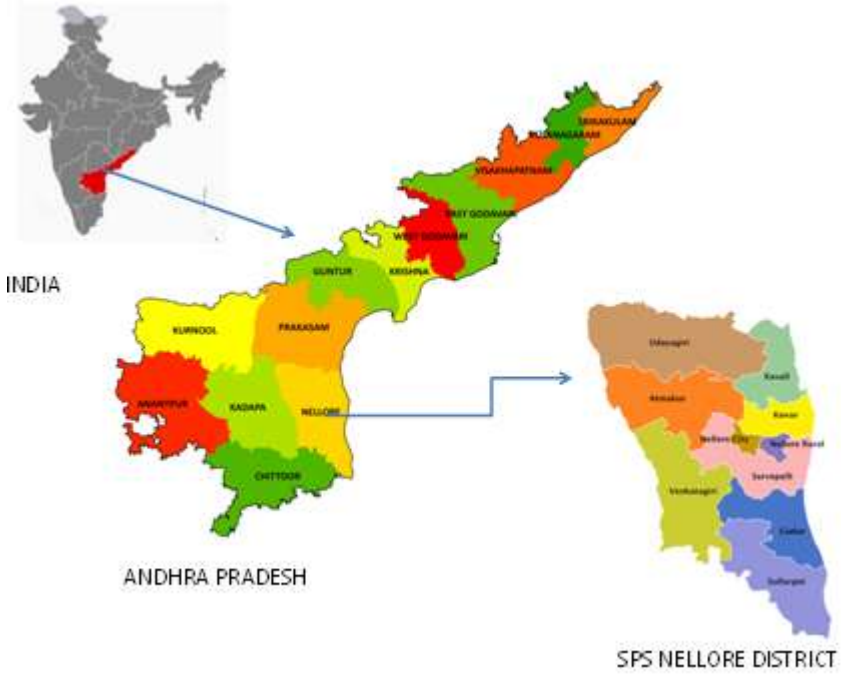



**Image 1:** Map of the Study area

## 3. Results and Discussion

**Animal Description and Habitat:**

**We describe the animal, as spotted in the Penusila Wildlife Sanctuary, Nellore.** *Mabuya* has an obtusely pointed snout, which is longer than the orbit (Images 2). Frontal is variable in length. *Mabuya* has well-developed frontoparitals and interparietal. As a characteristic feature, 5th or 6th supralabial is found to be subocular, and also equal in length to the preceeding labials. Of the four supraoculars observed, second supraocular is the largest and is in contact with the frontal. 5-7 supraciliaries are observed, the first being the largest. Temporal scales are small, almost identical to those upon the rest of the body.


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Dorsal scales are keeled, which are in 5 rows in many of the animals noticed. Occasionally 7 rows are found. Pre-anal scales and median subcaudal scales are small. Subconical tubercles are found on the ventral surface of palms and soles. Larger tubercles are present on the heels. *Mabuya carinata* can be identified in the field by scaly lower eyelid, numerous small scales on the underside of 4th toe, 30-34 scales round the body, legs reaching the elbow and absence of post-nasal. These observations are coinciding with those of earlier authors [19,20].

Typically, *Mabuya carinata* is found under litter, logs and abandoned places covered with scrub vegetation.

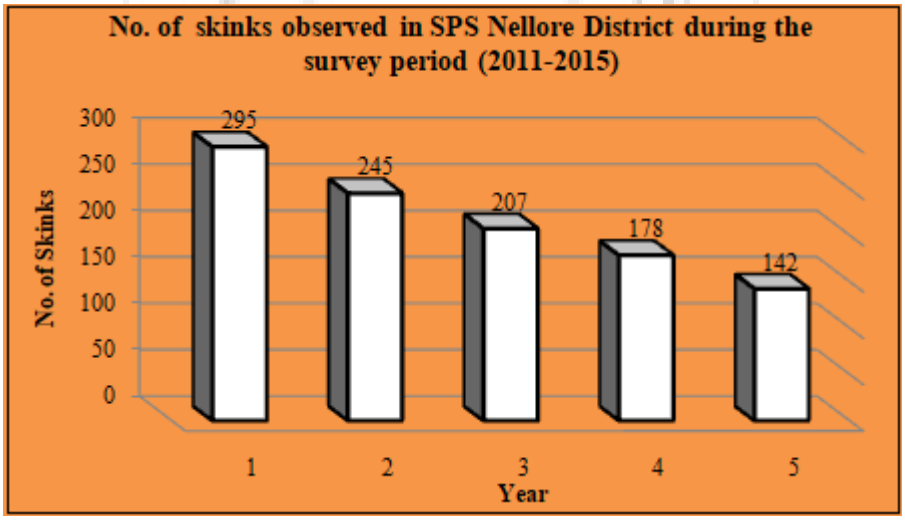


**Image 2:** Common Indian Skink in its natural habitat

**Population of *Mabuya* in SPS Nellore district during the study period**

| Sl. No | Year | No. of animals observed | % increase or decrease with reference to previous year |
|---|---|---|---|
| 01 | 2011 | 295 | -- |
| 02 | 2012 | 245 | -16.94 |
| 03 | 2013 | 207 | -15.51 |
| 04 | 2014 | 178 | -14.00 |
| 05 | 2015 | 142 | -20.93 |

In the year 2011, during the survey period, 295 skinks were observed in all the study locations. There was a reduction in skink population in the study locations by -16.94% during the next survey year. In the next survey year, i.e., 2013, skink population in the surveyed locations recorded a fall by 15.51%. During the next survey year also, there was a decline by 14.00%. During the survey year 2015, there was a negative growth of skink population in the surveyed locations by -20.93% . Altogether, there was a reduction in skink population by 51.86% from the year 2011 to the year 2015. As skinks are very much sensitive to environmental changes, if this decline is continued in the present scale, it is estimated that by 2020 skink population will become very much minimal, and they may face extinction.




Keeping in view the recent changes in the global warming profile and anthropogenic interference in herpetofaunal habitat, it is very much needed to safeguard this important genus in food chains.

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# PHYTOCHEMICAL ANALYSIS OF *OROXYLUM INDICUM* LEAF EXTRACTS ALONG WITH SCREENING FOR ANTIMICROBIAL AND ANTIOXIDANT PROPERTIES

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## Abstract

*Oroxylum indicum* belongs to family: Bignoniaceae (Jacaranda family) commonly known as Broken bones tree is widely distributed throughout South East Asia and India. The endangered forest tree known as *Oroxylum indicum* is having many unexplored medicinal properties. To report different phytochemicals like sterols, saponins, glycosides, flavonoids, alkaloids, tannins, phenols and quinones various tests were performed. The results of these phytochemical testing of crude methanol and ethanol extracts from leaves of *Oroxylum indicum* showed the presence of many important compounds used in the cure of various human ailments. The preliminary phytochemical screening study revealed that the leaf of *Oroxylum indicum* has presence of Flavonoids, Saponins Alkaloids,Sterols, Tannins ,Phenolic Compounds, Fats and Oils,. Glycosides, lignins. Whereas Anthraquinones, Anthocyanides, Coumarins ,Proteins, Carbohydrate, Indoles, Reducing sugars and Aminoacids are found to be absent in both the extracts. The extracts from *O. indicum* leaves collected from different provinces in Penchalakona of Nellore district were prepared by decoction and maceration with methanol, ethanol and evaluated their antimicrobial effects on three clinically isolated bacteria, *Bacillus subtilis MTCC 441,Staphylococcus aureus MTCC 737,Pseudomonas aeruginosa MTCC 1035* and a fungal pathogen *Candida albicans MTCC 3018* using disc diffusion assay. Methanol and ethanol extracts from *O. indicum* leaves at the concentration of 1000 mg/mL exhibited maximum antibacterial activity against *Staphylococcus aureus* with an inhibition zone of 15.9 mm and 14.1mm respectively. But it has no inhibitory affect on *Bacillus subtilis, Pseudomonas aeruginosa and Candida albicans.* The methanol and ethanol extracts from the leaves of this plant scavenged DPPH(1, 1Diphenyl-2picrylhydrazyl) free radicals with 65% and 63% inhibition and nitric oxide free radicals are scavenged by 72% and 71% respectively. The present study revealed the antioxidant potential of leaves of *Oroxylum indicum*. 2,2diphelyl 1-picrylhydrazyl (DPPH), and Nitric oxide are used as free radicals and scavenging potential and reductive ability assay of methanol and ethanol extract of leaves were performed to evaluate the inhibition percentage. From the results, it is clearly understood that the extracts from *O. Indicum* leaves have antioxidant effect along with antimicrobial nature, on clinically isolated pathogenic bacteria and it could be used for medicinal and pharmaceutical purposes in the future.

**Keywords:** *Oroxylum indicum*, Phytochemical analysis, Bioactive compounds, Antimicrobial and Antioxidant properties, Free radical Scavenging activity, Disc diffusion assay.

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# INTRODUCTION

Plants are the basis of many traditional medicines worldwide. Traditional medicines derived from plants are used by about 60% of the world's population. Though there are various approaches to control diseases because of their secondary complications, herbal formulations are preferred due to lesser side effects and low cost. The use of drugs and dietary supplements derived from green sources has been increased in recent years. Botanists, microbiologists, Ethno pharmacologists and chemists are searching the earth for phytochemicals and drugs which could be used for treatment of many stubborn infectious diseases in a green and natural way. While 30 to 50% of current pharmaceuticals are derived from plants, only few of them are used as antimicrobials. Traditional healers have long used plants to prevent or cure infectious conditions. Plants are rich in a wide variety of secondary metabolites, such as Terpenoids, Tannins, Alkaloids, Flavonoids, Saponins and Anthraquinones which have been found in vitro to have antimicrobial and anti oxidant properties. Leaves, stems and Roots of *Oroxylum indicum* are being used as an important drug component in the Indian Ayurvedic system for cure of various diseases and used as a tonic. ***Oroxylum indicum*** (Linn.), the plant used in this study is one of ten drugs named Dasamoola, is generally used in Ayurvedic system of medicine. Various studies indicated that sonapatha (common name of this plant in Ayurvedic medicine) possesses antioxidant, anticancer, hepato-protective, antimicrobial, analgesic and gastro-protective properties. Plants of *O.indicum* have been used as traditional medicine known to possess unique medicinal properties such as anti inflammatory, diuretic, anti-arthritic, antibacterial, anti-tussive and anti-fungal properties. The roots of *O.indicum* are known for anti-helminthic, anti-bronchitic, anti-luecodermatic, anti-rheumatic and anti-anorexic. The leaves and bark of stem are reported to possess flavonoids like baicalein, chrysin, oroxylin-A and scutellarin. The flavonoid baicalein is reported to have an anti-oxidant [1], hepato protective [2], anti-ulcer [3] and immuno-modularity activity [4]. This plant is used as an astringent, carminative, diuretic, stomachic, aphrodisiac and has high potential for stimulating digestion, curing fevers, coughs and preventing other respiratory disorders [5]. Bark of *O.indicum* is reported to be used to cure fevers, gastritis, liver disorders, as a purgative, for controlling hypertension, for treating headache [6] epilepsy, muscular sprain and in controlling hypertension [7] and general weakness [8] . The normal dose is reported 8 to 16 g of bark in the form of decoction, extract or powder [9,10]. The seeds are active in controlling chronic cough and gastralgia: 5 to 10 g daily in the form of a decoction or powder and also used as purgative. An alcoholic maceration of fresh bark is applied externally for lacquer allergic dermatitis. The fruits of *Oroxylum indicum* are acrid, sweet, stomachic, anthelmintic,

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and good in treating diseases of the heart and the throat, piles, bronchitis, used as an expectorant, improves the appetite, useful in leucoderma [11-16]. The aqueous extract of leaves of *Oroxylum indicum*

has been reported to possess significant anti-inflammatory activity [17]. The roots are used in dropsy and the leaves are reputed as an emollient. Tender fruits are described as carminative and stomachic [18]. The root of this plant is also one of the important ingredients in most commonly used ayurvedic formulations like dantyadyarista, brahma rasayana, dasamula, amartarista, dhanawantara ghrita, narayana taila [19]. The anti cancer potential of different parts of the plant has already been reported [20,21]. Inspite of its extensive use in folk, ayurvedic, herbal and tribal medicine the phytochemical analysis of leaves of *O. indicum* was not studied. Hence the present investigation has been under taken this analysis to screen different types of phytochemicals in *O.indicum* along with evaluation of antimicrobial and anti oxidant properties. *Oroxylum indicum* (Bignoniaceae), a broken bone tree is a local ornamental tree often grown for its strange appearance. It is mostly found along the river banks or slopes of the hills. The following are some of the local names/synonyms with which the tree is called in its respective regions of India.

**Table 1: Synonyms**

| **Language** | **Local name/Synonyms** |
|---|---|
| Hindi | Bhut-vriksha, Dirghavrinta, Kutannat, Manduk, Patrorna, Putivriksha, Shallaka, Shuran, Son, Vatuk. |
| Manipuri | Shamba |
| Sanskrit | Aralu,Shyonaka |
| Assamese | Toguna |
| Oriya | Tatelo |
| Bengali | Sona |
| Konkani | Davamadak |
| Kannada | Tattuna |
| Telugu | Manduka-parnamu,Pampena,Suka-nasamu,Tundilamu |
| Marathi | Tayitu,Tetu |
| Tamil | Cori-konnai,Palai-y-utaicci,Puta-puspam(the flower) |
| Malayalam | Palaqapayyani,Vashrppathiri, Vellappathiri |

Except in the western drier area, the plant is distributed throughout India and South East Asia. *Oroxylum indicum* Vent. (Bignoniaceae), a rare endangered and threatened medicinal plant widely used traditionally for treating several disorders [22]. The root bark and stem bark possess antiallergic properties and are used in treating allergic disease, hoarseness, gastralgia, diarrhoea, dysentery,

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urticaria, jaundice, asthma, sore throat, laryngitis, infantile, measles and erythema [22–23]. Antioxidants are now standing on the mainstay of the treatment and prevention of several diseases [23-24]. This has been used as a single drug or as a component of certain poly-herbal drug preparations in Indian system of medicine ie. Ayurveda. It is active ingredient of well known Ayurvedic formulations like Dashmularistha, Chyavanprash etc. [25]. Present research is directed towards finding naturally occurring antioxidants particularly of plant origin. The present study describes the phytochemicals present in *Oroxylum indicum* leaves and its antimicrobial and antioxidant properties.

**Botanical Description**

A small tree, 8-15 m tall, branched at top; bark light brown, soft with green juice and often with numerous corky lenticels. Leaves are 3-8 cm long, 2-3 pinnate with opposite pinnae, rachis very stout, cylindrical, leaflets 2-4 pairs, 7-13 cm long and 4-11 cm broad, ovate or elliptic, acuminate, glabrous, base rounded or sometimes cordate; petioles of the lateral leaflets 7-15 mm long. Flowers are numerous, in large erect racemes, 0.3-0.6 meter long or even more pedicels 6-31 mm long. Calyx 4 cm long, leathery, glabrous and oblong-campanulate. Corolla usually lurid-purple, reaching 10 cm long, fleshy lobes about 4 cm long with crisped margins. Stamens 5, slightly exerted beyond the corolla tube, one of them little shorter than the 4, filaments cottony at the base. Capsules 0.3-0.6 meter long and 5-9 cm broad, straight, tapering to both ends, flat, hardly 8 mm thick, acute, valves semi-woody. Seeds numerous, 6 cm long, winged all round except at the base( Kirtikar & Basu, 2001; Ayurvedic Pharmacopoeia of India) .The large leaf stalks wither and fall off the tree and collect near the base of the trunk, appearing to look like a pile of broken limb bones. The tree is a night-bloomer and flowers are adapted to natural pollination by bats. They form enormous seed pods that hang down from bare branches. Those long fruits curve downward and resemble the wings of a large bird or dangling sickles or swords in the night. The seeds are round with papery wings. Bark is off brown in colour. In India, the plants flower any time during August to February depending on climate. *O. indicum* is propagated naturally by seeds, which germinate in the beginning of the rainy season (June to September). Problems related with its natural propagation and indiscriminate exploitation for medicinal purpose has pushed *O. indicum* to the list of endangered plant species of India.

**Geographical Distribution*:*** *Oroxylum indicum* is native to the Indian subcontinent, in Indo-China, in the Himalayan foothills with a part extending to Bhutan and southern China and the Malaysia.

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**Taxonomical Classification:** *Oroxylum indicum* belongs to the family Bignoniaceae. Its taxonomical classification reported in literature is as given below.

**Table 2: Taxonomical Classification**

| **Kingdom** | **Plantae** |
|---|---|
| Division | Magnoliophyta |
| Class | Magnoliopsida |
| Order | Lamiales |
| Family | Bignoniaceae |
| Genus | Oroxylum |
| Species | Indicum |

**Fig.1: *Oroxylum indicum***



## MATERIALS AND METHODS

Leaves of *Oroxylum indicum* were collected from Penchalakona forest of Nellore disrict A.P.,in July 2016. The plant was identified by Prof. Dr. S.K.M.Basha, Department of Botany, Vikramasimhapuri University, P.G Centre, Kavali district of AndhraPradesh, India. The plant material was purified with distilled water and was shade dried for one month. Leaf sample of the material was ground into fine powder and stored in air tight containers at room temperature. All the specimens at different leaf stages were documented in the form of herbarium sheets which have been deposited in the Herbarium, Department of Botany, Vikramasimhapuri University, P.G Centre, and Kavali,Andhrapradesh, India. The powdered material was then extracted using solvents methanol and ethanol in the ratio 1:10 using Soxhlet apparatus. (Khan *et al*., 1988). The solvent was evaporated under reduced pressure in rotatory evaporator to get methanol and ethanol extracts. Antibacterial and antifungal activities of the four plant extracts were investigated by the disc diffusion method [26] .The supernatants were collected, covered, labelled and used for the screening of various phytochemicals. After extracting all colouring material, the solvent was removed by evaporating in a water bath, which gave rise to a solid isolate of extract used for antimicrobial and antioxidant screening.

**Phytochemical Analysis**

The photochemical analysis of the leaves was carried out to determine the presence of following bioactive compounds using the standard qualitative procedures.

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**Tests Performed for the Presence of Phytochemicals**

**A) Tests for Flavonoids**

1. **Shinoda test (Magnesium hydrochloride reduction test):** To the test solution few fragements of magnesium ribbon and concentrated hydrochloric acid were added drop wise and reddish to pink colour was resulted.
2. **Zinc Hydrochloride reduction test:** To test the sample solution for the flavonoids added a mixture of zinc dust and concentrated hydrochloric acid results in red colour.
3. **Lead acetate test:** When aqueous basic lead acetate was added to test sample produces reddish brown precipitate.
4. **Ferric chloride test:** To few ml of test samples taken separately, few drops of ferric chloride were added which resulted in the formation of blackish red precipitate.
5. **Alkaline reagent test:** When sodium hydroxide solution was added to the test samples formation of intense yellow colour, which turns to colour less on addition of few drops of dilute acid indicates the presence of flavonoids.

**B) Tests for Saponins**

**Foam test:** 5ml of extract was shaken vigorously to obtain a stable persistent froth. The froth was then mixed with three drops of olive oil and observed for the formation of an emulsion, which indicated the presence of saponins.

**C) Tests for Glycosides**

1. **Kellar Kiliani test:** 1ml of concentrated sulphuric acid was taken in a test tube then 5ml of extract and 2ml of glacial acetic acid with one drop of ferric chloride were added, formation of a blue colour.
2. **Raymond's test:** Test solution when treated with dinitrobenzene in hot methanolic alkali giving a violet colour.
3. **Molisch test:** When alpha naphthol and concentrated H2SO4 were added to test samples reddish violet ring at junction of two layers was resulted.
4. **Concentrated Sulphuric acid test:** Conc.H2SO4 was added to test sample which resulted in appearance of reddish colour.
5. **Legal's test:** The test samples when treated with pyridine and sodium nitroprusside solution blood red colour will be developed.
6. **Bromine water test:** When treated with bromine water test solution gives yellow precipitate.

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**D) Tests for Alkaloids**

1. **Dragendorff's test:** To 1 ml of each of the sample solution taken in a test tube few drops of Dragendorff's reagent (potassium bismuth iodide solution) was added. A reddish brown precipitate was observed indicating the presence of alkaloids.
2. **Meyer's test:** To 1ml of each of the sample solution few drops of Meyer's reagent (potassium mercuric chloride solution) was added. A creamy white precipitate was formed indicating the presence of alkaloids.
3. **Wagner's test:** To few ml of each of the sample solution, Wagner's reagent (Iodine in potassium iodide) was added, which resulted in the formation of reddish brown precipitate indicating the presence of alkaloids.
4. **Hager's test:** To 1 ml of each of the sample few drops of Hager's reagent (Picric acid) was added. Yellow precipitate was formed reacting positively for alkaloids.
5. **Tannic acid test:** When few ml of 10% Tannic acid was added to 1ml of each sample, a buff colour precipitate was formed giving positive result for alkaloids.
6. **FeCl 3 test:** One drop of FeCl 3solution was added to each of the test sample, formation of yellow precipitate was resulted reacting positively for alkaloids.

**E) Tests for Sterols**

1. **Libermann-Buchard test:** When samples were treated with few drops of acetic anhydride, boiled and few drops of concentrated sulphuric acid from the sides of the test tube were added, shows a brown ring at the junction of two layers and the upper layer turns green which shows the presence of steroids.
2. **Salkowski test:** Few drops of concentrated sulphuric acid were added to the test samples in chloroform, a red colour appears at the lower layer indicates the presence of sterols

**F) Tests for Tannins and Phenolic Compounds**

1. **Ferric chloride test:** When few drops of ferric chloride were added to sample solution a blackish precipitate appears.
2. **Gelatin test:** When gelatine and water were added to test samples formation of white precipitate was resulted.
3. **Lead acetate:** Few ml of test samples were taken in different test tubes followed by the addition of aqueous basic lead acetate. It results in the formation of reddish brown bulky preceipitate.

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4. **Alkaline reagent:** When sodium hydroxide solution was added to the sample solution results in the formation of yellow to red precipitate.
5. **Mitchell's test:** Tannins give a water soluble iron–tannin complex with iron and ammonium citrate or iron and sodium tartarate.
6. **Ellagic acid test:** When 5% glacial acetic acid and 5% sodium nitrite were added to test samples a muddy niger brown colour appears, which is a positive result for phenols.

**G) Tests for Fats and Oils**

1. **Stain test:** Press the small quantity of each extract between two filter papers, the stain on filter papers indicates the presence of the oils.
2. **Saponification test:** Added a few drops of 0.5N alcoholic potassium hydroxide to various extracts with a drop of phenolphthalein separately and heat on water bath for 1-2hours, formation of soap or partial neutralization of alkali indicates the presence of oils and fats.

**H) Tests for Lignins**

1. **Labat test:** When gallic acid is added to the test sample,it results in the formation of olive green colour.
2. **Furfuraldehyde test:** When furfuraldehyde is added to the test sample a red colour appears indicating the presence of lignin.

**I) Tests for Quinones**

**Alcoholic KOH test:** When alcoholic KOH was added to the test samples red to blue colour appears reacting positively for quinones.

**J) Terpenoids and steroids test**

1.50% $H_2SO_4$ is added along the sides of the test tube containing a mixture of methanolic HCl and acetic anhydride. If there is any change in color, from green to blue-green (sometimes via red or blue) indicates the presence of terpenoids and steroids.

**K) Anthroquinones test**

1. 5 g plant powder was shaken with 20 ml of benzene and filtered. To the filtrate 5 ml of 10% ammonium hydroxide solution was added and shaken well. Presence of pink red or violet color, in the ammonical phase indicates the presence of free anthroquinones (Fransworth, 1966).

**L) Anthocyanidin test**

To the plant extract was added equal volume of methanolic HCl. Appearance of red or purple color indicates the presence of anthocyanidins.

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**M) Coumarin test**

To the methanolic extract, a few drops of alcoholic sodium hydroxide were added. Formation of yellow color indicated the presence of coumarins.

**N) Proteins test (Millions test)**

2 ml of methanolic extract was boiled with a few drops of Million's reagent (Millions reagent is a solution of mercuric nitrate in nitric acid) results in the formation of red color indicates the presence of proteins.

**O) Carbohydrate test (Molish test)**

To the methanolic extract, c-naphthol solution (1gm dissolved in 100 ml of ethanol w/v) was added. Then conc. $H_2SO_4$ is added gently along the walls of the inclined test tube. Appearance of a red to violet color at the interface is taken as a positive reaction.

**P) Indole test**

If a violet color was developed on adding Ehrlich reagent to the alcoholic extract, it is considered as a positive reaction for indoles.

**Q) Test for reducing sugars**

To the 5 ml of methanolic extract, 5 ml of Benedict's reagent was added in a boiling test tube. The test tubes were incubated in boiling on water bath for 15-30 minutes. The formation of an orange red precipitate indicated the presence of reducing sugars.

**R) Test for amino acids**

To the methanolic extract, was added few drops of Ninhydrin solution and boiled. The formation of violet colour indicates the presence of amino acids.

**Determination of Antibacterial Activity of *O. Indicum* Leaf Extracts Using Disc Diffusion Assay:**

Sensitivity tests were performed by disc diffusion with standard antibiotics, following Kirby-Bauer method. The assessment of antimicrobial activity was done based on measurements of the diameter of inhibition zones (NCCLS, 1998). The assays were performed against three clinically isolated pathogenic bacteria *Bacillus subtilis MTCC 441,Staphylococcus aureus MTCC 737,Pseudomonas aeruginosa MTCC 1035* and a fungal pathogen *Candida albicans MTCC 3018* . Each extract was dissolved in 95% ethanol or sterile water at different concentrations (250, 500 and 1000 mg/mL). Then each solution was impregnated on to a small disc of filter paper and placed on the top of agar containing 100 µL of bacterial solution at a concentration of 1.5ˆ108 CFU/mL per plate (adjusted by comparing to 0.5 McFarland). Similarly, each plate carried a blank disk by adding solvent control

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alone in the centre, and antibiotic discs (6.0-mm diam) of (20 µg/ml, Streptomycin sulphate for bacteria) and Nystatin (20 µg/ml, for fungal) were also used as a positive control. All of the plates were incubated at 37°C for 18 hours for bacteria and at 28°C for 48 hours for fungi. The zones of growth inhibition around the discs were measured after 18 hours of in incubation at 37°C for bacteria and 48 hours for fungi at 28°C, respectively. The sensitivity of the microorganism species to the plant extracts was determined by measuring the sizes of inhibitory zones on the agar surface around the discs. All determinations were undertaken in triplicate and the average zone of inhibition was calculated with the standard deviation.

**Determination of In Vitro Antioxidant activity of *O.Indicum* Extracts Using DPPH Scavenging Method** [27]

**a) DPPH (1, 1-Diphenyl-2picrylhydrazyl) free radical scavenging activity**

- The ability of the sample to scavenge DPPH radicals were determined.
- 0.5 ml of aliquot of test at different concentrations (100 µg/ml and 200 µg/ml )in methanol was mixed with 0.5 ml of 100mM methanolic solution of DPPH.
- The mixture was incubated for 30 min in darkness and at ambient temperature.
- Absorbance was recorded at 517 nm.

**b) Nitric oxide radical scavenging activity**

1. The standard used here was Ascorbic acid. 100 µg/ml and 200 µg/ml solution of standard in methanol and ethanol were used for assay.
2. Sample solution was prepared by dissolving the sample in methanol and ethanol
3. 10 mg of each extract were dissolved in methanol and ethanol and solutions of 100 µg/ml and 200 µg/ml concentrations were prepared.
4. In this assay 0.5 ml of Sodium nitro prusside (5 mmol) in phosphate buffered saline pH 7.4, was mixed with different concentration of the sample and incubated at 25°C for 3 hrs.
5. A control without the test compound, but an equivalent amount of methanol and ethanol were taken. Control tube without the plant extract, but with equivalent amount of buffer was maintained in an identical manner.
6. Then 1.5 ml of Griess reagent (1% sulphanilamide, 2% phosphoric acid and 0.1% N-1-naphthyl ethylene diaminedihydrochloride) was added and incubated for 30 minutes.
7. The absorbance of the chromophore formed during diazotization of nitrite ions with suphanilic acid and its subsequent coupling with Napthyl ethyl enediamine was read at 546 nm. The experiment was repeated in triplicate.

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8. Absorbance was measured at 546 nm and the percentage scavenging activity was measured.

$$\text{Percentage inhibition} = \frac{\text{Absorbance of Control} - \text{Absorbance of Test}}{\text{Absorbance of Control}} \times 100$$

The percentage of inhibition for each reaction was then calculated, and EC50 values (µg/mL) were calculated from the linear equation from the curve between the percentage of inhibition and the solution's concentration. Each experiment was conducted in triplicate.

The EC50 value of each extract was expressed as the mean˘SD. The assays were performed as previously described [28-29].

## RESULTS

The results of the phytochemical screening to test the presence of Flavonoids, Saponins Glycosides,Alkaloids,Sterols, Tannins ,Phenolic Compounds, Fats and Oils, Lignins and Quinones, Terpenoids, Anthraquinones, Anthocyanides, Coumarins ,Proteins, Carbohydrate, Indoles, Reducing sugars and Aminoacids in the extracts from various parts of *Oroxylum indicum* are shown in Table 3.The preliminary phytochemical screening study revealed that the leaf of *Oroxylum indicum* has presence of Flavonoids, Saponins Alkaloids,Sterols, Tannins ,Phenolic Compounds, Fats and Oils,. Glycosides and lignins. Whereas Anthraquinones, Anthocyanides, Coumarins ,Proteins, Carbohydrate, Indoles, Reducing sugars and Aminoacids are found to be absent in both the extracts.

The methanolic and ethanolic leaf extracts of the plant *Oroxylum indicum* has shown prominent antimicrobial activity on tested pathogens, whereas the Methanol extract of plant has shown maximum inhibition on *Staphylococcus aureus* MTCC 737*(15.9 mm inhibition zone).* Ethanol extract of plant has shown maximum inhibition on *Staphylococcus aureus* MTCC 737*(14.1 mm inhibition zone )* and both the extracts have no effect on *Bacillus subtilis MTCC 441, ,Pseudomonas aeruginosa MTCC 1035* and a fungal pathogen *Candida albicans MTCC 3018* . The anti microbial activity is shown in table.4. With reference to the anti oxidant activity DPPH (1, 1 Diphenyl-2picrylhydrazyl) free radicals are scavenged by methanolic extract by 65% and ethanolic leaf extract by 63%. Nitric oxide free radicals are scavenged by methanolic leaf extracts by 72% and ethanolic leaf extracts by 71%. The anti oxidant activity is shown in table 5&6.

**Table 3: Analysis of Phytochemicals from methanolic and ethanolic leaf extracts of *Oroxylum indicum***

| S.NO | Name of the phytochemical | Name of the test | Methanolic leaf extract | Ethanolic leaf extract |
|---|---|---|---|---|
| 1. | Flavonoids | Shinoda test | + | + |
| | | Zn-HCl reduction test | + | + |
| | | Lead acetate test | + | - |

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| | | | | |
|---|---|---|---|---|
| | | $Fecl_3$ test | + | + |
| | | Alkaline reagent test | + | + |
| 3 | Saponins | Frothing test/Foam test | + | + |
| 4 | Glycosides: | Keller-Kilianii test | - | - |
| | | Raymond's test | - | - |
| | | Molisch test | - | - |
| | | Conc.$H_2SO_4$ test | - | - |
| | | Legal's test | - | - |
| | | Bromine water test | - | - |
| 5 | Alkaloids | Dragendorff test | + | + |
| | | Mayer's test | _ | - |
| | | Wagner's test | + | + |
| | | Hager's test | + | - |
| | | Tanicacid test | + | + |
| | | $Fecl_3$ test | + | + |
| 6 | Sterols: | Lieberman Burchardt test | -- | + |
| | | Salkowski test | + | + |
| 8 | Tannins and Phenolic Compounds | $FeCl_3$ test | + | + |
| | | Gelatin test | _ | - |
| | | Lead acetate test | + | + |
| | | Alkaline reagent test | + | - |
| | | Mitchell's test | + | + |
| | | Elagic acid test | + | + |
| 9 | Fats and Oils | Stain test | + | + |
| | | Saponification test | + | + |
| 10 | Lignins | Labat test | - | - |
| | | Lignin(furfuraldehyde) test | - | - |
| 11 | Quinones: | Alcoholic KOH test | - | - |
| 12 | Terpenoids | 50% $H_2SO_4$ Test | + | + |
| 13 | Anthraquinones | Benzene+ammonium hydroxide test | - | - |
| 14 | Anthocyanides | Methanolic HCl test | - | - |
| 15 | Coumarins | Alcoholic Sodium hydroxide | - | - |
| 16 | Proteins | Million's test | - | - |
| 17 | Carbohydrate test | Molish test | - | - |
| 18 | Indole test | Ehrlich reagent +alcoholic extract | - | - |
| 19 | Reducing sugars | Benedict's reagent test | - | - |
| 20 | Aminoacids | Ninhydrin test | - | - |

'+' Present, '--' Absent

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**Table 4: Antimicrobial activity of leaf extracts of *Oroxylum indicum***

| Solvent extracts | Zone of inhibition in mm | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Names of microbes | | | | | | | | | | | |
| | ***Bacillus subtilis*** | | | ***Staphylococcus*** | | | ***Pseudomonas*** | | | ***Candida albicans*** | | |
| Quantity (Micrograms) | 1000 | 500 | 250 | 1000 | 500 | 250 | 1000 | 500 | 250 | 1000 | 500 | 250 |
| Methanol | -N- | -N- | -N- | 15.9 | 15. | 13.9 | -N- | -N- | -N- | -N- | -N- | -N- |
| Ethanol | -N- | -N- | -N- | 14.1 | 13. | 12.1 | -N- | -N- | -N- | -N- | -N- | -N- |
| Streptomycin sulphate(µg/ml) (20µl) | 26±.8 | | | 22±.7 | | | 21±.9 | | | | | |
| Nystatin(µg/ml) (20µl) | - | | | - | | | - | | | 19±.7 | | |

**Table 5: Antioxidant activity of leaf extracts of *Oroxylum indicum***
**a) DPPH (1, 1 Diphenyl-2picrylhydrazyl) free radical scavenging activity**

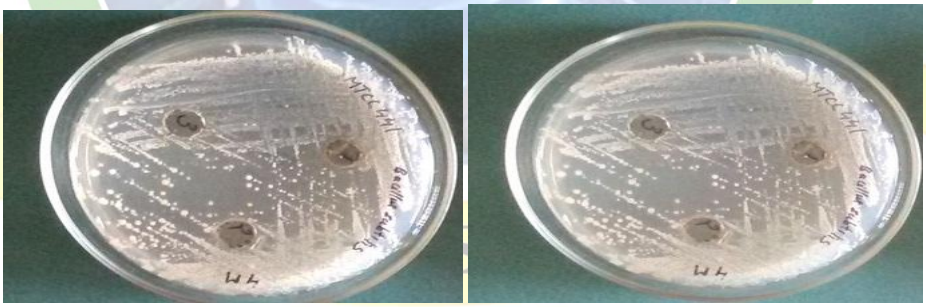
| S.No | Treatment | Concentration (µg/ml) | Absorbance at 517nm | |
|---|---|---|---|---|
| 1 | Control | - | 1.64<br>1.69<br>1.70 | 1.67 |
| 2 | Standard (Ascorbic acid) | 100 | 0.79<br>0.75<br>0.80 | 0.78 |
| | | 200 | 0.41<br>0.48<br>0.52 | 0.47 |
| 3 | Methanolic Leaf extract | 100 | 0.78<br>0.83<br>0.75 | 0.78(53%) |
| | | 200 | 0.58<br>0.61<br>0.55 | 0.58(65%) |
| 4 | Ethanolic Leaf extract | 100 | 0.69<br>0.73<br>0.78 | 0.73(56%) |
| | | 200 | 0.62<br>0.61<br>0.58 | 0.61(63%) |

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**Table 6: Antioxidant activity of leaf extracts of *Oroxylum indicum***
**b) Nitric oxide radical scavenging activity:**

| S.No | Treatments | Concentration (µg/ml) | Absorbance at 546nm | |
|---|---|---|---|---|
| 1 | Control | - | 1.50 | 1.5 |
| | | | 1.47 | |
| | | | 1.53 | |
| 2 | Standard (Ascorbic acid) | 100 | 0.61 | 0.62 |
| | | | 0.69 | |
| | | | 0.58 | |
| | | 200 | 0.34 | 0.34 |
| | | | 0.30 | |
| | | | 0.39 | |
| 3 | Methanolic Leaf extract | 100 | 0.54 | 0.53 (64%) |
| | | | 0.56 | |
| | | | 0.50 | |
| | | 200 | 0.39 | 0.41 (72%) |
| | | | 0.44 | |
| | | | 0.41 | |
| 4 | Ethanolic Leaf extract | 100 | 0.56 | 0.58 (61%) |
| | | | 0.58 | |
| | | | 0.61 | |
| | | 200 | 0.43 | 0.44 (71%) |
| | | | 0.47 | |
| | | | 0.42 | |

**1. *Bacillus subtilus***

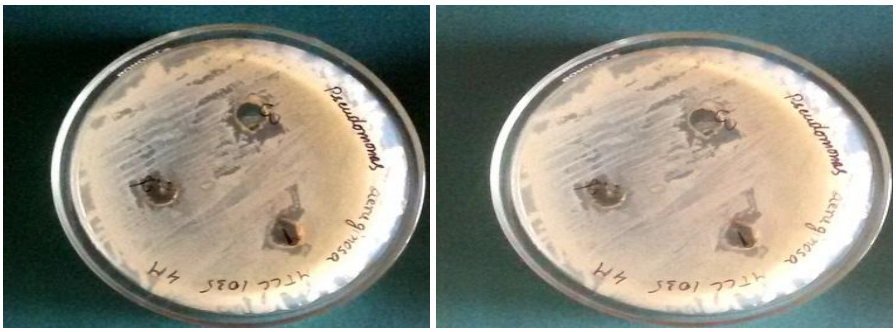


**2.*Staphylococcus aureus***



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**3.*Pseudomonas auriginosa***



**4.*Candida albicans***



## DISCUSSION

Background check reveals that the flavonoids (Rauha, 2000), sterols (Pereira et al., 2006) and phenolic compounds (Proestos, 2005) show antimicrobial activity against several pathogens (Eloff, 2004). Preliminary phytochemical analysis of *Oroxylum indicum* plant leaf extracts and its fractions shows the presence Flavonoids, Saponins Alkaloids, Sterols, Tannins, Phenolic Compounds, Fats and Oils,. Except Glycosides and lignins. Hence the antimicrobial activity exhibited by the Methanolic and ethanolic leaf extracts could be related with the concentrations of above said secondary metabolites present in these selected plant extracts. The results obtained here with antimicrobial activity support the folkloric claims regarding the plant and its medicinal values. This paper helps in formulating natural principles to combat drug resistance of certain bacteria. It is therefore, implied that isolation and proper characterization of the active constituents from the extracts of this plant species as possible antimicrobial and antioxidant agent. Secondary metabolites are chemicals produced by plants. Of these, Saponnins are known to possess hypocholesterolic, anti cancerous, anti mutagenic, anti fungal, zenotoxic anti cytotoxic, anti inflammatory, heamolytic, immune adjuvent, anti protozoal, spermicidal and clastogenic activities. Saponins have been used to control human heart diseases and can also control cholesterol levels. Tannins have insecticidal, mild diuretic, stomachic, antibacterial, antidote and

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haemostatic properties. Alkaloids comprised the vast single class of secondary plant metabolites. Alkaloids have anti fungal, antitumor, anti-amoebic, anti plasmodial, anti-bacterial and anti-ulcer activities. Glycosides show antidiabetic, cardiac, molluscidal, antibacterial, anti-HIV,anti-leukaemia,laxative,analgesic,antipyretic,aphrodisiac and antistress activities. Phenols have anti-microbial, anti-oxidant, anti-viral, vasodilatory and anti-inflammatory effects. In the present study, the methanol and ethanol extracts from *Oroxylum indicum* leaves were tested for their in vitro antimicrobial and antioxidant activities. The extracts from *O. indicum* leaves promoted moderate to intermediate antimicrobial activities against clinically isolated bacteria *Staphylococcus aureus* MTCC 737. The ethanol and methanol extracts from the leaves of *O. indicum* showed high in vitro antioxidant effects. Phytochemical study of the extracts showed some phenolics and flavonoids including baicalein. This compound promotes a strong antioxidant effect, and could be used as preparations from *O. indicum* in the future. Quantitative analysis of the active compound in *O. indicum* leaf extracts should be further investigated in the future. Therefore this research gives insight into the medical potential of the plant based drugs, and for further development of these drugs.

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# DROUGHT IN A P IMPACTS AND ADAPTIONS STRATEGIES WITH REFERENCE TO THE ALL MANDALS OF PRAKASAM DISTRICT BASED ON 2011 AGRICULTURAL YEAR

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## 1. OBJECTIVE OF THE STUDY

The Department of Planning, with the technical help of CRIDA, has also developed, as part of preparing a drought management plan, a real-time decision support system to forecast, and warn the farmers about, the likely upcoming drought and suggest actions such as cropping patterns, to mitigate these impacts. Research institutions, such as ICRISAT and the Agricultural University, have been conducting extensive research on drought resistant crops, appropriate agricultural strategies in drought prone regions and the socio-economic impact of drought in select rural communities. Among these districts in this project I have taken Prakasam District.

In Prakasam District Agriculture operations in Kharif season depends largely on South-West monsoon rains only in Prakasam District. Most of the area cultivated in Kharif is Rain fed. During the present Kharif season (South-west monsoon), 277.8 mm rainfall received as against the normal rainfall of 388.3 mm. The deficit rainfall is -28.5%. Agriculture and its allied sectors are the main source of income of the people in the District. In the south-west monsoon, 20 average rainy days recorded as against 28 normal rainy days. The rainfall received is not wide spread and only scattered. Prolonged dry spells i.e., 21 to 58 days have been continued in the most of the Mandals. Out of 56 Mandals in the District, scanty rainfall was recorded in 4 Mandals, deficit rainfall recorded in 36 Mandals and normal rainfall recorded in 14 Mandals.

**GENERAL DESCRIPTION OF THE DISTRICT**

## 1.2 INTRODUCTION

Ongole district was formed in the year 1970 by the amalgamation of backward areas of erstwhile Guntur, Nellore and Kurnool districts with head quarters at Ongole. Ongole district was later re-named as Prakasam district in the honor of great freedom fighter, Sri. T. Prakasam pantulu.

**Administrative divisions and planning unit**

Prakasam district is divided into 56 mandals and 1041 gram panchayats. The area of a mandal ranges between 15000 and 25000 ha after excluding forest area and non-agricultural land and a gram panchayat, on an average, extends over 1000 ha.

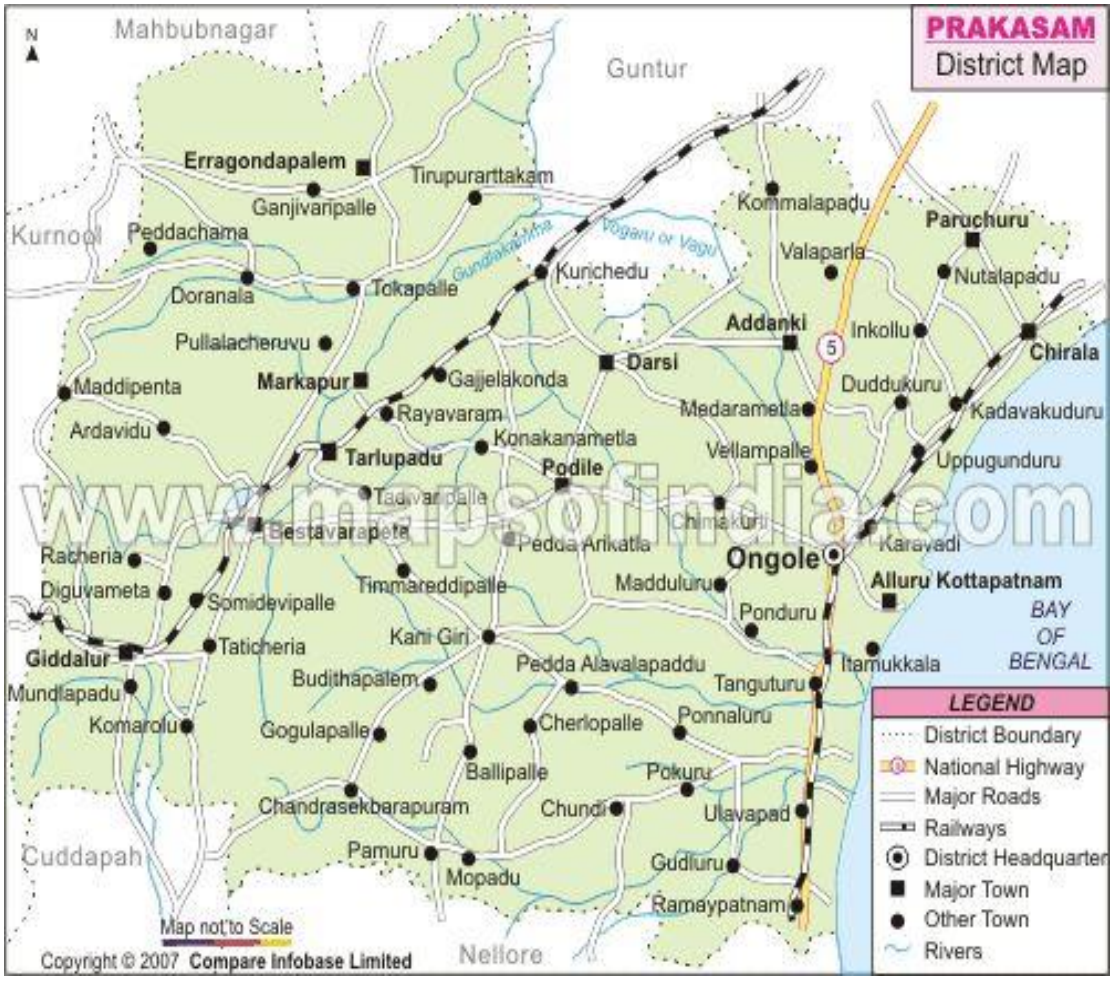
The 56 mandals in the district are listed below:

| | | | | | |
|---|---|---|---|---|---|
| 1 | Ongole | 21 | Tallur | 41 | Komarole |
| 2 | Kothapatnam | 22 | Mundlamur | 42 | Kanigiri |
| 3 | Tangutur | 23 | Darsi | 43 | Pamur |
| 4 | Chimakurthy | 24 | Podili | 44 | Veligandla |
| 5 | S.N.Padu | 25 | K.K.Mitla | 45 | H.M.Padu |
| 6 | Chirala | 26 | Kurichedu | 46 | C.S.Puram |
| 7 | Vetapalem | 27 | Donakonda | 47 | P.C.Palli |
| 8 | Chinaganjam | 28 | Marripudi | 48 | Kandukur |
| 9 | N.G.Padu | 29 | Y.Palem | 49 | Ponnalur |
| 10 | Parchur | 30 | Dornala | 50 | V.V.Palem |
| 11 | Inkollu | 31 | Tripuranthakam | 51 | Gudlur |
| 12 | Karamchedu | 32 | Pullalacheruvu | 52 | L.Samudram |
| 13 | Yaddanapudi | 33 | Markapur | 53 | S.Konda |
| 14 | Martur | 34 | Tarlupadu | 54 | Ulavapadu |
| 15 | J.Pangulur | 35 | Peddaraveedu | 55 | Zarugumalli |
| 16 | Santhamagulur | 36 | Cumbum | 56 | Kondepi |
| 17 | Ballikurava | 37 | Ardhaveedu | | |
| 18 | Addanki | 38 | Giddalur | | |
| 19 | Korisapadu | 39 | Racherla | | |
| 20 | Maddipadu | 40 | B.Peta | | |

These 56 mandals are aggregated in to 12 ADA circles.Since the gram panchayat is too small a unit to be considered as a planning and monitoring unit, the next unit in hierarchy i.e. mandal has been considered as the

planning unit for various agricultural and allied activities. Therefore, in this report, constraints, strategies and schemes relevant to each mandal have been worked out and are aggregated at ADA circle level for reporting purpose. An ADA circle comprises of three to six mandals and is akin to a taluk in other states in terms of geographical coverage. The data are finally aggregated at the district level.

## 2. DISTRICT MAP




## 2.1GENERAL STATISTICS

There are 1093 revenue villages in Prakasam district and they are organized in to 1043 gram panchayats.. Ongole and chirala ADA circles have the highest population, while Purchur and Singaraya Konda ADA circles have the lowest population. The scheduled caste population is concentrated more in Ongole, Addanki and Darsi ADA circles. The scheduled tribe population is concentrated more in Yerragonda palem and Chirala ADA circles . In 2011 census, Prakasam district had population of 3,397,448 of which male and female were 1,714,764 and

1,682,684 respectively. In 2001 census, Prakasam had a population of 3,059,423 of which males were 1,552,332 and remaining 1,507,091 were females.. There was change of 11.05 percent in the population compared to population as per 2001. In the previous census of India 2001, Prakasam District recorded increase of 10.88 percent to its population compared to 1991.

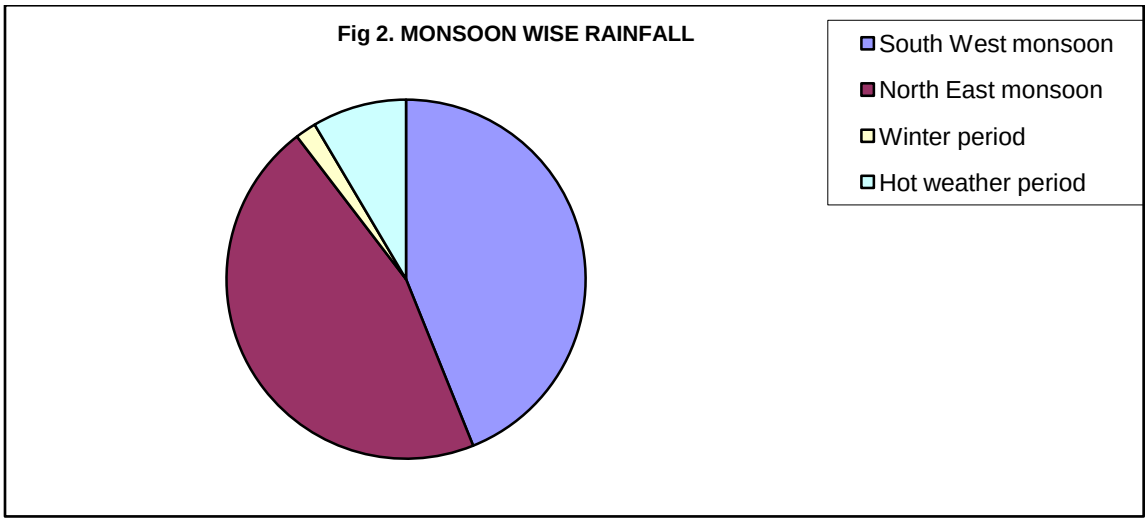
## 2.2 DISTRICT AT A GLANCE

### 2.2.1 Location and geographical units

The district lies between $14.57^{0'}$ and $16.17^{0'}$ northern latitude and $78.43^{0'}$ and $80.25^{0'}$ eastern longitude. The district is bounded by Bay of Bengal in the east, Nellore and Kadapa districts in the south, Kurnool district in the west and Guntur and Mahabubnagar districts in the North. The district comprises of three revenue divisions with 56 mandals. It has 1092 revenue villages and is organized in to 12 agricultural sub-divisions. The district is having 102 km long coastline spanning over eleven mandals.

### Rainfall

The rainfall of the district is influenced by both the south-west and north-east monsoons. Total normal rainfall of the district is 871.5 mm. The contribution from south west monsoon (June - Sept) is 388.3 mm and from north east monsoon (Oct-Dec) is 393.0 mm. The remaining rainfall of 89.5 mm is received in winter season (17.0 mm) and in hot summer period (73.2 mm) .




Drought is a common phenomenon in the district due to scanty and uneven rainfall in the monsoon seasons (south west & north east monsoon)

**Dry Spells**

During South-west monsoon period, dry spells recorded in 45 Mandals. Out of which Severe Dry spell (43 Days and above) recorded in 1 Mandal, Moderate Dry Spells (29 to 42 Days) in 16 Mandals and Mild Dry spells (21 to 28 Days) in 30 Mandals recorded. Due to these dry spells the crops like Redgram, Cotton, Chillies, Paddy, Groundnut etc. will suffer badly and Horticulture Crops like Sweet Orange, Batavia, Acid Lime etc, are also affected.

**Crop Coverage**

An extent of 1,87,439 Ha. area sown as against the Normal area of 2,33,580 Ha. which comes to 80%. Most of the area covered under Rain fed crops only. At present rain fed crops are in withering condition.

The predominant crops viz., Red gram (Ha.38,353), Cotton (54,083), Chilies (Ha.21,257) were cultivated in Prakasam District, which accounts 61% of the total Normal Area. The remaining 39% area sown in different crops during Kharif.

The present stage of the Cotton crop is Vegetative to picking stage and condition of the crop is stunted growth. The present sown crops viz., Bajra, Green gram, Red gram, Chilies and Vegetables are in withering stage and stunted growth.

**Horticulture Crops**

Horticulture is one of the thrust areas in the overall development of the Prakasam District. The major horticulture crops grown in the District are Sweet Orange, Mango, Sapota, Cashew, Papaya, Chilies and Vegetables. Depletion of water tables and drying of bore wells leading to dry-up of Sweet Orange gardens in upland area of the district.

Due to shortage of rainfall, discharge of water from Bore wells reduced in upland Mandals. Area under Vegetables particularly Tomato in upland areas is reduced to below 50% as against the normal area. 50% of Chilies crop grows under rain fed area, and growth of Chilies also effects adversely. The yield is expected to reduce in Sweet Orange, Acid Lime, Chilies and Vegetables above 50%. The Sweet Orange and Acid Lime gardens in upland mandals of the district started drying due to drying of bore wells.

## 2.3 TOPOGRAPHY AND AGRO-CLIMATIC CHARACTERISTICS

### A) Rivers

Gundlakamma, Manneru, Musi and Paleru rivers flow through the district. The Gundlakamma river flows at an altitude of about 2,700 ft near Gundla Brahmeswaram of Nallamala forest. It enters the plains through the Cumbum gorge. It runs in north-east direction and touches Mundlamur, Addanki, Maddipadu and Ongole Mandals and falls into Bay of Bengal near Devarampadu of Ongole mandal. The important tributaries are Kandaleru, Chilamaleru and Dornapuvagu. The total length of the river is about 265 Km, out of which about 220 Km is in the district. The projects across this river are the Thippayapalem reservoir, Duvvaleru Project, Cumbum and Bhavanasi tanks.

The river Manneru in the Veligondas at Balupalli of C.S.Puram mandal flows through Nellore district and takes a turn at Pentrala of Lingasamudram mandal in this district. It flows a distance of 112 Km and falls into Bay of Bengal near Karedu of Ulavapadu mandal. The Dokkalavagu and Nerellavagu fall into this river. It feeds Mopadu reservoir, Rallapadu reservoir and V.R.Kota channel.

The river Musi flows near Dokkalasala in the Veligondas. It flows first in the eastern direction and then in southern direction through Markapur, Darsi, northern boarder of Podili, Kondepi, Tangutur and Kothapatnam mandals and falls into the Bay of Bengal near Madanur of Kothapatnam mandal. It is joined by Gajjaleru, Dondaleru and Atleru in its course and it feeds tanks in Podili and Konakanamitla mandals.

## 2.4 LAND USE PATTERN AND LAND HOLDINGS

The total geographical area of the district is 17.14 lakh ha.

### Agrarian structure

Marginal and small farm category farmer together account for 79 per cent of the total land holdings, but their combined share in the land was only 44 per cent. 56 per cent of the land is owned by 21 per cent of the farmers belonging to medium and large farm categories.

## 2.5 IRRIGATION AND GROUND WATER

The area irrigated in Prakasam district is about 2.15 lakh ha, which represent 32% of the cultivable area. The details of area under different irrigation sources in the district are presented in table

## IRRIGATION
## MAJOR (NSP), MEDIUM AND MINOR IRRIGATION)

Irrigation Circle, Ongole is having Major (NSP) Medium (5 Projects) and Minor Irrigation (368 M.I.Tanks + 589 PR Tanks = 957 Tanks) with an ayacut of 4,29,747 Acres, 40,992 Acres and 1,36,532 Acres respectively in Prakasam District.

**Major NSP**

| Jurisdiction | Covering Mandals | Villages | Ayacut in Acres |
|---|---|---|---|
| M.85/3 onwards & M.18/0 of ABC | 25 Nos. | 50 | 4,29,749 |

**Medium Irrigation - 5 Nos.**

| Name of Project | Mandals | Villages | Ayacut in Acres |
|---|---|---|---|
| Rallapadu | 7 Nos. | 50 | 40992 |
| Mopadu | | | |
| Cumbum tank | | | |
| P.B.Anicut | | | |
| V.R.Kota anicut | | | |

**Minor Irrigation**

| | | |
|---|---|---|
| M.I.Tanks (368) | Entire Prakasam District | 1,36,532 Acres |
| P.R.Tanks (589) | | |

**Total ayacut in Prakasam District – 6,07,291 Acres**

## AYACUT DEVELOPED FOR THE LAST 2YEARS IN PRAKASAM DISTRICT

**Major Irrigation NSP**

| | **Wet** | **I.D.** | **Total** | |
|---|---|---|---|---|
| I.P.created ayacut in Acres | 180538 | 249209 | 429747 | |
| Khariff 2009-10 | 158109 | 170146 | 328253 | |
| Khariff 2010-11 | 169470 | 162915 | 332385 | (late khariff) |
| As on 21-11-2011 | 107100 | 58630 | 165730 | Transplantation in progress |

**Medium Irrigation (5 Nos.)**

| **Sl. No.** | **Name of Project** | **Registered ayacut** | **2009-10** | **2010-11** | **As on today** |
|---|---|---|---|---|---|
| 1 | Mopadu | 8040 | 8040 | 9600 | 200 |
| 2 | V.R.Kota | 5555 | 6500 | 5000 | -- |
| 3 | P.B.Anicut | 7262 | 6500 | 7000 | -- |
| 4 | Cumbum Tank | 6944 | 3180 | 1400 | -- |
| 5 | Rallapadu | 13191 | 13193 | 13191 | 5000 |
| | **Total** | **40992** | **37411** | **36193** | **5200** |

Note:- Transplantation is under progress

**Minor Irrigation:-** Transplantation is not yet started

**MAJOR IRRIGATION (NSP)**

**Statement showing the number of water distressed villages in Prakasam District as on 21.11.2011.**

| Sl. No | Name of Mandal | Wet | I.D. | Total | No.of villages | Water supplied to the villages | Distressed villages |
|---|---|---|---|---|---|---|---|
| 1 | Addanki | 16919 | 18617 | 35636 | 27 | 8 | 19 |
| 2 | Ballikurava | 7278 | 14043 | 21321 | 35 | 15 | 20 |
| 3 | Chimakurthy | 8637 | 25169 | 33806 | 45 | 16 | 29 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 4 | Chinaganjam | 2567 | 30 | 2597 | 3 | 0 | 3 |
| 5 | Darsi | 9196 | 21048 | 30244 | 58 | 7 | 51 |
| 6 | Donakonda | 878 | 53 | 931 | 7 | 3 | 4 |
| 7 | Eddanapudi | 1074 | 1718 | 2792 | 3 | 0 | 3 |
| 8 | Inkollu | 11360 | 11124 | 22484 | 18 | 6 | 12 |
| 9 | J.Pangulur | 8056 | 17820 | 25876 | 22 | 4 | 18 |
| 10 | Karamchedu | 12229 | 7838 | 20067 | 12 | 0 | 12 |
| 11 | Koresapadu | 2663 | 3760 | 6423 | 5 | 0 | 5 |
| 12 | Kothapatnam | 12797 | -- | 12797 | 7 | 0 | 7 |
| 13 | Kurichedu | 1891 | 4482 | 6373 | 15 | 9 | 6 |
| 14 | Maddipadu | 6959 | 3510 | 9469 | 10 | 0 | 10 |
| 15 | Martur | 5532 | 13154 | 18686 | 37 | 0 | 37 |
| 16 | Mundlamur | 1360 | 30592 | 44272 | 37 | 13 | 24 |
| 17 | N.G.Padu | 948 | -- | 948 | 3 | 0 | 3 |
| 18 | Ongole | 12490 | 4675 | 17165 | 18 | 0 | 18 |
| 19 | Parchur | 4459 | 3424 | 7883 | 6 | 2 | 4 |
| 20 | Pullalacheruvu | 1743 | 2148 | 3888 | 6 | 4 | 2 |
| 21 | S.N.Padu | 13387 | 16426 | 29813 | 43 | 11 | 32 |
| 22 | S.Magulur | 6622 | 9743 | 16365 | 19 | 8 | 11 |
| 23 | Talluru | 6937 | 17314 | 24251 | 28 | 10 | 18 |
| 24 | Tangutur | 7529 | 8037 | 15566 | 14 | 0 | 14 |
| 25 | Tripuranthakam | 7357 | 14671 | 22028 | 27 | 13 | 14 |
| | **Total** | **180538** | **249209** | **429747** | **505** | **129** | **376** |

**MEDIUM IRRIGATION**

**No. of distressed villages in Prakasam District**

| Name of Project | Name of Mandal | Ayacut | No.of villages | Water supplied to the villages | Distressed villages |
|---|---|---|---|---|---|
| Rallapadu | 1) Lingasamudram | 6954.60 | 5 | 1 | 4 |
| | 2) Gudlur | 6235.69 | 7 | 7 | 0 |
| | **Total** | **13190.29** | | | |
| Mopadu | Pamur | 12500 | 10 | Nil | 10 |

| | | | | | |
|---|---|---|---|---|---|
| Cumbum Tank | 1) Cumbum | 5350 | 16 | 7 | 9 |
| | 2) B.Peta | 1594 | 5 | 3 | 2 |
| | **Total** | **6944** | | | |
| P.B.Anicut | 1) Zarugumalli | 1131 | 1 | 0 | 1 |
| | 2) S.Konda | 6131 | 6 | 4 | 2 |
| | Total | 7262 | | | |
| V.R.Kota anicut | Kandukur | 5555 | 7 | 2 | 5 |
| | **Total** | **40992** | **57** | **24** | **33** |

***Water storage in Major Irrigation Project***

| *Sl. No.* | *Irrigation Project* | *Full level (FRL)* | *Live storage (Mcft.)* | | | *Last Year (Mcft.)* |
|---|---|---|---|---|---|---|
| | | | *Projected* | *Today* | *%* | |
| *1* | *Ramatheertham Balancing Reservoir* | *85.34 Mts. 1514 Mcft.* | *78.00 Mts. 400 Mcft.* | *76.0 Mts. 349 Mcft.* | *87.25%* | *83.60 Mts. 1290 Mcft.* |

***Water storage in Medium Irrigation Project***

| *Sl. No.* | *Irrigation Project* | *Full level (FRL)* | *Live storage (Mcft.)* | | | *Last Year (Mcft.)* |
|---|---|---|---|---|---|---|
| | | | *Projected* | *Today* | *%* | |
| *1* | *Cumbum Tank* | *2800 Mcft.* | *800 Mcft.* | *NIL* | *NIL* | *1088 Mcft.* |
| *2* | *Rallapadu* | *1106 Mcft.* | *1106 mcft.* | *776 mcft.* | *70.16%* | *1106 Mcft.* |
| *3* | *Mopadu Reservoir* | *2092 Mcft.* | *126* | *123* | *97.60%* | *603 Mcft.* |
| *4* | *V.R.Kota Anicut* | *20.72 ft.* | *10 Mcft.* | *6 Mcft.* | *60%* | *10 Mcft.* |
| *5* | *P.B.Anicut* | *13.34 ft.* | *15 Mcft.* | *3 Mcft.* | *20%* | *15 Mcft.* |

I submit that the following 38 mandals have been identified as eligible mandals for declaration of drought affected mandals as per the norms prescribed in drought manual.

| | | | CATEGORY – B | | | CATEGORY - C | |
|---|---|---|---|---|---|---|---|
| Sl. No. | Mandal | | Sl. No. | Mandal | | Sl. No. | Mandal |
| 1 | S.Magulur | | 1 | Chimakurthy | | 1 | Ongole |
| 2 | Pamur | | 2 | Addanki | | 2 | Kothapatnam |
| 3 | Donakonda | | 3 | Korisapadu | | 3 | S.N.Padu |
| 4 | Tarlupadu | | 4 | J.Pangulur | | 4 | Kandukur |
| 5 | Markapur | | 5 | Yaddanapudi | | 5 | Gudlur |
| 6 | Pedaraveedu | | 6 | Vetapalem | | 6 | V.V.Palem |
| 7 | Y.Palem | | 7 | Chinaganjam | | 7 | Kondepi |
| 8 | Tripurantakam | | 8 | Parchur | | 8 | Lingasamudram |
| 9 | Pullalacheruvu | | 9 | Inkollu | | | |
| 10 | Racherla | | 10 | Ponnalur | | | |
| | | | 11 | Kanigiri | | | |
| | | | 12 | H.M.Padu | | | |
| | | | 13 | P.C.Palli | | | |
| | | | 14 | Konakanamitla | | | |
| | | | 15 | Marripudi | | | |
| | | | 16 | Darsi | | | |
| | | | 17 | Tallur | | | |
| | | | 18 | Mundlamur | | | |
| | | | 19 | Kurichedu | | | |
| | | | 20 | Dornala | | | |

## GROUND WATER LEVELS

The Ground water levels in the district depend up on the rainfall and Ground water exploitation. The water levels are being monitored through 56 Piezometer bore wells and 150 Observation open wells.

The monthly average water levels of the district from the month of October, 2010 to October, 2011 is

| Water levels | | | Remarks |
|---|---|---|---|
| October, 2010 in Mts | October, 2011 in Mts | Fluctuations in Mts | |
| 6.00 | 9.37 | -3.38 | Fall in water levels |

The maximum water level is 42.0 m at Pullalacheruvu (V) & (M) which falls in Non-command and up land area. The minimum water level is 0.80 M at Parchur (V) & (M) which falls in command and coastal plain.

The net fall of ground water levels in the upland mandals is 4 to 17 m. The maximum water level at Tarlupadu mandal is 36.14 m during the month of October, 2011 and the minimum water level at Tripuranthakam mandal is 5.11 m.

The depletion of Ground water levels in the district is attributed to -26% of deficit rainfall during the water year 2011-12.

If the same weather conditions continuous, there is chance for further depletion of Ground water levels and leads to acute shortage of ground water for both drinking and irrigation purpose.

As per the GEC -2007 estimation out of 62 minor basins in the district, 06 basins fall in Over exploited category, 02 basins falls in Critical category, 07 in Semi critical category and remaining 47 basins falls in safe category.

As per AP WALTA 121 villages in the district are declared as over exploited villages where further ground water exploitation for irrigation is banned until the ground water conditions improves.

**RURAL WATER SUPPLY**

**Status of Habitations**

| | | |
|---|---|---|
| NSS | : | 235 |
| NC | : | 0 |
| PC1 (Up to 10 LPCD) | : | 282 |
| PC2 (10 to 20 LPCD) | : | 423 |
| PC3 (20 to 30 LPCD) | : | 376 |
| PC4 (30 to 40 LPCD) | : | 315 |
| FC (Above 40 LPCD) | : | 711 |
| Total | : | 2342 |

**Projects as on 18.11.2011**

| | | |
|---|---|---|
| No. of ongoing works | : | 16 |
| Habs to be covered | : | 805 |
| Population to be covered (in lakhs) | : | 7.74 |
| Estimated Cost (Rs. In Crores) | : | 240.40 |
| Expenditure incurred (Rs. In Crores) | : | 128.69 |

## 2.6ASSESSMENT OF ELIGIBILITY OF MANDALS FOR DECLARATION UNDER DROUGHT:

56 mandals are existing in the district are divided into three categories depending upon the annual average rainfall usually received.

**Category –A**: Annual Normal rainfall below 750 mm
(deficiency 15% and above)

**Category –B**: Annual Normal rainfall from 750 to 1000 mm
(deficiency 20% & above)

**Category –C**: Annual Normal rainfall above 1000 mm
(deficiency 25% and above)

The following four parameters have been prescribed for assessing the eligibility of a Mandal for declaration under drought affected Mandals.

1. 1st Parameter : Deficiency in rainfall(compulsory parameter)
2. 2nd Parameter : Compression or reduction in cropped area of 50% and above under all principal crops
3. 3rd Parameter : Reduction in crop yields of 50% and above.
4. 4th Parameter : Dry spells its impact on crop damages

Of the above 4 Parameters, 3 Parameters including rainfall parameter must be justified for a Mandal to become eligible for declaration of drought. Based on the above parameters, the Mandals eligible and ineligible for proposing them as drought Mandals in all three categories (Rainfall categories) are furnished in the annexure for kind perusal.

| | **sno.** | **MANDAL** | Cate-gory | **Parameter-I** | **Parameter-II** | **Parameter-III** | **Parameter-IV** | **Identified as Drought affected Mandal for Declaration** |
|---|---|---|---|---|---|---|---|---|
| | | | | **Deficiency in rainfall (compulsory parameter)** | **Compression or reduction in cropped area of 50% and above under all principal crops** | **Reduction in crop yields of 50% and above.** | **Dry spells its impact on crop damages** | |
| | 1 | ONGOLE(s17) | C | **Eligible** | **Eligible** | **Eligible** | | **Eligible** |
| | 2 | TANGUTUR | C | | **Eligible** | **Eligible** | | |
| | 3 | KOTHAPATNAM(s01) | C | **Eligible** | **Eligible** | **Eligible** | **Eligible** | **Eligible** |
| | 4 | N.G.PADU | B | | **Eligible** | **Eligible** | **Eligible** | |
| | 5 | CHIMAKURTHY(s16) | B | **Eligible** | **Eligible** | **Eligible** | **Eligible** | **Eligible** |
| | 6 | MADDIPAD | B | | **Eligible** | **Eligible** | **Eligible** | |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | U | | | | | | |
| | 7 | S.N.PADU(s02) | C | **Eligible** | **Eligible** | **Eligible** | **Eligible** | **Eligible** |
| | 8 | ADDANKI | B | **Eligible** | | **Eligible** | **Eligible** | **Eligible** |
| | 9 | KORISAPADU(s15) | B | **Eligible** | **Eligible** | **Eligible** | **Eligible** | **Eligible** |
| | 10 | J.PANGALUR(s14) | B | **Eligible** | **Eligible** | **Eligible** | **Eligible** | **Eligible** |
| | 11 | BALLIKURAVA | B | | **Eligible** | **Eligible** | | |
| | 12 | S.MAGULUR | A | **Eligible** | | **Eligible** | **Eligible** | **Eligible** |
| | 13 | MARTUR | B | | **Eligible** | **Eligible** | | |
| | 14 | YADDANAPUDI(s13) | B | **Eligible** | **Eligible** | **Eligible** | | **Eligible** |
| | 15 | CHIRALA | C | | **Eligible** | **Eligible** | **Eligible** | |
| | 16 | VETAPALEM | B | **Eligible** | **Eligible** | **Eligible** | | **Eligible** |
| | 17 | CHINAGANJAM(s12) | B | **Eligible** | | **Eligible** | **Eligible** | **Eligible** |
| | 18 | PARCHUR | B | | **Eligible** | **Eligible** | | |
| | 19 | INKOLLU | B | **Eligible** | **Eligible** | **Eligible** | **Eligible** | **Eligible** |
| | 20 | KARAMCHEDU | B | | **Eligible** | **Eligible** | | |
| | 21 | KANDUKUr | C | **Eligible** | **Eligible** | **Eligible** | | **Eligible** |
| | 22 | GUDLUR(s3) | C | **Eligible** | **Eligible** | **Eligible** | | **Eligible** |
| | 23 | V.V.PALEM(s04) | C | **Eligible** | **Eligible** | **Eligible** | **Eligible** | **Eligible** |
| | 24 | PONNALUR | B | **Eligible** | **Eligible** | **Eligible** | **Eligible** | **Eligible** |
| | 25 | KONDEP(s08) | C | **Eligible** | | **Eligible** | **Eligible** | **Eligible** |
| | 26 | ZARUGUMALLI(s09) | C | | **Eligible** | **Eligible** | | |
| | 27 | S.KONDA(s10) | C | | **Eligible** | **Eligible** | | |
| | 28 | ULAVAPADU | B | | **Eligible** | **Eligible** | | |
| | 29 | LINGASAMUDRAM(s07) | C | **Eligible** | **Eligible** | **Eligible** | **Eligible** | **Eligible** |
| | 30 | KANIGIRI | B | **Eligible** | | **Eligible** | **Eligible** | **Eligible** |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 31 | H.M.PADU | B | **Eligible** | **Eligible** | **Eligible** | **Eligible** | **Eligible** |
| | 32 | PAMUR | A | **Eligible** | **Eligible** | **Eligible** | **Eligible** | **Eligible** |
| | 33 | VELIGANDLA | B | | | **Eligible** | **Eligible** | |
| | 34 | C.S.PURAM | B | | **Eligible** | **Eligible** | | |
| | 35 | P.C.PALLI | B | **Eligible** | | **Eligible** | **Eligible** | **Eligible** |
| | 36 | PODILI | B | | | **Eligible** | **Eligible** | |
| | 37 | K.K.MITLA | B | **Eligible** | **Eligible** | **Eligible** | **Eligible** | **Eligible** |
| | 38 | MARRIPUDI | B | **Eligible** | | **Eligible** | **Eligible** | **Eligible** |
| | 39 | DARSI | B | **Eligible** | | **Eligible** | **Eligible** | **Eligible** |
| | 40 | TALLUR | B | **Eligible** | | **Eligible** | **Eligible** | **Eligible** |
| | 41 | MUNDLAMUR | B | **Eligible** | | **Eligible** | **Eligible** | **Eligible** |
| | 42 | DONAKONDA | A | **Eligible** | | **Eligible** | **Eligible** | **Eligible** |
| | 43 | KURICHEDU | B | **Eligible** | | **Eligible** | **Eligible** | **Eligible** |
| | 44 | TARLUPADU | A | **Eligible** | | **Eligible** | **Eligible** | **Eligible** |
| | 45 | MARKAPUR | A | **Eligible** | | **Eligible** | **Eligible** | **Eligible** |
| | 46 | DORNALA | B | **Eligible** | **Eligible** | **Eligible** | **Eligible** | **Eligible** |
| | 47 | PEDARAVEEDU | A | **Eligible** | | **Eligible** | **Eligible** | **Eligible** |
| | 48 | Y.PALEM | A | **Eligible** | | **Eligible** | **Eligible** | **Eligible** |
| | 49 | TRIPURANTHAKAM | A | **Eligible** | | **Eligible** | **Eligible** | **Eligible** |
| | 50 | PULLALACHERUVU | A | **Eligible** | | **Eligible** | **Eligible** | **Eligible** |
| | 51 | GIDDALUR | A | | **Eligible** | **Eligible** | | |
| | 52 | RACHERLA | A | **Eligible** | | **Eligible** | | |
| | 53 | KOMAROLE | A | | **Eligible** | **Eligible** | | |
| | 54 | B.PETA | B | | **Eligible** | **Eligible** | | |
| | 55 | CUMBUM | A | | | **Eligible** | **Eligible** | |
| | 56 | ARDHAVEEDU | A | | **Eligible** | **Eligible** | | |
| | **Total** | | **37** | **34** | **56** | **37** | **36** | |

## 3. METHODOLOGY

### 3.1 DISTRIBUTIONS

Three distributions are used in the fitting of the drought distribution. The first is exponential distribution that is known as a class of continuous probability distributions in probability theory and statistics with the following probability density function (pdf) and cumulative distribution function (cdf):

$$f(x) = \lambda e^{-\lambda x},\ x \geq 0,\ \lambda \geq 0 \qquad (1)$$

where $\lambda$ is the rate parameter of the distribution .$F(x)= 1- e^{-\lambda x}$ (2)

Next is gamma distribution that is known as a two-parameter family of continuous probability distributions in probability theory and statistics with the following probability density function (pdf) and cumulative distribution function (cdf):

$f(x)= \frac{e^{-x} x^{\lambda-1}}{\Gamma(\lambda)}$, $x \geq 0, \lambda > 0$. where $\Gamma(\lambda) = \int_0^{\infty} e^{-x} x^{\lambda-1}$ . (3)

The p.d.f. of gamma distribution with two parameters

$f(x)= \frac{a^{\lambda}}{\Gamma(\lambda)} e^{-ax} x^{\lambda-1}$, $x \geq 0, \lambda > 0$. (4)

Finally, weibull distribution that is known a continuous probability distribution in probability theory and statistics with the following probability density function (pdf) :

$$f(x;c,\alpha,\mu) = \frac{c}{\alpha}\left(\frac{x-\mu}{\alpha}\right)^{c-1} \exp\text{-}\left(\frac{x-\mu}{\alpha}\right)^{c-1} ;\ x>\mu, c>0. \qquad (5)$$

A drought threshold is an essential element in categorizing the drought events in drought analysis. Drought threshold is a constant demand where the droughts are defined as periods during which the discharge is below the threshold level. A threshold that applied commonly in monitoring rainfall and preparing drought alerts is at the seventieth percentile of the rainfall when the rainfall in a certain period is less than seventy percent of normal Precipitation.(Precipitation means the quantity of water falling to earth at a specific place with in specific period

of time)

In determining the threshold values, the data of rainfall amount are sorted in ascending order where the value at the seventy percent of the rainfall data is recognized as the seventieth percentile of the rainfall series, p70 which is then set as the threshold.

$$L = (PN)/100 \qquad (12)$$

where L is the number of measurements under the seventieth percentile, P=70 as the selected percentile and N is the total number of measurements in the data set. Therefore, the threshold is the $L^{th}$ value of amount of rainfall.

## 3.2 MAXIMUM LIKELIHOOD ESTIMATION

Maximum likelihood estimation (MLE) is a general and popular statistical method in fitting a statistical model to data and estimating the parameters of the corresponding model that maximize the probability or likelihood of the sample data.

Suppose $x$ is a continuous random variable with pdf $f(x;\theta_1,\theta_2,...,\theta_k)$ where $\theta_1,\theta_2,...,\theta_k$ are k unknown constant parameters which need to be estimated with an experiment conducted to obtain N independent observations, $x_1, x_2, ..., x_N$,

the estimation of parameters, $\hat{\theta}_1,\hat{\theta}_2,...,\hat{\theta}_k$ can be obtained by solving the differentiation of logarithmic likelihood function below:

$$\frac{d\sum_{i=1}^{N}\ln f(x_i;\theta_1,\theta_2,...,\theta_k)}{d\theta_j} = 0 \qquad (13)$$

where $j = 1,2,..., k$.

## 3.3 GOODNESS-OF-FIT TESTS

It is commonly applicable to verify the compatibility of a model and data by the statistical goodness-of-fit (GOF) tests. The GOF tests are applied in describing the fitness of a distribution to a set of observations. Measures of GOF typically summarize the discrepancy between observed values with the expected values under the specific

model selected.

The best fitted distribution will be determined based on the minimum error produced, which is measured by the techniques shown below:

(1) Akaike Information Criterion (AIC) is a method used for measuring the goodness-of-fit of an estimated statistical model that ranked based on the minimum error produced.

The formula of AIC is shown below:

$$AIC = 2k - 2\ln L \qquad (14)$$

where $k$ is the number of parameters in the statistical model, and $L$ is the maximized value of the likelihood function for the estimated model.

(2) Kolmogorov-Smirnov (KS) test is a form of minimum distance estimation that quantifies a distance between the empirical distribution function of the sample and the cumulative distribution function of the reference distribution.

The KS test statistic is defined as:

$$D = \max_{1 \le i \le N} \left( \left| F(x_i) - \frac{i-1}{N} \right|, \left| \frac{i}{N} - F(x_i) \right| \right)$$

where $x_i$ is the increasing ordered data, $F$ the theoretical distribution and $N$ is the number of sample size.

## 3.4. RESULTS AND DISCUSSION

### 3.4.1 Descriptive Statistics

The descriptive statistics computed are mean, variance, standard deviation, coefficient of variation, skewness, kurtosis and the maximum rainfall amount for each station. The summary of the descriptive statistics for each station is shown in Table 2.

**Table 2.** The descriptive statistics of the daily rainfall amount in prakasam

| Stations | Mean | Variance | Standard Deviation | Coefficient Variation | Skewness | Kurtosis | Maximum Amount |
|---|---|---|---|---|---|---|---|
| S01 | 7.0471 | 152.91 | 12.3660 | 1.7547 | 3.4581 | 21.560 | 137.5 |
| S02 | 5.8803 | 107.68 | 10.3770 | 1.7647 | 3.4151 | 25.040 | 152.0 |
| S03 | 6.1321 | 185.04 | 13.6030 | 2.2183 | 6.3572 | 73.591 | 234.8 |
| S04 | 6.5637 | 161.12 | 12.6930 | 1.9339 | 4.9975 | 45.891 | 188.0 |
| S05 | 6.8607 | 208.08 | 14.4250 | 2.1026 | 6.8322 | 85.481 | 261.0 |
| S06 | 5.6709 | 243.81 | 15.6140 | 2.7534 | 9.2645 | 157.100 | 398.0 |
| S07 | 5.5118 | 183.20 | 13.5350 | 2.4557 | 4.8424 | 38.444 | 189.5 |
| S08 | 5.4471 | 175.09 | 13.2320 | 2.4293 | 5.2733 | 50.828 | 227.0 |
| S09 | 7.1123 | 179.95 | 13.4140 | 1.8861 | 4.1730 | 32.092 | 172.0 |
| S10 | 4.5302 | 69.67 | 8.3469 | 1.8425 | 3.8164 | 24.391 | 87.8 |
| S11 | 7.0900 | 171.11 | 13.0810 | 1.8450 | 4.8445 | 43.850 | 183.7 |
| S12 | 5.4008 | 156.12 | 12.4950 | 2.3135 | 4.7372 | 40.403 | 196.0 |
| S13 | 5.5472 | 90.42 | 9.5091 | 1.7142 | 4.8446 | 64.779 | 204.7 |
| S14 | 6.8804 | 199.74 | 14.1330 | 2.0541 | 6.1923 | 80.647 | 298.0 |
| S15 | 6.0165 | 108.57 | 10.4200 | 1.7319 | 4.4725 | 45.706 | 193.3 |
| S16 | 5.9719 | 136.67 | 11.6910 | 1.9576 | 7.5171 | 143.760 | 311.0 |
| S17 | 5.4816 | 108.69 | 10.4250 | 1.9019 | 4.9849 | 55.252 | 205.3 |

From the summary, the mean or average of precipitation amount during the ten years period for all the stations lies between 4.50 mm per day and 7.20 mm per day with the highest mean value of 7.11 mm per day from S09 while the lowest mean of 4.53 mm per day from S10.

The variance for all the daily rain gauge stations is in the range of 69.60 $mm^2$ per $day^2$ to 243.90 $mm^2$ per $day^2$. The standard deviation for all the seventeen stations is ranged from 8.30 mm per day to 15.70 mm per day. S06 obtains the highest standard deviation with the value of 15.61 mm per day which indicates the large variation in the daily rainfall amount series while S10 receives the lowest standard deviation with the value of 8.35 mm per day which implies the small variation in the daily rainfall amount series. Furthermore, it is clear that the standard deviation for each station is always larger than the mean by referring to the fact that there are some effects caused by the extreme value to the large values in the raw data.

The coefficient of variations for the seventeen rain gauge stations will represent the irregularity of the daily precipitation between stations. However, the results of the coefficient of variation show that the values for each station are quite homogeneous where the range is between 1.70 and 2.80. S06 displays the highest value of coefficient of variation, which is 2.75 while S13 has the smallest value of coefficient of variation, which is 1.71.

The coefficient of skewness is used to verify the degree of asymmetric of a distribution around the mean. The values of skewness lie in between 3.40 and 9.30 where these positively results indicate that all the skewness are positively skewed for all stations. S06 receives the highest value of skewness with the value 9.26 which gives a clear indication that this station is very obviously skewed and the asymmetric tail is extending to the right while S02 with the smallest skewnes value of 3.42 indicates that the asymmetric tail is also extending to the right with less skewed.

The value of kurtosis can be used to determine the relative peakness or flatness of a distribution. The values of kurtosis are all positive in the range of 21.50 to 157.10. S06 obtains the highest value of kurtosis with the value 157.10 which implies the possibility of a leptokurtic distribution where the data set tend to have a distinct peak near to the mean with a heavy tail since the peak of distribution is too high around the mean. S01 receives the smallest value of kurtosis with the value 21.56 which indicates that the data set tend to have a flat peak near to the mean.

The maximum daily rainfall amount is ranged between 87.80 mm per day and 398.00 mm per day where S06 receives the highest maximum rainfall amount of 398.00 mm per day followed by S16 with the maximum rainfall amount of 311.00 mm per day. S10 on the other hand obtains the lowest maximum rainfall amount which is 87.80 mm per day.

### 3.4.2 Threshold

In finding the best fitted distribution to represent the drought events, it is essential to determine a threshold where the data fall below the corresponding threshold is categorized as drought and these data are used in the fitting of distribution. The threshold values for all the stations are shown in Table 3.

**Table 3.** The threshold values for each station

| Station | Threshold |
|---|---|
| S01 | 13.2 |
| S02 | 14.3 |
| S03 | 16.3 |
| S04 | 12.0 |
| S05 | 13.0 |
| S06 | 9.8 |
| S07 | 11.5 |
| S08 | 13.0 |
| S09 | 14.7 |
| S10 | 7.3 |
| S11 | 9.8 |
| S12 | 11.0 |
| S13 | 10.5 |
| S14 | 14.0 |
| S15 | 10.8 |
| S16 | 12.0 |
| S17 | 10.0 |

### 3.4.3 Goodness-of-Fit Tests

The best fitted distribution can be verified using Goodness-of-Fit (GOF) tests. In this study, three types of GOF tests were applied, namely Akaike Information Criterion (AIC), Kolmogorov-Smirnov (KS) test and Cramer-von-Mises (CVM). By referring to the definition of Goodness-of-Fit (GOF) tests, the best fitted distribution was selected based on the minimum error produced. The results of the GOF tests were shown in Table 4.

**Table 4.** The results of three GOF tests for daily rainfall amount in Prakasam.

| Station | AIC | | | KS | | |
|---|---|---|---|---|---|---|
| | EXP | GAM | WBL | EXP | GAM | WBL |
| S01 | 7960.2 | 7884.9 | 7859.2 | 0.07787 | 0.06198 | 0.05949 |
| S02 | 6895.3 | 6411.9 | 6353.4 | 0.19120 | 0.07673 | 0.07603 |
| S03 | 6477.0 | 6389.8 | 6355.3 | 0.09439 | 0.07187 | 0.06349 |
| S04 | 7655.7 | 7570.2 | 7550.1 | 0.07674 | 0.06658 | 0.06832 |
| S05 | 7548.7 | 7498.4 | 7471.9 | 0.07848 | 0.06515 | 0.06265 |
| S06 | 5733.3 | 5735.1 | 5734.9 | 0.11033 | 0.10661 | 0.10598 |
| S07 | 5419.0 | 5414.8 | 5416.1 | 0.07817 | 0.09110 | 0.08949 |
| S08 | 5590.2 | 5591.9 | 5592.2 | 0.10569 | 0.11010 | 0.10725 |
| S09 | 7684.6 | 7542.8 | 7511.3 | 0.25071 | 0.07525 | 0.06324 |
| S10 | 6491.4 | 6393.1 | 6362.7 | 0.09052 | 0.06713 | 0.06175 |
| S11 | 5849.8 | 5565.0 | 5501.9 | 0.16040 | 0.08455 | 0.06363 |
| S12 | 5629.6 | 5605.9 | 5612.3 | 0.11063 | 0.11242 | 0.10793 |
| S13 | 7421.7 | 7321.2 | 7292.6 | 0.08733 | 0.06568 | 0.06322 |
| S14 | 7435.5 | 7266.1 | 7244.3 | 0.09930 | 0.07411 | 0.07240 |
| S15 | 7711.2 | 7579.6 | 7523.6 | 0.11636 | 0.07236 | 0.06430 |
| S16 | 7276.2 | 7077.7 | 7030.3 | 0.12547 | 0.07248 | 0.06557 |
| S17 | 7055.0 | 6946.9 | 6918.2 | 0.09789 | 0.07122 | 0.06884 |

Table 4 shows the results of the three GOF tests for daily rainfall amount in Prakasam. The best fitted distribution is selected according to the minimum error produced.

From the results displayed above, many stations have resulted in weibull distribution to be the best fitted distribution to represent the drought event. Further, by using either the AIC, KS , it is found that weibull is still the distribution having the most minimum error .Therefore, weibull distribution is ranked first as the best fitted distribution in representing the drought events in Prakasam while gamma distribution is ranked second and exponential distribution is ranked last using all the results of GOF tests for each rain gauge station. Hence,

weibull distribution is the most appropriate distribution to represent the drought event in Prakasam.

## 3.5. CONCLUSIONS

The fitting of the most appropriate distribution to characterize the drought events starts with measuring the threshold value applied at the seventieth percentile. The data which fall below the threshold values is then used in the fitting distribution and weibull distribution has been found to be the best fitted distribution for the representation of the daily drought event in Prakasam District. However, gamma distribution is ranked second while exponential distribution is ranked last in the fitting of drought event in Prakasam District. Weibull is just like Gamma distribution is a two-parameters distribution. Clearly these two distributions outperform the exponential distribution that is a one-parameter distribution.

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# ON MINIMAX MULTI OBJECTIVE FRACTIONAL OPTIMALITY CONDITIONS WITH CONVEXITY

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***ABSTRACT***

***Under different forms of convexity conditions, sufficient Kuhn] Tucker conditions and three dual models are presented for the minimax fractional programming.***

## 1. INTRODUCTION

The necessary and sufficient conditions for generalized minimax pro-gramming were first developed by Schmitendorf [16]. Convexity assumptions in the sufficient optimality of [16] and also employed the optimality conditions to construct several dual problems which involve pseudo convex and quasiconvex functions, and they also derived weak and strong duality theorems.

Recently, Hanson [7] introduced the concept of a differentiable invex function which is a generalization of the convex function, and he proved the Kuhn Tucker sufficient optimality theorem and the duality theorem for the nonlinear programming problem involving differentiable invex functions. In this paper, Some definitions and notations are given in section 2.In section 2, We also establish the sufficient conditions for the minimax multi objective fractional programming problem with pseudo convexity. When the sufficient conditions are utilized, one parametric dual problem and two parametric-free dual problems may be formulated and duality results are presented in section 3,4and5

## 2. NOTATIONS AND PRELIMINARY RESULTS

Throughout, this paper, let $R^n$ be the *n*-dimensional Euclidean space and $R_q^n$ be its non-negative orthant. We now consider the following minimax fractional problem

$$\text{(FP) Minimize } F(x) = \sup_{y \in Y} \frac{f_i(x,y)}{h_i(x,y)}$$

$$\text{subject to } g_j(x) \le 0$$

Where

(a) Y is a component subset of $R^m$,

(b) $f_i(.,.) : R^n \times R^m \to R$ is a differentiable function with $f_i(x,y) \ge 0$,

(c) $h_i(.,.): R^n \times R^m \to R$ is a differentiable function with $h_i(x,y) > 0$,

(d) $g_j(.): R^n \to R^p$ is a differentiable function.

We let

$$J = \{1,2,..,p\}$$

$$J(x) = \{ j \in J \mid g_j(x) = 0\}$$

$$Y(x) = \left\{ y \in Y \middle| \frac{f_i(x,y)}{h_i(x,y)} = \sup_{Z \in Y} \frac{f_i(x,y)}{h_i(x,y)} \right\}$$

$$K = \left\{ (s,t,\bar{y}) \in N \times R_+^s \times R^{ms} \middle| 1 \le s \le n+1, t = (t_1,\ldots,t_s) \in R_+^s \right.$$

with $\sum_{i=1}^{s} t_i = 1$ and $\bar{y} = (y_1,\ldots, y_s)$ with $y_i \in Y(x), i = 1,\ldots, s \left. \right\}$.

In [5], Chandra and Kumar derived the following necessary conditions for optimality of (P):

THEROM 2.1 (Necessary Conditions)[5]. Let $x^*$ be a (P)-optimal solution and $\nabla g_j(x^*)$, $j \in J(x^*)$ be linearly independent. Then there exist $(s^*, t^*, \bar{y}) \in K, v^* \in R,$ and $\mu^* \in R_+^p$ such that

$$\sum_{i=1}^{s^*} t_i^* \{\nabla f_i(x^*, y_i) - v^* \nabla h_i(x^*, y_i)\} + \nabla \sum_{j=1}^{p} \mu_j^* g_j(x^*) = 0, \qquad (2)$$

$$f_i(x^*, y_i) - v^* h_i(x^*, y_i) = 0, i = 1,\ldots, s, \qquad (3)$$

$$\sum_{j=1}^{p} \mu_j^* g_j(x^*) = 0, \qquad (4)$$

$$\mu^* \in R_+^p, t_i^* \geq 0, \sum_{i=1}^{s^*} t_i^* = 1, y_i \in Y(x^*), i = 1,..., s^*. \quad (5)$$

In order the relax the convexity assumption in Theorem 2.1, we impose the following generalized convexity introduced by Hanson [7]:

Definition 2. 1. Let $\phi: X \to R$ (where $X \subseteq R^n$) be a differential function

(a) The function $\phi$ is said to be convex at $x_0$ if there exists for all $x \in X$,

$$\phi(x) - \phi(x_0) \geq (x - x_0)^T \nabla \phi(x_0).$$

Further, $\phi$ is said to be strictly convex at $x_0$ if there exists for all $x \in X$, $x \neq x_0$,

$$\phi(x) - \phi(x_0) > (x - x_0)^T \nabla \phi(x_0).$$

(b) The function $\phi$ is said to be pseudo convex at $x_0$ if there exists for all $x \in X$,

$$(x - x_0)^T \nabla \phi(x_0) \geq 0 \Rightarrow \phi(x) \geq \phi(x_0)$$

or equivalently

$$\phi(x) < \phi(x_0) \Rightarrow (x - x_0)^T \nabla \phi(x_0) < 0.$$

Further, $\phi$ is said to be strictly pseudo convex at $x_0$ if there exists for all $x \in X$, $x \neq x_0$,

$$(x - x_0)^T \nabla \phi(x_0) \geq 0 \Rightarrow \phi(x) > \phi(x_0)$$

Or equivalently

$$\phi(x) \leq \phi(x_0) \Rightarrow (x - x_0)^T \nabla \phi(x_0) < 0.$$

(c) The function $\phi$ is said to be quasi convex at $x_0$ if there exists for all $x \in X$,

$$\phi(x) \leq \phi(x_0) \Rightarrow (x - x_0)^T \nabla \phi(x_0) \leq 0.$$

Theorem 2.2 (Sufficient conditions).

Assume that $(x^*, \mu^*, v^*, s^*, t^*, \bar{y})$ satisfy relations (2)-(5). If

$\sum_{i=1}^{s} t_i^* (f_i(., y_i) - v^* h_i(., y_i))$ is a pseudo-convex function at $x^*$, then $x^*$ is an optimal solution of (P).

Proof: Let $x$ be any feasible solution of (P). From (1) and (4), we have

$$\sum_{j=1}^{p} \mu_j^* g_j(x) \le 0 = \sum_{j=1}^{p} \mu_j^* g_j(x^*).$$

Using the quasi-convexity of $\sum_{j=1}^{p} \mu_j^* g_j(.) = 0$ at $x^*$, we have

$$(x - x^*)^T \nabla \sum_{j=1}^{p} \mu_j^* g_j(x^*) \le 0. \qquad (6)$$

Relation (2) along with (6) yields

$$(x - x^*)^T \nabla \sum_{i=1}^{s^*} t_i^* (f_i(x^*, y_i) - v^* h_i(x^*, y_i)) \ge 0. \qquad (7)$$

Along with the facts that $\sum_{i=1}^{s^*} t_i^* (f_i(., y_i) - v^* h_i(., y_i))$ is a pseudo-convex at $x^*$,

we get from (7) and (3)

$$0 = \sum_{i=1}^{s^*} t_i^* (f_i(x^*, y_i) - v^* h_i(x^*, y_i)) \le \sum_{i=1}^{s^*} t_i^* (f_i(x, y_i) - v^* h_i(x, y_i)) .$$

Therefore , there exists a certain $i_0$ ,such that

$$0 \le f_i(x, y_{i_0}) - v^* h_i(x, y_{i_0}) .$$

It follows that

$$\sup_{y\in Y}\frac{f_i(x,y)}{h_i(x,y)} \geq \frac{f_i(x,y_{i_0})}{h_i(x,y_{i_0})} \geq v^* = \sup_{y\in Y}\frac{f_i(x^*,y)}{h_i(x^*,y)}.$$

Thus the proof of theorem is complete.

Remark 2.1. In theorem 2.2, If $\sum_{i=1}^{s^*} t_i^* ( f_i(.\ , y_i) - v^* h_i(., y_i))$ is a quasi-convex function at $x^*$ and $\sum_{j=1}^{p} \mu_j^* g_j(.)$ is a strictly pseudo-convex function at $x^*$, then the Theorem 2.2 also holds.

## 3. DUALITY MODEL

Making the use of the optimality conditions of the preceding section, we introduce a dual (DI) to the minimax problem (P) as follows:

(DI) $\max_{(s,t,\bar{y})\in} \sup_{(z,\mu,v)\in H_1(s,t,\bar{y})} v$, where $H_1(s,t,\bar{y})$ denotes the set of all triplets $(z,\ \mu, v) \in R^n \times R_+^p \times R_+$ satisfying

$$\sum_{i=1}^{s} t_i \{\nabla f_i(z\ , y_i) - v\ \nabla h_i(z, y_i)\} + \nabla \sum_{j=1}^{p} \mu_j g_j(z) = 0, \tag{8}$$

$$\sum_{i=1}^{s} t_i\ (f_i(z\ , y_i) - v\ h_i(z, y_i)) \geq 0, \tag{9}$$

$$\sum_{j=1}^{p} \mu_j g_j(z) \geq 0, \tag{10}$$

$$(s,t,\bar{y}) \in K.$$

If for a triplet $(s,t,\bar{y}) \in K$ the set $H_1(s,t,\bar{y})$ is empty, then we define the supremum over it to be $-\infty$.

THEOREM 3.1 (Weak Duality). Let $x$ and $(z,\mu,v,s,t,\bar{y})$ be (P)-feasible and be (DI)-feasible, respectively, and assume that $\sum_{i=1}^{s} t_i\ (f_i(.\ , y_i) - v\ h_i(., y_i))$ is a pseudo-convex function at $z$, and $\sum_{j=1}^{p} \mu_j g_j(.)$ is a quasi-convex function at $z$. Then $\sup_{y\in Y}(f_i(x,y)/h_i(x,y)) \geq v$.

Proof: By both the feasibility of $x$ and (10), we have

$$\sum_{j=1}^{p}\mu_j g_j(x) \le 0 \le \sum_{j=1}^{p}\mu_j g_j(z).$$

Using the quasi-convex of $\sum_{j=1}^{p}\mu_j g_j(.)$ at $z$, we have

$$(x-z)^T \nabla \sum_{j=1}^{p}\mu_j g_j(z) \le 0. \qquad (11)$$

consequently, (8) and (11) yield

$$(x-z)^T \nabla \sum_{i=1}^{s} t_i (f_i(z\ ,y_i) - v\ h_i(z,y_i)) \ge 0. \qquad \textbf{(12)}$$

**On account of pseudo-convexity of** $\sum_{i=1}^{s} t_i (f_i(.,y_i) - v\ h_i(.,y_i))$ at $z$, we get from (12) and (9)

$$0 \le \sum_{i=1}^{s} t_i (f_i(z\ ,y_i) - v\ h_i(z,y_i)) \le \sum_{i=1}^{s} t_i (f_i(x,y_i) - v\ h_i(x,y_i)).$$

**Therefore, there exists a certain** $i_0$ **, such that**

$$0 \le f_i(x,y_{i_0}) - v\ h_i(x,y_{i_0}).$$

It follows that

$$\sup_{y\in Y}\frac{f_i(x,y)}{h_i(x,y)} \ge \frac{f_i(x,y_{i_0})}{h_i(x,y_{i_0})} \ge v.$$

**Thus, the proof of the theorem is complete.**

**Remark 3.1. In Theorem 3.1, if** $\sum_{i=1}^{s} t_i (f_i(.,y_i) - v\ h_i(.,y_i))$ **is a quasi-convex function at** $z$ and $\sum_{j=1}^{p}\mu_j g_j(.)$ is a strictly pseudo-convex function at $z$, then Theorem 3.1 also holds.

**THEOREM 3.2 (Strong Duality). Assume that** $x^*$ is a (P)-optimal solution and $\nabla g_i(x)$, $j \in J(x^*)$ **is linearly independent. If in addition the hypothesis of Theorem 3.1 holds for all (DI)-feasible points** $(z,\mu,v,s,t,\bar{y})$, **then the two problems (P) and (DI) have the same external values.**

**Proof: By theorem 2.1 there exists** $(s^*, t^*, \bar{y}) \in K, (x^*, \mu^*, v^*) \in H_1(s^*, t^*, \bar{y})$ **such that** $(x^*, \mu^*, v^*, s^*, t^*, \bar{y})$ is a (DI)-optimal solution.

Since $v^* = f_i(x^*, y_i)/h_i(x^*, y_i)$, optimality of this feasible solution for (DI) follows from Theorem 3.1.

**THEOREM 3.3 (Strict Converse Duality). Let** $\bar{x}$ **and** $(z, \mu, v, s, t, \bar{y})$ be optimal solutions of (P) and (DI), respectively, and assume that $\sum_{i=1}^{s} t_i (f_i(.,y_i) - v\ h_i(.,y_i))$**is a pseudo-convex function at** $z$ for all $(s,t,\bar{y}) \in K, (x,\mu,v) \in H_1(s,t,\bar{y}), \sum_{j=1}^{p} \mu_j g_j(.)$ **is a quasi-convex function at** $z$ and, $\nabla g_i(\bar{x}), j \in J(\bar{x})$ **is linearly independent. Then** $\bar{x} = z$**; that is,** $z$ is a (P)-optimal solution and $\sup_{y \in Y}(f_i(z,y)/h_i(z,y)) = v$.

Proof: We shall assume that $\bar{x} \neq z$ and reach a contradiction. From Theorem 3.2 we know that

$$\sup_{y \in Y} \frac{f_i(\bar{x}, y)}{h_i(\bar{x}, y)} = v. \qquad (13)$$

By both the feasibility of $\bar{x}$ and (10), we have

$$\sum_{j=1}^{p} \mu_j g_j(\bar{x}) \leq 0 \leq \sum_{j=1}^{p} \mu_j g_j(z).$$

Using the quasi-convex of $\sum_{j=1}^{p} \mu_j g_j(.)$,we get from the inequality above

$$(\bar{x} - z)^T \nabla \sum_{j=1}^{p} \mu_j g_j(z) \leq 0. \qquad \textbf{(14)}$$

**Consequently, (8) and (14) yield**

$$(\bar{x} - z)^T \nabla \sum_{i=1}^{s} t_i (f_i(z\ , y_i) - v\ h_i(z, y_i)) \geq 0. \qquad (15)$$

On account of **strict pseudo-convexity of** $\sum_{i=1}^{s} t_i (f_i(.,y_i) - v\ h_i(.,y_i))$**at** $z$, we get

From (15) and (9)

$$0 \le \sum_{i=1}^{s} t_i \, (f_i(z\ , y_i) - v\ h_i(z, y_i)) < \sum_{i=1}^{s} t_i \, (f_i(x, y_i) - v\ h_i(x, y_i)).$$

Therefore, there exists a certain $i_0$ **, such that**

$$0 < f_i(x, y_{i_0}) - v\ h_i(x, y_{i_0}).$$

It follows that

$$\sup_{y \in Y} \frac{f_i(x, y)}{h_i(x, y)} \ge \frac{f_i(x, y_{i_0})}{h_i(x, y_{i_0})} > v = \sup_{y \in Y} \frac{f_i(z, y)}{h_i(z, y)}.$$

Which contradicts (13), and the proof is complete.

## 4. DUALITY MODEL II

In order to discuss another dual model for (P), we first state another version of Theorem 2.1. This is done by replacing the parameter $v^*$ with $f_i(x^*, y_i)/h_i(x^*, y_i)$ and by rewriting the multiplier functions associated with the inequality constraints. The result of Theorem 2.1 can be stated as follows.

THEOEM 4.1.If $x^*$ is an optimal solution of the problem (P) and $\nabla g_i(x),\ j \in J(x^*)$ is linearly independent, then there exists $(s^*, t^*, \bar{y}) \in K$ and $\mu^* \in R_+^p$ such that

$$\sum_{i=1}^{s^*} t^*_i \{h(x^*, y_i)\nabla f_i(x^*, y_i) - f_i(x^*, y_i)\nabla h_i(x^*, y_i)\} + \nabla \sum_{j=1}^{p} \mu^*_j g_j(x^*) = 0,$$

$$\sum_{j=1}^{p} \mu^*_j g_j(x^*) = 0,$$

$$\mu^* \in R_+^p, t_i^* \ge 0, \sum_{i=1}^{s^*} t^*_i = 1, y_i \in Y(x^*), i = 1, ..., s^*.$$

Now we introduce a dual (DII) to the minimax problem (P)

(DII) $\max_{(s,t,\bar{y})\in K} \sup_{(z,\mu)\in H_2(s,t,\bar{y})} f(z)$, where $H_2(s,t,\bar{y})$ denotes the set of $(z,\mu)\in R^m \times R_+^p$ satisfying

$$\sum_{i=1}^{s} t_i \{h(z,y_i)\nabla f_i(z,y_i) - f_i(z,y_i)\nabla h_i(z,y_i)\} + \nabla \sum_{j=1}^{p} \mu_j g_j(z) = 0, \tag{16}$$

$$\sum_{j=1}^{p} \mu_j g_j(z) \geq 0, \tag{17}$$

$y_i \in Y(z), i = 1,..., s,$

and

$$F(z) = \sup_{y\in Y} \frac{f_i(z,y)}{h_i(z,y)}. \tag{18}$$

If the set $H_2(s,t,\bar{y})$ is empty, then we define the supremum over it to be $-\infty$. Throughout this section, we simply denote $\psi(.)$ as

$$\sum_{i=1}^{s} t_i \{h(z,y_i) f_i(i,y_i) - f_i(.,y_i) h_i(.,y_i)\}.$$

THEOEREM 4.2 (Weak Duality). Let x be (P)-feasible and $(z,\mu,v,s,t,\bar{y})$ be (DII)-feasible, respectively, and assume that $\psi_1(.)$ is a pseudo-convex function at $z$, and $\sum_{j=1}^{p} \mu_j g_j(.)$ is a quasi-convex function at $z$. Then $\sup_{y\in Y}(f_i(x,y_i)/h_i(x,y_i)) \geq F(z)$.

Proof: By both the feasibility of $x$ and (17), we have

$$\sum_{j=1}^{p} \mu_j g_j(x) \leq 0 \leq \sum_{j=1}^{p} \mu_j g_j(z).$$

Using the quasi-convexity $\sum_{j=1}^{p} \mu_j g_j(.)$ at $z$, we have

$$(x-z)^T \nabla \sum_{j=1}^{p} \mu_j g_j(z) \leq 0. \tag{19}$$

Consequently, (16) and (19) yield

$$(x-z)^T \nabla \psi_1(z) \geq 0. \tag{20}$$

On account of pseudo-convexity of $\psi_1(.)$ at $z$, we get from (20)

$$0 = \psi_1(z) \leq \psi_1(.x).$$

Therefore, there exists a certain $i_0$, such that

$$0 \leq h_i(z, y_{i_0}) f_i(x, y_i) - f_i(z, y_i) h_i(x, y_{i_0}).$$

It follows that

$$\sup_{y \in Y} \frac{f_i(x,y)}{h_i(x,y)} \geq \frac{f_i(x, y_{i_0})}{h_i(x, y_{i_0})} \geq \frac{f_i(z, y_{i_0})}{h_i(z, y_{i_0})}. \tag{21}$$

Since $y_{i_0} \in Y(z)$, we have

$$F(z) = \frac{f_i(z, y_{i_0})}{h_i(z, y_{i_0})}. \tag{22}$$

Thus the proof of the theorem is complete.

Remark 4.1. In theorem 4.2, if $\psi_1(.)$ is a quasi-convex function at $z$, and $\sum_{j=1}^{p} \mu_j g_j(.)$ is a strictly pseudo-convex function at $z$, then Theorem 4.1 also holds.

Similar to the proof of Theorems 3.2, 3.3, we can establish Theorems 4.3, 4.4. Therefore, we simply state them.

THEOREM 4.3 (Strong Duality). If $x^*$ is a (P)-optimal solution and $\nabla g_i(x), j \in J(x^*)$ is linearly independent, and if in addition the hypothesis of Theorem 4.2 holds for all (DII)-feasible points $(z, \mu, s, t, \bar{y})$, then the two problems (P) and (DII) have the same external values.

THEOREM 4. 4 (Strict Converse Duality). Let $\bar{x}$ and $(z, \mu, v, s, t, \bar{y})$ be optimal solutions of (P) and (DII)-feasible points $(z, \mu, v, s, t, \bar{y})$, $\psi_1(.)$ is strictly pseudo-convex at $z$, and $\sum_{j=1}^{p} \mu_j g_j(.)$ is quasi-convex at $z$. Then $\bar{x} = z$ : that is, $z$ is a (P)-optimal solution.

## 5. DUALITY MODEL III

Based on (2) and (3), we obtain

$$\nabla \sum_{i=1}^{s^*} t_i^* f_i(x^*, y_i) - \frac{f_i(x^*, y_i)}{h_i(x^*, y_i)} \nabla \sum_{i=1}^{s^*} t_i^* h_i(x^*, y_i) + \nabla \sum_{j=1}^{p} \mu_j^* g_j(x^*) = 0, \text{ for all } i = 1,..., s^*.$$

Multiplying the above equations respectively by $t_i^*(h_i(x^*, y_i)$, $i = 1,..., s^*$, and adding them up, we have

$$\sum_{i=1}^{s^*} t_i^* f_i(x^*, y_i) \nabla \left[ \sum_{i=1}^{s^*} t_i^* f_i(x^*, y_i) + \sum_{j=1}^{p} \mu_j^* g_j(x^*) \right] - \sum_{i=1}^{s^*} t_i^* f_i(x^*, y_i) \nabla \left[ \sum_{i=1}^{s^*} t_i^* h_i(x^*, y_i) \right] = 0.$$

The above equation, together with (4), implies

$$\nabla \left( \frac{\sum_{i=1}^{s^*} t_i^* f_i(x^*, y_i) + \sum_{j=1}^{p} \mu_j^* g_j(x^*)}{\sum_{i=1}^{s^*} t_i^* h_i(x^*, y_i)} \right)$$

$$= \left( \sum_{i=1}^{s^*} t_i^* h_i(x^*, y_i) \right)^{-2} \times \left( \left[ \sum_{i=1}^{s^*} t_i^* h_i(x^*, y_i) \right] \nabla \left[ \sum_{i=1}^{s^*} t_i^* f_i(x^*, y_i) + \sum_{j=1}^{p} \mu_j^* g_j(x^*) \right] - \left[ \sum_{i=1}^{s^*} t_i^* f_i(x^*, y_i) + \sum_{j=1}^{p} \mu_j^* g_j(x^*) \right] \nabla \left[ \sum_{i=1}^{s^*} t_i^* h_i(x^*, y_i) \right] \right)$$

$$= \left( \sum_{i=1}^{s^*} t_i^* h_i(x^*, y_i) \right)^{-2} \times \left( \left[ \sum_{i=1}^{s^*} t_i^* h_i(x^*, y_i) \right] \nabla \left[ \sum_{i=1}^{s^*} t_i^* f_i(x^*, y_i) + \sum_{j=1}^{p} \mu_j^* g_j(x^*) \right] \right.$$

$$\left. - \left[ \sum_{i=1}^{s^*} t_i^* f_i(x^*, y_i) \right] \nabla \left[ \sum_{i=1}^{s^*} t_i^* h_i(x^*, y_i) \right] \right)$$

$$= 0.$$

Consequently, the result of Theorem 2.1 can be stated as follows.

THEOREM 5.1. If $x^*$ is an optimal solution of the problem (P) and $\nabla g_i(x)$, $j \in J(x^*)$ is linearly independent, then there exist $(s^*, t^*, \bar{y}) \in K$ and $\mu^* \in R_+^p$ such that

$$\nabla\left(\frac{\sum_{i=1}^{s^*} t_i^* f_i(x^*, y_i) + \sum_{j=1}^{p} \mu_j^* g_j(x^*)}{\sum_{i=1}^{s^*} t_i^* h_i(x^*, y_i)}\right) = 0,$$

$$\sum_{j=1}^{p} \mu_j^* g_j(x^*) = 0,$$

$$\mu^* \in R_+^p, t_i^* \geq 0, \sum_{i=1}^{s^*} t_i^* = 1, y_i \in Y(x^*), i = 1, \ldots, s^*.$$

We shall continue our discussion of the parameter-free duality model for (P) in this section by showing that the following variant of (DIII) is aiso the dual problem for (P):

(DIII) $\max_{(s,t,\bar{y}) \in K} \sup_{(z,\mu) \in H_2(s,t,\bar{y})} \dfrac{\left(\sum_{i=1}^{s} t_i f_i(z, y_i) + \sum_{j=1}^{p} \mu_j g_j(z)\right)}{\left(\sum_{i=1}^{s} t_i^* h_i(z, y_i)\right)}$ where $H_3(s,t,\bar{y})$ denotes the set $(z,\mu) \in R^m \times R_+^p$ satisfying

$$\nabla\left(\frac{\sum_{i=1}^{s} t_i f_i(z, y_i) + \sum_{j=1}^{p} \mu_j g_j(z)}{\sum_{i=1}^{s} t_i^* h_i(z, y_i)}\right) = 0. \qquad (23)$$

If the set $H_3(s,t,\bar{y})$ is empty, then we define the supremum over it to be $-\infty$. Throughout this section, we simply denote $\psi_1(.)$ as

$$\sum_{i=1}^{s} t_i h_i(z, y_i)\left[\sum_{i=1}^{s} t_i f_i(., y_i) + \sum_{j=1}^{p} \mu_j g_j(.)\right] - \left[\sum_{i=1}^{s} t_i f_i(z, y_i) + \sum_{j=1}^{p} \mu_j g_j(z)\right]\sum_{i=1}^{s} t_i h_i(., y_i).$$

We shall state weak duality, strong, and strict converse duality theorems for (P)-(DIII).

THEOREM 5.2 (Weak Duality). Let $x$ be (P)-feasible and $(z,\mu,s,t,\bar{y})$ be (DIII)-feasible, and assume that $\psi_2(.)$ is a pseudo-convex function at $z$. Then

$$\sup_{y\in Y}\frac{f_i(x,y)}{h_i(x,y)}\geq\frac{\sum_{i=1}^{s}t_i f_i(z,y_i)+\sum_{j=1}^{p}\mu_j g_j(z)}{\sum_{i=1}^{s}t_i h_i(z,y_i)}.$$

Proof: From (23), we have

$$\nabla\psi_2(z)=0. \tag{24}$$

By means of contradiction, we suppose that

$$\sup_{y\in Y}\frac{f_i(x,y)}{h_i(x,y)}<\frac{\sum_{i=1}^{s}t_i f_i(z,y_i)+\sum_{j=1}^{p}\mu_j g_j(z)}{\sum_{i=1}^{s}t_i^* h_i(z,y_i)}.$$

Thus we have an inequality

$$f_i(x,y)\sum_{i=1}^{s}t_i h_i(z,y_i)<h_i(x,y)\left[\sum_{i=1}^{s}t_i f_i(z,y_i)+\sum_{j=1}^{p}\mu_j g_j(z)\right] \text{ For all } y\in Y.$$

Furthermore, this above inequality implies

$$\left[\sum_{i=1}^{s}t_i f_i(x,y_i)\right]\left[\sum_{i=1}^{s}t_i h_i(z,y_i)\right]<\left[\sum_{i=1}^{s}t_i h_i(x,y_i)\right]\left[\sum_{i=1}^{s}t_i f_i(z,y_i)+\sum_{j=1}^{p}\mu_j g_j(z)\right].$$

Hence, we have another inequality

$$\left[\sum_{i=1}^{s}t_i f_i(x,y_i)+\sum_{j=1}^{p}\mu_j g_j(x)\right]\left[\sum_{i=1}^{s}t_i h_i(z,y_i)\right]-\left[\sum_{i=1}^{s}t_i h_i(x,y_i)\right]\left[\sum_{i=1}^{s}t_i f_i(z,y_i)+\sum_{j=1}^{p}\mu_j g_j(z)\right]$$

$$<\sum_{j=1}^{p}\mu_j g_j(x)\sum_{i=1}^{s}t_i h_i(z,y_i).$$

Using the fact that $\sum_{i=1}^{s} t_i h_i(z, y_i) > 0, \sum_{j=1}^{p} \mu_j g_j(x) \le 0$, and the latest inequality, we have

$$\psi_2(x) < 0 = \psi_2(z).$$

Using the fact that $\psi_2(.)$ is a pseudo-convex function at $z$, we have

$$(x - z)^T \nabla \psi_2(z) < 0. \qquad (25)$$

But (24) and (25) are not compatible. Thus, the proof is complete.

Remark 5.1. If we add the constraint $\sum_{i=1}^{s} t_i f_i(z, y_i) + \sum_{j=1}^{p} \mu_j g_j(z) \ge 0$ to the dual problem (DIII), and if $f_i(., y_i), -h_i(., y_i), g_j(.)$ are convex functions, and $(x - z)^T = x - z$ we can reduce Theorem 5.2 to Theorem 3.2, of Chandra and Kumar [5].

As a consequence of Theorems 5.1 and 5.2, we obtain the following strong duality theorem:

THEOREM 5.3 (Strong Duality). If $x^*$ is a (P)-optimal solution and $\nabla g_i(x), j \in J(x^*)$ is linearly independent, and if in addition the hypothesis of Theorem 5.2 holds for all (DIII)-feasible points $(z, \mu, s, t, \bar{y})$, then the two problems (P) and (DIII) have the same extremal values.

THEOREM 5.4 (Strict Converse Duality). Let $\bar{x}$ and $(z, \mu, s, t, \bar{y})$ be optimal solutions of (P) and (DIII), respectively, and assume that $\psi_2(.)$ is a strictly pseudo-convex function at $x$ for all $(s, t, \bar{y}) \in K, (z, \mu) \in H_3(s, t, \bar{y})$, and $\nabla g_i(x), j \in J(x^*)$ is linearly independent. Then $\bar{x} = z$; that is, $z$ is a (P)-optimal solution.

Proof: We shall assume that $\bar{x} \ne z$; and reach a contradiction. From Theorem 5.3 we know that

$$\sup_{y \in Y} \frac{f_i(\bar{x}, y)}{h_i(\bar{x}, y)} = \frac{\sum_{i=1}^{s} t_i f_i(z, y_i) + \sum_{j=1}^{p} \mu_j g_j(z)}{\sum_{i=1}^{s} t_i h_i(z, y_i)}.$$

Hence we have

$$f_i(\bar{x},y)\sum_{i=1}^{s}t_i\,h_i(z,y_i)\le h_i(\bar{x},y)\left[\sum_{i=1}^{s}t_i\,f_i(z,y_i)+\sum_{j=1}^{p}\mu_j g_j(z)\right]\quad\text{For all } y\in Y.$$

Furthermore, this above inequality implies

$$\left[\sum_{i=1}^{s}t_i\,f_i(\bar{x},y_i)\right]\left[\sum_{i=1}^{s}t_i\,h_i(z,y_i)\right]\le\left[\sum_{i=1}^{s}t_ih_i(\bar{x},y_i)\right]\left[\sum_{i=1}^{s}t_i\,f_i(z,y_i)+\sum_{j=1}^{p}\mu_j g_j(z)\right].$$

Hence, we have another inequality

$$\left[\sum_{i=1}^{s}t_i\,f_i(\bar{x},y_i)+\sum_{j=1}^{p}\mu_j g_j(\bar{x})\right]\left[\sum_{i=1}^{s}t_i\,h_i(z,y_i)\right]-\left[\sum_{i=1}^{s}t_ih_i(\bar{x},y_i)\right]\left[\sum_{i=1}^{s}t_i\,f_i(z,y_i)+\sum_{j=1}^{p}\mu_j g_j(z)\right]$$

$$\le\sum_{j=1}^{p}\mu_j g_j(\bar{x})\sum_{i=1}^{s}t_i\,h_i(z,y_i).$$

Using the fact that $\sum_{i=1}^{s}t_i\,h_i(z,y_i)>0,\sum_{j=1}^{p}\mu_j g_j(\bar{x})\le 0,$ and the latest inequality, we get

$$\psi_2(\bar{x})\le 0=\psi_2(z).$$

With the strict pseudo-convexity of $\psi_2(.)$, we have $(x-z)^T\nabla\psi_2(z)<0.$ that is,

$$(\bar{x}-z)^T\left\{\sum_{i=1}^{s}t_i\,h_i(z,y_i)\nabla\left[\sum_{i=1}^{s}t_i\,f_i(z,y_i)+\sum_{j=1}^{p}\mu_j g_j(z)\right]-\left[\sum_{i=1}^{s}t_i\,f_i(z,y_i)+\sum_{j=1}^{p}\mu_j g_j(z)\right]\left[\nabla\sum_{i=1}^{s}t_i\,h_i(z,y_i)\right]\right\}<0.\quad(26)$$

But (23) and (26) are not compatible. This completes the proof.

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ORIGINAL ARTICLE

# Exploratory Studies of (-)-Epicatechin, a Bioactive Compound of *Phyllanthus niruri*, on the Antioxidant Enzymes and Oxidative Stress Markers in D-galactosamine-induced Hepatitis in Rats: A Study with Reference to Clinical Prospective

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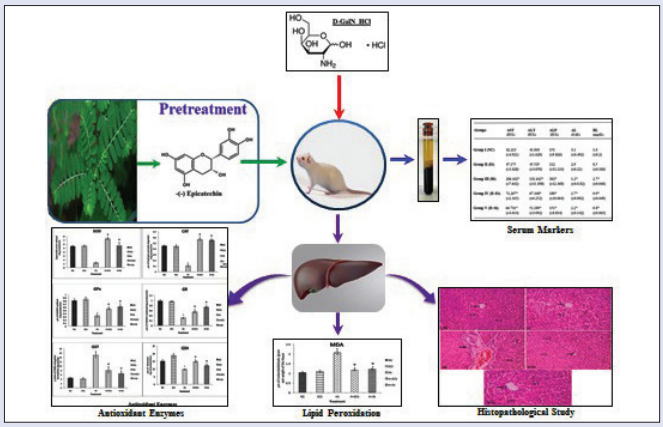
## ABSTRACT

**Background:** Hepatitis is a health problem affecting millions of people worldwide and it is the major risk factor for liver cirrhosis. In India, many plants are used to treat hepatitis. But little is known about the effects of (-)-epicatechin a bioactive compound of *Phyllanthus niruri* (PN) in hepatitis rats. **Objective:** The present study was designed to explore the antioxidant property of (-)-epicatechin isolated from PN in D-Galactosamine (D-GalN) induced hepatitis rats. **Materials and Methods:** The rats are divided into five groups as per the experimental design. (-)-Epicatchin pretreatment was given to the hepatitis rats for 21 days and biochemical analysis was carried out. The hepatic antioxidant enzymes like superoxide dismutase (SOD), catalase (CAT), glutathione peroxidase (GPx), and glutathione reductase (GR), glutathione S-transferase (GST), reduced glutathione (GSH), and malondialdehyde (MDA) and serum markers aspartate aminotransferase (AST), alanine aminotransferase (ALT), alkaline phosphatase (ALP), albumin, and bilirubin are estimated. **Results:** All the antioxidant enzymes activities and albumin levels are depleted in hepatitic rats. Whereas GST, ALP, AST, ALT activities and MDA, and bilirubin levels are elevated in hepatitis rats, (-)-epicatechin pretreatment increased all the antioxidant enzymes and decreased the GST, ALP, AST, ALT, and MDA levels in hepatitis rats. However, histopatholoigic studies also proves that (-)-epicatechin pretreatment decreased the tissue damage in hepatitis condition. This is the first report on the antioxidant enzymes and hepatoprotective effect of (-)-epicatechin in hepatitis rats. **Conclusion:** From this study, we conclude that (-)-epicatechin treatment decreased the oxidative damage in hepatitis rats.

**Key words:** (-)-Epicatechin, hepatitis, antioxidants enzymes, liver markers

## SUMMARY

- The present study was carried out to know the impact of (-)-epicatechin on antioxidant enzymes activities in hepatitis rats.
- From this study, we found that the antioxidant enzymes SOD, CAT, GPx, GR, GSH depleted in hepatitis rats and increased with (-)-epicatechin in hepatitis rats. MDA levels increased in hepatitis rats and decreased with (-)-epicatechin in hepatitis rats.
- From this study, we concluded that (-)-epicatechin will be useful to treat hepatotoxicity in rats.




**Abbreviations used:** *Phyllanthus niruri* (PN), D-Galactosamine (D-GalN),superoxide dismutase (SOD), catalase (CAT), glutathione peroxidase (GPx), and glutathione reductase (GR), glutathione s transferase (GST), reduced glutathione (GSH) and malondialdehyde (MDA) aspartate aminotransferase (AST), alanine aminotransferase (ALT), alkaline phosphatase (ALP), World Health Organisation (WHO), Indian Institute of Science (IISc), Nicotinamide adenine dinucleotide phosphate (NADPH), thiobarbituric acid reactive substances (TBARS),

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## INTRODUCTION

Hepatitis is a major public health problem worldwide, responsible for considerable morbidity and mortality from liver disease. According to World Health Organization (WHO) report, an estimated 600,000 persons die each year due to the acute or chronic consequences of hepatitis.[1] Types of hepatitis are A, B, C, D, E, F, and G. Developing countries like India is also struggling to manage the impact of hepatitis along with the growing burden of obesity, diabetes, hypertension, and coronary heart disease. Hence, hepatitis remains as clinical challenge and a problem of great importance today.

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Hepatitis may be induced by virus, alcohol, lipid oxidation products, and various drugs.[2] D-Galactosamine (D-GalN) is a hepatotoxicant, causing liver injury, which is closely related to human viral hepatitis due to their similarities in morphologic and functional features of hepatitis. Liver damage induced by D-GalN generally reflects in disturbance of liver cell metabolism, which leads to characteristic changes in the serum enzyme activities. It has been reported that GalN induces damage in rat hepatocyte, which results in increased production of reactive oxygen species.

*Phyllanthus niruri* (PN) Linn has been used in Ayurvedic medicine for over 2000 years and has been used in wide number of traditional ailments such as jaundice, gonorrhea, frequent menstruation, diabetes and liver-related disorders.[3] In PN many phytochemical constituents like flavonoids, alkaloids, terpenoids, lignans, polyphenols, tannins, coumarins, and saponins are seen. The bioactive compounds of *Phyllanthus* are astragalin, catechin, (+),(-)-epicatechin, catechin-3-o-gallate, epicorilagin, quercetin, geraniin, phyllnirurin, cymene, estradiol, fraternusterol, gallocatechin, limonene, lupeol, niranthin, mirphyllin, phyllanthin, hypophyllanthin, and so on.

(-)-Epicatechin is a flavan-3-ol, a secondary plant constituent belonging to the group of flavonoids and found in berries, grapes, apples, red wine, tea, cocoa, and phyllanthus.[4] (-)-Epicatechin has antidiabetic, anticancer, antilipidemic, antineoplastic, cardio protective, anti-inflammatory, and antioxidant properties.[5,6]

The present investigation was designed to explore the antioxidant and hepatoprotective effect of (-)-epicatechin in D-GalN-induced hepatitis in rats. There were no reports available on the effect of (-)-epicatechin on antioxidant defense system enzymes in hepatitis in rats. To the best of our knowledge, this is the first reported data on the antioxidant activity and hepatoprotective effect of (-)-epicatechin during hepatitis condition.

## MATERIALS AND METHODS

### Chemicals

All chemicals used in the present study are obtained from Sigma (St. Louis, MO, USA), Fisher Scientific (Pittsburg, PA, USA), Merck (Mumbai, India), Ranbaxy (New Delhi, India), and Qualigens (Mumbai, India).

### Isolation of bioactive compound (-)-epicatechin

Fresh plants of PN were locally collected in the months of October and November 2014 from seven hills of Tirupati, Andhra Pradesh, India, identified, and authenticated by botany taxonomist, Dr. Madhava Chetty, Department of Botany, S.V. University. A voucher specimen No. 2151 was retained in the Department of Botany, S.V. University, Tirupati. The bioactive compound of PN i.e., (-)-epicatechin was extracted by different methods. PN was grinded and ethanol added. The mixture was filtered and dried by using a rotary evaporator. The mixture is then washed with hexane. All other experimental work was carried out by using thin layer chromatography (TLC) and high-performance liquid chromatography (HPLC) and isolated pure bioactive compound (-)-epicatechin.[7]

### Induction of hepatitis

The rats are given D-GalN to induce hepatitis. Hepatitis was confirmed by estimating AST, ALT, and ALP in serum. AST, ALT, and ALP activities increased in rats, our results are similar with those from hepatitis subjects.

### Animals and experimental design

This experiment was carried in male Wistar rats (3 months old, weighing 180 ± 200 g) obtained from Indian Institute of Science (IISC), Bangalore. The animals were kept under standard laboratory conditions (temperature (27 ± 2°C), natural light dark cycle (photoperiod of 12-h light and 12-h dark), and humidity of 55–60%. The rats were given standard pellets diet (Lipton Rat Feed Ltd., Pune) and water *ad libitum* throughout the experimental period. The study design was approved by the animal ethical committee (Resolution No. 10/08/a/CPCSCA/IAEC/SVU/09-10/ZOOL/KRS/Dt.25.09.2009). After 7 days of acclimatization, animals were divided into five groups of six rats each.

**Group I normal control (NC)**: These rats received saline for 21 days and served as normal control.

**Group II (-)-epicatechin compound control treatment (Et)**: These rats received pretreatment of bioactive compound of PN (epicatechin 50 mg/kg body weight) for 21 days.

**Group III hepatitis control (Ht)**: A single injection of D-GalN (800 mg/kg body weight) was given intraperitoneally for the induction of hepatitis 48 h before sacrifice.

**Group IV hepatitis + (-)-epicatechin – 50 mg/kg body weight) treatment (H+Et)**: Hepatitis rats received pretreatment of bioactive compound ((-)-epicatechin) orally for 21 days.

**Group V hepatitis + Silymarin treatment (H+St):** Hepatitis rats received pretreatment of standard drug Silymarin (100 mg/kg body weight) orally for 21 days.

After 21 days of treatment, all the rats were sacrificed. Blood samples were collected in sterile plastic tubes and serum was separated by centrifugation at 3000 rpm for 10 min at 4°C. Liver tissue was quickly removed, washed in ice cooled 0.9% NaCl, and immersed in liquid nitrogen and immediately stored at -80°C for further biochemical analysis. Liver tissue was also used for histopathologic studies.

### Isolation of mitochondria

The isolation of mitochondria was done by using the methods of Kaushal *et al.*[8] The liver was placed in beakers containing chilled (-4°C) isolation media, which contained 0.25 M sucrose, 10 mM Tris-HCl buffer, pH 7.4, 1 mM EDTA, and 250 µg BSA/mL. The tissues were minced and washed repeatedly with the isolation medium to remove adhering blood and 10% (w/v) homogenates were prepared using homogenizer. The nuclei and cell debris were sedimented by centrifugation at 650*g* for 10 min and discarded. The supernatant was subjected to a further centrifugation at 7500*g* for 10 min. The resulting mitochondrial pellet was washed by suspending gently in the isolation medium and by re-sedimenting at 7500*g* for 10 min. Finally, the mitochondrion was suspended in the isolation medium.

### Measurement of antioxidant enzymes

SOD activity in liver was measured by the method of Misra and Fridovich.[9] The absorbance was read at 340 nm for 4 min and the activity was expressed as the amount of enzyme that inhibits the oxidation of epinephrine by 50%, which is equal to one unit. Whereas CAT activity was determined in the liver as described by Aebi[10] using Triton X-100 by measuring the absorbance at 240 nm for 60 s on a UV-Spectrophotometer (Hitachi U-2800).

GPx activity was estimated by Flohe and Gunzler.[11] GR activity was measured by the method of Carlberg and Mannervik[12] by monitoring the oxidation of nicotinamide adenine dinucleotide phosphate (NADPH) at 340 nm for 3 min. However, the levels of reduced glutathione (GSH) in liver was measured as described by Akerboom and Sies.[13] GST activity was assayed by the method of Habig *et al.*[14] Protein content in liver was determined by the method of Bradford.[15]

## Determination of the thiobarbituric acid reactive substances

The extent of liver lipid peroxidation in term of thiobarbituric acid reactive substance (TBARS) formation was measured as described by Ohkawa *et al.*[16]

## Estimation of serum markers

AST, ALT, ALP, albumin, and bilirubin are estimated in serum by kit methods.

## Free radical scavenging activity of PN

The free radical scavenging activity, i.e., DPPH of PN was determined spectrophotometrically by the method of Brand-Williams *et al.*[17]

The $H_2O_2$ free radical scavenging activity of PN is estimated by the method of Ruch *et al.*[18]

The reducing power was determined according to the method of Oyaizu.[19]

## Histopathologic studies

The liver tissues were fixed for 48 h in 4% paraformaldehyde, dehydrated by passing them successively in different mixtures of ethyl alcohol–water, cleaned in xylene, and embedded in paraffin. Sections of liver (3μ thick) were prepared, stained with hematoxylin and eosin (H&E 10×), and mounted using neutral (DPX) mountant for microscopic observation.

## Statistical analysis

Results are expressed as means ± standard deviation (SD). Variance analysis was done with Duncan's multiple comparison tests on data using the SPSS (Version 15, SPSS Inc., Chicago, IL, USA) and MS Office, Excel software for the significance of the main effects (factors), and treatments along with their interactions. Statistical significance was set at *P* less than 0.05. The *P* values are presented with the obtained data.

# RESULTS

## Free radical scavenging activity of PN

The free radical scavenging activity of PN was assessed by using DPPH, hydrogen peroxide, and reducing powers shown in Figure 1 . Interestingly, DPPH, hydrogen peroxide, and reducing power activity of PN demonstrated remarkable free radical scavenging effects with significant activity when compared with standard antioxidants. DPPH, hydrogen peroxide, and reducing powers of PN were increased with increase in the concentration levels. This shows that PN possess free radical scavenging activity [Figure 1].

## Effect of (-)-epicatechin on the antioxidant enzymes, SOD, CAT, GPx, GR, GST, and GSH

Figure 2 depicts the activities of antioxidant enzymes. When compared with normal control, the activities of all the liver antioxidant enzymes (SOD, CAT, GPx, GR, and GSH) are significantly decreased in hepatitis rats. However, (-)-epicatechin pretreatment in hepatitis rats SOD, CAT, GPx, GR, and GSH activities are increased. GST activity was increased in hepatitis condition. However (-)-epicatechin supplementation reverted back the GST activity to near normal in hepatitis rats. Our results showed that (-)-epicatechin pretreatment brought back all the antioxidant enzymes near to normal in hepatitis rats. Silymarin drug also showed a considerable effect in reverting the effects of hepatitis treated rats for all the enzymes.

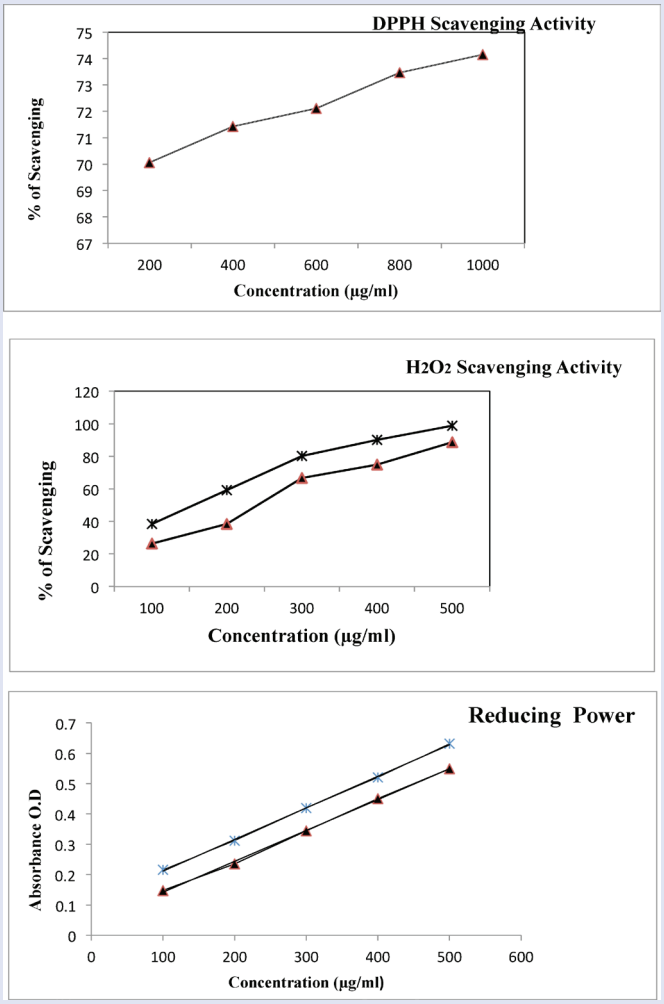



**Figure 1:** Free radical scavenging activity (DPPH, $H_2O_2$, reducing power) of PN and ascorbic acid as standards

## Impact of (-)-epicatechin on MDA levels

Oxidative tissue damage marker MDA levels significantly ($P < 0.05$) increased in D-GalN-induced hepatitis control rats than in normal control. However, (-)-epicatechin pretreatment progressively reduced ($P < 0.05$) oxidative tissue damage by decreasing the MDA levels compared with hepatitis control rats, which suggests that (-)-epicatechin could be able to retarded the hepatic tissue damage under D-GalN-induced hepatitis. Silymarin drug also showed the same effect in hepatitis rats [Figure 3].

## Effect of (-)-epicatechin on serum markers in hepatitis rats

Serum AST, ALT, ALP, bilirubin, and albumin are used as biochemical markers of hepatic tissue damage. Serum AST, ALT, ALP, and bilirubin levels significantly increased ($P < 0.05$) and albumin levels decreased in hepatitis rats over normal rats. However, pretreatment of (-)-epicatechin depleted AST, ALT, ALP activities, and bilirubin levels in hepatitis rats. But albumin levels elevated in hepatitis rats. (-)-Epicatechin supplementation prevented the hepatic tissue damage in hepatitis rats. Hence, all the serum markers levels are came back to near normal levels [Table 1].

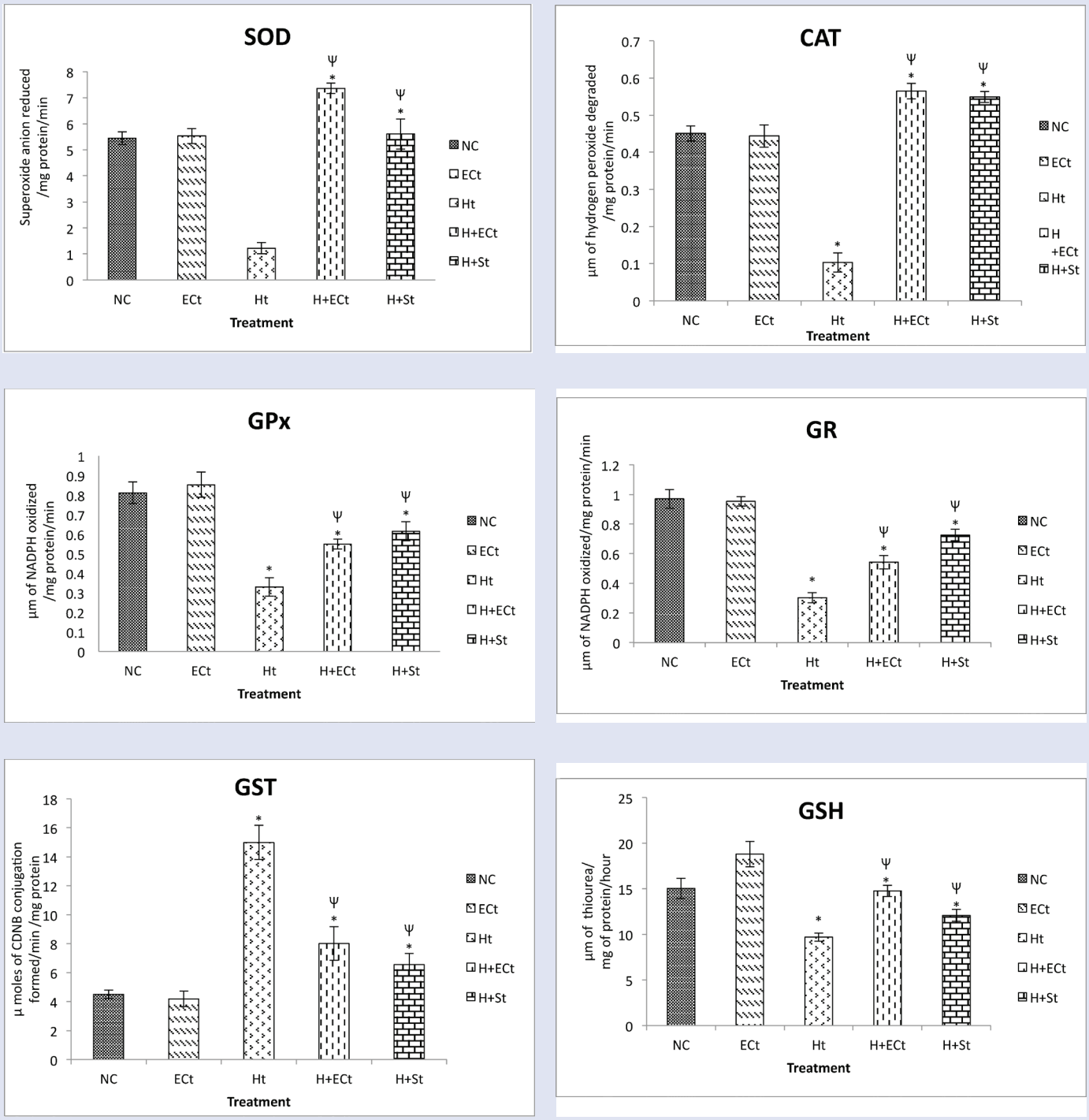



**Figure 2:** Effects of (-)-epicatechin and Silymarin on SOD, CAT, GR, GPx, GST activities, and GSH levels in the liver tissues of normal and hepatitis rats

## Effect of (-)-epicatechin on histopathologic changes of liver in D-GalN-induced hepatitis rats

In the present study, we observed degeneration of central vein, hepatocytes, and sinusoids in D-GalN-induced hepatitis control rats. Free radical production under hepatitis condition is more, hence in this condition, hepatic cell damage is seen. However, with (-)-epicatechin pretreatment, we observed regeneration of central vein, hepatocytes, and sinusoids in hepatitis rats. Which further confirms the hepatoprotective effect of the (-)-epicatechin. (-)-Epicatechin alone and Silymarin treatments did not show any change in the architecture of the liver as compared with normal control [Figure 4].

## DISCUSSION

Free radical production causes extensive damage to tissues and biomolecules leading to various disease conditions like diabetes, hepatitis, and cancer. Herbal treatment protects tissue damage against many diseases. Hence, an alternative solution to the problem is to consume natural antioxidants from food supplements and traditional medicines.

In the present study, we carried out the free radical scavenging activity of DPPH, $H_2O_2$, and reducing power of PN. These free radical scavenging assays have provide a good method to know the antioxidant activity. In this study, DPPH, $H_2O_2$, and reducing powers of PN showed good free radical scavenging activity [Figure 1].

Oxidative damage due to oxidative stress is the failure of the cell's defense against the deleterious effects of harmful agents. In our study, D-GalN decreased the activities of SOD and CAT enzymes in hepatitis rats. The inhibition of SOD activity in hepatitis rats may be attributed to inefficient scavenging of ROS, which might be implicated to oxidative inactivation of SOD.[20] CAT is a heme protein, which decomposes hydrogen peroxide and protects the tissues from highly reactive hydroxyl radicals. Our findings are supported by the previous studies, decline of SOD and CAT activity in D-GalN-induced hepatitis rats. However, pretreatment of (-)-epicatechin remarkably increased the SOD and CAT activity in D-GalN-induced hepatitis, it was indicated that (-)-epicatechin significantly prevents the superoxide anions and hydrogen peroxide radicals by SOD and CAT in D-GalN-intoxicated rats [Figure 2].

In our study, we observed the depleted activities of GR and GPx in hepatitis rats. D-GalN decreased the GPx and GR activities due to the free radicals, which led to interaction with these proteins and modulation of their action. GPx reduced the $H_2O_2$ to water in the presence of GSH and GR reduce the oxidized glutathione into reduced glutathione, which is essential for defense against free radicals. However, pretreatment of PN bioactive compound (-)-epicatechin substantially enhanced the GPx and GR activity either may be synthesis of GSH levels or may be decreased the free radicals by their antioxidant activity. Our results show the strong evidence of hepatoprotective effect of (-)-epicatechin that significantly reduces hepatic tissue damage in hepatitis rats [Figure 2].

GST plays a vital role in the detoxification of electrophiles produced by ROS via catalyzing the conjugation of electrophiles with GSH. In the current study, we reported that GST activity was increased in hepatitis rats. GST can remove free radicals, and their levels can reflect the antioxidant capacity of the tissue. Excessive oxidation in cells that causes reduction in GSH/GSSG may also affect other cellular events, hence GST activity was increased.[21] However, (-)-epicatechin pretreatment decreased GST activity in hepatitis rats. (-)-Epicatechin supplementation may decrease the production of toxic free radicals in hepatitis rats, so GST activity may decrease [Figure 2].

Glutathione is an important protein thiol that protects the cells against cytotoxic agents such as reactive oxygen species. GSH profoundly appeared in liver tissue, thus the liver has highly sophisticated protection from free radicals. However, in our study, GSH levels significantly decreased under D-GalN intoxication, indicating that GSH is highly vulnerable to toxic free radical mediated tissue damage. These results are in accordance with those of the earlier investigations that noticed that the tissue antioxidant status was being operated at diminished level in D-GalN-induced hepatitis, which may be due to either increased degradation or decreased synthesis of glutathione.[22] PN bioactive compound (-)-epicatechin increased the GSH levels in D-GalN-induced hepatitis rats. Pretreatment of (-)-epicatechin significantly defense the free radicals induced by D-GalN due to its free radical scavenging activities which reflected either decreased the utilization of GSH or may be enhance the synthesis the GSH by increasing the activity of GR.

Oxidative stress has been reported as one of the major causes of GalN-induced liver damage.[23] Excessive production of free radicals resulting from oxidative stress can damage lipids.[24] Increased lipid peroxidation in the organism is attenuated by the enzymatic antioxidant system and small molecule antioxidants. In the current experiment, we observed higher levels of MDA in hepatitis rats than normal control rats. The current data are in agreement with previously reported data.[25,26] However, D-GalN intoxication promotes to increase the free radical production in liver tissue, which can lead to tissue damage. These higher levels may due to the decreased activities of antioxidant enzymes in hepatitis rats. (-)-Epicatechin supplementation decreased the MDA levels in hepatitis rats. (-)-Epicatechin pretreatment may decrease the production of free radicals in hepatitis rats, this may cause downregulation of MDA levels. Thus, (-)-epicatechin had shown a potent chain breaking agent, which may prevent reaction between free radical and cell membranes interactions and protect the liver tissue under D-GalN intoxication.

AST, ALT, and ALP are the most common liver marker enzymes. AST is present in both the cytoplasm and mitochondria of hepatocytes, whereas ALT is present only in the cytoplasm. ALP is an enzyme that transports metabolites across cell membranes. ALT, AST, and ALP are also aminotransferases that could act as liver biomarkers. Many reports reported that under disease conditions, serum marker levels increases due to tissue damage and oxidative stress.[27] In hepatitis condition, AST, ALT, and ALP activities increased in serum.[27] In our results, similar consequences are observed, AST, ALT, and ALP activities elevated in serum due to D-GalN intoxication. (-)-Epicatechin pretreatment significantly reduces the elevated serum AST, ALT, and ALP activities in hepatitis rats. It was suggested that (-)-epicatechin possesses

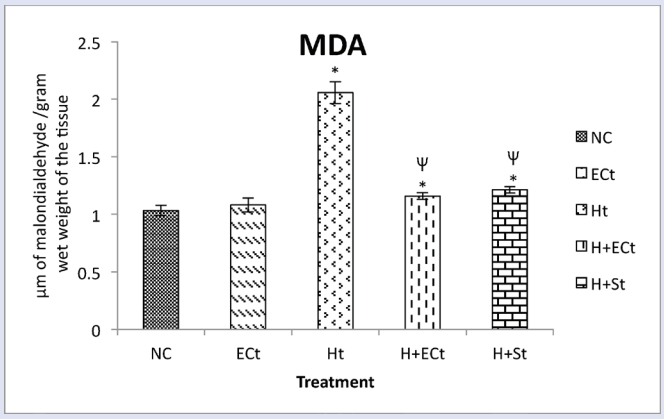



**Figure 3:** Effects of (-)-epicatechin and Silymarin on MDA levels in the liver tissues of normal and hepatitis rats. Data are expressed as means ± SD ($n$ = 6). *The values are significant compared with the following: control (*$P$ < 0.001) and hepatitic (*$P$ < 0.01) (Dunnett's multiple comparison test)

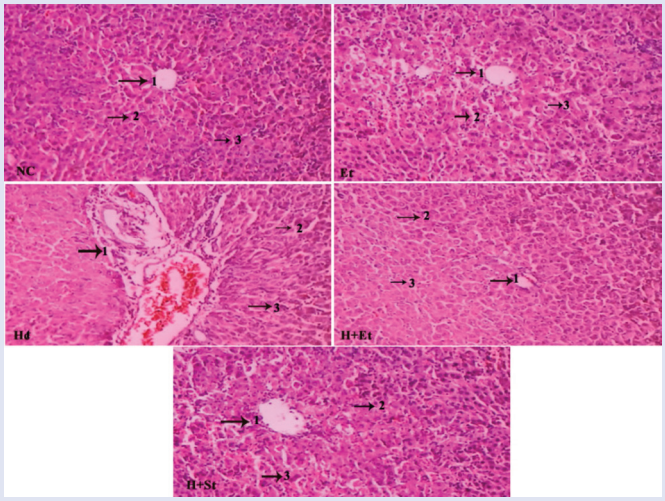



**Figure 4:** Effect of (-)-epicatechin on liver tissue during hepatitis condition

**Table 1:** Effect of (-)-Epicatechin on Serum markers in hepatitis rats

| Groups | AST (IU/L) | ALT (IU/L) | ALP (IU/L) | AL (G/dL) | BL (mg/dL) |
|---|---|---|---|---|---|
| Group I (NC) | 42.213 (±4.921) | 41.843 (±1.620) | 151 (±9.826) | 3.1 (±0.492) | 1.0 (±0.2) |
| Group II (Et) | 47.175 (±3.428) | 45.535 (±3.050) | 112 (±11.124) | 2.9 (±0.21) | 0.5 (±0.106) |
| Group III (Ht) | 206.442* (±7.642) | 131.642* (±11.398) | 302* (±12.368) | 1.2* (±0.0.82) | 2.7* (±0.046) |
| Group IV (H+Et) | 72.267* (±2.165) | 67.348* (±6.252) | 180* (±10.604) | 2.7* (±0.092) | 0.9* (±0.049) |
| Group V (H+St) | 66.731* (±4.614) | 51.189* (±3.092) | 151* (±8.814) | 2.2* (±0.142) | 0.8* (±0.063) |

All the values are means ± SD of six individual observations. * Significant at $p < 0.001$ with respect to normal control.

hepatoprotective activity in hepatitis rats [Table 1]. (-)-Epicatechin has a great potential against hepatitis condition. So (-)-epicatechin can be used as a health promoter for developing novel functional food ingredients and pharmaceutical preparations.[28]

In the current investigation, we reported an upregulation of bilirubin and a downregulation of albumin in the serum of hepatitis rats. During hepatitis condition, liver functions abnormally, hence all the hepatic markers are altered, which results in increased levels of bilirubin, accompanied by decreased levels of albumin.[29] Our results are in accordance with the previous studies showing that elevated levels of bilirubin and depleted levels of albumin in D-GalN-induced hepatitis.[30] However, (-)-epicatechin supplementation significantly declined the bilirubin and increased the albumin in hepatitis rats when compared with hepatitis control rats. (-)-Epicatechin pretreatment may suppressed the D-GalN toxicity in hepatic tissue by reducing the free radicals generation, which is reflected in the modulation of hepatic function as a result. We observed a decline in bilirubin and increased levels of albumin in hepatitis rats [Table 1].

Histopathologic studies of hepatitis liver showed disruption of sinusoids, degeneration of central vein, and hepatocytes, proving that free radicals production causes hepatic damage under hepatitis condition. When hepatitis rats pretreated with (-)-epicatechin, sinusoids, central vein and hepatocytes have regenerated. (-)-Epicatechin minimizes the production of free radicals in hepatitis-treated rats and protects the liver tissue from hepatitis-induced oxidative damage [Figure 4].

## CONCLUSION

This is the first report on hepatoprotective and antioxidant effect of (-)-epicatechin in hepatitis rats. From this study, we conclude that (-)-epicatechin bioactive compound isolated from PN modulated the antioxidant enzymes in hepatitis rats and also decreased the oxidative damage. Hence, (-)-epicatechin can be used as hepatoprotective and antioxidant agent against hepatitis. But more pharmacologic research work is required to find out the exact mechanism of (-)-epicatechin for its hepatoprotective activity in hepatitis condition.

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## Conflicts of interest

There are no conflicts of interest.

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ORIGINAL ARTICLE

# 6-Gingerol Prevents Free Transition Metal Ion [Fe (Ii)] Induced Free Radicals Mediated Alterations by *In vitro* and Ndv Growth in Chicken Eggs by *In ovo*

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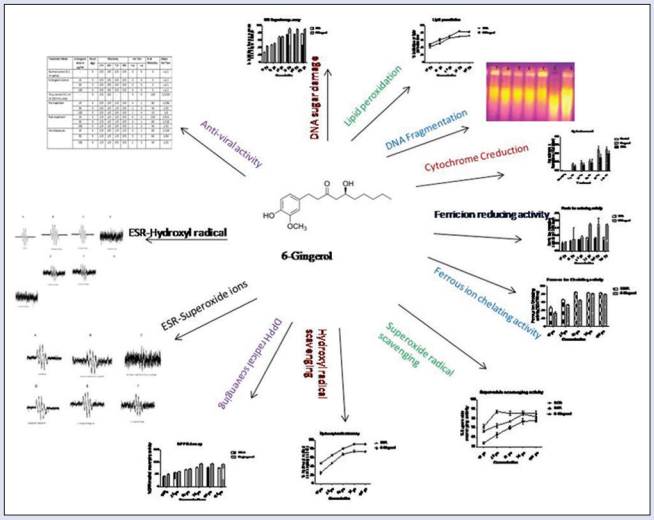
## ABSTRACT

**Background:** The study of free radicals and their reactions is implicated in the pathogenesis of various human diseases. Therefore, antioxidants treatment plays a pivotal role in preventing the free radical-induced diseases. **Objective:** The objectives of this study were to examine the protective role of 6-gingerol from free transition metal ion-induced alterations by *in vitro* and Newcastle disease virus (NDV) in chicken eggs by *in ovo*. **Materials and Methods:** In this study, lipid peroxidation, DNA sugar oxidation, chelation of ferrous ions, DNA fragmentation, Cytochrome c-oxidation, ferric ion reducing activities and DPPH, superoxide and hydroxyl radicals scavenging activity by ESR studies were examined with 6-gingerol by *in vitro*. Furthermore, antiviral activity was screened with 6-gingerol by *in ovo*. **Results:** *In vitro* results showed that 254 µM/ml of 6-gingerol firmly inhibited erythrocyte membrane lipid peroxidation by 85.28% and DNA sugar oxidation by 91.26% when compared with butylated hydroxyanisole 74.42% (554 µM/ml) and 78.30% (824 µM/ml), respectively. Whereas, chelating activity of 6-gingerol was 80.2% which nearly similar to the EDTA activity (50 µg/ml) shown 83.93%. In addition, 6-gingerol (254µM/ml) scavenged the superoxide, hydroxyl, DPPH radicals by 84.96%, 90.45%, and 94.63% respectively and the same was strongly supported with ESR studies. Further, 254 µM/ml of 6-gingerol inhibited the DNA fragmentation, Cytochrome c-oxidation and reducing the ferric ion by in vitro and antiviral activity shown on NDV at 100 µg/ml. **Conclusion:** This study could enlighten that the 6-gingerol has a good metal sequester property and it could prevent the free radicals by *in vitro* and NDV growth in chicken eggs by *in ovo*.

**Key words:** 6-Gingerol, antioxidants, cytochrome c, DNA fragmentation, lipid peroxidation

## SUMMARY

- 6-gingerol prevents free transition metal ion induced alterations
- 6-gingerol protects the DNA from metal ions induced free radicals
- 6-gingerol inhibits the NDV growth in chicken eggs.




**Abbreviations used:** NDV: Newcastle Disease Virus; ESR: Electron Spin resonance; SOD: Super oxide Dismutase; HA: *Hemagglutination*.

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## INTRODUCTION

The study of free radicals and their reactions has been led to increase the interest in the pathogenesis of human diseases. However, free transition metal ions induced free radicals interact the biomolecules and caused the oxidative damage. Thus, they play a major role in the contribution of oxidative stress-related diseases.[1] However, all aerobic animals have antioxidant defense system to counteract the harmful effects induced by free radicals.[2] Sometimes, these protective mechanisms are disrupted by various pathological conditions due to an increase of oxidative stress.[3]

Newcastle disease virus (NDV) causes Newcastle disease in all domestic and wild avian species. Its effect the egg production, hemorrhagic intestinal lesions, nervous disorders and respiratory distress.[4] Consequently, its effect on economic status of food production sectors in all around the world because of high mortality and morbidity was associated with disease.[5] Moreover, viral infections are accompanied with profound changes in cell/tissue metabolism, which lead to generate the reactive oxygen species. In this scenario, antioxidant supplementations were needed to overcome the oxidative stress. Although a number of synthetic

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antioxidants accomplish to be promising, their toxicity and side effects were restricted on their extensive prescription.

The phenolic compounds of plants have gained much attention due to their free radical scavenging and antioxidant activities with potential beneficial implications in human and animals health.[6] When they consumed with food, antioxidants minimize rancidity, retard the formation of toxic oxidation products, maintain nutritional quality, and increase shelf life.[7] Many medicinal plants have shown good antimicrobial activity. Several epidemiological studies have also been reported that the consumption of natural antioxidants reduced the risk of a number of chronic diseases.[8,9]

Ginger (*Zingiber officinale*) belongs to *Zingiberaceae* family. Since over 2000 years, ginger rhizome has been used worldwide as a spice and flavoring agent. Ginger has a long history of medicinal use for various diseases including dementia, fever, infectious diseases,[10] arthritis,[11] and diabetes.[12] Ginger rhizome contains biological active constituents including gingerol. Gingerols are found in greater abundance in fresh ginger.[13] Gingerol exhibit anti-inflammatory, antihyperglycemic, and anticancer activity.[14] To the best of our knowledge, there is no report related to ginger volatile compound 6-gingerol effect on free transition metal ion-induced free radical-mediated alterations and antiviral activity against NDV by *in vitro* and *in ovo* conditions. Therefore, we investigated the transition metal ion-induced free radical-mediated alterations and antiviral activity against NDV by 6-gingerol.

## MATERIALS AND METHODS

### Chemicals

6-Gingerol was purchased from TCI chemicals, China. 5,5'-dimethyl-l-pyrroline-N-oxide (DMPO), xanthine oxidase, cytochrome c, superoxide dismutase (SOD), and calf thymus DNA were purchased from Sigma-Aldrich, USA; remaining all chemicals were analytical grade and purchased from Sigma and HiMedia.

### *In vitro* studies

#### *Erythrocyte membrane lipid peroxidation*

Lipid peroxidation was induced in erythrocyte ghost by adopting the method of Dodge *et al.*[15] Lipid peroxidation was measured by the assessment of thiobarbituric acid reactive substances using Dahle *et al.*'s[16] method. Briefly, 6-gingerol was added at various concentrations ranging from 10 to 100 μg/ml to the reaction mixture. Butylated hydroxyanisole (BHA) was used as a positive control. The absorbance was measured calorimetrically at 535 nm. The percent inhibition of lipid peroxidation was calculated by comparing the absorbance of the test samples with negative control.

#### *Fenton reactant-induced DNA sugar damage*

Oxidative DNA sugar damage was measured by the following Sultan *et al.*'s[17] method. Briefly, 6-gingerol at various concentrations ranging from 10 to 100 μg/ml was added to the reaction mixture and absorbance was read at 535 nm using a Shimadzu ultraviolet (UV)-1800 Spectrophotometer (Tokyo, Japan). BHA was used as a positive control. The percent inhibition of DNA oxidation was measured by comparing the absorbance of the test sample with a negative control.

#### *Hydroxyl radical-mediated DNA damage*

DNA damage was measured on agarose gel by deoxyribose assay.[18] Briefly, 100 μg of calf thymus DNA was added to the 100 μl of reaction mixture and 10 μl of loading buffer was run on 1% agarose with ethidium bromide. The electrophoresis was conducted and DNA was visualized under a UV transilluminator (Bio-Rad, Sydney, Australia). BHA (50 and 100 μg/ml) was used as positive control.

#### *Cytochrome c reduction*

The cytochrome c-reducing capacity of 6-gingerol was measured using the method of Suter and Richter.[19] Briefly, 6-gingerol was added (10–100 μg) to the oxidative cytochrome c and absorbance was assessed at 550 nm using a Shimadzu UV-1800 Spectrophotometer. BHA was used as positive control.

#### *Test for ferric ion-reducing capacity ($Fe^{3+}$ to $Fe^{2+}$)*

The ferric ion-reducing capacity of 6-gingerol was assessed using the method followed by Wang *et al.*[20] Briefly, 6-gingerol was added at various concentrations ranging from 10 to 100 μg to the reaction mixture. The absorbance was recorded at 700 nm using Shimadzu UV-1800 spectrophotometer. Absorbance increases with an increase in ferric ion-reducing capacity.

#### *Test for ferrous ion-chelating activity*

Ferrous ion-chelating activity of 6-gingerol was assessed by the method proposed by Suter and Richter.[19] 6-gingerol at various concentrations ranging from 10 to 100 μg was added to the reaction mixture. The absorbance was measured at 700 nm using Shimadzu UV-1800 Spectrophotometer. Ethylenediaminetetraacetic acid (EDTA) (10–100 μg) was used as positive control. The percent of ferrous ion-chelating activity was measured by comparing the absorbance of the test samples with that of the negative control.

#### *Superoxide-scavenging activity*

Superoxide radical ($O^{-2}$)-scavenging activity was measured using the method followed by Lee *et al.*[21] Briefly, 6-gingerol was added at various concentrations ranging from 10 to 100 μg to the reaction mixture. The absorbance was measured calorimetrically at 560 nm. SOD (10–100 μg/3 ml) was served as positive control. The percent superoxide-scavenging activity was determined accordingly by comparing the absorbance of test samples with the negative control.

#### *Hydroxyl radical-scavenging activity*

Hydroxyl radical-scavenging activity was measured by deoxyribose assay.[18] Briefly, 6-gingerol was added at various concentrations ranging from 10 to 100 μg to the reaction mixture and absorbance was measured at 532 nm. BHA was used as positive control. The percent inhibition of hydroxyl radical-scavenging activity of 6-gingerol was evaluated by comparing with negative control.

#### *1,1-Diphenyl-2-picrylhydrazyl radical-scavenging activity*

1,1-Diphenyl-2-picrylhydrazyl (DPPH) radical-scavenging activity was evaluated by the method of Shimada *et al.*[22] Briefly, 6-gingerol was added to the reaction mixture at various concentrations ranging from 10 to 100 μg/ml. The absorbance was read at 517 nm in a Shimadzu UV-1800 Spectrophotometer. BHA at 400 μM was used as positive control. The percent DPPH radical-scavenging activity of 6-gingerol was calculated by decrease in absorbance at 517 nm in comparison with the negative control.

### Free radical-scavenging activity of 6-gingerol by electron spin resonance

Free radical-scavenging activity of 6-gingerol was determined by electron spin resonance (ESR) spectrophotometer. In this study, JES-FA200 model of X-band ESR (Japan) was used.

#### *Hydroxyl radical scavenging assay*

ESR studies were carried out by the method of Morales *et al.*[23] Briefly, 10 μl of 6-gingerol at various concentrations (10–100 μg/ml) was added to the reaction mixture. Ascorbic acid was used as a reference antioxidant. The ESR spectrum was recorded for every 60 s after the addition of $H_2O_2$.

### *Superoxide anion radical scavenging assay*

ESR studies were carried out using Morals *et al*.'s[23] method. Briefly, 10 µl of 6-gingerol at various concentrations (10–100 µg/ml) was added to the reaction mixture. SOD was used as a reference antioxidant. The ESR spectrum was recorded for every 120 s after the addition of xanthine oxidase at ambient temperature.

## Antiviral activity by *in ovo*

### *Virus*

Komarov mesogenic stain of NDV was obtained from Sri Venkateswara Veterinary University, Tirupati, Andhra Pradesh, India. In our study, 1024 hemagglutination (HA) units of NDV stock was prepared and it was preserved at −40°C until use. Embryonic infective dose ($EID_{50}$) was evaluated by the method of Reed and Muench[24] and it was found $10^{9.7}$ units/ml in chick embryos.

### *Embryonated chicken eggs*

Embryonated chicken eggs were obtained from the Poultry Department, Sri Venkateswara Veterinary University, Tirupati, Andhra Pradesh, India.

### *Inoculation of eggs*

After 9–12 days incubation of embryonated eggs, they were used for NDV infection and this was followed by the treatment with 6-gingerol. Eggs were mainly divided into six groups in which 2nd, 4th, 5th, and 6th groups were again divided each into three subgroups ($n$ = 5) based on the inoculation of 6-gingerol concentrations, 25, 50, and 100 µg/ml, respectively. They were perforated and immediately inoculated by the NDV and 6-gingerol as follows: Group-1 eggs were inoculated with 0.1 ml of phosphate buffered saline, Group-2 eggs were inoculated with 6-gingerol, and Group-3 eggs were treated with virus stock (1024 HA units), Group-4, i.e., pretreated group, where eggs were infected with 0.1 ml of stock virus after 1 h inoculation of 0.1 ml 6-gingerol, Group-5, i.e., posttreatment group, where eggs were treated with 6-gingerol after 1 h inoculation of virus, and Group-6 simultaneously treated group where eggs were treated with 0.1 ml of viral stock along with 6-gingerol. Embryo survival rate was observed daily for 5 days. Allantoic fluid was collected from all the groups for HA test to determine the viral titer in the eggs.

### *Hemagglutination test*

HA test was carried out according to OIE manual (1996) standard diagnostic test. HA test was performed and the observations were recorded. All tests were repeated in triplicates.

## Statistical analysis

Data were represented as mean ± standard deviation by Microsoft corporation , Redmond, Washington, United States GraphPad Software, San Diego, California, USA.

# RESULTS AND DISCUSSION

Some of the ginger nonvolatile pungent compounds (gingerols, shogaols, and zingerone) have antioxidant, anti-inflammatory, and gastroprotective activity,[25,26] and anticancer activity might be due to it's free radical scavenging activity.[26] The phenolic bioactive compounds could reduce the viral growth may due to their antioxidant activity.[27,28] However, the redox active metals play a major role in the generation of free radicals.[29] In stress condition, excess of superoxide release the iron from iron-containing molecules which generate the highly reactive hydroxyl radicals and make the changes in cell membrane, DNA, and other cellular molecules and which induce the diseases.[30] Therefore, in this study, we investigated the effect of 6-gingerol on free transition metal ion-induced free radical-mediated alterations by *in vitro* and antiviral activity on NDV by *in ovo*.

## Inhibition of ghost lipid peroxidation by 6-gingerol

Lipid peroxidation is a complex process occurring in cells and it induces the alterations in the membrane and generates potentially toxic products which are covalently interacting with proteins and DNA[31] bases and damaged. The inhibitory effect of 6-gingerol against ferrous sulfate and ascorbic acid induced ghost lipid peroxidation as shown in Figure 1a. 6-gingerol inhibits the lipid peroxidation at high level about 85.28% at low concentration (75 µg/ml) while BHA showed 73.42% at 100 µg/ml. The levels of lipid peroxidation products may use as biomarkers for the measurement of oxidative stress. Our *in vitro* results suggested that 75 µg/ml concentration of 6-gingerol significantly broke down the chain reaction of lipid peroxidation maybe by donating proton or electrons to the free radicals or chelation of ferrous ions in the Fenton reaction which prevents the generation of free radicals.

## Inhibitory effect of 6-gingerol on Fenton reactant-induced DNA sugar damage

The results shown in Figure 1b exhibit a positive relationship between the concentration of 6-gingerol and inhibition of oxidative DNA sugar damage. The maximum inhibition of DNA sugar damage by 91.26% at 75 µg/ml of 6-gingerol was observed when compared with BHA, which showed 78.30% at 125 µg/ml. Our results suggested that 6-gingerol may have the ability to combat against free radical-mediated degradation of DNA sugar moiety by their antioxidant and metal sequester property.[32,33]

## Protective effect of 6-gingerol on hydroxyl radical-mediated DNA damage

Increased production of reactive oxygen species concerned to increase the oxidative stress by deterioration of antioxidant mechanism which can lead to proliferate the DNA damage and it has been linked to various pathological disorders.[34] In the present study, calf thymus DNA was subjected to the Fenton reactants for 30 min; as shown in Figure 2a, high mobility of DNA (lane-2) was observed on agarose gel when compared with untreated DNA (lane-1) due to extensive DNA fragmentation by hydroxyl radical oxidation. Inhibition of DNA fragmentation of 6-gingerol was observed at various concentrations ranging from 25 to 100 µg/ml. The maximum inhibition of DNA fragmentation was observed at 75 µg/ml (lane 7) which was higher than the known synthetic antioxidant BHA (100 µg/ml) (lane 4). This effectiveness of the 6-gingerol to prevent oxidative DNA damage was concomitant to its hydroxyl radical-scavenging activity. This suggests that 6-gingerol might have the ability to combat free radical-mediated oxidative damage.

## 6-Gingerol cytochrome c reduction

In this study, cytochrome c has been used as a model protein. It is an electron transporter in the respiratory chain. 6-gingerol significantly reduced the oxidized cytochrome c in a concentration-dependent manner (25–100 µg/ml). The maximum cytochrome c-reducing capacity of 6-gigenrol was observed at 75 µg/ml which is higher than the known synthetic antioxidant BHA (100 µg/ml) [Figure 2b]. The earlier studies were shown similar results with the ethyl alcohol and water (1:1) extract of curry leaves which contain reducing compounds that reduce ferric-cytochrome c to ferro-cytochrome c.[35] Reduction of cytochrome c by 6-gingerol might also implemented to maintain the cytochrome c redox state which is an important to regulate the apoptosis.

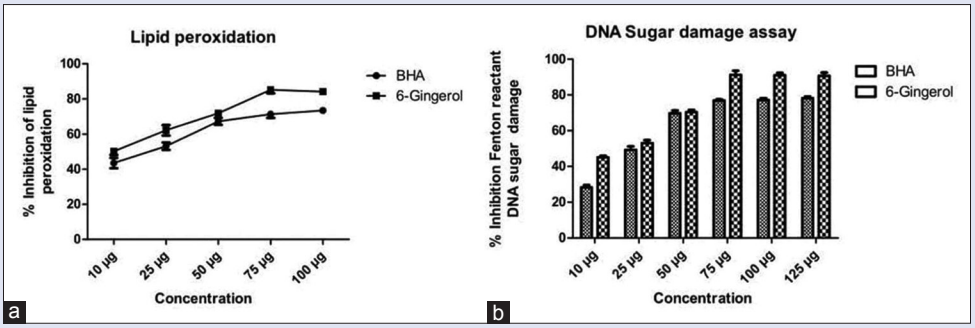



**Figure 1:** (a) Inhibition of rat red blood cell membrane lipid peroxidation by various concentration of 6-gingerol. (b) Inhibition of DNA sugar damage at various concentrations of 6-gingerol compared with butylated hydroxyanisole. The negative control was without any antioxidant or extract. Results are shown as mean ± standard deviation (*n* = 3)

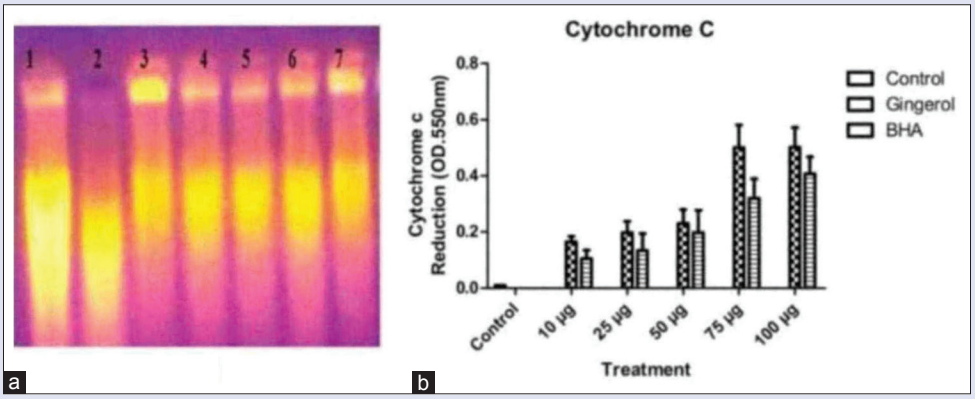



**Figure 2:** (a) Inhibition of hydroxyl radicals-mediated DNA degradation by 6-gingerol. Lane 1: calf thymus DNA untreated; lane 2: Calf thymus DNA + Fenton reactants lanes 3–7 show the results for calf thymus DNA + Fenton reactants solution + butylated hydroxyanisole (50 µg and 100 µg), 6-gingerol at 25, 50, and 75 µg, respectively. Butylated hydroxyanisole is a standard antioxidant. (b) Cytochrome c reduction capacity of 6-gingerol. The positive control was ascorbic acid. Results are shown as mean ± standard deviation (*n* = 3)

## 6-Gingerol ferric ion-reducing capacity

It was mainly depended on the substances those have dropping the electrons or hydrogen atoms for reducing the $Fe^{+3}$/ferricyanide into ferrous form and consequently terminate radical chain reaction. The previous studies have been reported that the extract of spices and herbs showed ferric ion-reducing activity.[35,36] In the present study, as shown in Figure 3a, the maximum reducing capacity of 6-gingerol (1.77 ± 0.10) was observed at lower concentration (75 µg/ml) when compared with BHA at 125 µg/ml concentration (0.912 ± 0.02). The reducing capacity of 6-gingerol might be due to their hydrogen-donating ability.

## 6-Gingerol ferrous ion-chelating activity

Iron is an essential mineral for normal physiology; when it is excess, it facilitates the formation of free radicals via Fenton reaction. The substances those were chelate the iron and removal of free iron from circulation could have valuable antioxidant capability. This can be a promising approach to prevent oxidative stress-induced diseases. Iron pro-oxidant property was last when it is chelated. Hence, we examined the chelation of $Fe^{+2}$ by 6-gingerol in a competitive way with potassium ferricyanide. Interestingly, as shown in Figure 3b, maximum (80.2%) $Fe^{+2}$ binding capability of 6-gingerol was found at 75 µg/ml as evidenced by the low absorption at 700 nm and its chelating effect is comparable with EDTA (50 µg/ml) which showed a chelating effect of 83.93%.

## 6-Gingerol superoxide radical-scavenging activity

The aerobic animals have able to suppressed superoxide anions by their antioxidant defense system when they are produced in certain limits. However, in excess, they cause cell damage.[21] In the present *in vitro* study, superoxide anions were generated via nitroblue tetrazolium (NBT) assay system. The results in Figure 4a showed superoxide anion-scavenging activity of 6-gingerol at various concentrations ranging from 10 to 100 µg/ml. The maximum superoxide anion-scavenging activity of 6-gingerol (84.96%) was observed at 75 µg/ml while it was 78.27% at 100 µg/ml of BHA. SOD was used as a positive control that showed 87.23% at 25 µg/ml concentration. The active inhibition of the NBT reduction by 6-gingerol suggests that 6-gingerol is a potential scavenger of superoxide anion. The previous studies have also been supported to our results; the ginger significantly scavenges the superoxide anions and acts as a dietary antioxidant *in vivo*.[37]

## 6-Gingerol hydroxyl radical-scavenging activity

Hydroxyl radicals are highly reactive substances and are easily to initiate the cell damage *in vivo* when compared with other reduced forms of dioxygen.[38] However, from our results [Figure 4b], 6-gingerol shown maximum hydroxyl radical-scavenging activity by 90.45% at 75 µg/ml which was higher than a well-known synthetic antioxidant BHA (77.25%) at 100 µg/ml. This implies that 6-gingerol may able to reduce the $Fe^{+3}$–EDTA reactions which was initiated the OH radicals using $H_2O_2$.

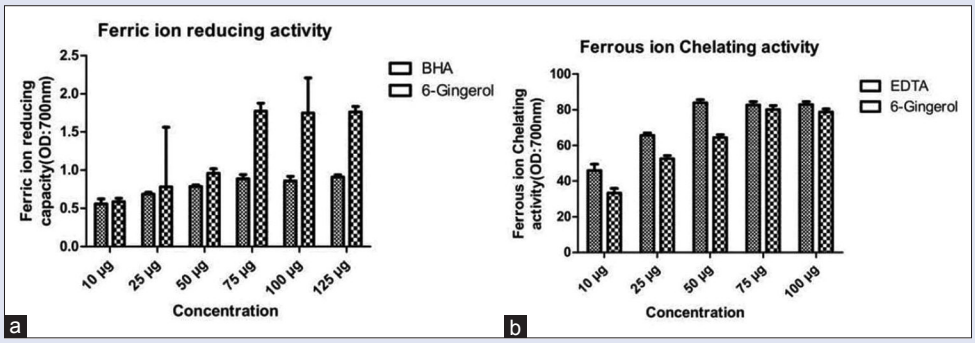



**Figure 3:** (a) Dose-dependent ferric ion-reducing capacity of 6-gingerol. Results are shown as mean ± standard deviation ($n$ = 3). The positive control was butylated hydroxyanisole. (b) Dose-dependent ferrous iron-chelating activity of 6-gingerol. The negative control was without any antioxidant or extract. Results are shown as mean ± standard deviation ($n$ = 3). Positive control was ethylenediaminetetraacetic acid

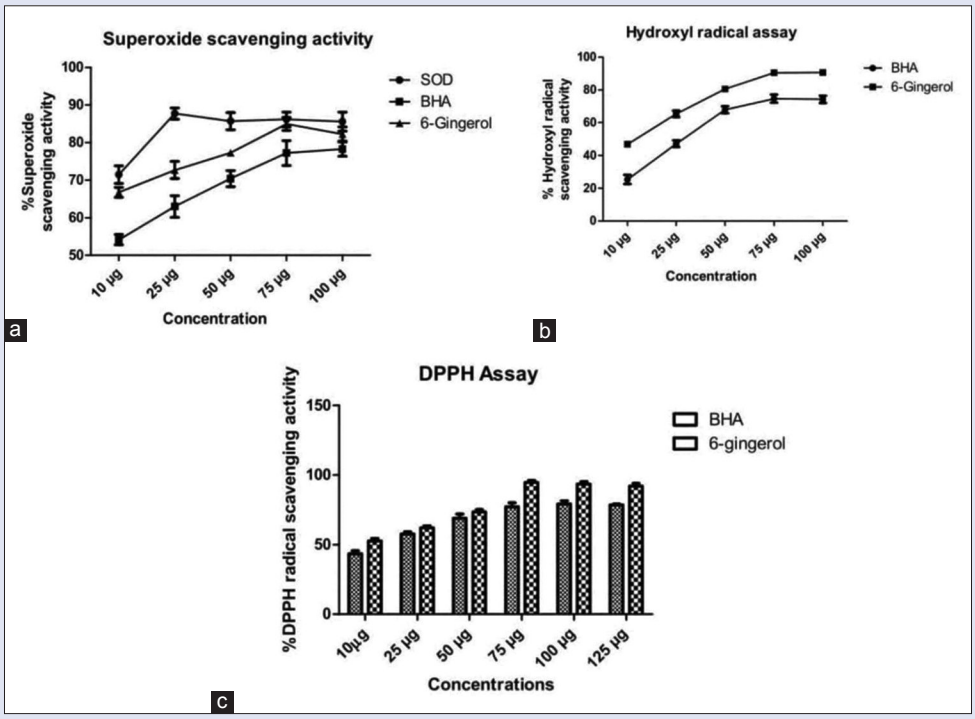



**Figure 4:** (a) The superoxide-scavenging activity of 6-gingerol. The negative control was without any antioxidant or extract. Positive control superoxide dismutase. (b) Hydroxyl radical-scavenging activity of various concentration of 6-gingerol in comparison with butylated hydroxyanisole. The negative control was without any antioxidant or extract. (c) Inhibition of 1,1-diphenyl-2-picrylhydrazyl radicals at various concentrations of 6-gingerol in comparison with butylated hydroxyanisole. Results are shown as mean ± standard deviation ($n$ = 3)

The earlier studies have demonstrated that phenolic compounds showed high antioxidant activity by donating electrons to the free radicals and suppress their activity.[35]

## 6-Gingerol 1,1-Diphenyl-2-picrylhydrazyl radical-scavenging activity

DPPH analysis is one of the tests used to prove the ability of 6-gingerol to act as donor of hydrogen atoms or electrons. The obtained results shown in Figure 4c explain 6-gingerol exhibited a significant effect on inhibition of DPPH radicals in dose-dependent manner. The maximum activity of 6-gingerol (94.66%) was observed at 75 µg/ml and it was higher than the known synthetic antioxidant BHA (79.19%) at 100 µg/ml. The results indicated that 6-gingerol is a powerful free radical scavenger compared with known antioxidant. The hydrogen-donating abilities of the phenolic compounds of the ginger are thought to be responsible for the inhibition of DPPH-free radical.[39]

## 6-Gingerol hydroxyl radical-scavenging activity by electron spin resonance

The ESR spectrum of DMPO-OH adducts showed a typical 1:2:2:1 quarted line. The ESR signal is proportional to the concentration of spin adducts in the solutions. The ESR signal significantly diminished with increase of 6-gingerol concentrations and it was higher at 75 µg/ml concentration [Figure 5a-g] when compared with other concentrations. Consequently, this activity was similar to the reference antioxidant ascorbic acid (75 µg/ml). This activity shown by gingerol may be due to (a) suppression of hydroxyl radicals formation by 6-gingerol in the Fenton reaction, (b) donation of proton or electron to radical spin

**Table 1:** Antiviral activity of 6-gingerol at various concentration

| Treatment Mode | 6-Gingerol dose in µg/ml | No. of eggs | Mortality | | | | HA Test | | % of mortality | Mean Ab Titre |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | 24 h | 48 h | 72 h | 96 h | +ve | -ve | | |
| Normal control (0.1 ml saline) | - | 5 | 0/5 | 0/5 | 0/5 | 0/5 | 0 | 5 | 0 | ≤1/2 |
| 6-Gingerol Control | 25 | 5 | 0/5 | 0/5 | 0/5 | 0/5 | 0 | 5 | 0 | ≤1/2 |
| | 50 | 5 | 0/5 | 0/5 | 0/5 | 0/5 | 0 | 5 | 0 | ≤1/2 |
| | 100 | 5 | 0/5 | 0/5 | 0/5 | 0/5 | 0 | 5 | 0 | ≤1/2 |
| Virus control (0.1 ml of 1024 HA units) | - | 5 | 2/5 | 3/5 | - | - | 5 | 0 | 100 | 1/1024 |
| Pre treatment | 25 | 5 | 0/5 | 2/5 | 2/5 | 0/5 | 4 | 1 | 80 | 1/256 |
| | 50 | 5 | 0/5 | 1/5 | 1/5 | 0/5 | 2 | 3 | 40 | 1/32 |
| | 100 | 5 | 0/5 | 1/5 | 0/5 | 0/5 | 1 | 4 | 20 | 1/8 |
| Post treatment | 25 | 5 | 2/5 | 1/5 | 2/5 | 0/5 | 5 | 0 | 100 | 1/512 |
| | 50 | 5 | 2/5 | 1/5 | 1/5 | 0/5 | 4 | 1 | 80 | 1/128 |
| | 100 | 5 | 1/5 | 1/5 | 0/5 | 0/5 | 2 | 3 | 40 | 1/32 |
| Simultaneously | 25 | 5 | 2/5 | 0/5 | 1/5 | 1/5 | 4 | 1 | 80 | 1/128 |
| | 50 | 5 | 1/5 | 1/5 | 1/5 | 0/5 | 3 | 2 | 60 | 1/64 |
| | 100 | 5 | 1/5 | 1/5 | 0/5 | 0/5 | 2 | 3 | 40 | 1/32 |

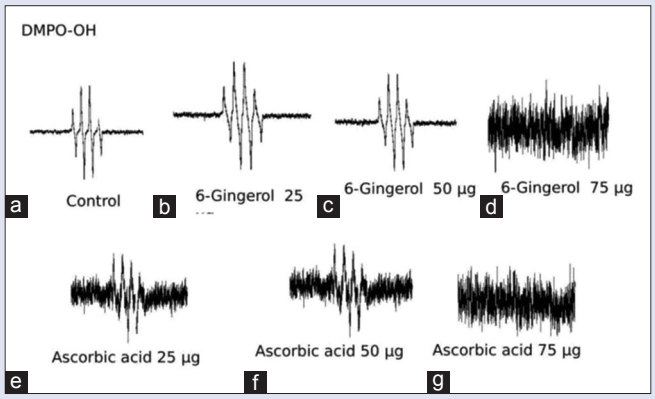



**Figure 5:** Quenching effect of various concentrations of 6-gingerol using 5,5′-dimethyl-l-pyrroline-N-oxide to trap the OH radical. Examples of electron paramagnetic resonance spectra signal ranging from 326–346 mT: (a) Control; (b-g) Effects of concentrations ranging from 10 to 75 µg/ml. The positive control was ascorbic acid

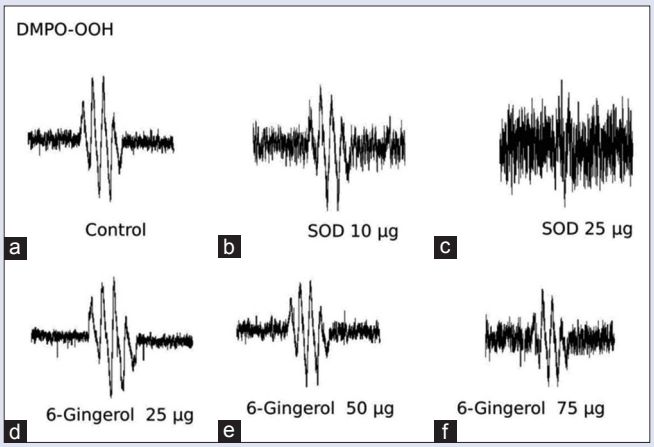



**Figure 6:** Quenching effect of various concentrations of 6-gingerol using 5,5′-dimethyl-l-pyrroline-N-oxide to trap the O2 radical. Examples of electron paramagnetic resonance spectra signal ranging from 326 to 346 mT: (a) = control; (b-f) Effects of concentrations ranging from 10 to 75 µg/ml. The positive control was superoxide dismutase

adduct, and (c) competition between 6-gingerol and the spin trap agent for the hydroxyl radical.[40,41]

## Superoxide anion radical-scavenging activity of 6-gingerol by electron spin resonance

The results obtained are as shown in Figure 6a-f, the intensity of the signals virtually abolished with increasing of 6-gingerol concentrations from 10 to 100 µg/ml, and it was higher at 75 µg/ml of 6-gingerol concentration when compared with other concentrations. However, this activity was similar with the antioxidant enzyme SOD at 25 µg/ml concentration.

In this study, ESR signals of DMPO-OOH were gradually decreased when increased the concentration of 6-gingerol, it may be due to (a) the fact that 6-gingerol inhibits the xanthine oxidase activity and (b) transformation of superoxide anion to oxygen.[42,43]

## Inhibition of Newcastle disease virus growth in chicken eggs by 6-gingerol

NDV has a single-stranded negative probing filamentous RNA.[44] At present, there is no specific treatment for NDV, and it was only controlled by the vaccination. Recently, there has been a growing interest in plants as natural sources for the treatment of viral diseases as therapeutics.

The results from our *in ovo* study, as shown in Table 1, showed that normal control and 6-gingerol alone treated embryonic eggs were not shown any agglutination in HA test and mortality whereas untreated NDV-infected eggs have shown agglutination in HA test (1/1024 virus titer) and all infected eggs died within 48 h. Six-gingerol pretreated viral infected eggs shown 80%, 40%, and 20% mortality rate at concentrations of 25, 50, and 100 µg/ml of 6-gingerol, respectively, whereas in HA test, their viral titer values 1/256, 1/32, and 1/8, respectively. Six gingerol posttreated group eggs showed 100%, 80% and 40% mortality rate at various concentrations of 25, 50, and 100 µg/ml 6-gingerol and their viral titer values were 1/512, 1/128, and 1/32, respectively. Virus and 6-gingerol (1:1 v/v) simultaneously treated group showed 80%, 60%, and 40% mortality rate at various concentrations of 25, 50, and 100 µg/ml of 6-gingerol and their titer values were 1/128, 1/64, and 1/32, respectively.

Several studies made a comparative evaluation of the antioxidant and the antiviral activities of plant extracts and naturals substances. The higher amount of phenolic compounds particularly flavonoids and tannins are known to possess good antiviral activities.[27,28] In our *in ovo* study, 6-gingerol pretreatment significantly exerts antiviral activity in a dose-dependent manner which indicates that 6-gingerol inhibited the viral growth. Post and simultaneously 6-gingerol treated NDV-infected

eggs have shown low titer value in HA test and mortality when compared with NDV control. This could be suggested that 6-gingerol has ability to prevent the NDV growth at some extent. The antiviral effect of 6-gingerol on NDV might be due to killing the virus and/or interfering with viral multiplication[45] or may it exhibit protease inhibition, and hence interferes with cleavage of hemagglutinin neuraminidase and fusion protein, which are important to glycoproteins for NDV attachment and multiplication or virucidal effect.[46,47]

## CONCLUSION

Our research results clearly demonstrated that 6-gingerol has shown a good metal sequesters property by recuperation of free transition metal ion-induced free radical alterations by *in vitro* and it also inhibits the NDV growth in embryonic chicken eggs by *in vivo*. Thus, this study provides a basis for developing a valuable food additive to protect from the free radical-induced alterations and NDV in chickens


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### Conflicts of interest

There are no conflicts of interest.


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## II SEMESTER







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# ANIMAL DIVERSITY-II

# BIOLOGY OF CHORDATES



SREENIVAS-CHAKRAPANI-ANILKUMAR




*II SEMESTER*

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## ANIMAL DIVERSITY-II

# BIOLOGY OF CHORDATES

**MODULE-I (PROTOCHORDATES)**

1.1. General Characters and Classification of Chordates upto classes.

1.2 Salient features of Urochordata and Cephalochordata Salient features of Cyclostomes

1.3 General Characters and Classification of Fishes upto sub class level,

1.4. Structure and life-history of *Herdmania*, Significance of retrogressive Metamorphosis.

# MODULE-I

## INTRODUCTION

Animal kingdom is basically divided into two sub kingdoms:

(a) Nonchordata- including animals without notochord.

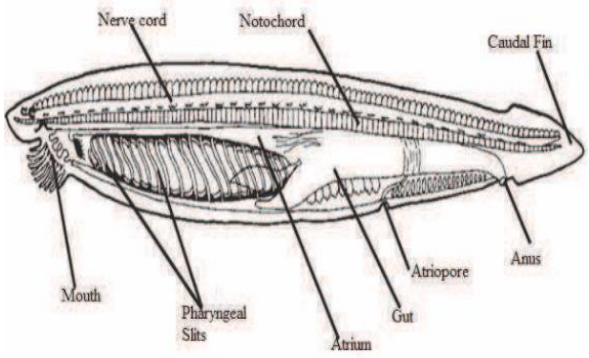
(b) Chordata- This comprising animal having notochord or chorda dorsalis. While the Chordata has a notochord at some stage during the life, it is not known to exist in the Nonchordata.

- The Chordata is the animal phylum with which everyone is most intimately familiar, since it includes humans and other vertebrates However, not all chordates are vertebrates.

- All chordates have the following features at some stage in their life (in the case of humans and many other vertebrates, these features may only be present in the embryos).

- Pharyngeal slits – a series of openings that connect the inside of the throat to the outside of the

"neck". These are often, but not always, used as gills.




- Dorsal tubular nerve cord – A bundle of nerve fibers which runs down the "back". It connects the brain with the lateral muscles and other organs.

Pharyngeal slits dorsal nerve cord & Notochord

- Notochord – cartilaginous rod running underneath, and supporting, the nerve cord.

- Post-anal tail – an extension of the body posts the anal opening.

## ORIGIN OF CHORDATES

It is believed that chordates originated from invertebrates. However, it is difficult to determine from which invertebrate group of the chordate developed.

It is almost constant that chordate ancestors were soft bodied animals. Hence, they were not preserved as fossil.

Many theories have been put forward to explain the evolution of chordates, few of them are as follows:

### (a) COELENTERATE THEORY:

According to this theory chordates developed from coelenterates.

It is belived that radial symmetry coelenteron, cnidoblasts etc, disappeared and advanced characters developed to give rise the chordates.

This theory infers that chordate might have acquired higher characters independently. This theory is not acceptable.

**(b) ANNELID THEORY:** This theory suggests that the chordates have evolved from an annelid stock, like many chordates the annelids show bilateral symmetry, metasmerism, head, lateral coelome complete digestive tract, closed circulatory system, haemoglobin, etc.




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# ANIMAL DIVERSITY-II

# BIOLOGY OF CHORDATES

**MODULE-II (FISHES & AMPHIBIA)**

2.1. *Scoliodon*: Morphology, structure of Heart, Brain and sense organs.

2.2. Migration in fishes and types of scales - Dipnoi fishes

*2.3 Characters and Classification of Amphibia upto orders*

*2.4. Rana* : Morphology, respiratory system, structure of heart, Brain and reproductive systems only.

# MODULE-II

**External Features of Dogfish (Scoliodon):**

**Shape, Size and Colour:**

Dogfish (Scoliodon) has a long, laterally compressed spindle-shaped body tapering at both ends. The fully grown specimen measures from 30 to 60 cm in length. The colour of the body is dark grey above and pale white beneath, while the portions of the caudal fin are more or less dark. Body surface is rough due to backwardly directed spines of placoid scales embedded in the dermis.

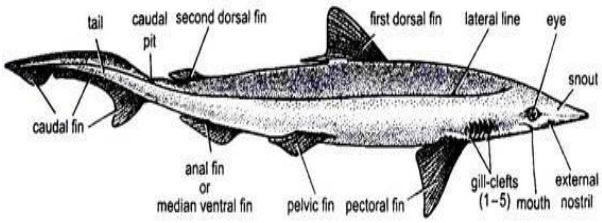



Fig. 14.1. *Scoliodon*. External features.

**Division of Body:**

The body is divisible into head, trunk and tail, though there are no distinct boundaries between these regions.

**(i) Head:**

The head is strongly compressed dorso-ventrally and is produced in front into a wedge-shaped snout or rostrum.

**(ii) Trunk:**

The trunk is almost elliptical in transverse section. Its thickest part lying in front of the middle of the body. The trunk gradually tapers behind into the tail.

**(iii) Tail:**

The tail is laterally compressed and is bent upwards at a small angle and fringed with a caudal fin. Such a tail is known as heterocercal tail.

**Fins:**

Dogfish (Scoliodon) is provided with two sets of fins which are flattened expansions of the skin supported by cartilaginous rods and horny fin rays- these are unpaired or median fins and paired lateral fins.

**(i) Median Fins:**

The median fins are two dorsal fins, a ventral or anal fin and a caudal fin. The first dorsal fin is large and triangular in shape and is situated a little in front of the middle of the body. It has a basal lobe. The second dorsal fin is also triangular in outline but is very small and is situated midway between the first dorsal and the tip of the tail. The caudal fin extends along the dorsal and ventral




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# ANIMAL DIVERSITY-II

# BIOLOGY OF CHORDATES

**MODULE-III (REPTILIA)**

*3.1. Characters and Classification of Reptiliaupto orders*

3.2. *Calotes*: Morphology, digestive system, urinogenital system and Brain

3.3. Identification of Poisonous snakes

# MODULE-III

**REPTILIA: CHARACTERS AND CLASSIFICATION**

Reptiles are cold-blooded vertebrates, breath by lungs and having the body covered by scales or scutes.

General characters:

- They are inhabitants of terrestrial and aquatic (both marine and freshwaters) environments.
- Their skin is dry, cornified and usually covered by **epidermal** scales or scutes. There are a few integumentary scent glands secreting pheromones during breeding seasons.
- Single external nasal opening is present on the snout. Ear drums are slightly depressed.
- Two pairs of pentadactyle limbs are present. The limbs end in clawed digits.
- The cloacal opening is either transverse or longitudinal.
- A post-anal tail is present.
- The heart is composed of two auricles and a partially divided ventricle. There are right and left systemic arches.
- The kidney is metanephric type.
- Mullerian duct persists as oviduct in female and Wolffian duct is retained as vas deference in male. Males possess copulatory organs.
- Twelve pairs of cranial nerves are present.
- Vomero-nasal organ (Organ of Jacobson) is well-developed.
- Single occipital condyle in the skull is present for the attachment with atlas.
- Mandible consists usually six pieces of bones.
- Vertebrae are procoelous. Sternum is greatly developed with ribs.
- Cleidoic eggs are large. The calcareous shell serves for protection against desiccation and external injury. The shell is porous for gaseous exchange.
- Fertilisation is internal.
- Embryos are provided with extra-embryonic membranes, like amnion, chorion and allantois.

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# ANIMAL DIVERSITY-II

# BIOLOGY OF CHORDATES

**MODULE-IV (AVES & MAMMALS)**

4.1. General characters of Aves and Classification of Mammals- comparison of Prototheria, Metatheria and Eutheria
4.2. Pigeon (*Columbia livia*) : Exoskeleton, respiratory system, structure of heart,
4.3. Migration in birds and its significance, Flight adaptation in birds
4.4. Dentition in Mammals,

# MODULE-IV

# GENERAL CHARACTERS OF AVES

## Introduction:

Class Aves includes birds, bipedal vertebrates. Birds are unique in having feathers as their exoskeleton. Aves originated from therapod dinosaurs in Jurassic period and modernized in the cretaceous period. **T.H.Huxley** called birds "G**lorified reptiles"**. **J.Z. Young** described them as the "**Masters of air**" . Ornithology is the study of birds.

## General characters of Aves

- Birds are cosmopolitan and found in all continents, seas and most islands.
- Their wide occurrence is due to their power of flight, which enables them to reach places unreachable to other animals.
- Most of them can fly and a few have lost the power of flight.

## Body temperature:

- They are **homeothermic** (**warm blooded**) and the body temperature provides high metabolic rate for quick energy supply.
- Birds are **endothermic**, and expend a lot of energy to keep warm.

## Body form and appendages:

- The body is boat shaped and streamlined.
- It is divisible into **head, neck, trunk** and **tail.**
- The forelimbs are modified into wings for flight which are supported by powerful flight muscles attached to the sternum.
- Each fore limb has 1 to 3 digits and each hind limb has 1 to 4 digits.
- The hind limbs are used for perching, walking, hopping, wading, swimming etc.
- Skin is dry and thin except for uropygial or oil gland on the tail.
- Body is covered by epidermal horny skeleton of feathers which conserve body heat, help in flight and provide colouration to the birds.

## Endoskeleton:

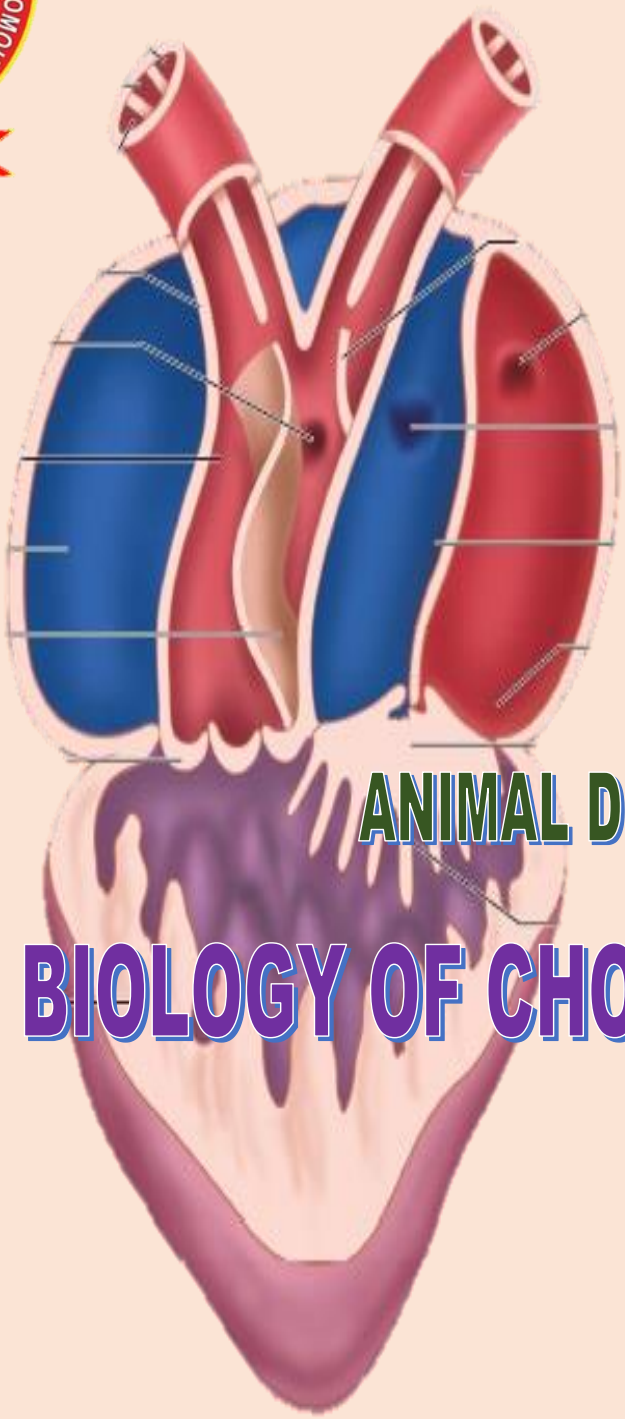
- The endoskeleton is bony, but delicate and light.
- Skull is **monocondylic**, i.e., with single occipital condyle.
- Sternum is usually large and with a median keel for the attachment of flight muscles.
- Bones are pneumatic, i.e., contain air cavities to reduce weight.

## Digestive system:

- Mouth has a wide gap and jaws are covered with horny sheaths to form strong beaks.
- Beaks are adapted to various modes of feeding: seed-crushing, fruit-scooping, fish-tearing, nectar-sipping, wood-chiselling, grain-pickling etc.
- Teeth are absent and food is swallowed un masticated.
- The **crop** stores and softens food.
- Alimentary canal often has additional chambers; **crop and gizzard.**
- Gizzard is muscular to crush and churn the softened food.
- Some birds keep stone in the gizzard to effectively crush seeds and grains. Alimentary canal leads to the cloaca.
- The cloaca is divided into three linear compartments: i.e., anterior **coprodaeum** middle **urodaeum**

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# Portrayal of the Poor and Oppressed in the Select Novels of Charles Dickens and Mulk Raj Anand: A Comparative Study

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**Abstract**: Charles Dickens, the greatest English novelist of the Victorian Era, attempts to draw the attention of his readers with the theme of poverty, one of the central problems in some of his novels. Mulk Raj Anand, an eminent Indian writer in English, is notable for his depiction of the lives of the poorer castes in traditional Indian society in his novels. The present article aims at making a comparative study of the poor and oppressed people in the novel *Oliver Twist* by Charles Dickens, and *Untouchability by* Mulk Raj Anand. The problem of poverty was very serious in English society of the late 19th century, and so Charles Dickens chose this theme as one of the central themes of some of his novels including *Oliver Twist* (1839). This novel represents the Victorian English society where the poverty is next to enormous wealth. Mulk Raj Anand's debut novel *Untouchability* exposes the oppression, injustice, exploitation to the whole community of the outcastes in India. This novel covers the span of a decade from 1930 to 1940 when poverty, slavery and the inhuman exploitation of the masses were at the peak. Both the writers in their novels focus on the poor, suffering and wretchedness of the poor. The outcastes are exploited by almost all on the economic level too. To both the writers, exploitation of man is immoral and impermissible, particularly the poor and the illiterate. Both of them depict the lifestyle of the poor and the upper class.

## I. INTRODUCTION

Dickens was not only the first great urban novelist in England, but also one of the most important social commentators who used fiction effectively to criticize economic, social, and moral abuses in the Victorian era. Dickens showed compassion and empathy towards the vulnerable and disadvantaged segments of English society, and contributed to several important social reforms.

Dickens believed in the ethical and political potential of literature, and the novel in particular, and he treated his fiction as a springboard for debates about moral and social reform. In his novels of social analysis Dickens became an outspoken critic of unjust economic and social conditions.

Dickens was not the first novelist to draw attention of the reading public to the deprivation of the lower classes in England, but he was much more successful than his predecessors in exposing the ills of the industrial society including class division, poverty, bad sanitation, privilege and meritocracy and the experience of the metropolis. In common with many nineteenth-century authors, Dickens used the novel as a repository of social conscience

Mulk Raj Anand a socially committed novelist has produced a good deal of literature. He has written more than a dozen novels and about seventy short stories. He focused his attention on the sufferings, misery and wretches of the poor as a result of the exploitation of of the downtrodden classes of the Indian society. His themes mainly deals with the poverty, society hunger and exploitation.charless dickens is one of the greatest novelist in the English literatures. He wrote about the real world. He wrote about the poor people and social injustice

The theme of poverty remains on the central problems that Charles dickens focuses and attempts to draw attention to his readers. The problem of poverty becomes a serious social and economic burden of English society of the late 19th century. The two writes are compared here as their themes were more related with the poor and oppressed people and social exploitation. Mulk Raj Anand was also called as Indian Charles dickens.

Oliver Twist (1837-39), which represents a radical change in Dickens's themes, is his first novel to carry a social commentary similar to that contained in the subsequent Condition-of-England novels Dickens explores many social themes in Oliver Twist, but three are predominant: the abuses of the new Poor Law System the evils of the criminal world in London and the victimisation of children. The critique of the Poor Law of 1834 and the administration of the workhouse is presented in the opening chapters of Oliver Twist. Dickens gives the most uncompromising critique of the Victorian workhouse, which was run according to a regime of prolonged hunger, physical punishment, humiliation and hypocrisy Oliver fell on his knees, and clasping his hands

together, prayed that they would order him back to the dark room—that they would starve him—beat him—kill him if they pleased—rather than send him away with that dreadful man [1]

In Oliver Twist Dickens presents a portrait of the macabre childhood of a considerable number of Victorian orphans. The orphans are underfed, and for a meal they are given a single scoop of gruel. Oliver, one of the oppressed children, dares to ask for more gruel and is severely punished.

The evening arrived; the boys took their places. The master, in his cook's uniform, stationed himself at the copper; his pauper assistants ranged themselves behind him; the gruel was served out; and a long grace was said over the short commons. The gruel disappeared; the boys whispered each other, and winked at Oliver; while his next neighbours nudged him. Child as he was, he was desperate with hunger, and reckless with misery. He rose from the table; and advancing to the master, basin and spoon in hand, said: somewhat alarmed at his own temerity: 'Please, sir, I want some more.' [2]

This scene, which has become "the most familiar incident in any English novel" strongly appealed to the Victorian conscience. Dickens challenged the Victorian idea of charity for the so-called "deserving poor". He showed persuasively that the workhouse was a failed attempt to solve the problem of poverty and unwanted children.

Anand's novel Untouchable expresses his great advocacy of the marginalized and defenceless against their age long humiliation, persecution and oppression. Anand himself observes Great author is to highlight the cause of the dumb and the deserted, the lowly and the lost of an adverse society. The author also flings a harsh irony on the snobbery and hypocrisy, ostentation and fabrication of the aristocratic people who, sometimes One of the prime concerns of a stoop low to achieve the end. A writer, the prince of the pen, is the true voice of the million mass particularly of the untouchable and the vulnerable victimized by undeserved tyranny and injustice from the time immemorial. And this is what prompted Mulk Raj Anand to present the deplorable description of the destitute

In this article there were a lot of similarities in the works of Charles dickens oliver twist and Mulk Raj Anand untouchable .First if we go for the work of Charles dickens. Charles Dickens in this novel Oliver Twist depict English society of Victorian age which is full of contrasts where the poverty is next to snornious wealth, and where spiritual richness is often overshadowed by the material desperate social portions of the characters of novels.dickens pores a question whether poverty is really a sinn or something really bad that make people fall lower and lower in the social ladder or probably it is just a poor material portion of individuals.

In the novel untouchable by Mulk raj anand covers the san from 1930 to 1940 when poverty slavers and the inhuman exploilation of the masses were at the peak .In this Novel untouchable by Mulk raj anand the characters in this novels belongs to downtreden society.There was a poverty and slavery in this Novel,the authorisation of high class society on low class society, hunger and poverty is potrayed in this Novels.So, in there two novel both the writers used the themes of poverty, hunger, social status and human exclopitation .

Charles dickens depicts the opprersive nature of the 19$^{th}$ century society and subjection of the poor and poverty.while Mulk raj anand depicted the poor and oppressive nature of 21$^{st}$ century society and its subjection of the poor and poverty. Both the novels oliver twist and untouchable well illustrate the situation and condition of the lower class Juxtapore against the lavish liver of middle classes and the aristocracy.In oliver twist oliver is the protagonist, he is an orphan. Oliver twist and his companions suffered the tortures of slow staruation for many days.the powerful pathor and visual imagery which dicken user in deserileing Oliver is a martuful creation to intensify the gravity of circumstances in which Oliver finds himself. The staruation of the poor at athe work houses was also a reflection of the hunger encountered by the paupers outside the poor work houses.

In untouchable Bakha is the protagonist. Anand is the first Indian novelist to have depicted in the novel from the stigma of this eveil which isolates a man from his own society. The character in his novels belongs to the down trodelen society. The characters are normal, simple, credible human being unaware of their social conditions.Bhaka shouts for foods and begs for food.The woman comes out and throws a chapatti for him, he suffered with hunger all the day. M.K Naïk writes "Untouchable is a scathing incident of Hindu society and irony is the weapon of this indictment"[3]

There were many situations in oliver twist where oliver was insulted many times, from his birth, when oliver goes to the workhouse, he is introduced to ten fat gentleman and one who was particularly fat with very round red face. The fat gentle men are juxtaposed against the children at the poor houses who were starved as evidenced by the scene in which the older children forced oliver to ask for more food. In the novel it is stated that the immater were fed on the small quantities of oatmeal, three meals of thin gravel a day and half a roll on Sundays. The same way untouchable by Mulk raj anand also depicts the related circumstances, Bakha a sweeper boy and a latrine clean starts his day welcomed by the abuses of his latrines with a brush and bucket.After cleaning roads and toilets in house, he goes to an alley nearby to beg for food. When bakha returns home, he tells his father They think we are mere dirt because we clean their dirt" [4]

He starts shouting or food but nobody responds tired of the hectic schedule he sleeps on the wooden platform in front of a house.The woman comes out of the house on the call of a sadhu.She shouts at Bakha for polluting her house.She asks him to clean the drain to get a piece of bread. Mean while a woman from neighbouring house gives him a chapatti .Mulk raj anand in his article "The source of potest in my Novels" say I wished to create the folk, the lumpens and the suppressed, oppressed, repressed, those who have seldom appeared in our literature"[5]

In oliver twist the poor were actually oppressed and those who were not living in the work house were forced to work and they could no longer be provided with any aid.In Victorian age the authorities believed that the paupers were lazy and idle, yet hey failed to understand that they were poor because of lack of employment and if they did final any work at all, it was always low paying petty work like sweeping and repairing roads.Even though the poor laws were snacted to arrist the poor, they did nothing to change their plight or improve their situation.The poor were furthered exploited by physical and emotional abuses. and takes him to his home lifting on his hand. The thankless mother of the child shouts at him for defiling her house. For the work he did they throw the bread of slice on him as they do to animals so they workhard, they were ill treated due to their poverty, hunger and low_ class. Oh! You eater of masters what have you done ?....Give me my child ...you have defiled the houses besides wounding my son"[6] In case of Mulk raj untouchable in period from 1930 to 1960's in India the poor end lower cartes were treated very badly, there were some invidents that happend in a day to Bakha. He receives a slap from the high cart Brahmin for defiling him by his touch makes him aware of his true identity. An other incident he faces at another moment of humiliation at the steps of the temple that increases the rage of his soul. Once when he saved the child from accident

In untouchable the themes of exploitation are best expressed through the character of sohini Bakha's sister. She not only excmplifier caste expoitation but also six exploitation.Gulabo a washer woman, a caste superior to other cartes exploits sohini, she being of the low carte among he outcartes would naturally be looked down upon by Gulabo. She becomes the victim of sexual exploitation due to here carte and poverty.

Dickens successfully portrays the child exploitation in Oliver twist . He potrays it as the abuse of them in 19$^{th}$ century Britian. Most of there children are orphans and also members of the low class, therefore they were economically desparate and they were forced to endure by means of survivial even if it meant accepting maltreatment. In oliver twist olivers feels alone, he dislikes being alone and having no body to care for him, where as in untouchable Bakha also feels alone though he has a father lakhe who is not piety enough towards his son and daughter and always abuses him with his bad words.

Dickens showed compassion and empathy towards the vulnerable and disadvantaged segments of English society, and contributed to several important social reforms. Dickens's deep social commitment and awareness of social ills are derived from his traumatic childhood experiences when his father was imprisoned in the Marshallese Debtors' Prison under the Insolvent Debtors Act of 1813, and he at the age of twelve worked in a shoe-blacking factory In his adult life Dickens developed a strong social conscience, **an** ability to empathise with the victims of social and economic injustices

Mulk Raj also have the child hood experiences which he portrayed in untouchable Bakha's character is modelled after one of Anand's childhood friends, who was humiliated by his own mother for being a sweeper boy but whom Anand adored as a hero. Anand could never forget that sweeper boy and the insult and humiliation that he received by Anand's family. He gave voice to his views against the exploitation of a sweeper-boy through the character of Bakha in his very first novel *Untouchable*.

Dickens explores many social themes in Oliver Twist, but three are predominant: the abuses of the new Poor Law system, the evils of the criminal world in London and the victimisation of children... Dickens gives the most uncompromising critique of the Victorian workhouse, which was run according to a regime of prolonged hunger, physical punishment, humiliation and hypocrisy. Mulk Raj also explores social themes in untouchable he focused his attention on the sufferings, misery and wretchedness of the poor as a result of the exploitation of the downtrodden class of the Indian society. Religious hypocrisy, feudal system, East-West encounter, the place of woman in the society, superstitions, poverty, hunger and exploitation are his common themes.

In Untouchable Bakha suffers without any fault of his own. The slap he receives from the high caste Brahmin for defiling him by his touch makes him aware of his true identity. Soon after this he faces another moment of humiliation at the steps of the temple that increases the rage in his soul. But the molestation of his sister by the priest turns him violent to which he reacts aggressively. But his hereditary serfdom acts as a handicap to his spontaneous rebellion. In both the cases oliver in oliver twist and bakha in untouchability become rebellious towards the attitude of their superiors. He is simultaneously an exploited person and a rebel. He is scapegoat of the rigid caste system. Injustice inflicted upon him makes him rebellious. Excessive buses and insult makes him think about retaliation. At such moments he feels like a tiger at a bay. Saros Cowasjee in her book *So Many Freedoms* rightly says, But he is a tiger in a cage, securely imprisoned by the conventions his superiors have built up to protect themselves against the fury of those whom they exploit. [7]

## II. CONCLUSION

In the comparative study of both the novels oliver twist by Charles dickens and untouchable by Mulk Raj Anand there were a lot of similarities related to the poverty and oppression .Though the countries were different, traditions were different, culture changes but the poverty remains the same. Both the protagonists Oliver Twist and Bakha suffered throughout the novel because of poverty and oprresion. There were many similarities in writings of both the authors.

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# "A Study of Human Heart": Little Dorrit by Charles Dickens

Abstract

The present paper aims at describing about the novel Little Dorrit by Charles Dickens. This is about how a girl of tender age in a family come across many problems and how she overcome all those hurdles in her life and how she saves her family which includes her father who was imprisoned for a long period for his debts and her brother and sister. By the end of the article we find her life ended happily and how she was blessed with a happy life, who helped her to solve her problems and ended her tragic life. The role played by her throughout novel to overcome her problems.

Key words: Charles Dickens, Little Dorrit, problems, solve, overcome.

## Introduction

Charles Dickens is remembered today as one of the greatest and most popular writers of the novel ever to have lived. Dickens captured the spirit of his age in both a profound and entertaining way. He wrote wit and humour, but he also wrote about the everyday tragedies of life he saw around him. Dickens was the greatest of English 19th century novelists but also captured the spirit of the times in which he lived. His own life and the age in which he lived were tightly intertwined, more so than with most writers.

Dickens believed in the ethical and political potential of literature, and the novel in particular, and he treated his fiction as a springboard for debates about moral and social reform. In his novels of social analysis Dickens became an outspoken critic of unjust economic and social conditions. Dickens was not the first novelist to draw attention of the reading public to the deprivation of the lower classes in England, but he was much more successful than his predecessors in exposing the ills of the industrial society including class division, poverty, bad sanitation, privilege and meritocracy and the experience of the metropolis. In common with many nineteenth-century authors, Dickens used the novel as a repository of social conscience.

Marshal sea prison is a place which stood within high walls in the London borough of Southwark. These walls encircled squalid houses which contained all manner of people all of whom shared a common fate for one reason each had the disgrace of being in debt. Rather than being granted the liberty to earn money to repay their creditors, they languished in prison. Mr.Dorrit was one such man. His complex business affairs had failed, and for the past 22 years he and his children had lived in one house within the prison. For all the 22 years of her life, the Marshal Sea was the only home little Dorrit known.

In Marshal sea prison Mr.Dorrit saw his wife die in prison, and there his children had grown up .The passing years had made this shably, soft mannered debtor respectful figure among other prisoners, gradually earning him the title of “Father of Marshal sea “In this grand capacity Mr.Dorrit would welcome new prisoners with pomp and gravity and receive money it became traditional to pay him upon departure.

“It became a not unusual circumstance for letters to be put under his door at night, enclosing half a crown, two half –crowns, now and then at long intervals even a half –

a-sovereign, for the Father of marshalsea, and with the compliments of collegian taking leave (LD.P.80)"

Arthur settled and earned a lot of money in business and decided to return back to London where his mother stayed. In past 20 years he had been working in china with his father. He returned back and felt there was no change and development in London. He found his family in its familiar gloom and darkness. The house brought him back all painful memories. His parents believed that suffering in life would gain them forgiveness for their sins when they die. Arthur is 40 years old .he feels he became old and decided to spend rest of his life in London with his mother. But his mother was not happy for his return from china. She is confined to wheel chair. Arthur handed his mother an old fashioned watch in a heavy case. He said it was his father's last wish to present this before he died. The watch has the letters DNF inside it. He asked his mother the meaning of it. She felt very anger and bitterness. She can neither forget nor forgive. At that movement Arthur noticed a girl for first time, a girl sitting in the shadows was employed in some needle work. She was working with his mother. The girl was very calm, she never ate the food given to her but she take to home. She worked for 12 hours; his mother has a good concern for her.

As the days passed Arthur grew increasingly curious about the girl who worked so quietly for his mother for 12 hours a day. The truth about little dorrit he came to know was that with love and devotion she worked hard to support her family. She had learned needle work from a milliner in the marshal sea prison, so she could earn money for her father.

She has secured work as a dancer for her sister Fanny and had found numerous jobs for her slovenly brother Tip. They all relied on her .They all took her for granted. Little Dorrit might have been little in body but not in spirit. This is the life to which Little Dorit returned as she fitted through the prison gaiter watched by Arthur clennam .One day he made up a story for the gate keeper, handed over a little money and was shown to Mr.Dorrit room. Little dorrit was alarmed when she opened the door to her employers son, but his eyes treated her to trust him. She introduced him to her father as a friend. Arthur invited little dorrit to walk with him outside the prison.

"Thus they emerged upon the iron bridge, which was as quite after the roaring streets, as though it had been open country. The wind blew roughly, the wet squalls came rattling past them, skimming the pools on the road and pavement, and raining them down into river. (LD.P.114)

Mean while she explained everything about her family and about her father.Arthur agreed that a man cannot be blamed simply for being poor. Arthur said that many good people are there who have fallen on misfortune through no fault of their own. Arthur expressed his wish to be a friend of Dorrit. He also asked her to tell the names of creditors so that he may try to persuade them to cancel defects Little Dorrit said thought for a movement .She said there was somebody called Barnacle .He works in circumlocution office.

Arthur mind was full of questions that night about little Dorrit, he questioned himself, why he was trying to help her. What reason could his mother have to treat Little Dorrit with unequal kindness He thought that Mr.Dorrit debts had something to do with the Arthurs business He also thought Dorrit confinement in prison and his mothers self imprisonment in her room both be part of a deal she had struck with heaven. The Circumlocution office was the main office of the British government, specialising in meetings, committees, complaining forms. It never made any decisions nor took any positive actions. It insisted to squash original ideas and dam pick independence and inventiveness. The works of thousands good people with projects that might benefit the people of Briton were lost under piles of papers in circumlocution office.

The Barnacles were a large, very important family they held all the most powerful positions in the circumlocution office just as Barnacles cling to a ship of state. If the ship sank with them clinging to it, that was the ships problem, not theirs. After 5 days of queuing and filling in forms at the circumlocution office, Arthur finally had the houner of meeting at Barnacles but the junior to Barnacles said he had not got appointment .Arthur felt very disappointed .He said to fill a another form ,send to another department ,for sign from there to other department.

Barnacle junior said about this, Arthur suggested it was not the way to do business, but the junior said, if you want you can, otherwise stop filling them. Arthur sat with his head in his hands outside the circumlocution office, wandering what to do. Next to him a soft weary voice observed, Arthur turned and saw a person who was very smartly dressed, gray haired man at his side. His name was Daniel Doyce. Arthur introduced himself about how 12 years ago; he invented something and thought he could make useful to their country. He said that he had been wasting his time and money in circumlocution office, trying to advance his invention he was the inventer, public offender and outlaw.

Arthur also introduced about himself ,he said about his work hope" bleeding heart yard", he said it was an appropriate named for a place where peoples hopes had been crunched .Hence then Introduced his friend Mr.Pancks who was a rent collector, he introduced him to Arthur. Pancks said he has a great in rest tracking family histories. Pancks explained, he said he can find all orts of things forgotten wills, Estates that Avnet been claimed. Arthur briefly explained his business at the circumlocution office. He explained everything of Mr.Dorrit. Then Pancks promised that he will find out information.

Arthur gladly accepted Doyce offer of a job taking care of his company finances. They became very close friends. Arthur felt very happy over bleeding heart yard and spending his time with Little Dorrit. Once Little Dorrit came to his office and said that her mother's servant Mr.Flinwinch in the shadows by the prison gate, and also another man with strange black spiny. By the time Pancks got in and introduced himself to Little Dorrit and asked to give her palm and said about her future. Arthur work in Bleeding heart yard brought him into contact with a gentleman called Mr.Meagles and his beautiful daughter Pet Meagles. Arthur remains of himself that he was 40 years old, Far too old to fall in love.

It was a very good thing for Arthur that he had resolved not to fall in love, for otherwise he would have grown to hate the handsome wealthy Mr.Gowam who would have been his rival in Pets love. against the will of her father Pet Meagles loved Mr.Gowdam, and agreed to marry him when Arthur heard of their Intended marriage .He went along for a walk by the river, carrying a bunch of roses he had intended to give to Pet as the roses were go into the river, the roses floated away on the river .Arthur went to marshal sea several times to see Little Dorrit.

"He put the roses in his breast and they walked on for a little while, slowly and silently, under the umbrageous trees. Then he asked her, in a voice of cheerful kindness, was there anything else that she would say to him as her friend and her father's friend, many years older than herself (LD.P.398)"

But whenever he called she was too busy to see him. Once they meet each other left the confines of the prison and walked side by side. Dear Little Dorrit soothed Arthur. He asked her why she was avoiding him, did she have a secret love with anyone, and Dorrit said not at all and said she was busy.

"They were very near the end of their walk, and they now came out of the gateway to finish it. Nothing would serve Maggie but they must stop at the grocer's window, short of their destination, for her to show her learning (LD.P.122)"

By the time Arthur and Dorrit returned to Marshal Sea Mr.Pancks was waiting at the gate. He was carrying a huge file full of papers. He said to Dorrit, as good fortune Arthur feeling a Fluttered of anticipation, took Pancks to his side and spoke hurriedly. Arthur made Dorrit to sit on a stone bench and held her hands in his face and said that his father can be a free man, he had inherited great wealth. Little Dorrit felt a dizzying sensation, as thought she was been physically lifted from the scholar around her.

All the three went to Mr.Dorrit in his old gray room wearing old gray gown and black cap. Dorrit informed his father about their fortune. She said the wall was gone, and you are prosperous. Arthur explained everything about the inheritance, Mr.Dorrit demanded to see Pancks and he was happy to pay him some money. His priority was to incur that his family should be worthy of noble and dignified family name of Dorrit. All wore new clothes, they all claimed into their carriage but they not found Little Dorrit. They saw Arthur carry Dorrit in his hands, and said to them that they forgot her, when she went to change her dress she fainted away.

The Dorrit family escape from the prison was a grand occasion people cheered from the yeard as the great gate opened. Anybody with sufficient wealth to be accepted by society knew of Mr.Merdle he was immensely rich and it was rumoured that every business he ever touched turned to gold, whether it be banking or building Mr.Merdle did everything that society accepted of him. Mr.Merdle was a reserved man and his wife was dissatisfied. It was to society that Mr.Dorrit and his family were now introduced .Mr.Dorrit had instructed his three children never to mention the Marshalsea. They must abandon all their previous habits of humility and present themselves as anybody's equals. They has a son Edmund Sparker who started at fanny in admiration from the movement he saw her. Mrs.merdle was keen to encourage this relationship with such a fine family. Within weeks arrangements had been made for Mrs.Merdle and her son to join the Dorrit family on a grand tour of the Alps and Italy.

A few weeks later Arthur received a letter from Dorrit and come to know about her sister marriage and about her. Arthur feels as he missed Little Dorrit terribly. Daniel Doyce had finally decided to his invitation to Russia, when he was meeting with great success. He

had left Arthur in a charge of the business in Bleeding Heart Yard. Doyce feels he had perfect confidence in Arthurs ability .He suggested him not to make risky investment. Arthur shared his partner's opinion. He says he had seen men lost all their money by making unsafe investments. Arthur said his mother about the Dorrits family change of fortune, then his mother felt happy and said to herself that she did nothing harm to her and felt relived.

Pancks suggested Arthur to invest Doyce money in Merdles and it would be as safe as house. He believed and investment in merdles so Doyce's property would double. Mr.Dorrit felt to accompany Fanny and Edmund back to London for their wedding. During the long journey back to Italy Mr.Dorrit felt ill and tied. He experienced a strange yearning for his former life in Marshalsea, yearning which made his heart ache .After they have arrived in Italy, Little Dorrit noticed the change in her father. He looked shrunken and old, ate little and asleep often.

A few days later some friends held a dinner to welcome the traveller back from London. In the dinner some of other guest insulted him as Ladies and gentleman, welcome to Marshal Sea both the father and daughter were pale and felt ashamed. As he wasted away next few days. Finally his spirit broke free of all earthly Concerns, Little Dorrit wept bitterly or her father death. Week later Arthur came to know about two news and shock, His head in his hand. One is that he got letter from Little Dorrit about her father death, and other his very bad news about Mr.Merdle had slit his wrist with penknife and was the news in morning news paper.

Arthur had gone against Doyce advice and invested Doyce money in Mr.Merdle business; he wept with regret and felt he had ruined his father. Arthur however was not so fortunate taking solely responsibility for Doyce new debts, he allowed himself to lead into the Marshal sea. He was placed and looked into Mr.Dorrits old room. He felt lonely and sighed for Little Dorrit days passed and Arthurs health and spirit sank under the weight that bore down on him .He was sure that he would die there, because it was so difficult to breathe .He slipped slowly into a fever a week later when he opened his life, there was a vases full of roses and in the corner, he found Little Dorrit knitting in the corner of the room, he was shocked to see her there. Her father hasn't invested everything in Merdle, she was poor again but she was not ruined, and was happier than before.

"I have nothing in the world. I am as poor as when I lived here. When papa came over to England, he confided everything he had to the same hands, and it is all swept away O, my dearest and best, are you quite sure you will not share my fortune with me now? (LD.P.976)"

Mrs.Clennem collected a legal document from her desk and moves out of her house and went to Dorrit and said she must explain herself to her and said she done a great wrong to her. She said by a complex maze of business intrigue and wills, little Dorrit was left with money and said she had kept it from her. She said that she had to restore it before she dies and asked Dorrit to forgive. She took the legal document from her bag and handed over to Dorrit, she read and forgave her.

By the time Dorrit reaches the prison Mr.Doyce was in Arthur room and they were in discussion about debts and Doyce excused Arthur and said Arthur you will have a new and prosperous career .Little Dorrit threw the document into the flames and never revealed to Arthur about the will. Arthur was released and both went too directly from Marshal Sea to the church where together they took their first step towards a modest useful and happy life.

"They all gave place when the singing was done and little Dorrit and her husband walked out of the church alone. They paused for a moment on the steps of the Portico, looking at the fresh perspective of the street in the autumn morning suns bright rays, and then went down (LD.P.986)"

From that day onwards they felt forever blessed as they followed life path together sunshine and shade, and lived very happily.

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# PORTRAYAL OF CHILDHOOD AND SUFFERING IN CHARLES DICKENS' *DAVID COPPERFIELD*

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***Abstract:***

*The present paper aims at studying the suffering of children and their living conditions in Victorian era. It is well known by the great development of the industrial revolution which had officially begun in 1950.It marks the most fundamental transformation of human life in the history of life. It created profound changes in the society; the worst was child labor a phenomenon that culminated in that period. The growing of population made a world of children, who lived in the work houses and were expected to work at the age of six or seven. Apart from this dickens also portrays the brutal treatment of children at the work houses. The present selected paper for research is David Copperfield which is Charles dickens Master piece and autobiographical novel which shows the social background of English society at that time. It is a novel that recounts poverty is bad. It is poverty that leaves David isolated and without a future as a child laborer in London. The research paper shows how a ten years David faced his hurdles in his childhood and how he suffered to have his own living as an orphan boy and how he get out of this sufferings and how his fate ended with his new happy life.*

*Key words: Copper Field, suffering, childhood and poverty.*

**Introduction:**

Charles Dickens was one of the great literary geniuses of all time and one of the most popular. He was nicknamed as the "Inimitable" and it can be argued that in all of English literature his creativity is revealed only by Shakespeare .He was enormously complex man. The present paper aims at presenting an Orphan boy's childhood and suffering in one of his masterpiece novel *David Copper Field* which is considered as his autobiographical novel also. In Most of his novels he mainly focuses on the poor and oppressed lives of children.

**Childhood and Suffering of David Copperfield:**

David Copperfield was born at Blunder stone a village in Suffolk. He was born with a Caul or membrane that covers the head of infant



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that means he would be fortune in life. As a boy David experienced the loss of his parent, he knows in early years that his father died six months before he was born, when his mother Clara was six months pregnant .His father has a sister Betsey Trotwood, who never agreed to the marriage of her brother to Clara. They were separated to this reason. His aunt Betsey came to see Clara after his brother's death, she believed that the new born child was a girl, and she has to become the God mother to that child. Miss Betsey came to know that the child in Clara's lap was a boy; she rushed out of the house, never to enter the door again.

> "She went like a discontented fairy; or like one of those supernatural beings, whom it was popularly supposed I was entitled to see; and never came back any more."(Dickens, 24)

David at last reaches to the safe hands of his aunt after all his sufferings from then onwards he leads a happy life. With the gradual passage of time as an Orphan boy David spends his happy days with his mother and his nurse Peggotty. All the three become accustomed to a new happy life. David's happiness ends when one day Clara entered the house with Mr. Murdstone, a gentleman with beautiful black hair and Whiskers though the gentleman patted David with affection yet the boy didn't like him or his deep voice.

Clara and Murdstone decided to get married, David was sent away with Peggotty to her brother's house in Yarmouth, as David was too young to be told about the decision. Two weeks passed away Peggotty and David came back to home after a long journey. David found his mother married to Murdstone, he came to live with Clara along with his sister Jane Murdstone. From then everything changed. Mr. Murdstone treated David very harshly and in order to escape from the unhappiness of his life David lays his only pleasure in reading books that his father left them to him. It became clear that reading books can be seen as the only shelter for David to escape from the cruel treatment of Mr. Murdstone.

These books became his best friends in isolation. On one occasion David failed in successful completion of some lessons while David's mother was teaching him. David witnessed a cane in the hand of Mr. Murdstone, thus he was interrupted and feels afraid and forgets what his mother taught him. In the mean time Mr. Murdstone ordered him to walk up to his room, suddenly David surprised by the behavior of Mr. Murdstone of beating him.

> *"He had my head in a vice, but I twined him somehow, and stopped him for a*




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> *moment, entreating him not to beat me. It was only for a moment that I stopped him, for he cut me heavily an instant afterwards, and in the same instant I caught the hand with which he held me in my mouth, between my teeth, and bit it through. It sets my teeth on edge to think of it" (Robert E. lougy, 414)*

David cried and pleased him to don't beat him and told him that he can't learn with their attendance. Moreover David tried to stop him and in order to defend himself he bites Mr. Murdstone in his hand. As a reaction to this Mr. Murdstone beats David again harshly as if he beat him to death, as a result of his misbehavior with his step father David was imprisoned for five days, David sees no one but only Miss. Murdstone who brings to him bread, meat and milk. David suffers a lot from the length of these five days. Thus he resembles them with years instead of days that had gone from his life. "Shall I never forget those lessons?" His biting of Murdstone's hand "Sets my teeth on edge to think of it" and the subsequent hours of punishment with the accompanying "Oppression of remembrance" are the memories that the narrator will "never forget" (Rosemary Mundhenk, 332)

David explains the long hours especially at night that makes him uncertain and doubt of knowing the time whether it is morning or not. As a consequence of this punishment of imprisoned and in the evening of the five day, Peggotty informs David that he will be send to school in London as it was decided by Mr. Murdstone. When Peggotty informs David about the decision of Mr. Murdstone of sending him abroad, he feels sad and began to blame himself and ask question to himself as what he had done to have been sent to hardest school.

Of course they hate him. It became clear from the beginning; they harshly, steadily and sullenly over looked at him. Mr. Murdstone had a desire to throw him away abroad to get rid of him. The changed circumstances cast a devasting effect on Clara's health and she soon realized the ghastliness of her decision to marry Mr. Murdstone. However by the time, it had been too late and the two devils had entered her peaceful life to bring loads of miseries.

School is a place from which people acquire knowledge, encounter with each other and learns a lot of information .But peoples sometimes struggle to get their success with the cruel treatment of head master and teachers as it is occurred



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in a vast number of dickens novels in his several works. Dickens tackled the subject of children at schools especially in his novel *David Copperfield*.

David was sent away to a brooding school in London, a miserable school under the oversight of Mr. Creakle, who has a harsh treatment with the boys of the school .He, was sent much before the start of the term. Mr. Murdstone designed a plan to get rid of David as a result of his misbehavior with him. David was surprised as he was received everywhere with the name of Murdstone instead of Copperfield. The school was enclosed with a high brick wall and looked very strong and dull.

The first thing Mr. Murdstone done to David as a punishment for him is that he sent him to the school in holiday, when there is no one in the school. It became clear that Mr. Murdstone send David to Salem house school in a holiday as a retribution for David's behavior with Murdstone. The second bad thing that Mr. Murdstone done to David is that he told Mr. Creakle to treat David cruelly that emerged from his first meeting with him, when Mr. Creakle meet David for the first meeting with him. When Mr. Creakle meets David for the first time, he told him that he knows his step father Mr. Murdstone. David spends three months in Salem house unhappy and suffering but his worst thing that makes David suffer a lot during this time. "To make the matter worse, he was forced to wear a placard that bore the words "Take care of him, he bites". (Terry O'Brien, 9)

David suffers psychologically more than physically from the sign that he was obliged to wear, David became a game to other boys in school, and they enjoyed his placard too much. Tom traddles was the first boy to return from holiday befriended David. The only person who supports David during this time was Steer forth, who takes care of him in Salem house.

The time came for boys to visit their homes. David reached home and spends happily two days with his mother, Peggotty and his little brother. The next day Mr. Murdstone along with his sister Jane came home, everything changed again. David was restricted to spend time with Peggotty. The day came David have to leave home and go to school. His mother Clara bid him bye with the little brother in his hand. That was the last time he saw his mother and brother.

> *"I looked out, and she stood at the garden-gate alone, holding her baby up in the arms for me to see. It was cold still weather; and*



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*not a hair of her head, or a fold of her dress, was stirred, as she looked intently at me, holding up her child."(Dickens, 133)*

One day when in school he was called by Mr. Creaks .He was informed that his mother was seriously ill after his arrival and was dead now. His grief not stopped by the news. He immediately reached home and attended the funeral of his mother. Peggotty was very affectionate with David and explained how his mother died. After his mother's death poor David felt very loanly. Miss. Peggotty was dismissed from the works. Mr. Barkins and Peggotty got married in a private ceremony at a church which was attended by Copperfield.

After the death of his mother David was removed from school and Mr. Murdstone sends him to work at the "Blacking Factory "thrown away in a very little age of ten. David was surprised by this action; he didn't think that Mr. Murdstone could do something like that by sending him to work. While sending to blacking factory Mr. Murdstone said some terms to David that he will earn enough for himself to provide for his eating, drinking and pocket money. He also said his lodges will be arranged by Murdstone. The next day he was sent to London with Mr. Quinion to begin the world on his own account. The duty assigned to David in the blacking house is to keep labels on the empty bottles, washing the bottles or corks to be fitted.

*"When the empty bottles ran short, there were labels to be pasted on full ones, or corks to be fitted to them, or seals to be put upon the corks ,or finished bottles to be packed in casks."(Terry O'Brien, 34)*

Mr. Quinion introduced Mr. Micaber to David, who was an agent and took orders on commission. Micawber was introduced to David on the subject of his lodgings and to stay with him. The salary for David at blacking house was 6 shillings a week. David was taken to Mr. Micawber family for his lodgings. Theirs is a funny family and were affectionate with David. Mr. Micawber was sent to jail due to his debts and was again released soon. But Micawber family decided to go to Polymath and left London. David decided he wouldn't stay in London without Micawber and resolved to run away to his aunt Miss. Betsy Trotwood on the suggestion of Micawber.

*"I had resolved to run away –To go, by some means or other, down into the country, to the relation I had in the world, and tell my story to my aunt, Miss Betsey". (Dickens, 187)*

David has faced many struggles on his way to reach his aunt Miss. Trotwood. His money was stolen on his way along



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with his bag, he sold his clothes and earns some money, but it was not sufficient to reach his aunt.

At last he reached his aunt in Dover. By the time he reached there he was thirsty, hunger and tied. His aunt never liked boys and not accepted him to enter his house, but David explained everything about him and his relationship with her and about his step father Mr. Murdstone and his sufferings. She was convinced and took him by her love and affection and offered him food. Miss. Trotwood sent a letter to Mr. Murdstone about David's arrival to her house. Both Mr. Murdstone and Jane came to his aunt house.

> *"Thus I began a new life, in a new name, and with everything new about me. Now that the state of doubt was over, I felt for many days, like one in a dream." (Dickens, 225)*

But David refused to go along with them. David's aunt adopted David and kept along with her. Miss Trotwood renamed David name as Trotwood Copperfield. His aunt decided to send him to Canterbury for his further studies. By this David's suffering ended and lived very happily with his God Mother.

**Conclusion:**

David by the end reaches his God mother house Miss Trotwood; she takes the complete responsibility of the boy. Though David has faced many problems at a very small age, all his struggles come to an ends and after he reaches his Aunt house. From then onwards David leads a very peaceful and happy life with his one and only relative Miss Trotwood. David within a short period forgets his past bad memories and sufferings and lives a wonderful life with his Aunt.

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# The Role of Blended Learning in Teaching English at Under Graduate Level

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**Abstract**
In order to be successful in their teaching, teachers always look for different ways to increase the quality of their teaching. These days the use of computers and new technologies play pivotal role in teaching a foreign language, particularly English. In this situation computer-based distance learning courses that are supported by e-learning have emerged. E-learning is also exploited in the 'blended learning'. The term 'blended learning' is defined as 'a combination of online learning and face-to-face learning'. This has been defined in different ways by different people. Blended Learning instruction is a new teaching and learning approach that is being promoted at many higher educational institutions and universities at under graduate level, involving an integration of learning technologies and face-to-face teaching. It emerges as one of the most widespread teaching modalities used nowadays in the educational field, mainly by Universities and Higher Education Institutions mainly at under graduate level. Based on the concept of blended learning, it can be assumed that the introduction of this form in teaching and learning process can improve the efficiency of the educational process in a changing standard of modern education. So it is hoped that the blended learning approach is likely to emerge as the predominant instructional model in the future particularly at under graduate level.

**Key words:** teaching, computers, blended learning, e-learning

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In order to be successful in the process of their teaching, teachers always look for different ways to increase the quality of their teaching. These days the use of computers and new technologies play pivotal role in teaching a foreign language, particularly English. In this connection, Brown says 'Teachers of English have a mission to help everyone in the world to communicate with each other and solve global problems. Of course, this is so because of the global status of English' (Brown, 1991). In this situation, computer-based distance learning courses have emerged. 'One of the supports of the distance learning is e-learning. Sometimes e-learning is also exploited in the so-called 'blended learning'.

The term blended learning originated in 'the business world in connection with corporate training' (Sharma and Barrett, 2007), then 'was employed in higher education' (MacDonald, 2006), and lastly it appeared in language teaching and learning. The research on blended learning reveals that this type of learning is used to increase the quality of learning. As opined by Dziuban, et al, 'Many researchers believed that blended learning is an essential learning process to enhance the efficiency and quality of learning because the blended learning supports all the benefits of pedagogical approaches that combine effectiveness and socialization opportunities of the classroom with the technological enhance active learning possibilities of the online environment' (Dziuban, Hartman, & Moskal, 2004, P.2).

The term 'blended learning', in general, is defined as 'a combination of online learning and face-to-face learning'. However, this has been defined in different ways by different people. Blended learning has been described as 'a pedagogical approach that combines effectiveness and socialization opportunities of the classroom with the technologically enhanced active learning possibilities of the online environment' (Dziuban, Hartman, & Moskal, 2004). Graham considers 'blended learning as an approach, and defines it as a learning approach that combines different delivery methods and styles of learning. The blend could be between any forms of instructional technology (e.g., Videotape, Web-based learning, CD-ROM, etc.)' (Graham, 2006). Rooney said, 'Appearance of the information technologies in teaching foreign languages led to appearance of a relatively new method, called blended learning. The term is most commonly defined as a combination of online and face-to-face instruction' (Rooney, 2003). Lieser & Taff define as, "Technology has been used inside and outside of the classroom for teaching and learning in many ways. Blended learning is a formalized model that provides individualized learning for students using a combination of face-to-face and technology-based learning in a planned, systematic way" (Lieser & Taff, 2013). Harvey elaborates, "The amount of technology used and time for students to spend with the technology depends on the implementation of the blended learning model. Blended learning is a flexible approach that combines face-to-face teaching/learning with remote (usually internet-based) learning" (Harvey, 2004–9). Bliuc et al. regards blended learning as the set of "learning activities that

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involves a systematic combination of face-to-face interactions and technologically-mediated interactions between students, teachers, and learning resources" (Bliuc et al, 2007, P. 234). Based on the definition by C. Graham "three components of blended learning can be singled out:

- face-to-face learning that represents a traditional format when instructors and students meet during classes;
- self-study learning that assumes different types of activities, such as search on the Internet, webquests, etc, performed by students unassisted;
- online collaborative learning – an online cooperative work of students and instructors in forms of webinars, wikis, Skype conferences, etc." (Graham, 2005).

The role of blended learning in teaching English at under graduate level is useful, and blended learning facilitates the students acquire language with utmost interest. According to Thorne 'blended learning is the most logical and natural evolution of our learning and it suggests an elegant solution to the challenges of tailoring learning and development to the needs of learners. Thus, blended learning represents an opportunity to integrate the innovative and technological advances offered by online learning with the interaction and participation offered in the best of traditional learning. Blended Learning emerges as one of the most widespread teaching modalities used nowadays in the educational field, mainly by Universities and Higher Education Institutions' (Thorne, 2003). Blended Learning instruction is a new teaching and learning approach that is being promoted at many higher educational institutions and universities at under graduate level, involving an integration of learning technologies and face-to-face teaching, and it can not only hone the English language proficiency of learners, but also allow them to have more access to the language of native speakers.

Previous studies investigating the effectiveness of the blended learning approach have reported that 'it meets the educational needs of students such as enhancing flexibility and convenience, allowing the attainment of higher achievement and attitude levels, and improving language learning skills as well as developing critical thinking skills (Lee & Chong, 2007). Another aspect of blended learning is whether it deepens learning engagement and increases motivation in learning. Sucaromana finds that 'students who are taught in a blended learning environment have higher levels of intrinsic motivation, a better attitude toward the learning subject, and even better satisfaction with the learning climate than a face-to-face only environment. However, studies have reported on students' apprehension, anxiety and confusion when interacting with online materials' (Sucaromana, 2013). This type of experience is very common when students have no sufficient exposure to technological innovations in the classrooms. Moreover, ambiguous instructions and guidelines may cause students to become lost and disengaged, and so innovations involving technology should be integrated appropriately and effectively within

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classrooms in order to improve and maximize the learning outcomes of the students. This study posits that the incorporation of self-access online reinforcement exercises would have positive pedagogical impact on them.

The role of teacher in implementing this blended learning approach is prominent. With reference to English Language Teaching using blended approach, Sharma suggests 'for blended learning to be effective the two component parts should be integrated with the technology complementing and not replacing the efforts of the teacher' (Sharma, 2007). According to Lewis, "technology is nothing without a teacher and a plan" (Lewis , 2009, P. 9).

Language learning is such a complex process that it is impossible to offer a single solution to all our problems, and to arrive at the perfect approach or technique for language learning in Indian context. Perhaps the best method is the one which works, and this varies from context to context. Any method which creates conditions for learning to take place is good. It should enable the learner to acquire the strategies of learning rather than merely equipping him with knowledge. What is important for the teacher, therefore, is to find out what approach and what method will enable him to realize a particular objective under a set of particular circumstances. Since it is felt that blended learning at under graduate level is useful, it is preferable that teachers and educationalists can make it an integral part in their curriculum. Focus should be drawn to learning center instruction. Blended learning offers approaches to solving one of the main tasks of modern traditional education, i.e. the implementation and development of each student's potential abilities. Based on the concept of blended learning, it can be assumed that the introduction of this form of training to teaching practice can improve the efficiency of the educational process in a changing paradigm of modern education. The blended learning approach is likely to emerge as the predominant instructional model in the future.

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# Phytochemical Analysis and Antibacterial Activities of *Boswellia Ovalifoliolata*

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**Abstract:** ***Different parts of Boswellia Ovalifoliolata were collected from different localities of Udayagiri hills of Velugonda hill range, Eastern Ghats, Nellore Dt, Andhra Pradesh, India. The methanolic extracts of various parts of the plants were qualitatively screened for phytochemicals using standard procedures which revealed the presence of various important bioactive chemical entities. Antibacterial activity of the methanolic extracts of stem bark and gum were evaluated against Bacillus subtilis, Staphylococcus aureus, and Gram negative bacteria Proteus vulgaris, Pseudmonas aeruginosa. The methanolic extracts of these plant parts have exhibited significant broad spectrum antibacterial activities.***

**Keywords:** Phytochemicals, Antibacterial, Ethnobotanical

## 1. Introduction

The treasure of traditional medicine, the plant kingdom has components of therapeutic values. More than 80 percent of the global population depends on the traditional medicine for improvement health, resistance and maintenance of good health. These Phytochemicals extracted from various parts of the plants act as natural antimicrobial agents. The metabolites extracted from the plants have curative properties and they can be used to treat outrageous infections and chronic diseases. One of the emerging global threats is multidrug resistance in pathogens. Hence the need of the hour is to search for novel antimicrobial agents. An abundant research work is going on to investigate the antimicrobial activity of various plant parts. A large number of antimicrobial chemical components of medicinal plants were identified and now they are under usage for treating offensive microbial infections and chronic diseases.

The Gum and stem bark of *Boswellia Ovalifoliolata* a member of Burseraceae have several therapeutic values. Oleo gum resin is used against ulcers, dysentery, joint pains and inflammations. Gum is used externally to cure arthritis (Y,N) (Nagaraju, 1992 ; Vedavathy, 1992). Gum with the fresh leaf juice is given in ulcers in mouth and throat (Vedavathy, 1992). Shade dried gum is powdered and dissolved in water. The extract obtained is mixed with curd and given orally to cure amoebic dysentery (Nagaraju, 1992). Gum powder of the plant is mixed with white precipitate of pounded stem of *Tinospora cordifolia* and honey , given orally in small quantity (10 ml),two times a day to cure hydrocele (I) (Vedavathy *et al.,* 1997a,b). Gum powder of *Boswellia ovalifoliolata* and *Boswellia serrata* and the fruit powder of *pedalium murex* are made into a paste. This is applied externally on the affected part of the testicles to cure hydrocoel . The treatment is continued for a fort-night (Y,Ye,I).

Stem bark and resin are shade dried and made into powder. About one tea spoonfuls of the mixture is given daily with sour milk on empty stomach for a month to cure stomach ulcers (Y,I).

## 2. Materials and Methods

The collected plant materials were cleaned, shade dried, powdered coarsely in a blender and then stored in air-tight containers for future use. The methanolic extracts of various parts of the plants were qualitatively screened for phytochemicals using standard procedures.

Fluorescence analysis was carried out following Chase and Pratt (1949) and Kokoski *et al.* (1958). The selected powdered drugs were studies both in visible light and Ultra-Violet light for their fluorescence characters.

The Pharmacognostical study includes morphology of the plant, macro and microscopical studies of the drug. Plant materials like gum and stem bark were collected for the studies. Following the techniques of Johansen (1940), Wallis (1967) and Trease and Evans (1985) the parts of the plants used as drug (stem bark, gum ) were fixed in 70% alcohol for 24 hours. Free hand sections taken were stained with safranin and light green and the permanent slides were prepared. Histochemical tests were carried out by treating the sections with solutions of phloroglucinol, chloral hydrate and hydrochloric acid as per Trease and Evans (1985). Maceration was carried out for the study of various cells and tissues. The small pieces of the materials were macerated with nitric acid and potassium chloride as per Trease and Evans (1985). The measurements of tissues (Quantitive microscopy) were carried out using ocular and stage micrometers (Erma-Japan) following Wallis (1967).Line drawing were drawn by using a Camera Lucida (mirror type). Photographs of the plants and the crude drug were taken by using a Minolta camera.

## 3. Experimental Studies

**Alkaloids test:** The methanolic extract was evaporated to dryness and the residue obtained was digested with 1% Hydrochloric acid. The resulting acidic solution was divided into two parts. To one part was added Mayer's reagent and to the second part dragendorff's reagent. Appearance of precipitate or turbidity indicates the presence of alkaloids.


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**Preparation of reagents**

**a) Mayer's reagent:** 1.3 g of Mercuric chloride and 5g of Potassium iodide were dissolved separately in 60 ml and 10 ml of double distilled water and both the solutions were mixed and diluted to 100 ml.

**b) Dragendorff's reagent:** 8g of the Bismath nitrate was dissolved in 20 ml of conc. nitric acid and 27.2g of Potassium iodide in 50 ml of double distilled water. Both the solutions were allowed to stand till $KIO_3$ crystallized out. Supernatant was decanted and final volume was adjusted to 100 ml.

**c) Flavonoids:** The plant extract was tested for flavonoids by shinoda's reaction. To a few ml of Methanolic extract, conc. Hydrochloric acid, Magnesium powder and a few fragments of Mg metal was added. The presence of flavonoids was identified by the development of pink or magneta or red coloured flame.

**d) Terpenoids (Liebermann-Burchard's test):** The Liebermann-Burchard's reaction was carried out by adding 0.5 ml of $H_2SO_4$ along the side of the test tube containing a mixture of Methanolic HCl and Acetic anhydrate (0.5 ml each). Formation of colour from green to bluish-green (sometimes via red or blue) indicate the presence of terpenoids.

**e) Steroids (Salkaowski reagent):** Development of wine red colour on adding con. $H_2SO_4$ and $CHCl_3$ to the Methanolic extract indicate the positive test for steroidal compounds.

**f) Lignins:** The plant extract was tested for the presence of lignins by adding conc. HCl and 2% Forfuraldehyde. Development of red colour indicates the presence of lignans.

**g) Indoles:** The development of voilet colour in the methanolic extract on adding Ehrilich reagent is considered as a positive reaction test.

**h) Carbohydrates (Molisch test):** To the methanolic extract, α-napthol solution (1.0g dissolved in 100 ml of each ethanol w/v) was added. Then Conc. $H_2SO_4$ was added gentlyalong the walls of the inclined test tube. Formation of a red to voilet colour indicate the presence of carbohydrates.

**i) Test for reducing sugars:** 2ml to 5ml of Benedict's reagent, 5ml of the test solution was added. The tubes were incubated in boiling water on water bath for 10-30 minutes. The development of an orange red precipitate indicate the presence of reducing sugars.

**j) Protiens (Million's test):** Million's reagent (solution of Mercuric nitrate in nitric acid) was added to 20 ml of boiling Methanolic extract. Formation of white precipitate that gradually turns red upon heating was observed for the presence of proteins.

**k) Phenolic compounds:** To the test solution 1-4 drops of 1% Ferric chloride was added. Appearance of intense colour in the extract was observed for the presence of phenolic compounds.

**l) Anthocyanidins:** The formation of red or purple colour with the plant extract, on adding equal volume of Methanolic HCl was taken as a positive reaction for anthocyanidins.

**m) Anthraquinones:** 20ml of benzene was added to 5g of plant powder and filtered. To the filtrate 5ml of 10% Ammonium hydroxide solution was added and shaken well. The formation of pink, red or violet colour in the ammonical phase indicate the presence of anthraquinones (Wall *et al.,* 1954 anf Frans Woath, 1966).

**n) Saponin test:** The plant extract was evaporated to dryness. Tap water was added and shaken vigorously in a graduated cylinder for 15 minutes. Formation of a persistent foam was taken as a positive reaction test.

**o) Tannins:** The Methanolic extract was concentrated and the residue was dissolved in water and tested with 1% Gelatin solution and 1% Gelatin salt solution (1g gelatin dissolved in 10g NaCl w/w) to separate volumes. The appearance of white precipitate indicate the presence of tannins.

**Preliminary phytochemical screening of Stem bark and gum of *Boswellia Ovalifoliolata* ( Methanolic Extract )**

| Compound | Stem Bark | Gum |
|---|---|---|
| Alkaloids | - | + |
| Flavonoids | + | + |
| Indoles | + | - |
| Leucoantho-cyanins | + | - |
| Steroids | + | - |
| Carbohydrates | + | + |
| Phenols | + | + |
| Steroidal nucleus | + | - |
| Saponins | + | + |
| Tannins | + | + |
| Proteins | + | - |
| Lignins | + | + |
| Methylenedioxy functional compounds | - | - |

## 4. Screening for Selective Secondary Constituents

### A. Phenolic compounds:

**a) Extractive procedure:**

The phenolic constituents were extracted by following the method given by Bate Smith (1954) and Ibrahim and Towers (1960). About 25g of healthy plant material was macerated with 100ml of 2N Hydrochloric acid.(HCL). The homogenate was digested on a boiling water bath for about half-an-hour. The contents were cooled and filtered through Whatman No.1 filter paper. The filtrate was extracted repeatedly with peroxide free diethyl ether. All the extracts were pooled and concentrated to 100ml and was treated three times with 25ml of 5% anhydrous sodium carbonate solution. The pooled carbonate solution was adjusted to pH 2.0 with Conc. Hydrochloric acid.

The acidified fraction at pH 2.0 was extracted with equal volumes (25ml) of fresh diethyl ether thrice. The combined other extracts were washed with distilled water repeatedly till all traces of hydrochloric acid was removed. The ether soluble water was removed by freezing the extract. The ether was evaporated to dryness on water bath at $98^0$C and the resulting phenolic compound residue was dissolved in 1ml of 95% ethanol. This was stored at low temperature in dark container for ready use.

**b) Identification**

About 2g of fresh weight equivalent to the final alcoholic extract was spotted on 23x29cm whatmann No.1


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Chromatographic filter paper with the help of micro pipette. The origin of the spot area was dried immediately with the help of hair-drier. Two dimensional ascending Chromatographic technique was adapted with benzene-acetic acid-water (60:70:30 v/v/v, upper layer) in the direction and sodium formate-formic acid-water (10:1:200 w/v/v) in the second direction. The Chromatographic chambers were saturated with the above solvent systems one day before the development of the Chromatograms at 22 to $24^0$c. The sheets after development were removed from the chambers and dried at room temperature. The dried sheets were observed under Ultra violet light and flourescent regions were marked. The papers while exposing to Ammonia vapours were also observed under UV light and new flourescent spots were marked.

The seperated phenolic compounds on the Chromatograms were identified by comparision of $R_f$ values and individual spot colours of Chromogenic sprays. The final confirmation was made with authentic samples by co-chromatography.

**c) Chromogenic spray reagents:**

**i) Diazotized sulphanilic acid reagent:**
25ml of freshly prepared 5% sodium nitrate was slowly added to 5ml of sulphanilic acid solution (900mg of sulphanilic acid was dissolved in 9ml of Conc. HCl and the solution was diluted to 100ml with $H_2O$) at $0^0$c. To intensify the colours of the developed spots, 20% Sodium Carbonate solution was sprayed to the wet sheets (sprayed at $0^0$c immediately after spraying the above solution).

**ii) Diazotized *p*-Nitraniline reagent:**
10ml of *p*-nitraniline reagent (1.5g of *p*-nitraniline was added to 45 ml of Conc. HCl and was made up to 950ml with distilled water) was mixed with 0.2ml of 5% Sodium nitrate and 10ml of 10% Sodium carbonate solution.

**Table:** Phenols

| Compound | Stem bark | Gum |
|---|---|---|
| Digallic acid | - | - |
| Gallic acid | + | + |
| Ellagic acid | - | - |
| Aesculetin | - | - |
| Cis-p-coumaric acid | - | - |
| iso-chlorogenic acid | - | - |
| Chlorogenic acid | + | + |
| Caffeic acid | - | - |
| Protocatechuic acid | + | - |
| Gentistic acid | + | + |
| Scopoletin acid | + | - |
| Phloretic acid | + | + |
| ρ-Hydroxy benzoic acid | + | + |
| α-Resorcyclic acid | - | - |
| β-Resorcyclic acid | + | - |
| trans-ρ-coumaric acid | + | - |
| Vanillic acid | + | + |
| P-coumarylquinic acid | - | - |
| Cis-p-coumaric acid | + | - |
| Meliotic acid | + | + |
| Cis-Ferulic acid | + | - |
| Trans-Ferulic acid | - | - |
| Coumarin | + | + |
| Salycyclic acid | + | + |
| Cinnamic acid | + | + |
| Syringic acid | - | - |

**Table:** $R_f$ values and colour reactions of Phenolic compounds on Paper Chromatograms

| Compound | $R_f$ values in solvent | | U.V fluorescence | | Silphanilic Reagent | P-Nitraniline Reagent |
|---|---|---|---|---|---|---|
| | **1** | **2** | **Without $NH_3$** | **With $NH_3$** | | |
| Digallic acid | 0.3 | 0.7 | None | Blue violet | Violet | Violet |
| Gallic acid | 0.5 | 0.7 | violet | Violet | Violet | Violet |
| Ellagic acid | 0 | 0.3 | None | Blue green | Blue green | Blue green |
| Aesculetin | 0.3 | 0.3 | white blue | Very bright blue | Brown | Grey |
| Cis-p-coumaric acid | 0.4 | 0.8 | Light blue | Deep blue | Dark brown | Blue |
| iso-chlorogenic acid | 0 | 0.3 | Faint blue | Duckegg green | Light orange | Brown |
| chlorogenic acid | 0 | 0.8 | Faint blue | Duckegg green | Orange | Brown |
| Caffeic acid | 0.1 | 0.4 | Blue | Bright blue | Buff | Light brow |
| Protocatechuic acid | 0.1 | 0.6 | None | None | Buff | Light brown |
| Gentistic acid | 0.1 | 0.7 | Bright blue | Yellow | Buff | Blue white |
| Scopoletin acid | 0.3 | 0.5 | Bright blue | Very bright blue | Yellow | Brown |
| Phloretic acid | 0.7 | 0.8 | None | None | Yellow | Purple white |
| ρ-Hydroxy benzoic acid | 0.4 | 0.7 | None | None | Bright yellow | Light pink |
| α-Resorcyclic acid | 0.2 | 0.8 | None | None | Brown | Orange brown |
| β- Resorcyclic acid | 0.3 | 0.8 | None | None | Dark brown | Brown |
| trans-ρ-coumaric acid | 0.5 | 0.5 | Light blue | deep blue | Light brown | Blue |
| Vanillic acid | 0.8 | 0.6 | None | None | Orange | Purple |
| P–coumarylquinic acid | 1 | 0.6 | None | None | Light yellow | Yellow |
| Cis-ρ-coumaric acid | 0.4 | 0.8 | Light blue | deep blue | Dark brown | Blue |
| Meliotic acid | 0.5 | 0.8 | None | None | Orange yellow | Purple |
| Cis-Ferulic acid | 0.9 | 0.7 | Light blue | Blue | Purple | Blue green |
| trans-Ferulic Acid | 0.8 | 0.3 | Light blue | Blue | Purple | Blue green |
| Coumarin | 1 | 0.7 | None | None | Yellow | Violet |
| Salycyclic acid | 0.9 | 0.3 | Dark blue | Dark violet | Yellow | Pink |
| Cinnamic acid | 1 | 0 | None | None | Yellow | Green |
| Syringic acid | 0.9 | 0.5 | None | None | red | Dark blue |


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**Solvents:**

1. Benzene**:**Acetic acid **:** Water → 60:70:30
2. Sodium Formate**:** Formic acid**:**Water → 10 :1 :200

**B. Flavonoids Compounds**

**a) Extractive procedure**

The flavonoid compounds were extracted according to the method given by Markham (1982). About 5g of powdered plant material was extracted in two steps. First 18ml of Methanol and 2 ml of water (9:1) were added, shaken well and kept for one day at room temperature. The supernatant solution of the extract was taken and transferred to another test tube. Secondly Methanol and water of 5ml each (1:1) was added to the remaining residue, stirred well and the mixture left for 24 hours. The two extracts were combined, mixed well and filtered through cotton wool. Later the filtrate was evaporated to about 1/3 the original volume till most of the methanol was removed. The resultant aqueous extract was extracted with chloroform repeatedly for 3 times. The solvent extracted aqueous chloroform layer was evaporated to dryness under vaccum in a rotary evaporator. The dried residue was saturated with 1 ml of 95% alcohol and stored in a dark place at low temperature.

**b) Identification**

The extracts containing flavonoids were separated in suitable quantities on Whatmann No.1 Chromatographic filter paper(23x29 cm) adopting the ascending technique using the solvent system Iso-propyl alcohol **:** Ammonia (25%) **:** Water(8:1:1:v/v/v) and n-butanol:acetic acid: water(4:1:5v/v/v) (top layer was used).The dried Chromatograms were examined under UV lamp and the fluorescent spots were marked. The papers while exposed to Ammonia Vapours were also observed under UV lamp and the new fluorescent regions were marked. The flavonoid compounds were identified by comparing the $R_f$ values and colours with those of the authentic samples on the Chromatograms. Co-Chromatographic studies were conducted with authentic markers to confirm the identification.

**C) Chromogenic spray reagents**

**Diazotized sulphanilic acid reagent (Markham, 1982) :**0.3% solution of sulphanilic acid in 8% HCl (25ml) was mixed with 5% Sodium nitrite solution(1.5ml) just before use. The Chromatographic sheets were sprayed with this mixture and with a 20% solution of anhydrous Sodium carbonate.

**1% Alcoholic ferric chloride:**1 g of Ferric chloride was dissolved in alcohol and made up to 100ml.

**1% Alcoholic Aluminium chloride:**1g of Aluminium chloride was dissolved in alcohol and made up to 100ml, just before spraying of the chromatographic sheets

**Table:** Flavonoids:

| Compound | Stem Bark | Gum |
|---|---|---|
| Quercetin | + | + |
| Rutin | + | + |
| Myricetin | - | - |
| Luteolin | + | - |
| Apigenin | - | - |
| Orientin | + | - |
| Vitexin | + | + |

**Table**: $R_f$ values and colour reactions of Flavonoids on Paper Chromatograms:

| Compound | $R_f$ values in solvent | | U.V Fluorescence | | Sulphanilic Reagent | 1% Alcoholic Ferric Chloride | 1% Alcoholic Aluminium Chloride |
|---|---|---|---|---|---|---|---|
| | **1** | **2** | **Without NH3** | **With NH3** | | | |
| Quercetin | 0.3 | 0.6 | yellow | Light yellow | Bright yellow | Green | Yellow |
| Rutin | 0 | 0.6 | Orange brown | Yellow | Green | Olive | Grey yellow |
| Myricetin | 0.1 | 0.4 | Yellow | Bright yellow | Light yellow | Olive | Grey yellow |
| Luteolin | 0.4 | 0.8 | Dull yellow | Yellow | Light red | Pale green | Pale yellow |
| Apigenin | 0.6 | 0.9 | Red brown | Red brown | Pink | Pale green | None |
| Orientin | 0.8 | 0.3 | Yellow | Yellow green | Grey | None | None |
| Vitexin | 0.9 | 0.4 | Dull yellow | yellow | Bright red | none | None |

**Solvents:**

1. Iso-propyl alcohol**:**Ammonia(25%) **:**Water → 8:1:1 & n-butanol**:**Acetic acid**:**Water → 4:1:5

**C. Amino acids**

**a) Extractive procedure**

Amino acids were extracted following the method of Das Chowdary *et al.,* (1967). About 5g of plant material was cut into small pieces and plunged immediately into a round bottomed flask containing 20ml of 80% Ethanol. It was reflexed for 30 minutes over a boiling water bath. The boiled material was ground in mortar using additional volumes of 10ml ethanol 80% (v) and centrifuged at 2000 rpm. The supernatant was collected and the Ethanol removed in vaccum. The aqueous extract was passed through Dowex 50W-X8 ($H^+$ from 20-50 mesh) column (1x10cm). the amino acids were eluted from the column with 50ml of 2N Ammonium hydroxide. The elute was evaporated to dryness and the residue was saturated with 95% Ethanol(1ml).

**b) Identification**

The extracts containing amino acids were seperated on Whatmann No.1 Chromatographic filter paper(23x28 cm) employing two-dimensional ascending technique using the solvent system:

1) Sec. butanol **:** Formic acid **:** Water(75:13:12v/v/v)-1st direction.
2) Buffer saturated phenol (1:2v/v)-2nd direction(6.3 g of Sodium citrate and 3.7g of Potassium dihydrogen phosphate were dissolved in 100ml of distilled water. To this 200ml of distilled phenol was added)

The amino acids were identified based on comparision of $R_f$ values, colours and with those of authentic samples by co-chromatographic studies.


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**C) Chromogenic spray reagents:**

**Ninhydrin:**It was prepared by dissolving 200 mg of Ninhydrin in 98ml of n-butanol with 2ml of glacial acetic acid

**Table:** Amino acids:

| Compound | Stem Bark | Gum |
|---|---|---|
| Aspartic acid | + | - |
| Arginine | + | - |
| Asparagine | + | + |
| α-Alanine | + | + |
| β-Alanine | + | + |
| 2-Aminobutyric acid | - | + |
| Cystaine | + | + |
| Cystine | + | + |
| Glutamic acid | + | - |
| Glutamine | + | - |
| Glycine | + | - |
| Histidine | + | + |
| Isoleucine | + | - |
| Leucine | + | + |
| Lycine | + | + |
| γ-Methylene glutamic acid | - | - |
| γ-Methylene glutamine | - | + |
| Norleucine | - | + |
| Ornithine | + | - |
| Phenylalanine | - | - |
| Proline | + | + |
| Serine | + | + |
| Threonine | + | + |
| Tryptophan | - | - |
| Valine | + | + |
| Tyrosine | - | - |

**Table:** $R_f$ values and colour reactions of Amino acids on Paper Chromatograms:

| Compound | $R_f$ values in solvent | | Colour with Ninhydrin |
|---|---|---|---|
| L-Aspartic acid | 0.05 | 0.10 | Light violet |
| DL-Arginine | 0.10 | 0.60 | Violet |
| DLAsparagine | 0.19 | 0.41 | Violet |
| α-Alanine | 0.26 | 0.28 | Light violet |
| β-Alanine | 0.42 | 0.77 | Deep violet |
| DL-2-Aminobutyric acid | 0.55 | 0.70 | Light violet |
| L-Cystaine | 0.38 | 0.61 | Deep violet |
| L-Cystine | 0.23 | 0.53 | Violet |
| L-Glutamic acid | 0.17 | 0.20 | Violet |
| L-Glutamine | 0.14 | 0.82 | Violet |
| L-Glycine | 0.09 | 0.38 | Violet |
| L-Histidine | 0.08 | 0.52 | Violet |
| DL-Isoleucine | 0.68 | 0.82 | Violet |
| L-Leucine | 0.79 | 0.83 | Deep violet |
| L-Lycine | 0.79 | 0.83 | Deep violet |
| γ-Methylene glutamic acid | 0.20 | 0.68 | Violet |
| γ-Methylene glutamine | 0.30 | 0.71 | Violet |
| DL-Norleucine | 0.96 | 0.68 | Violet |
| DL-Ornithine | 0.04 | 0.27 | Light violet |
| DL-Phenylalanine | 0.60 | 0.90 | Light violet |
| L-Proline | 0.39 | 0.89 | Yellow |
| DL-Serine | 0.20 | 0.23 | Deep violet |
| DL-Threonine | 0.28 | 0.35 | Deep violet |
| DL-Tryptophan | 0.50 | 0.76 | Violet |
| DL-Valine | 0.59 | 0.77 | Deep violet |
| L-tyrosine | 0.52 | 0.65 | Light violet |

**Solvents:**

1. Sec. butanol **:** Formic acid **:**Water → 75**:**13**:**12
2. Buffer**:**Phenol → 1:2

**D. Anthocyanidins:**

**a) Extractive procedure:**The anthocyanidin constituents were extracted according to the method described by Harborne (1973). About 5g of plant material was immersed in 20ml of 2N HCl in a boiling test tube and heated for 30-40 minutes at6 $100^0$c. The extract was cooled and filtered. The filtrate was washed twice with 20 ml of ethyl acetate to remove flavones. The remaining aqueous extract was further heated at $80^0$c for 3 minutes to remove the last traces of ethyl acetate. The pigment was re-extracted again with a small volume of Iso-amyl alcohol. The Ethyl acetate extract was evaporated to dryness on a boiling water bath. The anthocyanid in the residue was diluted with 1ml of 1% Methanolic HCl and preserved at low temperature in dark for future use.

**b) Identification:**

The extracts containing anthocyanidins was separated on 23 x 29 cm Whatmann No.1 Chromatographic filter paper. Unidimensional Chromatographic ascending technique was employed with Conc. Hydrochloric acid, Formic acid, Water (2**:**5**:**3 v/w/v) and n-butanol**:** Acetic acid **:** water(4:1:5). The Chromatograms developed from the said solvent systems were taken out from the glass chambers and dried at room temperature. The fluorescent regions of dried papers were marked under UV light. The $R_f$ values and colours of the spots were determined by comparing with those of the authentic markers on the Chromatograms.

**Table 4a:**

| **Compound** | Stem Bark | Gum |
|---|---|---|
| Cyanidin | + | - |
| Petunidin | + | - |
| Delphinidin | - | - |

**Anthocyanidins:**

**Table:** $R_f$ Values and Colours of Anthocyanidins on Paper Chromatograms:

| Compound | $R_f$ values in solvent | | Visible Colour | U.V. fluorescence | |
|---|---|---|---|---|---|
| | **1** | **2** | | **without $NH_3$** | **with $NH_3$** |
| 1 | 0.4 | 0.7 | Meganta | pink | blue green |
| 2 | 0.3 | 0.5 | Purple | mauve | Mauve |
| 3 | 0.2 | 0.4 | Purple | mauve | blue green |

**Solvents:**

1) Conc. Hydrochloric Acid **:** Formic Acid**:**Water → 2**:**5**:**3
2) n-butanol **:** Acetic Acid **:** Water → 4**:**1**:**5

**Thin layer Chromatography (TLC):**

**E. Lipids:**

**a) Extractive procedure:**

Lipids were extracted following the method adopted by Hoppe and Heitefuss (1974). A solvent mixture consisting of 30ml Chloroform, 60ml of Methanol and 20 ml Water(1**:**2**:**0.8 v/v/v) was taken and allowed to boil. About 5g of plant material was homogenized in the above solvent mixture. The contents were filtered and taken separately. The residual mixture was treated with 70ml Methanol and


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the filtrate taken. The residue was again washed with 100ml Chloroform. All the above filtrate mixtures were taken in a separating funnel and 90ml of water added. The mixture now contains Chloroform**:** Methanol**:** Water in the ratio of 2**:**2**:**1.8 respectively and the mixture were allowed to settle. The lower lipid layer containing chloroform was separated and transferred into a breaker. The upper water layer was treated with 50ml of Chloroform successively for three times. All the extracted Chloroform layers were evaporated to dryness in a vacuum by rotary evaporation maintained at $40^0$C. The residue was treated with 2ml of Benzene to remove the traces of chlorophyll if present. Now the final lipid residue was dissolved in 2 ml of Chloroform and stored at low temperature in dark until use.

**b) Identification**

Thin layer plates were prepared by spreading a slurry of silicagel-G (50g in 100ml distilled water) to 105 mm thickness over thin glass plates. The glass plates were air dried and stored at room temperature. Before using, the plates were heated at $110^0$c for 30 minutes in a hot air oven for activation. Using micropipette, one gram equivalent of lipid extract was taken and potted on TLC plates. The spotted areas were allowed for immediate dryness with the help of a drier. The dried plates were run in uni dimensional ascending Chromatography by using TLC glass chambers. The chambers were saturated with developing solvents one day before the plates were developed.

**Solvent systems:**

1) Chloroform**:** Methanol**:** Acetic acid**:** Water (170**:**25**:**25**:**3 v/v/v/v)
2) Acetone**:** Benzene**:** Water(91**:**30**:**8 v/v/v).

The plates were placed in airtight tanks. The developed plates were removed and dried at room temperature and exposed to Iodine vapours to visualize all the lipid compounds.

The TLC plates were sprayed with 25% Sulphuric acid reagent with the help of an automizer for the clear detection of various lipid layers. The lipids were identified by comparision of $R_f$ values, color and with those of authentic samples by Co-Chromatographic studies.

**c) Chromogenic spray reagent:**

The TLC plates were sprayed with 25% Sulphuric acid and heated to $230^0$c for 15 minutes, and the colour observed. Glycolipids gave red brown while phospholipids gave bright, red and other lipids gave pale brown colour spots on white background

**Table 5a:** Lipids

| Compound | Stem Bark | Gum |
|---|---|---|
| Phosphatidyl serine | + | + |
| Phosphatidyl inositol | + | - |
| Phosphatidyl Clioline | - | - |
| Phosphatidyl Ethanolamine | - | - |
| Digalactosyl Diglyceride | + | - |
| Phosphatidyl glycerol | + | + |
| Sulphoquinovosyl Diglyceride | + | + |
| Monogalactosyl Diglyceride | + | + |
| Steryl glycoside | + | + |

**Table 5b:** Rf values and colour reaction of lipids on thin layer Chromatograms

| Compound | $R_f$ values in solvent | Colour with iodine vapours | Colour with $H_2SO_4$(25%) |
|---|---|---|---|
| 1 | 0.09 | + | + |
| 2 | 0.13 | + | + |
| 3 | 0.18 | + | + |
| 4 | 0.23 | + | + |
| 5 | 0.33 | + | + |
| 6 | 0.41 | + | + |
| 7 | 0.57 | + | + |
| 8 | 0.81 | + | + |
| 9 | 0.87 | + | + |

Solvent :
$CHCl_3$: MeOH:HOAc :$H_2O$ → 170:25:25:3

## 5. Determination of ash values

The object of ashing crude drugs is to remove all traces of organic matter which may otherwise interfere in an analytical determination. The inorganic salts naturally occurring in drug or adhering to it or deliberately added to as a form of adulteration are removed by gradual incineration of the drug. Thus the residue remaining after incineration of the powdered drug is known as ash content. The ash values are a criterion to judge the identity or purity and quality of the crude drug.

**a) Determination of total ash:**

Total ash usually consists of Phosphates, Silicates and Carbonates of Potassium, Calcium and Magnesium. About 2 gm of the air dried powdered drug was accurately weighed and taken in a tared silica crucible, which was previously ignited and weighed. The powdered drug was spread as a fine even layer at the bottom of the crucible. The crucible containing the drug was gradually incinerated in a muffle furnace by increasing the temperature. It was heat dull red hot until free from carbon or converted into ash. Later the crucible was allowed to cool and kept in desiccators. The residue was weighed the percentage of total ash calculated with reference to the air dried sample. The residue was weighed the percentage of total ash calculated with reference to the air dried sample. The procedure was repeated till constant result was obtained.

**b) Determination of acid insoluble ash:**

Acid insoluble ash is a part of total ash insoluble in dilute Hydrochloric acid. The acid insoluble ash content is determined and recommended for certain drugs may be coated with dirt and sand. The total ash obtained as described above was treated with 25ml of 10% Hydrochloric acid and boiled for 5 minutes. The insoluble matter was filtered and collected on ashless filter paper (Whatman No.42) and the paper washed with hot water. The insoluble ash was ignited and weighed in a tared silica crucible. The acid insoluble ash of the drug was repeated to get constant results.

**c) Determination of water soluble ash:**

The total ash obtained from the above process was boiled with 25 ml of distilled water for 5 minutes. The insoluble ash was filtered through ash less filter paper (Whatman


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No.42). The residue was once again washed with water and ignited up to temperature not exceeding 450°c and converted into ash. The difference between the weight of total ash and insoluble matter represent the weight of water soluble ash. The percentage of water soluble ash was calculated with reference to the air dried drug.

**B. Determination of extractive values:**

Extractive values indicate the nature of the constituents present in a crude drug. Based on the diversity in chemical nature and properties of the contents of the drug, various solvents were used for the determination of extractives. The solvents used for extraction dissolve appreciable quantity of substances desired. The methods used to find out the extractive values were as follows.

**a) Determination of alcohol soluble extract:**

Alcohol is an ideal solvent frequently employed to determine various chemical contents like Tannins, Resins etc. Generally, Ethyl alcohol is used for determination of alcohol-soluble extractive. Dilute Alcohol a may also be used in some cases, depending upon solubility of constituents in a crude drug. In the present work, the author used 100 ml of 90% Alcohol for determining crude drug was macerated with 100 ml of 90% Alcohol in a stoppered flask for 24 hours. It was shaken frequently every 6 hours and allowed to stand to 18 hours. Then the extract was filtered rapidly through filter paper, taking precaution against loss of alcohol, about 25 ml of the filtrate was evaporated to dryness in a tared flat bottomed shallow dish, transferred to the oven and dried at 105°C and weighed. The percentage of alcohol soluble extract was calculated with reference to the air dried drug.

**Table:** Ash value of various parts *Boswellia ovalifoliolata*

| S.No. | Part(s) | Total Ash (%) | Acid insoluble ash (%) | Water insoluble ash (%) |
|---|---|---|---|---|
| 1 | Stem bark | 13.5 | 2.50 | 2.00 |
| | Gum | 6.00 | 1.60 | 1.50 |

**Table:** Extractive value of the various parts *Boswellia Ovalifoliolata*

| S.No. | Part(s) | 90% alcohol Soluble Extract (%w/w) | Water Soluble Extract (%w/w) | Chloroform Soluble Extract (%w/w) | Pet.Ether Soluble Extract (%w/w) |
|---|---|---|---|---|---|
| 1 | Stem bark | 17.6 | 22.4 | 4.8 | 3.4 |
| | Gum | 10.5 | 9.2 | 1.5 | 1.3 |

## 6. Fluorescence Studies

**Introduction:**

When physical and extractive value methods are inapplicable, especially powdered drugs, the fluorescence studies method will be useful to identify the drug. The study of fluorescence of powdered drugs as a means of identification appears to possess distinct possibilities of practical application (Chaudhuri Rai 1969). The ultra-violet light (200-400mu) is very active where several crude drugs show characteristic useful for their evaluation. Goodwin (1953) presented an excellent survey of fluorescent compounds in plants and the application of fluorimetry to their assay.

Fluorescence analysis was carried out following Chase and Pratt (1949) and Kokoski *et al.* (1958). The selected powdered drugs were studies both in Visible light and Ultra-Violet light for their fluorescence characters.

About one gram of the dried plant powder was extracted with 10 ml of the absolute alcohol. The tube containing Alcoholic extract of plant powder was placed at a distance of 14 cm from the source of Ultra-Violet tube and fluorescence observed. 2 ml of Alcoholic extract was treated with following reagents with the help of 1 ml pipette with 10 divisions.

Reagent I - Saturated Aqueous solution of $AgNO_3$
Reagent II - 0.1N Aqueous solution of NaOH
Reagent III - 5% Aqueous solution of HgCl2
The following tests were applied for fluorescence study

**Test 1**

a) Add 1 drop of Reagent I to 2ml of Alcoholic extract. It was shaken and fluorescence was observed.
b) 3 drops of Reagent II were added to the above (i.e.,a) and fluorescence observed immediately.

**Test 2**

a) Add 2 drops of Reagent II to 2 ml of Alcoholic extract, shaken and the colour of fluorescence was observed.
b) One drop of reagent III was added to the above containing extract (i.e.,a) shaken and noted the colour of fluorescence.
c) One more drop of Reagent III was added to the above (i.e.,a) shaken and noted the colour of fluorescence.
d) To the above (i.e.,c) 2 more drops of Reagent III were added, shaken and observed colour of fluorescence.

Dry powder also studies with the specified reagents. To the dry powder, a few drops of the following reagents were added separately and fluorescence observed immediately under Ultra-Violet tube light.

1) Powder as such 2) In NaOH in methanol 3) In NaOH in water 4) In HCl 5) 50% $HNO_3$ 6) 50% $H_2SO_4$. P
2) **Table: Fluorescence analysis of the Alcoholic extract of the selected powdered drugs of *Boswellia ovalifoliolata*:**

| Treatment of Powder | Stem bark | Gum |
|---|---|---|
| Colour of the extract in visible light | D. r | P. y |
| Colour of the extract under UV light | Y | B |
| Test - I | | |
| Step 1<br>Reagent I(drop) | Pu | L. b |
| Step 2<br>Reagent II(3drops) | D.br | B |
| Test - II | | |
| Step 1<br>Reagent II(2 drops) | Fl. pu | B |
| Step 2<br>Reagent III(1 drop) | De. pu | L. b |
| Step 3<br>Reagent III(1 drop) | G | L. b |
| Step 4<br>Reagent III(2 drops) | D. g | B |


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**Table:** Fluorescence analysis of the dry powder of selected drugs with various reagents under U.V. light

| Treatment of powder | Stem Bark | Gum |
|---|---|---|
| Powder in visible light | D. br | P. y |
| Powder in U.V light | D. pu | L. b |
| Powder + NaOH in Methanol | Fl. p | L. g |
| Powder + HCl | V | B |
| Powder + 50% $HNO_3$ | G. P | Pu |
| Powder + 50% $H_2SO_4$ | Pu | Brt.b |

B = Blue ; Bl. r = Blood red; Br. g = Brownish green; Brt. b = Bright blue; Brt. fl. g = Bright fluorescent green;
D.b = Dark blue; D.br = Dark brown; D.g = Dark green; D.p = Dark pink; D.pu = Dark purple; D.r = Dark red; D.y = Dark yellow; De.g = Deep green; De.pu = Deep purple; De.v = Deep violet; D. y. brn = Dark Yellowish Brown; Fl. b = fluorescence blue; Fl. g = Fluorescence green; Fl. p. g = Fluorescence pale green; Fl. pu = Fluorescence purple.

G = Green; G.br = Greenish brown; G. pu = Greenish purple; G. o = Greenish orange; G. v = Greenish violet; G. y = Greenish yellow; H. Fl. g = High green fluorescence. I. fl. g = Intensified green fluorescence.L. b = Light blue; L.br = Light brown; L. g = Light green, L.y.br = Light yellowish brown; O. r = Orange red; Ol. g = Olive green; P = pink; Pu. g = Purplish green; P. y = Pale yellow; R=Red; R. y = Reddish yellow. V= Violet; Y= Yellow; Y.br = Yellowish brown; Y. g =Yellowish green; Y. r = Yellowish red.

**Table:** Histochemical tests for stem bark of *Boswellia ovalifolilata:*

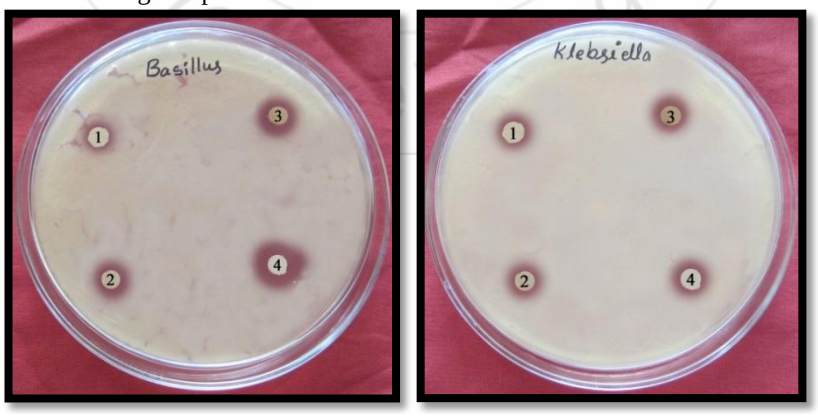
| Drug | Reagent | Test for | Reaction | Result |
|---|---|---|---|---|
| Section | Iodine solution | Starch | Blue colour | + |
| Section | 10% Ferric chloride solution + alcohol | Tannins | Black colour | + |
| Section | Sudan III solution | Oil globules | No change | - |
| Section | Conc.Hcl | Crystals | Effervescence | + |
| Section | Pinch of Phloroglucinol +dil.Hcl + Alcohol | Lignin | Magenta colour (Fibres) | + |

**Antibacterial Activity**

The plant's secondary products may exert their action by resembling endogenous metabolites, ligands, hormones, signal transduction molecules or neurotransmitters and thus have beneficial medicinal effects on humans due to similarities in their potential target sites. The presence of antimicrobial substances in the higher plants provide a source of inspiration for novel drug compounds as plants derived medicines have made significant contribution towards human health. The antimicrobial compounds from plants may inhibit microbial growth by different mechanism than those presently used antimicrobials and may have a significant clinical value in treatment of resistant microbial strains. Therefore, random screening of plants for active chemicals is as important as the screening of ethnobotanically targeted species (Principle, 1989)**.**

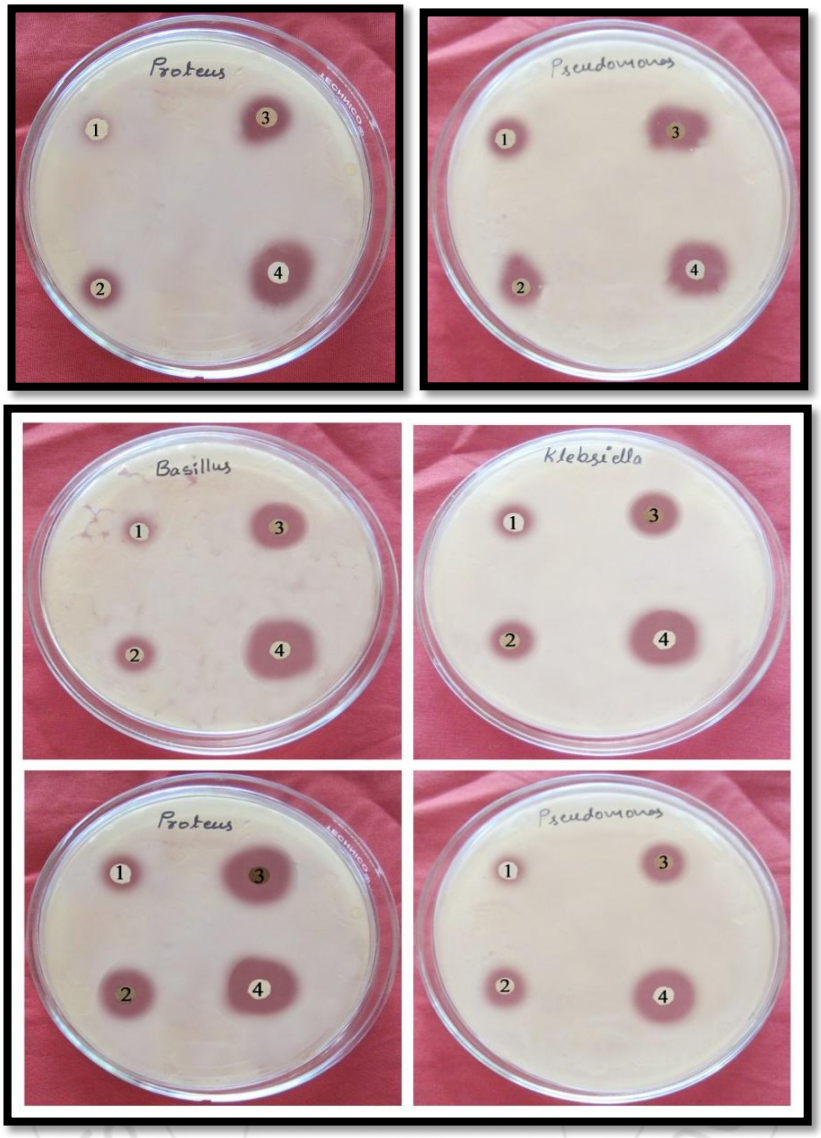
**Bacterial Cultures:**
The bacterial cultures were procured from the Department of Microbiology, Sri Venkateswara Institute of medical Sciences (SVIMS), Tirupati, Andhra Pradesh. Pathogenic Gram positive bacteria such as *Bacillus subtilis*, *Staphylococcus aureus*, and Gram negative bacteria *Proteus vulgaris*, *Pseudmonas aeruginosa*, were maintained on nutrient agar slants at $4^0$C until further used for experimental studies**.**

**Antibacterial activity of *Boswellia ovalifoliolata*:**

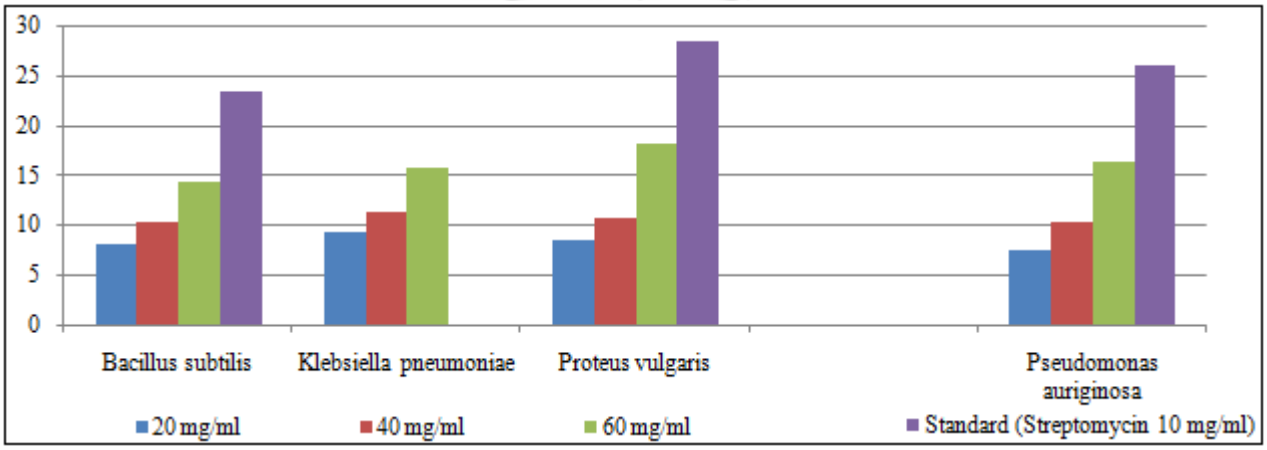




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| S. No | Name of the microorganism | 20 mg/ml | 40 mg/ml | 60 mg/ml | Standard (Streptomycin 10 mg/ml) |
|---|---|---|---|---|---|
| 1 | Bacillus subtilis | 8.14± 0.24mm | 10.32 ±0.61mm | 14.35 ± 0.34mm | 23.45 ± 0.65mm |
| 2 | Klebsiella pneumonia | 9.32 ± 0.56mm | 11.45 ± 0.32mm | 15.8 ± 0.71mm | 24. 4 ± 0.53mm |
| 3 | Proteus vulgaris | 8.43 ± 0.64 | 10.7 ± 0.89mm | 18.24 ± 0.46mm | 28.53 ± 0.74mm |
| 4 | Pseudomonas auriginosa | 7.54 ± 0.23 mm | 10.3 ± 0.45mm | 16.32 ± 0.29mm | 26.25 ± 0.36 mm |





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## 7. Results

Present investigation, anti bacterial activity of four selected medicinal plant, on pathogenic bacterial strains, all exhibited significant antibacterial activity. Methanol stem extract of *Boswellia ovalifoliolata* at the concentration 60 mg/ml showed potent antibacterial activity. *P. vulgaris* (18mm) was more susceptible, followed by *P. aeruginosa* (16mm), *K. Pneumonia* (15mm) and *B. subtilis* (14mm).

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# ETHNOBOTANICAL STUDY OF DURGAMKONDA OF VELIGONDA HILL RANGE, EASTERN GHATS, ANDHRA PRADESH

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**Abstract - Durgamkonda of Veligonda Hill Range, Eastern Ghats, Andhra Pradesh is floristically rich area where plants of various categories are growing spontaneously in their natural habitat. Durgamkonda is known for wide variety of Medicinal Plants that have been in existence identified and utilized since hundreds of years by local tribes. The present study aims at documentation of Medicinal Plants used by tribes for various purposes. Durgamkonda is the most important part of veligonda situated near Udayagiri forest of Nellore District.**
**Key words: Durgamkonda – Ethnobotany - Medicinal Plants —MPCA– Tribes.**

## I. INTRODUCTION

The area of Durgamkonda reserve forests covers aroung 5029.60 hectors of land. There is significant number of rare species of endemic flora and fauna, most of the area is under the conservation region. Udayagiri was also known as Kondyapalem in ancient times. It lies at the foot of Udayagiri hill which is about 938 meters above the sea level. The hill fort is supposed to have been built by Langula Gajapathi, a Hindu King.

Udayagiri is a mandal in Nellore district of Andhra Pradesh. Udayagiri hill (Sanjeevini hill) is situated on the southern part of Udayagiri town. It is the southernmost part of the Eastern Ghats. It comprised of dry deciduous forests and located at $14.8667^0$N, $79.3167^0$E. It has an average elevation of 3261 ft above the sea level. Durgampalli, Duragampalli road, Loddivagu (Loddi river), Salvapet, Kona canal, Kona,Tapaka, Chinna masjid (Small Mosque) Pedda masjid(Big Mosque) and fort are the main places of the hill. Herbarium species were deposited at Department of Botany, Vikrama Simhapuri University P. G Centre, Kavali.

## II. STUDY AREA

Durgamkonda of Udayagiri Durgam is a sacred Groove and off shoots of Eastern ghats is an abode for rich Bio-diversity.Total number of plants in our study from udayagiri hills is 295 species of 290 genera and 83 families with genus-species ratio is 4.5:3.7:1 .The presence of 295 species concludes that udayagiri forests as one of the phyto-diversity rich spot of Nellore district. Dicotyledons are represented by 260 species belonging to 270 genera of 35 families. Monocotyledons include 30 speies belonging to 20 genera of 11 families.

The ratio of dicotylidons to monocotylidons is 10:1.For species and 10.3:1 for genus Based on habit flora comprises 121 species (37%) under trees followed by 76 species shrubs (20%) and 107 species herbs (31%) and 37species of climbers (11%).37% of flora comprises trees ,33% of flora comprises herbs 21% of flora comprises shrubs and 11% of flora comprises climbers.

*Hardwickia binata and Pterocarpus santalinus* occur here and there over the veligondas. Anogeissus latifolia occurs in patches in the slopes of yerra konda. The principal ranges of hills bearing forests of the veligondas, the

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yerrakonda and the Udayagiri duragam hills. The veligonda range, the yerrakonda ( yerra means Red) are called so because these hills contain a number of *Hardwickia binata* (yepi) trees. The young red leaves of these trees give a distinctive colour to their general aspect in summer.

*Hardwickia binata* is one of the dominant components in forests especially near foot hills and low elevation up to 300 m but due to over exploitation and slow regeneration it became threatened species in Veligonda hill range

Much stress is given to collect data on use of these plants by tribals namely yanadis ,tribal medicine.The ethno-medical data was prepared from house-wives who knew/practice of herbal medicine, village physicians, tribals, Yanadi, Yerukula and Nakkala.

## III. EXPERIMENT AND RESULT

**DISTRBUTION OF IMPORTANT SPECIES IN DURGAM KONDA - DENSITY WISE:**

| | | | | |
|---|---|---|---|---|
| 1. | Chirumanu | - | *Anogeissus latifolia* | - 40% |
| 2. | Billudi | - | *Chloroxylon swietenia* | - 4% |
| 3. | Gotti | - | *Zyziphus xylophyrus* | - 15% |
| 4. | Jana | - | *Grewia damine* | - 8% |
| 5. | Redsanders | - | *Pterocarpus santalinus* | - 12% |
| 6. | Nakkina | - | *Canthium dicoccum* | - 3% |
| 7. | Ooti | - | *Diosphyros ferrea* | - 7% |
| 8. | Usiri | - | *Emblica officinalis* | - 1% |
| 9. | Kondaregu | - | *Commiphora caudata* | - 3% |
| 10. | Others | - | | - 7% |

**Important species found in Durgamkonda of Udayagiri hills**

| | | | |
|---|---|---|---|
| 1. | Chirumanu | - | *Anogeissus latifolia* |
| 2. | Billudu | - | *Chloroxylon swietenia* |
| 3. | Gotti | - | *Zyziphus xylophyrus* |
| 4. | Jana | - | *Grewia damine* |
| 5. | Redsanders | - | *Pterocarpus santalinus* |
| 6. | Nakkina | - | *Canthium dicoccum* |
| 7. | Ooti | - | *Diosphyros ferrea* |
| 8. | Usiri | - | *Emblica officinalis* |
| 9. | Mayuri siki | - | *Actinopteris radiata* |
| 10. | Sarapappu | - | *Buchanania Lanzan* |
| 11. | Nelavemu | - | *Andrographis paniculata* |
| 12. | Musti | - | *Strychnos nuxvomica* |
| 13. | Kunkudu | - | *Sapindus emarginatus* |
| 14. | velama | - | *Anogeissus latifolia* |
| 15. | Rela | - | *Cassia fistula* |
| 16. | Karaka | - | *Terminalia chebula* |
| 17. | Beedi leaves | - | *Diospyros Melanoxylon* |
| 18. | Maredu kommulu | - | *Decalepis hamiltonii* |
| 19. | Beera | - | *Luffa acutangula* |
| 20. | Kalivi | - | *Carissa carandas* |
| 21. | Gumpena | - | *Lannea coromandelica* |
| 22. | Pala | - | *Manikara Hexandra* |
| 23. | Yepi | - | *Hardwickia binata* |
| 24. | Munkudu | - | *Atlanta monophylla* |
| 25. | Magabeera | - | *Anisomeles malabarica* |
| 26. | Somichettu | - | *Soymida febrifuga* |
| 27. | Kondakasintha | - | *Toddalia asiatica* |
| 28. | Adavi ulli | - | *Urginea indica* |
| 29. | Chedu jilakara | - | *Vernonia anthelmintica* |
| 30. | Bodatharam | - | *Sphaeranthus indicus* |
| 31. | Karrathumma | - | *Prosopis chelelsis* |
| 32. | Chitramudam | - | *Plumbago zeylanica* |
| 33. | Addasaram | - | *Adathoda vasica* |

34. Tangedu - *Cassia auriculata*

**MINOR FOREST PRODUCTS OF DURGAMKONDA OF UDAYAGIRI HILLS OF VELIGONDA HILL RANGE**

*Buchanania lanzan* (Sarapappu) seed: - The species occurs scattered in all the ranges but the seeds are collected only in Udayagiri Range.

*Strychnos nux-vomica* (Musti) seed:- The species occur scattered in all the ranges. The ripe fruits are collected from December to April .The proper time to start the collection is when the bats begin to eat the fruits.

*Sapindus emarginatus* (Kunkudu) Fruits:- Fruits ripe in April and the collection is made in May. Fruits used as substitute of soap.

*Tamarindus indica* (Chinta) Fruits:- Trees occur in scattered manner in all the ranges. The fruits ripe in February-March. Pods & leaves are used for culinary purpose.

*Murraya Koenigii* (Karivepaku) Leaves:- The leaves are collected and dispatched to consumption centers in Udayagiri division as well as to Madras. Leaves are used to flavor curries etc.

*Anogeissus latifolia* (Chirumanu)wood: The only species which occur in fair profusion. Wood is used as Timber.

*Cassia fistula* (Rela) Bark:- The species occur diffusely in hilly tracts of Udayagiri hill range. Stem bark and fruit pulp are used as laxative.

*Cassia auriculata* (Tangedu) Bark:- The species occur diffusely in plain areas of Udayagiri range. Powdered root bark is taken internally for cooling effect.

*Terminalia chebula* (Karaka)Fruits:- The species is found in fair abundance in interior ranges of Udayagiri hills. Fruits of myrobalan are of medicinally important. Wood is a valuble timber.

*Diospyros melanoxylon* (Beedi aaku)Leaves:- These occurs diffusely in all the Udayagiri hill ranges. Leaves are used in the preparation of Beedis.

*Accacia leucophloea* (Tella thumma) Bark :- Bark is used for tanning and in alcohol distillation. Gum is indigenous medicine.

*Viscum auriculatum* (Badanika) Stem:- Paste of plant applied to wounds.

*Terminalia bellerica* (Thandra) Fruits :- Fruit is used as astringent and a remedy for cough. Wood used as timber.

*Menecylon umbellatum* (Alli)Leaves :- Yellow dye from the leaves used for dyeing clothes and mats.

*Trichosanthes cucumerina* (Adavi potla)Roots :- Roots used to cure bronchitis. Leaves used in bilious disorders.

*Mytragyna parvifolia* (Batta Ganapa) Stem :- Wood used for furniture.

*Terenna asiatica* (Korivi) Leaves :- Leaves used in Skin deceases and swellings.

*Wrightia tinctoria (*Reppala) Bark :- Decoction of bark and leaves are taken for stomach disorders.

*Hemidesmus indicus* (Sugandhapala) Roots :- Roots used for cooling effect and blood purification.

*Strychnos potarorum* (Chilla) Seeds :- Seeds are used to clear turbid water and in eye diseases.

*Lucas aspera* (Tummi) Leaves:- Leaf juice used in treating jaundice and scorpion sting.

*Plumbago zeylanica* (Chitramulam) Root:- Roots used as appetizer and in skin diseases.

*Salvadora persica* (Varagogu) Leaves :- Twigs used as tooth cleaners, decoction of leaves in asthma and cough.

*Gmelina asiatica* (Gummadi) Fruits :- Ripe fruits used in removing dandruff.

*Chionanthes zeylanica* (Punagani) Roots :- Root bark used to control white discharge in ladies.

*Boswellia serrata* (Adavi sambrani):-Stem – stomach ulcers, diabetes. Leaf - mouth and throat ulcers. Gum – dysentery, inflammations, joint pains, arthritis, amoebic, dysentery, hydrocele, diabetes.

*Aegle marmelos* (L) (Maredu):-Whole plant – Venereal diseases, digestive and abdominal disorders, eye diseases, stupor, pyrexia, dropsy, vomiting, piles, intermittent fever. Leaf – Diabetes, fruit astringent, digestive stomachic, dysentery cooling agent.

*Gymnema sylvestre* (Retz) (Podapatri):-Root – Hydrocele, polyuria, poisoning. Leaf- Diabetes, diuretic, fruit stomachic, alexitaric, bronchitis, cardiac diseases.

*Gmelina arborea* (Roxb) (Gummadi teku):- Root – Cardiac diseases, dysuria, aphrodisiac, expectorant, demulcent. Leaf –Diabetes. Fruit-Diabetes.

*Gloriosa superba* (L) (Adavi Nabhi):- Tuber – Tonic, stomachic, anthelmintic, abortifacient, gonorrhea, ulcers, neuralgic pains, skin troubles, gout, rheumatism, piles, skin diseases, leprosy, wounds, snake bite and scorpion string. Leaf juice–Lice killer.

*Hardwickia binata Roxb* :- Bark yields resinuous gum and fibre leaf used as green manure

*Asparagus racemosus* Wild (Pilliteegalu):- Tuber – Herbal tonic, diuretic, galactogogue, urinary diseases, gynaecological disorders, diseases of nervous system, hyperacidity, gastritis, menorrhagia, eye diseases. Root, leaf – diabetes, cough, diarrhea, pain, skin diseases, nervous and rheumatic complaints.

*Andrographis paniculata* (Brum.f) (Nelavemu):- Whole plant – Febrifuge, astringent, anodyne, tonic, diabetes. Leaf – anthelmintic, malarial fever, skin diseases, general debility, discontinuation of menstrual cycle.
*Tinospora cordifolia* (Wild) (Kappa teega):- Root – Snake bite. Stem – Fissures in the sole, snake bite.
*Cassia senna* L (Senna):- Leaf and Fruit – Laxative, purgative, constipation, febrifuge, gout, worm infestation, skin diseases, abdominal and blood disorders.
*Piper longum* L (Pippallu):- Leaf and Fruit – Counter irritation, diabetes, analgesic, expectorant, inflammations, carminative, insomnia tonic, cough, cold, bronchitis, stimulant, lever disorders, fever, indigestion.
*Santalum album* L (Srigandhamu):- Heart wood and wood – Diabetes, oil- verenal diseases, refrigerant, expectorant, herpis worm infestation, dysuria.
*Strychnos colubrina* L. (Teega Mushti):- Wood – Fever. Root – Rheumatism, Anthelmintic, cutaneous disorders. Fruit – Mania.
*Strychnos potatorum* L.f (Chillaginja Chettu):- Seed – Tonic, diabetes, diarrhea, gonorrhea, cardiac diseases, abdominal diseases, stomachic, water purifier.

**\ENDEMISM:**
A good number of plants seemed to be endemic to these parts of Eastern Ghats. But specific mention may be made of *Pterocarus santalinus.* It is an interesting species in that it is more prevalent in this area than in the adjoining districts viz. Kurnool and Chittoor. It has edaphic preference at higher elevations *Shorea tumbaggaia* is rare but occurs in this forests only, found associated with Red sanders at high elevation. *Croton scabiosus* is another associate of Red sanders. A few more endemics like *Decalepis hamiltoni, Glossocardia, Sympagis petiolares, Hugonia mystax, Terminalia pallid,* also occur in this forest.
**Rare plants:** Owing to intensive studies in the area a good number of species have been discovered first time or recorded after a lapse of at least seventy years. Some of them by their occurrence here show continuity or extended distribution in the Udayagiri Hills. *Desmodium pryonii, Hibiscus purpureus, Rhynchosia rufesens, Rhynchosia rothii, Rhynchosia densiflora, Asyneuma fulgens.*

From the foregoing information it is clear that the area harbours a good number endemics and rare plants. It seems to be due to a combination of factors of edaphic, climatic as well as genetic structure in total. Thus these parts of Eastern Ghats forming at ecological islands support specific gene pool niche. Any disturbance due to biotic interference leading to degradation of forests, the prevailing semi arid climate and thermal regime, give scope for thrival of exotics resulting in the unusual change in natural ecosystems

The field work carried out at intervals has facilitated the researcher to record the data in various surveys. The survey resulted in collection of more than 225 medicinal plants used for different ailments along with the ethno medicinal data from 30 informants.
The following are the vulnerable plants in Udayagiri hill range

1. *Sterculia villosa*
2. *Aegle marmelos*
3. *Gymnema sylvestre*
4. *Oroxylum indicum*
5. *Gloriosa superba*
6. *Shorea tumbuggaia*
7. *Rubia cordifolia*
8. *Eubhorbia fusiformis*
9. *Stemona tuberosa*
10. *Hildergardia populifolia*
11. *Phyllanthus indofischeri*

**IV.CONCLUSION**
Ethnobotanical study of a particular region depicts its ecological, hydrological. Topographical, historical identification. Documentation of all indentified species of Durgamkonda of Udayagiri forest in the present study would serve as a reference for the students and teachers of Botany and others interested to get knowledge. This study also helps in the addition of new species to district flora. For the proper utilizing of forest resources, meticulous and estimated strategy need to be evolved without causing deterioration to the flora. There are efforts to develop infrastructure like Roads, electricity etc... To make this as one of the best tourist spot in the State. It can be developed as Andhra Ooty, if funds allotted. The climatic condition is semi arid with mixed type of vegetation consists of semi evergreen dry deciduous scrub forest. Hence it is suitable Medicinal plant conservative area.

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# Medicinal Plant Resources of Nagarjuna Sagar Srisailam Wildlife Sanctury (Rajiv Gandhi Wild Life Sannctuary)

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***Abstract*** **-The Nagarjunasagar Srisailam Wildlife Sanctuary (also known as Rajiv Gandhi ….) occurs on the Nallamala Ranges (78°30'— 79°28'E; 15°53'—16°43'N) in Andhra Pradesh at elevations varying from 100 to 917 m. The area consists mostly (80%) of the area is gently rolling to steeply hilly (incl. a ref. in support).. These ranges include many plateaus of which Amrabad, Srisailam, Peddacheruvu, Sivapuram, Nekkanti are noteworthy.**

**The present paper refers to 214 species belonging to 175 genera, 91 families. Out of 91 families, 85 are of angiosperms, five are of Pteridophytes and one is a gymnosperm. The medicinal ferns of Pteridophytes are *Adiantum caudatum, Actinopteris radiate, Christella dentate, Hemionitis arifolia,* and *Lygodium flexosum. Cycas beddomei* is the only one gymnosperm. There are 60 (27.02%) herbs, 41 shrubs (18.46%) 77 trees(34.68%), and 33(14.86%) climbers. 34.68% of medicinal plants constitute trees.**

***Key Words:– Eastern Ghats, Deities – Tribes.***

## I. INTRODUCTION:

The Nagarjunasagar Srisailam Wildlife Sanctuary (also known as Rajiv Gandhi ….) occurs on the Nallamala Ranges (78°30'— 79°28'E; 15°53'—16°43'N) in Andhra Pradesh at elevations varying from 100 to 917 m. The Elevation varies from 100 m (330 ft) to 917 m (3,009 ft) above mean sea level.

Nargarjunasagar Srisailam Wildlife Sanctuary was declared as a sanctuary in 1978 and made a part of 'Protect Tiger'in 1983. In 1992, the reserve was renamed as Rajiv Gandhi Wildlife Sanctuary. Apart from tigers, the reserve is home for Over 150 bird species also occur here. Srisailam and Nagarjunasagar dams serve as water sources.

The perennial water sources are generally located in the valleys and the plateaus suffer from acute scarcity of water during summers. The Krishna River cuts its basin almost 200 m deep over a distance of 130 km through the reserve. The mean temperatures are 16°C in June (name the months) winter (December) and 43°C in summer (May) (name the months).

## II. STUDY AREA

Nargarjunasagar Srisailam Wildlife Sanctuary was declared as a sanctuary in 1978 and made a part of 'Protect Tiger'in 1983. In 1992, the reserve was renamed as Rajiv Gandhi Wildlife Sanctuary.

The main types of forest biomes in the reserve are : southern tropical dry deciduos forest *Hardwickia* forest and Deccan thorn scrub forests with much Euphorbia scrub. Important plant species here are : *Anogeissuslatifolia* ( axlewood ) , Cleisthanthus collinus (odcha) , *Terminalia* spp., *Pterocarpus marsupium* , *Hardwickia binata* (anjan tree), *Boswellia serrata* (Indian frankincense or Salai ) , *Tectona grandis* ( teak ), *Mundulea sericea* and *Albizia* spp. (silk plants). (Champion H.G., Seth.S.K.1968).

## III. MATERIALS AND METHODS

Field trips were undertaken during the four seasons-viz,Summer,Monsoon,Autumn and Winter in2014–2016. Details such as vegetative, flowering and fruiting stages of the plant species were observed.. The plant specimens were collected and determined using Gamble (1967) and Hooker (1897). During the field work, the specimens collected for the preparation of herbarium were processed following Jain and Rao (1977).


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## IV. RESULTS

Table:1 list of species of Nagarjuna sagar srisailam wild life sanctuary

| S.No | Botanical Name | Vernacular name | Family | Habit | Medicinal Uses |
|---|---|---|---|---|---|
| 1 | Abuliton indicum (L.)Sweet.Hort.Brit. | Duvvenakaya/ Tutturubenda | Malvaceae | Shrub | Haematuria |
| 2 | Acacia leucophloea (Roxb.) Willd. | Tella tumma | Mimosaceae | Tree | Diuretic |
| 3 | Accacia nilotica (L.) Willd. | Nallatumma | Mimosaceae | Tree | Cough;Diarrhoea |
| 4 | Achyranthes aspera L. | Uttareni | Amaranthaceae | Herb | Piles;Dieretic |
| 5 | Actinopteris radiata (Koenig ex Sw.) | Mayuri shika | Actinopteridaceae | Herb | Skin diseases |
| 6 | Adiantum caudatum L. | Raja hamsa | Adiantaceae | Herb | Diabetes |
| 7 | Adiantum lunulatum Burm.f. | Chitrapadu | Adiantaceae | Herb | Ulcers;Dysentery |
| 8 | Aegle marmelos (L.) | Maredu / Bilva | Rutaceae | Shrub | Dysentery |
| 9 | Aerva lantana (L.) | Pindikura | Amaranthaceae | Herb | Urinary diseases |
| 10 | Ageratum conyzoides L. | Goat weed | Asteraceae | Herb | Nervine tonic |
| 11 | Alangium salvifollium (L.f.) | Udaga / Ankolamu | Alangiaceae | Tree | Dog bite |
| 12 | Albizia amara (Roxb.) | Cheekireni | Mimosaceae | Tree | Inflamation |
| 13 | Albizia odoratissima (L.f.) Benth. | Chinduga | Mimosaceae | Tree | Leprosy |
| 14 | Alstonia scholaris L. | Edakulapala | Apocynaceae | Climber | Abdominal pains;Dysentery |
| 15 | Andrographis paniculata (Burm.f.) Wall. | Nelavemu | Acanthaceae | Herb | Fever |
| 16 | Androghapis nallamlayana Ellis. | Kachugadda | Acanthaceae | Herb | Leucorrhoea |
| 17 | Anisomelea malabarica (L.) | Moga-Bira | Lamiaceae | Shrub | Diarrohoea;Eczema |
| 18 | Annona reticulata L. | Ramaphalam | Annonaceae | Tree | Astringent |
| 19 | Anogeissus latifolia (Roxb.ex Dc.) | Chirimanu / Elamas | Combretaceae | Tree | Bitter tonic;Astring |
| 20 | Argemeone mexicana L. | Kusuma / Brahmadandi | Pepepaveraceae | Herb | Syphillis |
| 21 | Aristolochia braceteolata Lam. | Gadidagadapa | Aristolochiaceae | Herb | Skin diseases; Diabetes |
| 22 | Aristolochia indica L. | Easwari | Aristolochiaceae | Herb | Snake bite |
| 23 | Arisaema tortuosum Schott | Rollavagu | Araceae | Herb | Kill worms in Cattle |
| 24 | Asperagus gonclados Baker | Pilliteegalu | Liliaceae | Herb | Galactagogue;Diabetes |
| 25 | Atalantia monophylla (L.) | Munukudu | Rutaceae | Shrub | Fever; Antiseptic |
| 26 | Azadirachta indica A.Juss. In Mem.Mus.Natl. | Vepa | Meliaceae | Tree | Skin diseases |
| 27 | Azima tetracantha Lam. | Tella uppili | Salvadoraceae | Shrub | Leprosy; Eczema |
| 28 | Bacopa monnieri (L.) Pennel | Brahmi | Scrophulriaceae | Herb | Memory booster |
| 29 | Baliospermum montanum (Willd.) | Konda audamu | Euphorbiaceae | Shrub | Stomach Pain;Laxative |
| 30 | Bamboosa arundinaceae(RETz.)Roxb. | Bongu Veduru | Bambusiaceae | Bush | Leprosy;Wounds |
| 31 | Bauhinia racemosa Lam.t | Are fibres | Caesalpinaceae | Tree | Malaria fever |
| 32 | Bauhinia vahlii Wight&Arn | Camel'sfoot climber | Caesalpiniaceae | Perennial creeper | Aphrodisiac;Dysentery |
| 33 | Blumea mollis (D.Don)Merr | Kukka pogaku | Asteraceae | Herb | Dropsy; Throat Infection |
| 34 | Boerhavia diffusa L. | Attamamidi | Nyctaginaceae | Herb | Urinary disorders |
| 35 | Boswelia serrata Roxb. | Sambrani | Burseraceae | Tree | Arthritis |
| 36 | Buchanania lanzam Spreng. | Morli | Anacardiaceae | Tree | Leucorrhoea |
| 37 | Buchanania oxilaris(Desr)Ramam. | Sara | Anacardiaceae | Tree | Boils; Cardio tonic; Wounds |
| 38 | Caesearia elliptica (Roxb.) | Chilakaduddi | Flacourtiaceae | Tree | Diabetes;Diuretic |
| 39 | Canscora diffusa (Vahl) R.Br | Shankhupuhi | Gentianaceae | Herb | Piles; Skin diseases |
| 40 | Capparis sepiaria L. | Nalla uppili | Capparaceae | Shrub | Febrifuge |
| 41 | Cardiospermum halicacabum L.Sp. | Buddakakara | Sapindaceae | Climber | Nervous disorders;Rhematism |
| 42 | Careya arborea Roxb. | Budda darimi | Barringtoniaceae | Tree | Eye diseases; Skin sores |
| 43 | Carmona retusa (Vahl) | Nomuchettu / Barranki | Boraginaceae | Shrub | Snake bite; Sterility |
| 44 | Canthium dicocum Teij.&Binn. | Nalla balusu | Rubiaceae | Tree | Fever;Diarrhoea |
| 45 | Cassia absus L.Sp. | Chanupala vittulu | Caesalpinaceae | Herb | Constipation; Cough |
| 46 | Cassia auriculata L. | Tangedu | Caesalpiniaceae | Shrub | Diabetes |
| 47 | Cassia fistula L.Sp. | Rela | Caesalpinaceae | Tree | Diabetes |
| 48 | Cassia italica (Mill.)Spreng. | Nelatangedu | Caesalpinaceae | Herb | Bone fracture |
| 49 | Cassia montana Meyne ex.Roth. | Pyditangedu | Caesalpinaceae | Shrub | Body Pains |
| 50 | Cassia occidentalis L.Sp. | Kasintha | Caesalpinaceae | Shrub | Laxative |
| 51 | Cassine glauca Kuntze | Neridi | Celastraceae | Tree | Eczema;Antidote |
| 52 | Cassytha filiformis L. | Sitamma savaralu | Lauraceae | Climber | Hair tonic; Dysentery |


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|---|---|---|---|---|---|
| 53 | Catunaregam spinosa (Thung.) | Manga | Rubiaceae | Shrub | Astringent;Dysentery |
| 54 | Centella asiatica (L.) | Saraswathi | Apiaceae | Herb | Brain tonic |
| 55 | Celastrus paniculatus Willd. | Errasurugudu | Celastraceae | Tree | Brain tonic;Scabies |
| 56 | Celosia argentea L | Gunnugu | Amaranthaceae | Herb | Eczema;Ulcers |
| 57 | Chloroxylon swietenia DC.Prodr. | Billudu | Meliaceae | Tree | Rheumatism; Astringent |
| 58 | Chlorophytum arundinaceum Baker | Adavi ulli | Liliaceae | Herb | Aphrodisiac;Hydrocele |
| 59 | Cipadessa baccefera (Roth)Miq. In Ann.Mus | Ranaberi | Meliaceae | Shrub | Diabetes;Wounds |
| 60 | Cleome viscosa L | Yerraemiti | Cleomaceae | Herb | Wounds |
| 61 | Cissampelos pareira L.Var.hirsuta | Visha boddi | Menispermaceae | Shrub | Dropsy;Diabetes |
| 62 | Cissus quadrangularis L. | Nalleru | Vitaceae | Herb | Leucorrhoea;Piles |
| 63 | Cissus vetigenia L.Sp.Pl. | Adavi gummidi | Vitaceae | Climber | Wounds |
| 64 | Clerodendrum serratum Moon | Gantu bharangi | Veranaceae | Shrub | Febrifuge;Diabetes |
| 65 | Cocculus hirsutus (L.) Diels in Engl. | Dusari Teega | Menispermaceae | Climber | Rheumatism |
| 66 | Cochlospermum religiosum (L.) Alston | Konda gogu | Cochlospermaceae | Tree | Dysentery;Gonorrhoea |
| 67 | Coldenia procumbens L. | Hamsapadu | Boraginaceae | Herb | Rheumatism |
| 68 | Commifera caudata(Wightand Arn.)Engler | Kondaravi | Burseraceae | Tree | Rheumatism |
| 69 | Cordia dichotoma Forst.f | Bankamanu / Nakkera | Boraginaceae | Tree | Bronchial disorders; Fever |
| 70 | Costus speciosus (Koen.) | Adavi allam/Chengalva cost | Costaceae | Herb | Snake bite |
| 71 | Ctenolepis gracini (Burm.f.) | | Cucurbitaceae | Climber | Boils;Wounds |
| 72 | Curculigo orchioides Gaertn.,Fruct. | Nelathati | Hypoxidaceae | Herb | Asthma;Anaemia |
| 73 | Cymopogon flexuosus(L.) Rendle | Nimma gaddi | Poaceae | Herb | Citral oil |
| 74 | Dalbergia latifolia Roxb. | Jittagi / Iridi | Fabaceae | Tree | Leprosy;Ulcers |
| 75 | Dalbergia paniculata Roxb.Pl.Cor.t. | Pacchari | Fabaceae | Tree | Filarial Swelling |
| 76 | Datura metal L. | Nalla ummetta | Solanaceae | Herb | Epilepsy |
| 77 | Datura stromonium L. | Ummetta | Solanaceae | Shrub | Asthma;Narcotic |
| 78 | Decalepis hamiltonii Wight & Arn | Maredu kommulu | Asclepediaceae | Shrub | Haemorrhage;Appetizer |
| 79 | Decaschistia crotonifolia Wight &Arn | Adavigogu | Malvaceae | Shrub | Hydrocele |
| 80 | Deccannia pubscens (Roth) | Konda manga | Rubiaceae | Tree | Sores |
| 81 | Derris scandens (Roxb.) | Nalla teega | Fabaceae | Climber | Snake bite |
| 82 | Desmodium pulchellum (L.) Benth | Dayyapu jada | Papilionaceae | Shrub | Diarrhoea;Aphrodisiac |
| 83 | Desmodium triflorum (L.) Dc. | Munta mandu | Fabaceae | Herb | Galactagogue;Dysentery; |
| 84 | Dillenia pentagyna roxb. | Chinna kalinga | Dilleniaceae | Tree | Cooling agent for cattle |
| 85 | Diospyros ebenum Koen. | Nalla uti | Ebenaceae | Tree | Astringent |
| 86 | Diospyos melanoxylon Roxb. | Tumikaku | Ebenacaea | Tree | Astringent;diuretic |
| 87 | Dioscorea pentaphylla L. | Yeleru tiga | Dioscoreacea | Vine | Leprosy;Dysentery |
| 88 | Dodonea viscosa (L.)Jacq.Enum. | Bandaru | Sapindaceae | Shrub | Bone fractures; Antipyretic |
| 89 | Eclipta prostrata (L.) | Gunta galijeru | Asteraceae | Herb | Asthma; Jaundice |
| 90 | Enicostema axillare (Lam.) | Gulividi | Gentianaceae | Herb | Scabies;Gout |
| 91 | Erithroxylon monogynum Roxb. | Devadari | Erythroxylaceae | Tree | Diuretic;Febrifuge |
| 92 | Euphorbia hirta L. | Nanabala | Euphorbiaceae | Herb | Cough;Dysentery |
| 93 | Euphorbia nivulia Buch.Ham | phorbiaAkujamudu | Euphorbiaceae | Shrub herb | Ruefacient;Diabetes |
| 94 | Evolvulus alsinoides(L.) | Vistikantha | Convolvulaceae | Herb | Asthma;Fevers |
| 95 | Ficus benghalensis L.Sp. | Marri | Moraceae | Tree | Rheumatism |
| 96 | Ficus hispida | | Moraceae | Shrub | Leucoderma |
| 97 | Ficus microcarpa L. | Pittamarri | Moraceae | Tree | Wounds;Diabetes |
| 98 | Flacouria indica (Burm.f.)Merr. | Putikada | Flacourtiaceae | Shrub | Astringent;Appetiser |
| 99 | Ficus tinctoria Forst.f.subsp.parasitica (willd.)Corner | Tellabarica | Moraceae | Medium sized tree. | Fever;Stringent |
| 100 | Gardenia resinifera Roth. | Erribikki | Rubiaceae | Tree | Constipation; Bronchitis |
| 101 | Givotia moluccaina(L.) | Tella poliki | Euphorbiaceae | Tree | Drandruf;Psoriasis |
| 102 | Gloriosa superba L.Sp.Pi. | Nabhi / Nagetigadda | Liliaceae | Climber | Abortifacient;Leprosy |
| 103 | Glycosmis pentaphylla (Retz) DC. | Gonji | Rutaceae | Shrub | Diabetes; Eczema |
| 104 | Gymnema sylvestre (Retz) | Podapatri | Asclepediaceae | Shrub | Diabetes |
| 105 | Gyrocarpus americanus jacg | Kummari puliki | Hernandiaceae | Tree | Cancer |
| 106 | Gyrocarpus asiaticus Willd. | Taniki /Nalla poliki | Hernandiaceae | Tree | Cancer |


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| 107 | Haldinia cordifolia (Roxb) | Rudra ganapa | Rubiaceae | Tree | Stomachic |
| 108 | Hardwickia binata Roxb. | Yepi | Caesalpiniaceae | Tree | Rheumatism |
| 109 | Hedtitus peberula (G.Don)Arn. | Chiruveru | Rubiaceae | Herb | Asthma;bronchites |
| 110 | Hedyotis affinis Roem and Schult. | Gorlaum | | Herb | Gonorrhoea |
| 111 | Hedyotis corymbosa (L.) | Vermela – vemu | Rubiaceae | Herb | Stomachic;diarrhoea |
| 112 | Hedyotis herbacea L. | Chiriveru | Rubiaceae | Herb | Febrifuge,Rheumatism |
| 113 | Helicters isora L. | Gooba thada | Sterculiaceae | Shrub | Desentery;Diabetes |
| 114 | Hemidesmus indicus(L.) var.inducus | Sugandhapala | Periplocaceae | Herb | Cooling Bevarage;Cardio tonic |
| 115 | Hemionitis arifolia (Burm.f.) Moore | Rama bhanam | Hemionitidaceae | Herb | Antidiabetes |
| 116 | Hiptage benghalensis (L.)Kurz | Madhavi tega | Malphigiaceae | Climber | Liver disorders;Dysentery |
| 117 | Holarrhena antidysenterica (Roxb. exFleming) | Kola musthi / pala / kodisapala | Apocynaceae | Tree | Diabetes;Antidysentric |
| 118 | Holostemma ada-kodein Schultes | Tella jilledu / Peyyi baddu | Asclepediaceae | Climber | Diabetes;Gonorrhoea |
| 119 | Holarrhena pubescens (Roxb.ex.Flemming) Wall | Kodicipala | Apocynaceae | Tree | Mouth Ulcers;Diabetes |
| 120 | Holoptelea integrifolia (Roxb.)Planch. | Nemlinara | Ulmaceae | Tree | Piles;fistula;Scabies |
| 121 | Hybanthus enneaspermus (L.) Muell.Arg.Fragm. | Ratna purusha | Violaceae | Herb | Impotency;Antidote |
| 122 | Ichnocarpus frutescens (L.)R.Br. | Palateega | Apocynaceae | Climber | Blood Purifier |
| 123 | Indigofera cassioides | Kondaneeli | Papilionaceae | Errect shrub | Cough |
| 124 | Ipomea mauritiana jacq. | Vidarkada | Convolvulaceae | Cimber | Galactogogue |
| 125 | Ixora arborea Roxb.ex.Smith | Gorivi | Rubiaceae | Tree | Urinary disorders; Dysentery |
| 126 | Ixora pavetta Andr.Bot.Repos.t. | Korivi/ Papidi | Rubiaceae | Tree | Urinary disorders; Dysentery |
| 127 | Jasminum auriculatum Vahl. | Adavimalli | Oleaceae | Climber | Dropsy;Expectorent |
| 128 | Justicia adhatoda L. | Addasaram | Acanthaceae | Shrub | Asthma; Diabetes |
| 129 | Lannea coromandalica(Houtt.)Merr. | Gumpidi | Anacardiaceae | Tree | Nervous diseases; Diabetes |
| 130 | Lantana camara L. | Phallikampa | Verbanaceae | Shrub | Cuts; Wounds |
| 131 | Leonotis nepetiifolia (L)R.Br.Prodr | Ranabheri | Lamiaceae | Herb | Burns; Rheumatism |
| 132 | Lepidogathis cristataWilld. | Nakkapeethiri | Acanthaceae | Herb | Dandruf;Dental problems |
| 133 | Lepisanthes tetraphylla (Wall.) Radf. | Sali kunkudu | Sapindaceae | Tree | Skin diseases;Dandruf |
| 134 | Limnophila indica (L.) | Sambrani | Scrophulriaceae | Herb | Dysentery;Carminative |
| 135 | Litsea glutinosa (Lour.)Robin. | Pullamamidi | Lauracea | Tree | Bone fracture |
| 136 | Lygodium flexuosum (Linn.) | Mekasannu | Schizaeaceae | Climber | Scabies;Eczema |
| 137 | Madhuca longifolia (Koen.)Macbr. | Ippa | Sapotaceae | Tree | Diabetes;Vigour |
| 138 | Maeruva oblongifolia (Forsk.) | Magasirigadda | Capparidaceae | Shrub | Diabetes;Stimulant |
| 139 | Manikara hexandra (Roxb.) | Pala | Sapotaceae | Tree | Aphrodisiac; Ulcers |
| 140 | Maytenus emarginata (Willd.)Ding.Hou | Danthi | Caelastraceae | Tree | Dysentery;Gastrointestinal problems |
| 141 | Momordica charantia L.Var.muricata Willd | Buddakakara | Cucurbitaceae | Climber | Rheumatism;Diabetes |
| 142 | Ochna obtusata DC. | Errijambi | Ochnaceae | Shrub | Asthma;Menustral complaints |
| 143 | Olax scandens Roxb. | Mekabanda | Olacaceae | Climber | Fevers;Anaemia |
| 144 | Opilia amentacea Roxb. | Nallamekabanda | Opilaceae | Climber | Snake bite |
| 145 | Oroxylum indicum (L.) Ven | Bapana Pumpena | Bignoniaceae | Tree | Rheumatism;Oedema |
| 146 | Paracalyx scariosa (Roxb.)Ali. | Adavitellakandi | Papilionaceae | Climbing Shrub | Dysentery;Astringent |
| 147 | Pavonia xylanica (L.)Cav. | Adavi puttudu / Chiru benda | Malvaceae | Herb | Antihelmenthic;Febrifuge |
| 148 | Peristrophe paniculata (Frossk).Brummitt | Chebera | Acanthaceae | Herb | Wounds;Skin diseases |
| 149 | Phyllanthus amarus Schum&Thonn | Nelausiri | Euphorbiaceae | Herb | Jaundice |
| 150 | Phyllanthus embllica L. | Nelli / Usiri | Euphorbiaceae | Tree | Asthma |
| 151 | Physalis minima L. | Budama | Solanaceae | Herb | Fevers |
| 152 | Piper nigrum Linn. | Adavi miriyalu | Piperaceae | Herb | Muscle pain;Sprains |
| 153 | Piper sylevestre. | Toka mereyalu | Piperaceae | Climber | Rubefacient;Diabetes |
| 154 | Piper trioicum Roxb.Ham.ex.Miq. | Pamumiriyalu | Piperaceae | Climber | Rubefacient;Diabetes |
| 155 | Plumbago zeylanica Linn. | Tella chitramulam | Plumbaginaceae | Herb | Leucoderma;Scabies |
| 156 | Polygonum glabrum willd. | Golucu chettu | Polygonaceae | Herb | Jaundice;Febrifuge |
| 157 | Pouzolzia zeylanica (L.)Benn. | Uchchlagadda | Urticaceae | Herb | Snake bite;Galactogogu |


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| | | | | | |
|---|---|---|---|---|---|
| 158 | Premna tomentosa Willd | Narava/ Namari | Verbanaceae | Tree | Jaundice;Dropsy |
| 159 | Pseudarthria vicida(Linn.) | Antrita Mayakuponna | Fabaceae | Shrub | Rheumatism;Asthma |
| 160 | Pterospermum xylocarpum (Gaertn.) | Tada | Sterculiaceae | Tree | Leucorrhoea |
| 161 | Pupalia lapacea (L.) Juss. | Antudu chettu | Amaranthaceae | Herb | Cough;Fever |
| 162 | Rivea hypoicraterufirnus (Desr.) | Boddi teega | Convolvulaceae | Shrub | Parturition |
| 163 | Pueraria tuburosea Roxb.exWilld. | Chenchu gadda / Bhoochakra | Fabaceae | Climber | Asthma;Lactogogue |
| 164 | Salvadora persica L. | Nalla uppili/ Varagogu | Salvadoraceae | Tree | Asthma; Joint Pains |
| 165 | Sansevieria roxburghiana Schult.f. | Saganara | Agavaceae | Herbs | Cough;Piles |
| 166 | Santalum album L. | Chandanam , Srigandham | Santalaceae | Tree | Diuretic;Diabetes |
| 167 | Sarchostemma acidum (Roxb.)Voigt. | Pullangi tiga | Asclepiadaceae | Leafless Climbing succulent, jointed shrub | Rejuvenate;Odema |
| 168 | Scoparia dulcis L. | Mrugandhi chettu | Scrophulariaceae | Herb | Diabetes;Astringent |
| 169 | Schleichera oleosa (Lour) | Pushka | Sapindaceae | Tree | Macassar oil |
| 170 | Schrebera swleteniodes Roxb. | Mokkem chettu | Oleaceae | Tree | Leprosy;Diabetes |
| 171 | Scilla hyacinthina (Roth) | Nakkeragadda | Liliaceae | Herb | Diuretic |
| 172 | Shorea roxburghii G.Don Gen.Syst | Jalari | Dipteerocarpaceae | Tree | Astringent;Rheumatism |
| 173 | Solanum melanogena L.varinsanum L. | Chiruvanga | Solanaceae | Shrub | Toothache |
| 174 | Smilax zeylanica Linn. | Phirangichekka | Liliaceae | Climber | Diabetes;Syphilis |
| 175 | Solanum surrattense Burm.F. | Errivanga | Solanaceae | Tree | Diuretic;Cough |
| 176 | Solanum trilobatum L. | Mulla mushti | Solanaceae | Climber | Bronchites |
| 177 | Soymida febrifuga (Roxb) | Somi | Meliaceae | Tree | Dysentery;Diarrhoea |
| 178 | Sphaeranthus indicus L. | Bodasaram | Asteraceae | Herb | Rejuvenate;Diabetes |
| 179 | Strychnos nux vomica L. | Musti | Loaniaceae | Trees | Rheumatism;Leprosy |
| 180 | Strychnos potatorum L.f. | Musthi | Loganiaceae | Tree | Gonorrhoea |
| 181 | Sterculia urens Roxb. | Kovila chettu | Sterculiaceae | Tree | Diabetes |
| 182 | Suregada angustifolia (Baill.ex Muell.Arg) | Sapranchi | Euphorbiaceae | Shrub | Leprosy;Ankel pains |
| 183 | Syzygium cumini (L.) | Neredu | Myrtaceae | Tree | Urinary Calculi |
| 184 | Syzygium alternifolium (Wight) Walp. | Mogi | Myrtaceae | Tree | Diabetes;Joint Paints |
| 185 | Tarenna asiatica L. | Kommi | Rubiaceae | Shrub | Eczema;Cough |
| 186 | Tephorosia purperia (L.) Pers | Yempali | Papilionaceae | Under Shrub | Asthma;Snake bite |
| 187 | Terminalia alata Roth | Nallamadhi | Combretaceae | Tree | Constipation;Diabetes |
| 188 | Terminalia arjuna (DC.) Wight&Arn) | Arjuna / Tella maddi | Combretaceae | Tree | Obesity;Heart diseases |
| 189 | Terminalia bellirica (Gaertn.) | Thandra / tani | Combretaceae | Tree | Hypertention;Tridosa |
| 190 | Terminalia pallida Brandis | Tella karaka | Combretaceae | Tree | Dysentery;Cough |
| 191 | Terminallia chebula Retz. | Karaka | Combretaceae | Tree | Jaundice;Piles |
| 192 | Tinospora cordifolia (Willd.)Hook.f. &Thoms | Tippa teega | Menispermaceae | Climber | Diarrhoea;Cough |
| 193 | Toddalia asiatica. L.Lam.Var floribunda | Konda nimma | Rutaceae | Shrub | Gonorrhoea |
| 194 | Tribulus terrestris L. | Palleru | Zygophyllaceae | Herb | Retention of Urine;Leucorrhoea |
| 195 | Trichosanthes cucumerina Linn. | Chedu potla | Cucurbitaceae | Climber | Diabetes;Hepatoprotective |
| 196 | Trichosanthes tricuspidata Lour. | Papara | Cucurbitaceae | Climber | Headache;Sores |
| 197 | Tridax procumbens L. | Gaddi chamanthi | Asteraceae | Herb | Antiseptic |
| 198 | Tylophora indica (Burm.f.) | Kakkupala | Asclepediaceae | climber | Asthma |
| 199 | Vanda spathulata L. | Nusti bhadhanika | Orchidaceae | Herb | Asthma;Consumption |
| 200 | Vanda roxburghii Nicolson in Salda | Veduru bhadhanika | Orchidaceae | Herb | Fevers;Rheumatic swellings |
| 201 | Vanda tessellate (Roxb.) Hook.ex.G.Don | Badanika | Orchidaceae | Epiphyte | Rheumatic Swellings ;Bone fractures |
| 202 | Ventilago denticulata Willd. | Surati / Surudu | Rhamnaceae | Climber | Sprains; Malaria fever |
| 203 | Vernonia anthelmintica (L.) | Adavi jeelakarra | Asteraceae | Herb | Digestion |
| 204 | Vernonia cinerea (L.) Less | Sahadevi | Asteraceae | Errect herb | Blood disorders;Antihelmenthic |
| 205 | Vettiveria zizanioides (L.) | Vattiveru | Poaceae | Herb | Diabetes;Cooling agent |
| 206 | Viscum articulatum Burm.f. | Badanika | Viscaceae | Shrub | Epilepsy;Ulcers |
| 207 | Vitex altissima L.f.syppl. | Nemaliadugu | Verbanaceae | Tree | Leprosy; Cardiac diseases |
| 208 | Walsura trifolia (A.Juss) | Valudu | Meliaceae | Tree | Emmenagogue |


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|---|---|---|---|---|---|
| 209 | Wattakaka volubilis (L.f.) | Kallisi | Asclepediaceae | Climber | Snake bite; Body Pains |
| 210 | Withania somnifera (Linn.) | Ashwagandha | Solanaceae | Herb | Fever;Aphrodisiac |
| 211 | Wrightia arborea(Dennst.)Mabb | Peddapala | Apocynaceae | Tree | Dysentery;Skin diseases |
| 212 | Wrightia tinctoria (Roxb.)R.Br. | Reppala | Apocynaceae | Tree | Cough;Antihelmenthic |
| 213 | Ziziphus mauritiana Lam.Encycl. | Regu | Rhamnaceae | Tree | Diarrhoea;Scorpion Sting |
| 214 | Ziziphus xylopyrus (Retz.) | Gotti | Rhamnaceae | Tree | Diarrhoea;Asthma |
| | | Critically Endangered Plants (CE) | | | |
| 1 | Actinopteris radiata (SW) Lin. | Mayura sikha | Polypodiaceae | Herb | Skin diseases |
| 2 | Arisaema tortuosum Schott | Rollavagu | Araceae | Herb | Kill worms in cattle |
| 3 | Aristolochia indica Linn. | Eswari | Aristolochaceae | Climber | Snake bite |
| 4 | Aristolochia bracteata RETz. | Gadidagodapaku | Aristolochaceae | Herb | Skin diseases;Diabetes |
| 5 | Cochlospermum religiosum (L.) Alston | Kondagogu | Cochlospermaceae | Herb | Dysentery;Gonorrhoea |
| 6 | Costus speciosus(koen.) | Adaviallamu | Zinziberaceae | Herb | Snake bite |
| 7 | Decalepis hamiltonni Wt&Arn | Maredu Kommulu | Asclepiadaceae | Climber | Haemorrhage;Appetizer |
| 8 | Gymnema sylvestre (RETz) | Meshashrungi | Asclepiadaceae | Climber | Diabetes |
| 9 | Henuornitis arifolia (Burm.f) | Ramabanamu | Adiantaceae | Lithophyte herb | Antidiabetes |
| 10 | Lygodium flexuosum (Linn) | Bangaruteega | Shizeaceae | Climber fern | Scabies;Eczema |
| 11 | Piper trioicum Roxb Ham.ex.Miq. | Pamumiriyalu | Piperacae | Climber | Rubefacient;Diabetes |
| 12 | Piper nigrum Linn. | Adavimiriyalu | Piperaceae | Climber | Muscle pains;Sprains |
| 13 | Plumbago zeylanica Linn. | Chitramulamu | Plumbaginaceae | Bush | Leucoderma;Scabies |
| 14 | Pueraria tuberosa (Willd.) | Darigummadi | Fabaceae | Climber | Asthma;Lactogogue |
| 15 | Tylophora indica (Burmf.) | Mekameyniaku | Asclepiadaceae | Climber | Asthma |
| 16 | Vanda spathulata (Linn.) | Badanika | Orchidaceae | Epiphyte | Asthma;Consumption |
| 17 | Vanda tessellata (Roxb.) | Badanika | Orchidaceae | Epiphyte | Rheumatic swellings;Bone fractures |
| 18 | Withania somuifera (Linn.) | Ashwagandha | Solanaceae | Herb | Fever;Aphrodisiac |
| | | Endangered Plants (EN) | | | |
| 1 | Alstonia scholaris R. | Edakula ponna | Apocynaceae | Tree | Abdominal pains;Dysentery |
| 2 | Boswellia serrata Roxb. | Konda sabrani | Burseraceae | Tree | Arthrites |
| 3 | Caesearia elliptica (Roxb.) | Chilakaduddi | Flacourtiaceae | | Diuretic;Diabetes |
| 4 | Canthium dicocum Teij.& Binn. | Nallabalusu | Rubiiaceae | Tree | Fever;Diarrhoea |
| 5 | Cardiospermum halicacabum Linn. | Peddabudda | Sapindaceae | Climber | Nervours disorders;Rheumatism |
| 6 | Careya arborea Roxb. | Budda burusu | Barringtiniaceae | Tree | Eye diseases;Skin Sores |
| 7 | Centella asiatica Urb. | Saraswathiaku | Apiaceae | Herb | Brain tonic |
| 8 | Chlorophytum arundinaceum Baker | Adavi Ulli | Liliaceae | Herb | Aphrodisiac;Hydrocele |
| 9 | Dillenia pentagyna Roxb. | Chinna kalinga | Dilliniaceae | Tree | Cooling agent for cattle |
| 10 | Flacouria indica (Burm. f.)Merr. | Putikada | Flacourtiaceae | Shrub | Astringent;Appetiser |
| 11 | Gloriosa superba Linn. | Nabhi | Liliaceae | Herb | Abortifacient;Leprosy |
| 12 | Hemidesmus indicus (Linn.R.Br.) | Sugandhapala | Asclepiadaceae | Twinnig Shrub | Cooling beverage;Cardio tonic |
| 13 | Hybanthes ennaespermus (Linn.) | Ratnapurusha | Violaceae | Herb | Impotency;Antidote |
| 14 | Ipomoea mauritiana Jacq. | Vidarkanda | Convolvulacaeae | Climber | Galactogogue |
| 15 | Opilia amentaceae Roxb. | Adavi bandedi | Opiliaceae | Tree | Snake bite |
| 16 | Oroxylum indicum (Linn.) | Pampini | Bignoniaceae | Tree | Rheumatism;Oedema |
| 17 | Schleichera oleosa (Lour) | Pushka | Sapindacaeae | Tree | Macassar oil |
| 18 | Smilax zeylanica Linn. | Phirangichekka | Loganiaceae | Climber | Diabetes;Syphilis |
| 19 | Strychnos nux –vomica Linn. | Nagamustni | Loganiaceae | Tree | Rheumatism;Leprosy |
| 20 | Strychnos potatorum Linn. | Chillagingalu | Loganiaceae | Tree | Gonorrhoea |
| 21 | Syzygium alternifolium (Wt.) | Movi | Myrtaceae | Tree | Diabetes;Joint pains |
| 22 | Trichosanthes cucumerina Linn. | Chedu potla | Cucurbitaceae | Climber | Diabetes;Hepatoprote |
| 23 | Vernonia anthlemintica (Linn.) | Adavi jeelakarra | Asteraceae | Shrub | Digestion |
| | | Near Threatened Plants (NT) | | | |
| 1 | Aegle marinelos (Linn.) | Maredu | Rutaceae | Tree | Dysentery |


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| | | | | | |
|---|---|---|---|---|---|
| 2 | Androghaphis paniculata Wall | Nelavemu | Acanthaceae | Herb | Fever |
| 3 | Argemone mexicana Linn. | Verri kusuma | Papavaraceae | Shrub | Syphilis |
| 4 | Asperagus gonclados Baker | Pilliteegalu | Liliaceae | Herb | Galactogogue;Diabetes |
| 5 | Baliospermum montanum (Willd.) | Konda audamu | Euphorbiaceae | Shrub | Stomach pain;Laxative |
| 6 | Cassine glauca Kuntze | Neridi | Caelastraceae | Tree | Eczema,Antidote |
| 7 | Caelatrus paniculatus Willd. | Errasurugudu | Celastraceae | Tree | Brain tonic;Scabies |
| 8 | Clerodendrum serratum Moon | Gantu bharangi | Verbanaceae | Shrub | Febrifuge;Diabetes |
| 9 | Commifera caudata Engler | Kondamamidi | Burseraceae | Tree | Rhematism |
| 10 | Cordia dichotoma Forst. | Banka Iriki | Boraginaceae | Tree | Bronchial disorders |
| 11 | Ctenolepis garcini (Burm.f.) | | Cucurbitaceae | Climber | Boils;Wounds |
| 12 | Curculogo orchaiodes Gaetn | Nelathadi | Hypoxidaceae | Herb | Asthma;Anaemia |
| 13 | Euphorbia nivulia Buch. | Aku jamudu | Euphorbiaceae | Tree | Diabetes; |
| 14 | Holostemma ada-kodein Schult. | Pala gurija | Asclepiadaceae | Climber | Diabetes;Gonorrhoea |
| 15 | Maeruva oblangifolia (Forsk) | Magaubsirigadda | Capparaceae | Shrub | Stimulant;Diabetes |
| 16 | Ochna obtusata DC | Kukka-Mogu | Ochnaceae | Tree | Asthma;Menustral complaints |
| 17 | Pseudarthria vicida (Linn.) | Antrita Mayakuponna | Fabaceae | Shrub | Rheumatism;Asthma |
| 18 | Schrebera swleteniodes Roxb. | Mokem Chettu | Oleaceae | Tree | Leprosy;Diabetes |
| 19 | Soymida febrifuga (Roxb.) | Somi/Somintha | Meliaceae | Tree | Dysentery;Diarrhoea |
| Rare Plants | | | | | |
| 1 | Andrographis nallamalayana | Nelavemu | Acanthaceae | | Leucorrhoea |
| 2 | Gyrocarpus americanus Jacq. | Kummari puliki | Hernandiaceae | Tree | Cancer |

## VI DISCUSSION

Nagarjunasagar Srisailam Wildlife Sanctuary in the Eastern Ghats is a rich biodiversity landscape of Deccan. The total number of medicinal plant species collected in this study from Nagarjunasagar Srisailam Wildlife Sanctuary is 214 species of 175 genera belonging to 91 families. Among these 18 Critically Endangered Plants (CE); 23 Endangered Plants (EN); 19 Near Threatened Plants (NT) ; 2 rare Plants are recorded.

## VII CONCLUSION

This report will be useful for researchers in the field of Ethanobotany, Ethanomedicine, Taxonomy, and Pharmacology for further studies. The tribals and local people who reside near and around the Sanctuary still depend on the plants to cure various ailments .This study also aims to create awareness among the non-tribal main stream society so as to realise the value of the sustainable biodiversity of wild life sanctuary. Numerous anthropogenic activities like developmental projects, eco-tourism, modernization, urbanization, overexploitation, over grazing are the major threats for the wild life sanctuary. This recognizes the need to conserve its biological resources. Wild life sanctuaries depict cultural, traditional, sociological, biological, economical values and are the chief method of in-situ conservation of biodiversity. Conservation of biological resources and of the indigenous traditional knowledge is essential for sustainable development and managing natural resources the world over.The history of indigenous knowledge as an old as the human race. This knowledge has always been very important for the people who generate it.It is a matter of survival for them. Two Rare medicinal plants *Andrographis nallmalayana*,and *Gyrocarpus americanus* Jacq.were found in the study area

## ACKNOWLEDGMENT

The authors are thankful to all the local people who shared their knowledge on ‘medicinally useful plants’ throughout. In and around the villages of the wild life sanctuary. .


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Fig.1-Map of Nagarjunasagar Srisailam Tiger Reserve (Rajiv Gandhi Wild Life Sanctuary)




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# Phytochemical Analysis and Antibacterial Activities of *Pimpinella tirupatiensis* against *Bacillus subtilis*, *Klebsiella pneumoniae*, *Proteus vulgaris* and *Pseudomonas aeruginosa*

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**Abstract:** ***The human culture directly or indirectly was influenced by plants from the time immemorial. The progress of human civilization was accompanied by the use of plants and nature throughout the ages. Plants are fundamental to almost all life on earth providing protection and sustenance to other organisms. Plants which are nature's precious gift to mankind have health improving properties. Nature has served as a rich repository of medicinal plants for thousands of years and an improve number of modern drugs have been isolated from natural sources notably of plant origin. Herbal medicine, based on their traditional uses in the form of powders, liquids or mixtures, has been the basis of treatment for various ailments in India since ancient times. There are numerous references for the use of plants as therapeutic agents both in the works of Indian medicine and other works of antiquity. Plants have played a major role as the basic source for the establishment and enhancing the economy of developing countries like India. To elevate the medicinal properties, root tubers of Pimpinella tirupatiensis were collected from different localities of tirumal hills, Eastern Ghats, Andhra Pradesh, India. The methanolic extracts of root tubers were qualitatively screened for phytochemicals by using standard procedures which revealed the presence of various important bioactive chemical entities. Antibacterial activity of the methanolic extracts of root tubers were evaluated against Bacillus subtilis, Klebsiella pneumoniae and Proteus vulgaris, Pseudomonas aeruginosa. The methanolic extracts of root tubers have exhibited significant broad spectrum antibacterial activities.***

**Keywords:** Herbal medicine, Therapeutic agents, Phytochemicals, Root tubers

## 1. Plant Material Collection

During the exploration of ethno-medico-botanical survey, the root tubers of *Pimpinella tirupatiensis* were collected from different localities of Tirumal hills, Eastern Ghats, Andhra Pradesh, India. The root tubers were thoroughly washed with water and sufficient quantity of samples collected and chopped off into small fragments and shade dried. The dried samples were ground to make coarse powder (each 1 kg) and stored in polythene containers at room temperature. These samples were used for the detection of various secondary metabolites. Phytochemical screening was done following standard procedure adopted by Harborne (1973) and Gibbs (1974).

**Table 1-a:** Preliminary Phytochemical screening of *Pimpinella tirupatiensis* (Root tubers - Methanolic Extract)

| | |
|---|---|
| Alkaloids | + |
| Flavonoids | + |
| Indoles | - |
| Leucoantho-cyanins | + |
| Steroids | + |
| Carbohydrates | + |
| Phenols | + |
| Steroidal nucleus | - |
| Saponins | + |
| Tannins | + |
| Proteins | + |
| Lignins | + |
| Methylenedioxy functional compounds | + |

## 2. Screening for selective secondary constituents:

### A. Phenolic compounds

**a) Extractive procedure**

The phenolic constituents were extracted by following the method given by Bate Smith (1954) and Ibrahim and Towers (1960). About 25g of healthy plant material was macerated with 100ml of 2N Hydrochloric acid.(HCL). The homogenate was digested on a boiling water bath for about half-an-hour. The contents were cooled and filtered through Whatman No.1 filter paper. The filtrate was extracted repeatedly with peroxide free diethyl ether. All the extracts were pooled and concentrated to 100ml and was treated three times with 25ml of 5% anhydrous sodium carbonate solution. The pooled carbonate solution was adjusted to pH 2.0 with Conc. Hydrochloric acid.

The acidified fraction at pH 2.0 was extracted with equal volumes (25ml) of fresh diethyl ether thrice. The combined other extracts were washed with distilled water repeatedly till all traces of hydrochloric acid was removed. The ether soluble water was removed by freezing the extract. The ether was evaporated to dryness on water bath at $98^0$C and the resulting phenolic compound residue was dissolved in 1ml of 95% ethanol. This was stored at low temperature in dark container for ready use.


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**b) Identification**

About 2g of fresh weight equivalent to the final alcoholic extract was spotted on 23 x 29 cm whatmann No.1 Chromatographic filter paper with the help of micro pipette. The origin of the spot area was dried immediately with the help of hair-drier. Two dimensional ascending Chromatographic technique was adapted with benzene-acetic acid-water (60:70:30 v/v/v, upper layer) in the direction and sodium formate-formic acid-water (10:1:200 w/v/v) in the second direction. The Chromatographic chambers were saturated with the above solvent systems one day before the development of the Chromatograms at 22 to $24^0$c. The sheets after development were removed from the chambers and dried at room temperature. The dried sheets were observed under Ultra violet light and fluorescent regions were marked. The papers while exposing to Ammonia vapours were also observed under UV light and new fluorescent spots were marked.

The separated phenolic compounds on the Chromatograms were identified by comparison of $R_f$ values and individual spot colours of Chromogenic sprays. The final confirmation was made with authentic samples by co-chromatography.

**Table 1b:** Phenols

| | |
|---|---|
| Digallic acid | - |
| Gallic acid | - |
| Ellagic acid | - |
| Aesculetin | + |
| Cis-p-coumaric acid | + |
| iso-chlorogenic acid | + |
| Chlorogenic acid | + |
| Caffeic acid | - |
| Protocatechuic acid | + |
| Gentistic acid | + |
| Scopoletin acid | + |
| Phloretic acid | + |
| ρ-Hydroxy benzoic acid | + |
| α-Resorcyclic acid | + |
| β-Resorcyclic acid | + |
| trans-ρ-coumaric acid | + |
| Vanillic acid | + |
| Pcoumarylquinic acid | - |
| Cis-ρ-coumaric acid | + |
| Melilotic acid | + |
| Cis-Ferulic acid | + |
| trans-Ferulic acid | + |
| Coumarin | + |
| Salycyclic acid | + |
| Cinnamic acid | + |
| Syringic acid | + |

**Table 1c:** $R_f$ values and colour reactions of Phenolic compounds on Paper Chromatograms

| Compound | $R_f$ values in solvent | | U.V fluorescence | | Silphanilic reagent | P-Nitraniline reagent |
|---|---|---|---|---|---|---|
| | **1** | **2** | **Without $NH_3$** | **With $NH_3$** | | |
| Digallic acid | 0.29 | 0.69 | None | Blue violet | Violet | Violet |
| Gallic acid | 0.45 | 0.66 | violet | Violet | Violet | Violet |
| Ellagic acid | 0.02 | 0.28 | None | Blue green | Blue green | Blue green |
| Aesculetin | 0.28 | 0.33 | white blue | Very bright blue | Brown | Grey |
| Cis-p-coumaric acid | 0.42 | 0.77 | Light blue | Deep blue | Dark brown | Blue |
| iso-chlorogenic acid | 0.01 | 0.31 | Faint blue | Duckegg green | Light orange | Brown |
| chlorogenic acid | 0.01 | 0.76 | Faint blue | Duckegg green | Orange | Brown |
| Caffeic acid | 0.06 | 0.38 | Blue | Bright blue | Buff | Light brown |
| Protocatechuic acid | 0.05 | 0.58 | None | None | Buff | Light brown |
| Gentistic acid | 0.14 | 0.68 | Bright blue | Yellow | Buff | Blue white |
| Scopoletin acid | 0.30 | 0.51 | Bright blue | Very bright blue | Yellow | Brown |
| Phloretic acid | 0.66 | 0.77 | None | None | Yellow | Purple white |
| ρ-Hydroxy benzoic acid | 0.38 | 0.68 | None | None | Bright yellow | Light pink |
| α-Resorcyclic acid | 0.16 | 0.83 | None | None | Brown | Orange brown |
| β- Resorcyclic acid | 0.28 | 0.75 | None | None | Dark brown | Brown |
| trans-ρ-coumaric acid | 0.50 | 0.45 | Light blue | deep blue | Light brown | Blue |
| Vanillic acid | 0.78 | 0.57 | None | None | Orange | Purple |
| P–coumarylquinic acid | 0.97 | 0.64 | None | None | Light yellow | Yellow |
| Cis-ρ-coumaric acid | 0.42 | 0.77 | Light blue | deep blue | Dark brown | Blue |
| Melilotic acid | 0.51 | 0.76 | None | None | Orange yellow | Purple |
| Cis-Ferulic acid | 0.89 | 0.65 | Light blue | Blue | Purple | Blue green |
| trans-Ferulic acid | 0.80 | 0.31 | Light blue | Blue | Purple | Blue green |
| Coumarin | 0.99 | 0.66 | None | None | Yellow | Violet |
| Salycyclic acid | 0.93 | 0.31 | Dark blue | Dark violet | Yellow | Pink |
| Cinnamic acid | 0.96 | 0.04 | None | None | Yellow | Green |
| Syringic acid | 0.92 | 0.48 | None | None | Red | Dark blue |

**B. Flavonoids Compounds**

**a) Extractive procedure**

The flavonoid compounds were extracted according to the method given by Markham (1982). About 5g of powdered plant material was extracted in two steps. First 18ml of Methanol and 2 ml of water (9:1) were added, shaken well and kept for one day at room temperature. The supernatant solution of the extract was taken and transferred to another test tube. Secondly Methanol and water of 5ml each (1:1) was added to the remaining residue, stirred well and the mixture left for 24 hours. The two extracts were combined, mixed well and filtered through cotton wool. Later the filtrate was evaporated to about 1/3 the original volume till


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most of the methanol was removed. The resultant aqueous extract was extracted with chloroform repeatedly for 3 times. The solvent extracted aqueous chloroform layer was evaporated to dryness under vaccum in a rotary evaporator. The dried residue was saturated with 1 ml of 95% alcohol and stored in a dark place at low temperature.

**b) Identification**

The extracts containing flavonoids were separated in suitable quantities on Whatmann No.1 Chromatographic filter paper(23x29 cm) adopting the ascending technique using the solvent system Iso-propyl alcohol **:** Ammonia (25%) **:** Water(8:1:1:v/v/v) and n-butanol:acetic acid: water(4:1:5v/v/v) (top layer was used).The dried Chromatograms were examined under UV lamp and the fluorescent spots were marked. The papers while exposed to Ammonia Vapours were also observed under UV lamp and the new fluorescent regions were marked. The flavonoid compounds were identified by comparing the $R_f$ values and colours with those of the authentic samples on the Chromatograms. Co-Chromatographic studies were conducted with authentic markers to confirm the identification.

**C. Chromogenic spray reagents**

**Diazotized sulphanilic acid reagent (Markham, 1982) :**0.3% solution of sulphanilic acid in 8% HCl (25ml) was mixed with 5% Sodium nitrite solution(1.5ml) just before use. The Chromatographic sheets were sprayed with this mixture and with a 20% solution of anhydrous Sodium carbonate.

**1% Alcoholic ferric chloride:**1 g of Ferric chloride was dissolved in alcohol and made up to 100ml.

**1% Alcoholic Aluminium chloride:**1g of Aluminium chloride was dissolved in alcohol and made up to 100ml, just before spraying of the chromatographic sheets.

**Table 2a:** Flavonoids

| | |
|---|---|
| Quercetin | + |
| Rutin | + |
| Myricetin | + |
| Luteolin | + |
| Apigenin | + |
| Orientin | - |
| Vitexin | + |

**Table 2b:** $R_f$ values and colour reactions of Flavonoids on Paper Chromatograms

| Compound | $R_f$ values in solvent | | U.V. fluorescence | | Sulphanilic Reagent | 1% Alcoholic Ferric Chloride | 1% alcoholic Aluminium Chloride |
|---|---|---|---|---|---|---|---|
| | 1 | 2 | Without NH3 | With NH3 | | | |
| Quercetin | 0.26 | 0.64 | yellow | Light yellow | Bright yellow | Green | Yellow |
| Rutin | 0.03 | 0.57 | Orange brown | Yellow | Green | Olive | Grey yellow |
| Myricetin | 0.07 | 0.43 | Yellow | Bright yellow | Light yellow | Olive | Grey yellow |
| Luteolin | 0.44 | 0.78 | Dull yellow | Yellow | Light red | Pale green | Pale yellow |
| Apigenin | 0.61 | 0.91 | Red brown | Red brown | Pink | Pale green | None |
| Orientin | 0.78 | 0.31 | Yellow | Yellow green | Grey | None | None |
| Vitexin | 0.91 | 0.42 | Dull yellow | yellow | Bright red | none | None |

**Solvents:** 1. Iso-propyl alcohol **:** Ammonia(25%) **:** Water (8:1:1)
2. n-butanol**:** Acetic acid **:** Water(4:1:5)

**C. Amino acids**

**a) Extractive procedure**

Amino acids were extracted following the method of Das Chowdary *et al.*, (1967). About 5g of plant material was cut into small pieces and plunged immediately into a round bottomed flask containing 20ml of 80% Ethanol. It was refluxed for 30 minutes over a boiling water bath. The boiled material was ground in mortar using additional volumes of 10ml ethanol 80% (v) and centrifuged at 2000 rpm. The supernatant was collected and the Ethanol removed in vaccum. The aqueous extract was passed through Dowex 50W-X8 ($H^+$ from 20-50 mesh) column (1x10cm). the amino acids were eluted from the column with 50ml of 2N Ammonium hydroxide. The elute was evaporated to dryness and the residue was saturated with 95% Ethanol (1ml).

**b) Identification**

The extracts containing amino acids were seperated on Whatmann No.1 Chromatographic filter paper(23x28 cm) employing two-dimensional ascending technique using the solvent system:

1) Sec. butanol**:** Formic acid **:** Water(75:13:12v/v/v)-1$^{st}$ direction.

2) Buffer saturated phenol (1:2v/v)-2$^{nd}$ direction(6.3 g of Sodium citrate and 3.7g of Potassium dihydrogen phosphate were dissolved in 100ml of distilled water. To this 200ml of distilled phenol was added)

The amino acids were identified based on comparision of $R_f$ values, colours and with those of authentic samples by co-chromatographic studies.

**C) Chromogenic spray reagents**

**Ninhydrin:** It was prepared by dissolving 200 mg of Ninhydrin in 98ml of n-butanol with 2ml of glacial acetic acid.

**Table 3a:** Amino acids

| | |
|---|---|
| Aspartic acid | - |
| Arginine | + |
| Asparagine | + |
| α-Alanine | + |
| β-Alanine | + |
| 2-Aminobutyric acid | - |
| Cystaine | + |
| Cystine | + |
| Glutamic acid | + |
| Glutamine | + |
| Glycine | - |
| Histidine | + |
| Isoleucine | + |


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| | |
|---|---|
| Leucine | + |
| Lycine | - |
| γ-Methylene glutamic acid | - |
| γ-Methylene glutamine | - |
| Norleucine | - |
| Ornithine | + |
| Phenylalanine | - |
| Proline | + |
| Serine | + |
| Threonine | - |
| Tryptophan | - |
| Valine | + |
| Tyrosine | - |

**Table 3b:** $R_f$ values and colour reactions of Amino acids on Paper Chromatograms

| Compound | $R_f$ values in solvent | | Colour with Ninhydrin |
|---|---|---|---|
| L-Aspartic acid | 0.05 | 0.10 | Light violet |
| DL-Arginine | 0.10 | 0.60 | Violet |
| DLAsparagine | 0.19 | 0.41 | Violet |
| α-Alanine | 0.26 | 0.28 | Light violet |
| β-Alanine | 0.42 | 0.77 | Deep violet |
| DL-2-Aminobutyric acid | 0.55 | 0.70 | Light violet |
| L-Cystaine | 0.38 | 0.61 | Deep violet |
| L-Cystine | 0.23 | 0.53 | Violet |
| L-Glutamic acid | 0.17 | 0.20 | Violet |
| L-Glutamine | 0.14 | 0.82 | Violet |
| L-Glycine | 0.09 | 0.38 | Violet |
| L-Histidine | 0.08 | 0.52 | Violet |
| DL-Isoleucine | 0.68 | 0.82 | Violet |
| L-Leucine | 0.79 | 0.83 | Deep violet |
| L-Lycine | 0.79 | 0.83 | Deep violet |
| γ-Methylene glutamic acid | 0.20 | 0.68 | Violet |
| γ-Methylene glutamine | 0.30 | 0.71 | Violet |
| DL-Norleucine | 0.96 | 0.68 | Violet |
| DL-Ornithine | 0.04 | 0.27 | Light violet |
| DL-Phenylalanine | 0.60 | 0.90 | Light violet |
| L-Proline | 0.39 | 0.89 | Yellow |
| DL-Serine | 0.20 | 0.23 | Deep violet |
| DL-Threonine | 0.28 | 0.35 | Deep violet |
| DL-Tryptophan | 0.50 | 0.76 | Violet |
| DL-Valine | 0.59 | 0.77 | Deep violet |
| L-tyrosine | 0.52 | 0.65 | Light violet |

**Solvents:** 1. Sec. butanol **:** Formic acid **:**Water(75**:**13**:**12)
2. Buffer**:** Phenol(1:2)

**D. Anthocyanidins**

**a) Extractive procedure**

The anthocyanidin constituents were extracted according to the method described by Harborne (1973).

About 5g of plant material was immersed in 20ml of 2N HCl in a boiling test tube and heated for 30-40 minutes at6 $100^0$c. The extract was cooled and filtered. The filtrate was washed twice with 20 ml of ethyl acetate to remove flavones. The remaining aqueous extract was further heated at $80^0$c for 3 minutes to remove the last traces of ethyl acetate. The pigment was re-extracted again with a small volume of Iso-amyl alcohol. The Ethyl acetate extract was evaporated to dryness on a boiling water bath. The anthocyanidin in the residue was diluted with 1ml of 1% Methanolic HCl and preserved at low temperature in dark for future use.

**b) Identification**

The extracts containing anthocyanidins was separated on 23 x 29 cm Whatmann No.1 Chromatographic filter paper. Uni-dimensional Chromatographic ascending technique was employed with Conc. Hydrochloric acid, Formic acid, Water (2**:**5**:**3 v/w/v) and n-butanol **:** Acetic acid **:** water (4:1:5). The Chromatograms developed from the said solvent systems were taken out from the glass chambers and dried at room temperature. The fluorescent regions of dried papers were marked under UV light. The $R_f$ values and colours of the spots were determined by comparing with those of the authentic markers on the Chromatograms.

| | |
|---|---|
| Cyanidin | + |
| Petunidin | - |
| Delphinidin | - |

**Table 4b:** $R_f$ Values and Colours of Anthocyanidins on Paper Chromatograms

| Compound | $R_f$ values in solvent | | Visible colour | U.V. fluorescence | |
|---|---|---|---|---|---|
| | **1** | **2** | | **without $NH_3$** | **with $NH_3$** |
| 1 | 0.38 | 0.68 | Magenta | Pink | blue green |
| 2 | 0.26 | 0.50 | Purple | Mauve | Mauve |
| 3 | 0.15 | 0.40 | Purple | Mauve | blue green |

**Solvents :** 1. Conc. Hydrochloric acid **:** Formic acid **:** Water(2**:**5**:**3)
2. n-butanol **:** Acetic acid **:** Water(4**:**1**:**5).

**E. Lipids**

**a) Extractive procedure**

Lipids were extracted following the method adopted by Hoppe and Heitefuss (1974). A solvent mixture consisting of 30ml Chloroform, 60ml of Methanol and 20 ml Water(1**:**2**:**0.8 v/v/v) was taken and allowed to boil. About 5g of plant material was homogenized in the above solvent mixture. The contents were filtered and taken separately. The residual mixture was treated with 70ml Methanol and the filtrate taken. The residue was again washed with 100ml Chloroform. All the above filtrate mixtures were taken in a separating funnel and 90ml of water added. The mixture now contains Chloroform**:** Methanol**:** Water in the ratio of 2**:**2**:**1.8 respectively and the mixture were allowed to settle. The lower lipid layer containing chloroform was separated and transferred into a breaker. The upper water layer was treated with 50ml of Chloroform successively for three times. All the extracted Chloroform layers were evaporated to dryness in a vacuum by rotary evaporation maintained at $40^0$C. The residue was treated with 2ml of Benzene to remove the traces of chlorophyll if present. Now the final lipid residue was dissolved in 2 ml of Chloroform and stored at low temperature in dark until use.

**b) Identification**

Thin layer plates were prepared by spreading a slurry of silicagel-G (50g in 100ml distilled water) to 105 mm thickness over thin glass plates. The glass plates were air dried and stored at room temperature. Before using, the plates were heated at $110^0$c for 30 minutes in a hot air oven for activation.

Using micropipette, one gram equivalent of lipid extract was taken and potted on TLC plates. The spotted areas were allowed for immediate dryness with the help of a drier. The


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dried plates were run in uni dimensional ascending Chromatography by using TLC glass chambers. The chambers were saturated with developing solvents one day before the plates were developed.

**Solvent systems**

1) Chloroform**:** Methanol**:** Acetic acid**:** Water (170**:**25**:**25**:**3 v/v/v/v)
2) Acetone**:** Benzene**:** Water(91**:**30**:**8 v/v/v).

The plates were placed in airtight tanks. The developed plates were removed and dried at room temperature and exposed to Iodine vapours to visualize all the lipid compounds.

The TLC plates were sprayed with 25% Sulphuric acid reagent with the help of an automizer for the clear detection of various lipid layers. The lipids were identified by comparision of $R_f$ values, color and with those of authentic samples by Co-Chromatographic studies.

**c) Chromogenic spray reagent**

The TLC plates were sprayed with 25% Sulphuric acid and heated to $230^0$c for 15 minutes, and the colour observed. Glycolipids gave red brown while phospholipids gave bright, red and other lipids gave pale brown colour spots on white background.

**Table 5 a:** Lipids

| | |
|---|---|
| Phosphatidyl serine | - |
| Phosphatidyl inositol | + |
| Phosphatidyl Clioline | + |
| Phosphatidyl ethanolamine | - |
| Digalactosyl diglyceride | + |
| Phosphatidyl glycerol | + |
| Sulphoquinovosyl diglyceride | + |
| Monogalactosyl diglyceride | + |
| Steryl glycoside | + |

**Table 5b:** Rf values and colour reaction of lipids on thin layer Chromatograms

| Compound | $R_f$ values in solvent | Colour with iodine vapours | Colour with $H_2SO_4$ (25%) |
|---|---|---|---|
| Phosphatidyl serine | 0.09 | + | + |
| Phosphatidyl inositol | 0.13 | + | + |
| Phosphatidyl Clioline | 0.18 | + | + |
| Phosphatidyl ethanolamine | 0.23 | + | + |
| Digalactosyl diglyceride | 0.33 | + | + |
| Phosphatidyl glycerol | 0.41 | + | + |
| Sulphoquinovosyl diglyceride | 0.57 | + | + |
| Monogalactosyl diglyceride | 0.81 | + | + |
| Steryl glycoside | 0.87 | + | + |

Solvent : $CHCl_3$ : MeOH : HOAc : $H_2O$ (170:25:25.3).

**Physicochemical studies**

For several years, the crude drugs were identified by comparison only with the standard descriptions available. But recently, due to advancement in the field of Pharmacognosy, various techniques are followed to the standardization of crude drugs. Among such techniques, ash and extractive values are considered very important in promoting the quality and in establishing the Pharmacopeial standards of the drug.

Substandard quality of many drugs is due to either faulty collection or incorrect storage. When the constituents of a drug cannot be readily estimated by any other means, ash and extractive values are very useful especially for their evaluation. To prove its acceptability as a drug, studies of ash and extractive values are basically required in determining the quality and purity of selected crude drug.

**Materials and Methods**

The physical constants like ash and extractive values were determined by standard methods (Anonymous, 1985 and Kokate, 1991).

## 3. Experimental Studies

**A. Determination of ash values**

The object of ashing crude drugs is to remove all traces of organic matter which may otherwise interfere in an analytical determination. The inorganic salts naturally occurring in drug or adhering to it or deliberately added to as a form of adulteration are removed by gradual incineration of the drug. Thus the residue remaining after incineration of the powdered drug is known as ash content. The ash values are a criterion to judge the identity or purity and quality of the crude drug.

**a) Determination of total ash**

Total ash usually consists of Phosphates, Silicates and Carbonates of Potassium, Calcium and Magnesium. About 2 gm of the air dried powdered drug was accurately weighed and taken in a tared silica crucible, which was previously ignited and weighed. The powdered drug was spread as a fine even layer at the bottom of the crucible. The crucible containing the drug was gradually incinerated in a muffle furnace by increasing the temperature. It was heat dull red hot until free from carbon or converted into ash. Later the crucible was allowed to cool and kept in desiccators. The residue was weighed the percentage of total ash calculated with reference to the air dried sample. The residue was weighed the percentage of total ash calculated with reference to the air dried sample. The procedure was repeated till constant result was obtained.

**b) Determination of acid insoluble ash**

Acid insoluble ash is a part of total ash insoluble in dilute Hydrochloric acid. The acid insoluble ash content is determined and recommended for certain drugs may be coated with dirt and sand. The total ash obtained as described above was treated with 25ml of 10% Hydrochloric acid and boiled for 5 minutes. The insoluble matter was filtered and collected on ashless filter paper (Whatman No.42) and the paper washed with hot water. The insoluble ash was ignited and weighed in a tared silica crucible. The acid insoluble ash of the drug was repeated to get constant results.

**c) Determination of water soluble ash**

The total ash obtained from the above process was boiled with 25 ml of distilled water for 5 minutes. The insoluble ash was filtered through ash less filter paper (Whatman No.42). The residue was once again washed with water and ignited up to temperature not exceeding $450^o$c and converted into ash. The difference between the weight of total ash and


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insoluble matter represent the weight of water soluble ash. The percentage of water soluble ash was calculated with reference to the air dried drug.

**B. Determination of extractive values**

Extractive values indicate the nature of the constituents present in a crude drug. Based on the diversity in chemical nature and properties of the contents of the drug, various solvents were used for the determination of extractives. The solvents used for extraction dissolve appreciable quantity of substances desired. The methods used to find out the extractive values were as follows.

**a) Determination of alcohol soluble extract**

Alcohol is an ideal solvent frequently employed to determine various chemical contents like Tannins, Resins etc. Generally, Ethyl alcohol is used for determination of alcohol-soluble extractive. Dilute Alcohol a may also be used in some cases, depending upon solubility of constituents in a crude drug. In the present work, the author used 100 ml of 90% Alcohol for determining crude drug was macerated with 100 ml of 90% Alcohol in a stoppered flask for 24 hours. It was shaken frequently every 6 hours and allowed to stand to 18 hours. Then the extract was filtered rapidly through filter paper, taking precaution against loss of alcohol, about 25 ml of the filtrate was evaporated to dryness in a tared flat bottomed shallow dish, transferred to the oven and dried at 105$^{o}$C and weighed. The percentage of alcohol soluble extract was calculated with reference to the air dried drug.

**Table 6:** Ash value of Root tubers

| S.No. | Plant species | Part(s) | Total ash (%) | Acid insoluble ash (%) | Water insoluble ash (%) |
|---|---|---|---|---|---|
| 1. | ***Pimpinella tirupatiensis*** | Tuber | 9.50 | 3.00 | 1.75 |

**Table 7:** Extractive value of the root tubers

| S.No. | Species | Part(s) | 90% alcohol soluble extract (% w/w) | Water soluble extract(%w/w) | Chloroform soluble extract(%w/w) | Pet.Ether soluble extract(%w/w) |
|---|---|---|---|---|---|---|
| 1 | *Pimpinella tirupatiensis* | Tuber | 17.92 | 12 | 2.4 | 0.9 |

**Antibacterial Activity**

The presence of antimicrobial substances in the higher plants provide a source of inspiration for novel drug compounds as plants derived medicines have made significant contribution towards human health. The antimicrobial compounds from plants may inhibit microbial growth by different mechanism than those presently used antimicrobials and may have a significant clinical value in treatment of resistant microbial strains. Therefore, random screening of plants for active chemicals is as important as the screening of ethnobotanically targeted species (Principle, 1989).

**Materials and Methods**

**Collection of medicinal plants**: Selected medicinal plant, *Pimpinella tirupatiensis* has been used in the present study and it was collected from Tirumala hills, Eastern Ghats, Andhra Pradesh, India.

**Bacterial Cultures:** The bacterial cultures were procured from the Department of Microbiology, Sri Venkateswara Institute of medical Sciences (SVIMS), Tirupati, Andhra Pradesh, India. Pathogenic Gram positive bacteria such as *Bacillus subtilis*, *Klebsiella pneumoniae*, and Gram negative bacteria *Proteus vulgaris*, *Pseudomonas aeruginosa* were maintained on nutrient agar slants at 4$^{0}$C until further used for experimental studies.

**Preparation of the medium**

**Nutrient Agar media (P.H 7.0)**

For the preparation of 1 lt of Nutrient Agar media ingredients like 1.5 g of beef extract, 1.5 g of yeast extract, 5 g of peptic digest of animal tissue and 5 g of sodium chloride were weighed and added in 500 ml of distilled water and heated with agitation to dissolve the constituents. Finally, the volumes were made upto 1 lt. Before the addition of agar (15 g) the pH of the medium was adjusted to 7.0 by adding few drops of 0.1 N NaOH or HCl using digital pH meter ( Elico Pvt. Ltd., Hyderabad). These were then sterilized by autoclaving at 15 lbs pressure at 120$^{0}$ C for 15 min; cooled to 40$^{0}$ C and approximately 20 ml of medium was poured to each 90mm sterilized petridish.

**Preparation of inoculum:**

**Bacteria:** 18 hrs old bacterial broth cultures were used as inoculae after adjusting its population to 10$^{6}$ CFU/ ml (Colony Forming Units) using 0.9% (w/v) sterile saline by the method described by Forbes *et al*.,(1990).

**Preparation of plant extract:** The methanolic extracts of the four selected medicinal plants were prepared by dissolving 10gm of fine powder of each medicinal plants separately in 100 ml of methanol solvent. The contents were kept in orbitary shaker for 48 h. Then the extract was filtered and it is dried in hot air oven at 40$^{0}$ C. Then the extract was stored under refrigeration at 4$^{0}$ C for further studies.

**Preparation of sterile disc:** Whatman's No.3 filter paper was punched into 5 mm disc form and they sterilized, each sterile disc was incorporated individually with 20 – 60 mg/ml of extracts using micropipette. Precautions were taken to prevent the flow of the solvent extract from the discs to the outer surface. The condensed extracts were applied in small quantities on discs and they were allowed to dry in air. Then they were stored at 4$^{0}$ C.

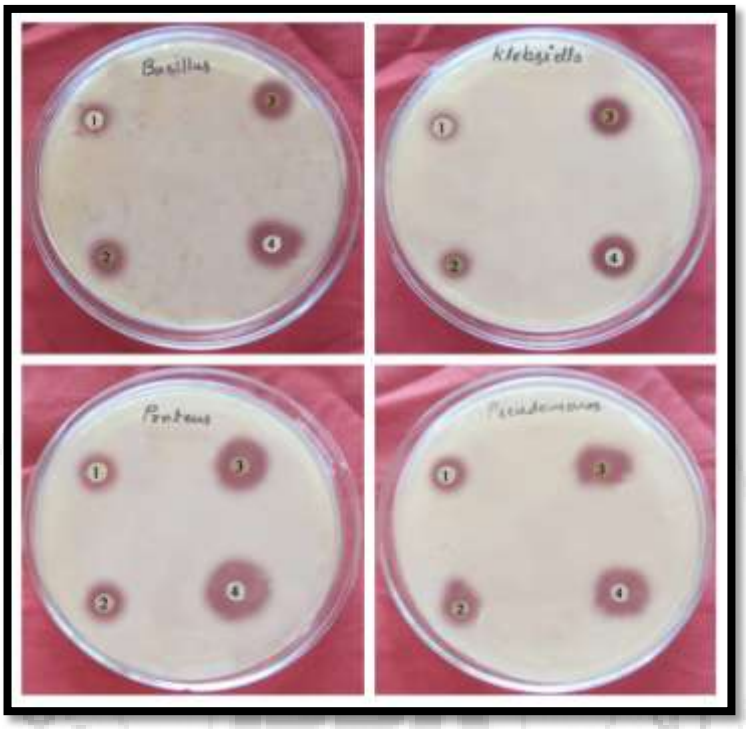
**Assay of antimicrobial activity using Disc diffusion method:** The antimicrobial activity was performed by employing the disc diffusion method adopted by Bauer *et al.*, (1966) and Cruickshank (1968). The 20 ml of sterilized Muller Hinton Agar was poured into sterile petriplates, after solidification, 100 µl of fresh culture of human pathogens were swabbed on the respective plates. Sterile discs of Whatman No. 1 filter paper of about 6 mm were prepared.

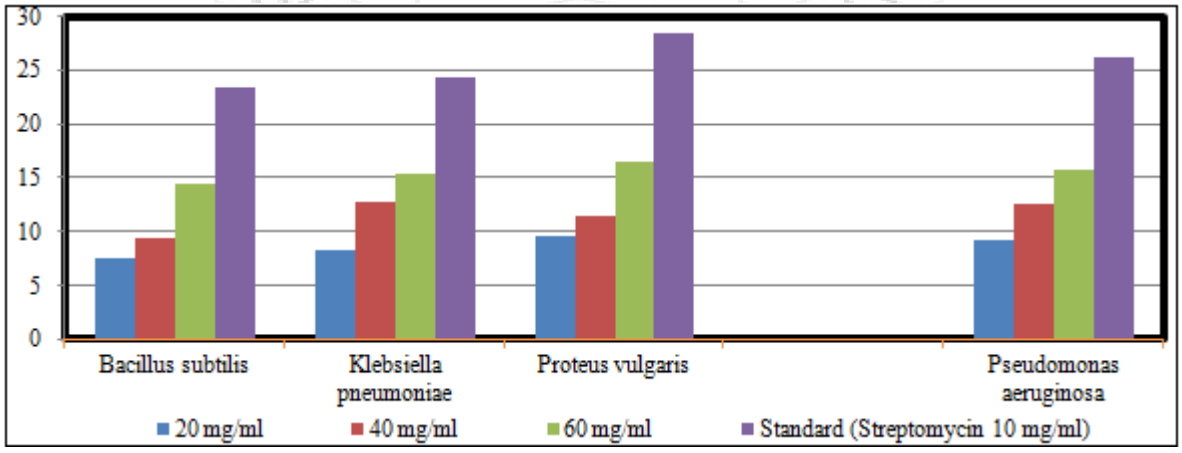

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The discs were kept over the agar plates using sterile forceps at various concentrations (20, 40, and 60 mg/ml). Streptomycin 10mg/ml containing disc used as standard control. The plates were incubated for 24 h at $37^0$ C and the diameter of the inhibition zones was recorded. The assessment of antimicrobial activity was based on measurement of inhibition zones formed around discs. A zone of inhibition around the disc indicates that the compounds, which diffused into the agar from the disc, inhibited the growth of the organism.

**Antibacterial activity of *Pimpinella tirupatiensis*:**

| *S. No* | *Name of the microorganism* | *20 mg/ml* | *40 mg/ml* | *60 mg/ml* | *Standard (Streptomycin 10 mg/ml)* |
|---|---|---|---|---|---|
| 1. | *Bacillus subtilis* | 7.5 ± 0.45 mm | 9.4 ± 0.6mm | 14.52 ± 0.89mm | 23.45 ± 0.65mm |
| 2. | *Klebsiella pneumoniae* | 8.2 ± 0.24mm | 12.8 ± 0.89mm | 15.34 ± 0.59mm | 24. 4 ± 0.53mm |
| 3. | *Proteus vulgaris* | 9.5 ± 0.23mm | 11.35 ± 1.2mm | 16.5 ± .64mm | 28.53 ± 0.74mm |
| 4. | *Pseudomonas auriginosa* | 9.2 ± 0.54mm | 12.5 ± 0.16mm | 15.82 ± 0.44mm | 26.25 ± 0.36 mm |






## 4. Results

Present investigation, antibacterial activity of *Pimpinella tirupatiensis* on pathogenic bacterial strains, the plant exhibited significant antibacterial activity. Methanol root extract of *Pimpinella tirupatiensis* at the concentration 60 mg/ml, *P.vulgaris* (16.5mm) was more susceptible, followed by *P. aeruginosa* (15.8mm), *K.pneumonia* (15.3mm), and *B.subtilis* (14mm).

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# Phytochemical Analysis and Antibacterial Activities of *Terminalia pallida* against *Bacillus subtilis*, *Klebsiella pneumoniae*, *Proteus vulgaris*, and *Pseudmonas aeruginosa*

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**Abstract:** ***Indian medicine is known as the richest, the first and the foremost among other branches of medical knowledge that is available elsewhere on the globe. Much of the information was amply recorded by experienced individuals of this art. The earliest written record of the preparation and use of medicine from plants is in the Rig-Veda, Atharvanaveda documented more details on medicinal herbs and their varied utility. Throughout the history of man, plant drugs have played a vital role in healing and curing illness. Many indigenous methods were in use for centuries to treat various ailments. To elevate the medicinal properties, Different parts of Terminalia pallida were collected from different localities of Veligonda hill range, Eastern Ghats, Nellore Dt, Andhra Pradesh, India. The methanolic extracts of various parts of the plants were qualitatively screened for phytochemicals by using standard procedures which revealed the presence of various important bioactive chemical entities. Antibacterial activity of the methanolic extracts of stem bark and fruit were evaluated against Bacillus subtilis, Klebsiella pneumoniae and Proteus vulgaris, Pseudomonas aeruginosa. The methanolic extracts of these plant parts have exhibited significant broad spectrum antibacterial activities.***

**Keywords:** Stem bark, Antibacterial, Bioactive

## 1. General Introduction

Organic analytical study is one of the important and rapidly extending areas of plant drugs useful in pharmacognostical studies. The study helps in standardizing and differentiating the drugs and to provide adequate data for laying down pharmacopoeial standards. The Phytochemical evaluation of the selected crude drugs involves 1) organic analysis for active principles and 2) chromatography of different extracts.

**Preliminary Phytochemical studies**

## 2. Introduction

Phytochemical constituents are the basic source for the establishment of several pharmaceutical industries. The constituents present in a drug or plant play a significant role of crude drug. It is a qualitative chemical evaluation which indicates spectrum of chemical constituents present in a plant drug. Thus the Phytochemical screening is very important in identifying new sources of therapeutically and industrially important compounds like alkaloids, flavonoids, phenolic compounds, saponins, steroids, tannins, terpenoids etc. In pharmacognostical study, detection of these active principles are of great importance since many plant based drugs like aconite, atropine, brucine, caffeine, codeine, colchicines, digitoxin, digoxin, ephedrine, morphine, papaverine, pilcorpine, physostigmine, protopine, quinine, reserpine, scopolamine, strychnine, vinblastine, vincristine and taxol are widely used now-a-days in medicine for production of various pharmaceutical drugs. n general the organic compounds in plants can be categorised into three groups viz., primary metabolites, secondary metabolites and semantides. The primary metabolites (carbohydrates, proteins, lipids, cellulose and chlorophyll) are the basic constituents of the plant. They occur universally in the plant and play a vital role in the function of cell.

The compounds that are responsible for therapeutic effect are usually the secondary metabolites. These are selective and accumulate in the various parts of the plant cells. They synthesize either for a particular plant or may be translocated from other areas of active synthesis in the plant. Semantides are the information carrying molecules. DNA is primary, RNA is secondary and proteins are tertiary semantides.

**Plant Material Collection**

During the exploration of ethno-medico-botanical survey, the stem bark and fruits of *Terminalia pallida* were collected from different localities of Veligonda hill range, Eastern Ghats, Nellore Dt, Andhra Pradesh, India. These plant parts (Stem bark and fruit) were thoroughly washed with water and sufficient quantity of samples collected and chopped off into small fragments and shade dried. The dried samples were ground to make coarse powder (each 1 kg) and stored in polythene containers at room temperature. These samples were used for the detection of various secondary metabolites. Phytochemical screening was done following standard procedure adopted by Harborne (1973) and Gibbs (1974).


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## 3. Experimental Studies

**Alkaloids test:** The methanolic extract was evaporated to dryness and the residue obtained was digested with 1% Hydrochloric acid. The resulting acidic solution was divided into two parts. To one part was added Mayer's reagent and to the second part dragendorff's reagent. Appearance of precipitate or turbidity indicates the presence of alkaloids.

**Preparation of reagents**

1) **Mayer's reagent:** 1.3 g of Mercuric chloride and 5g of Potassium iodide were dissolved separately in 60 ml and 10 ml of double distilled water and both the solutions were mixed and diluted to 100 ml.
2) **Dragendorff's reagent:** 8g of the Bismuth nitrate was dissolved in 20 ml of conc. nitric acid and 27.2g of Potassium iodide in 50 ml of double distilled water. Both the solutions were allowed to stand till $KIO_3$ crystallized out. Supernatant was decanted and final volume was adjusted to 100 ml.
3) **Flavonoids:** The plant extract was tested for flavonoids by shinoda's reaction. To a few ml of Methanolic extract, conc. Hydrochloric acid, Magnesium powder and a few fragments of Mg metal was added. The presence of flavonoids was identified by the development of pink or magenta or red coloured flame.
4) **Terpenoids (Liebermann - Burchard's test):** The Liebermann-Burchard's reaction was carried out by adding 0.5 ml of $H_2SO_4$ along the side of the test tube containing a mixture of Methanolic HCl and Acetic anhydrate (0.5 ml each). Formation of colour from green to bluish-green (sometimes via red or blue) indicate the presence of terpenoids.
5) **Steroids (Salkaowski reagent):** Development of wine red colour on adding con. $H_2SO_4$ and $CHCl_3$ to the Methanolic extract indicate the positive test for steroidal compounds.
6) **Lignans:** The plant extract was tested for the presence of lignins by adding conc. HCl and 2% Forfuraldehyde. Development of red colour indicates the presence of lignans.
7) **Indoles:** The development of voilet colour in the methanolic extract on adding Ehrilich reagent is considered as a positive reaction test.
8) **Carbohydrates (Molisch test):** To the methanolic extract, α-napthol solution (1.0g dissolved in 100 ml of each ethanol w/v) was added. Then Conc. $H_2SO_4$ was added gentlyalong the walls of the inclined test tube. Formation of a red to voilet colour indicate the presence of carbohydrates.
9) **Test for reducing sugars:** To 5ml of Benedict's reagent, 5ml of the test solution was added. The tubes were incubated in boiling water on water bath for 10-30 minutes. The development of an orange red precipitate indicates the presence of reducing sugars.
10) **Protiens (Million's test):** Million's reagent (solution of Mercuric nitrate in nitric acid) was added to 20 ml of boiling Methanolic extract. Formation of white precipitate that gradually turns red upon heating was observed for the presence of proteins.
11) **Phenolic compounds:** To the test solution 1-4 drops of 1% Ferric chloride was added. Appearance of intense colour in the extract was observed for the presence of phenolic compounds.
12) **Anthocyanidins:** The formation of red or purple colour with the plant extract, on adding equal volume of Methanolic HCl was taken as a positive reaction for anthocyanidins.
13) **Anthraquinones:** 20ml of benzene was added to 5g of plant powder and filtered. To the filtrate 5ml of 10% Ammonium hydroxide solution was added and shaken well. The formation of pink, red or violet colour in the ammonical phase indicates the presence of anthraquinones (Wall *et αl.,* 1954 anf Frans Woath, 1966).
14) **Saponin test:** The plant extract was evaporated to dryness. Tap water was added and shaken vigorously in a graduated cylinder for 15 minutes. Formation of a persistent foam was taken as a positive reaction test.
15) **Tannins:** The Methanolic extract was concentrated and the residue was dissolved in water and tested with 1% Gelatin solution and 1% Gelatin salt solution (1g gelatin dissolved in 10g NaCl w/w) to separate volumes. The appearance of white precipitate indicates the presence of tannins.

**Table 1 (a):** Preliminary Phytochemical screening of *Terminalia pallida* (Methanolic Extract)

| Compoud | *Terminalia pallida* | |
|---|---|---|
| | Stem Bark | Fruit |
| Alkaloids | - | - |
| Flavonoids | + | + |
| Indoles | + | + |
| Leucoantho-cyanins | + | - |
| Steroids | + | - |
| Carbohydrates | + | + |
| Phenols | + | + |
| Steroidal nucleus | + | - |
| Saponins | + | + |
| Tannins | + | + |
| Proteins | + | + |
| Lignins | + | + |
| Methylenedioxy functional compounds | - | - |

## 4. Screening for Selective Secondary Constituents

**A. Phenolic compounds**

**a) Extractive procedure**

The phenolic constituents were extracted by following the method given by Bate Smith (1954) and Ibrahim and Towers (1960). About 25g of healthy plant material was macerated with 100ml of 2N Hydrochloric acid.(HCL). The homogenate was digested on a boiling water bath for about half-an-hour. The contents were cooled and filtered through Whatman No.1 filter paper. The filtrate was extracted repeatedly with peroxide free diethyl ether. All the extracts were pooled and concentrated to 100ml and was treated three times with 25ml of 5% anhydrous sodium carbonate solution. The pooled carbonate solution was adjusted to pH 2.0 with Conc. Hydrochloric acid.

The acidified fraction at pH 2.0 was extracted with equal volumes (25ml) of fresh diethyl ether thrice. The combined


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other extracts were washed with distilled water repeatedly till all traces of hydrochloric acid was removed. The ether soluble water was removed by freezing the extract. The ether was evaporated to dryness on water bath at $98^0$C and the resulting phenolic compound residue was dissolved in 1ml of 95% ethanol. This was stored at low temperature in dark container for ready use.

**b) Identification**

About 2g of fresh weight equivalent to the final alcoholic extract was spotted on 23 x 29 cm whatmann No.1 Chromatographic filter paper with the help of micro pipette. The origin of the spot area was dried immediately with the help of hair-drier. Two dimensional ascending Chromatographic technique was adapted with benzene-acetic acid-water (60:70:30 v/v/v, upper layer) in the direction and sodium formate-formic acid-water (10:1:200 w/v/v) in the second direction. The Chromatographic chambers were saturated with the above solvent systems one day before the development of the Chromatograms at 22 to $24^0$c. The sheets after development were removed from the chambers and dried at room temperature. The dried sheets were observed under Ultra violet light and fluorescent regions were marked. The papers while exposing to Ammonia vapours were also observed under UV light and new fluorescent spots were marked.

The separated phenolic compounds on the Chromatograms were identified by comparison of $R_f$ values and individual spot colours of Chromogenic sprays. The final confirmation was made with authentic samples by co-chromatography.

**c) Chromogenic spray reagents**

**i) Diazotized sulphanilic acid reagent**

25ml of freshly prepared 5% sodium nitrate was slowly added to 5ml of sulphanilic acid solution (900mg of sulphanilic acid was dissolved in 9ml of Conc. HCl and the solution was diluted to 100ml with $H_2O$) at $0^0$c. To intensify the colours of the developed spots, 20% Sodium Carbonate solution was sprayed to the wet sheets (sprayed at $0^0$c immediately after spraying the above solution).

**ii) Diazotized *p*-Nitraniline reagent**

10ml of *p*-nitraniline reagent (1.5g of *p*-nitraniline was added to 45 ml of Conc. HCl and was made up to 950ml with distilled water) was mixed with 0.2ml of 5% Sodium nitrate and 10ml of 10% Sodium carbonate solution.

**Table 1b:** Phenols

| Compoud | *Terminalia pallida* | |
|---|---|---|
| | Stem Bark | Fruit |
| Digallic acid | + | + |
| Gallic acid | + | + |
| Ellagic acid | - | + |
| Aesculetin | - | - |
| Cis-p-coumaric acid | - | - |
| iso-chlorogenic acid | - | - |
| Chlorogenic acid | + | + |
| Caffeic acid | - | - |
| Protocatechuic acid | + | + |
| Gentistic acid | - | - |
| Scopoletin acid | - | - |
| Phloretic acid | + | + |
| ρ-Hydroxy benzoic acid | + | + |
| α-Resorcyclic acid | + | + |
| β-Resorcyclic acid | - | + |
| trans-ρ-coumaric acid | + | - |
| Vanillic acid | + | + |
| Pcoumarylquinic acid | + | - |
| Cis-ρ-coumaric acid | + | + |
| Melilotic acid | + | - |
| Cis-Ferulic acid | + | + |
| trans-Ferulic acid | + | - |
| Coumarin | + | + |
| Salycyclic acid | + | - |
| Cinnamic acid | + | + |
| Syringic acid | + | - |

**Table 1c:** $R_f$ values and colour reactions of Phenolic compounds on Paper Chromatograms

| Compound | $R_f$ values in solvent | | U.V fluorescence | | Silphanilic reagent | P-Nitraniline reagent |
|---|---|---|---|---|---|---|
| | **1** | **2** | **Without $NH_3$** | **With $NH_3$** | | |
| Digallic acid | 0.29 | 0.69 | None | Blue violet | Violet | Violet |
| Gallic acid | 0.45 | 0.66 | violet | Violet | Violet | Violet |
| Ellagic acid | 0.02 | 0.28 | None | Blue green | Blue green | Blue green |
| Aesculetin | 0.28 | 0.33 | white blue | Very bright blue | Brown | Grey |
| Cis-p-coumaric acid | 0.42 | 0.77 | Light blue | Deep blue | Dark brown | Blue |
| iso-chlorogenic acid | 0.01 | 0.31 | Faint blue | Duck egg green | Light orange | Brown |
| chlorogenic acid | 0.01 | 0.76 | Faint blue | Duckegg green | Orange | Brown |
| Caffeic acid | 0.06 | 0.38 | Blue | Bright blue | Buff | Light brown |
| Protocatechuic acid | 0.05 | 0.58 | None | None | Buff | Light brown |
| Gentistic acid | 0.14 | 0.68 | Bright blue | Yellow | Buff | Blue white |
| Scopoletin acid | 0.30 | 0.51 | Bright blue | Very bright blue | Yellow | Brown |
| Phloretic acid | 0.66 | 0.77 | None | None | Yellow | Purple white |
| ρ-Hydroxy benzoic acid | 0.38 | 0.68 | None | None | Bright yellow | Light pink |
| α-Resorcyclic acid | 0.16 | 0.83 | None | None | Brown | Orange brown |
| β- Resorcyclic acid | 0.28 | 0.75 | None | None | Dark brown | Brown |
| trans-ρ-coumaric acid | 0.50 | 0.45 | Light blue | deep blue | Light brown | Blue |
| Vanillic acid | 0.78 | 0.57 | None | None | Orange | Purple |
| P–coumarylquinic acid | 0.97 | 0.64 | None | None | Light yellow | Yellow |
| Cis-ρ-coumaric acid | 0.42 | 0.77 | Light blue | deep blue | Dark brown | Blue |
| Melilotic acid | 0.51 | 0.76 | None | None | Orange yellow | Purple |
| Cis-Ferulic acid | 0.89 | 0.65 | Light blue | Blue | Purple | Blue green |
| trans-Ferulic acid | 0.80 | 0.31 | Light blue | Blue | Purple | Blue green |


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| | | | | | | |
|---|---|---|---|---|---|---|
| Coumarin | 0.99 | 0.66 | None | None | Yellow | Violet |
| Salycyclic acid | 0.93 | 0.31 | Dark blue | Dark violet | Yellow | Pink |
| Cinnamic acid | 0.96 | 0.04 | None | None | Yellow | Green |
| Syringic acid | 0.92 | 0.48 | None | None | red | Dark blue |

**Solvents:** 1. Benzene **:** Acetic acid **:** Water(60:70:30);
2. Sodium formate **:** Formic acid **:** Water(10 :1 :200)

**B. Flavonoids Compounds**

**a) Extractive procedure**

The flavonoid compounds were extracted according to the method given by Markham (1982). About 5g of powdered plant material was extracted in two steps. First 18ml of Methanol and 2 ml of water (9:1) were added, shaken well and kept for one day at room temperature. The supernatant solution of the extract was taken and transferred to another test tube. Secondly Methanol and water of 5ml each (1:1) was added to the remaining residue, stirred well and the mixture left for 24 hours. The two extracts were combined, mixed well and filtered through cotton wool. Later the filtrate was evaporated to about 1/3 the original volume till most of the methanol was removed. The resultant aqueous extract was extracted with chloroform repeatedly for 3 times. The solvent extracted aqueous chloroform layer was evaporated to dryness under vaccum in a rotary evaporator. The dried residue was saturated with 1 ml of 95% alcohol and stored in a dark place at low temperature.

**b) Identification**

The extracts containing flavonoids were separated in suitable quantities on Whatmann No.1 Chromatographic filter paper(23x29 cm) adopting the ascending technique using the solvent system Iso-propyl alcohol **:** Ammonia (25%) **:** Water(8:1:1:v/v/v) and n-butanol:acetic acid: water(4:1:5v/v/v) (top layer was used).The dried Chromatograms were examined under UV lamp and the fluorescent spots were marked. The papers while exposed to Ammonia Vapours were also observed under UV lamp and the new fluorescent regions were marked. The flavonoid compounds were identified by comparing the $R_f$ values and colours with those of the authentic samples on the Chromatograms. Co-Chromatographic studies were conducted with authentic markers to confirm the identification.

**C. Chromogenic spray reagents**

**Diazotized sulphanilic acid reagent (Markham, 1982) :**0.3% solution of sulphanilic acid in 8% HCl (25ml) was mixed with 5% Sodium nitrite solution(1.5ml) just before use. The Chromatographic sheets were sprayed with this mixture and with a 20% solution of anhydrous Sodium carbonate.

**1% Alcoholic ferric chloride:**1 g of Ferric chloride was dissolved in alcohol and made up to 100ml.
**1% Alcoholic Aluminium chloride:**1g of Aluminium chloride was dissolved in alcohol and made up to 100ml, just before spraying of the chromatographic sheets.

**Table 2a:** Flavonoids

| Compoud | *Terminalia pallida* | |
|---|---|---|
| | Stem Bark | Fruit |
| Quercetin | + | + |
| Rutin | + | + |
| Myricetin | + | + |
| Luteolin | - | + |
| Apigenin | + | + |
| Orientin | - | - |
| Vitexin | + | - |

**Table 2b:** $R_f$ values and colour reactions of Flavonoids on Paper Chromatograms

| Compound | $R_f$ values in solvent | | U.V. fluorescence | | Sulphanilic Reagent | 1% Alcoholic Ferric Chloride | 1% alcoholic Aluminium Chloride |
|---|---|---|---|---|---|---|---|
| | 1 | 2 | Without NH3 | With NH3 | | | |
| Quercetin | 0.26 | 0.64 | yellow | Light yellow | Bright yellow | Green | Yellow |
| Rutin | 0.03 | 0.57 | Orange brown | Yellow | Green | Olive | Grey yellow |
| Myricetin | 0.07 | 0.43 | Yellow | Bright yellow | Light yellow | Olive | Grey yellow |
| Luteolin | 0.44 | 0.78 | Dull yellow | Yellow | Light red | Pale green | Pale yellow |
| Apigenin | 0.61 | 0.91 | Red brown | Red brown | Pink | Pale green | None |
| Orientin | 0.78 | 0.31 | Yellow | Yellow green | Grey | None | None |
| Vitexin | 0.91 | 0.42 | Dull yellow | yellow | Bright red | none | None |

**Solvents:** 1. Iso-propyl alcohol **:** Ammonia(25%) **:** Water (8:1:1)
2. n-butanol**:** Acetic acid **:** Water(4:1:5)

**D. Amino acids**

**a) Extractive procedure**

Amino acids were extracted following the method of Das Chowdary *et al.*, (1967). About 5g of plant material was cut into small pieces and plunged immediately into a round bottomed flask containing 20ml of 80% Ethanol. It was reflexed for 30 minutes over a boiling water bath. The boiled material was ground in mortar using additional volumes of 10ml ethanol 80% (v) and centrifuged at 2000 rpm. The supernatant was collected and the Ethanol removed in vaccum. The aqueous extract was passed through Dowex 50W-X8 ($H^+$ from 20-50 mesh) column (1x10cm). the amino acids were eluted from the column with 50ml of 2N Ammonium hydroxide. The elute was evaporated to dryness and the residue was saturated with 95% Ethanol (1ml).

**b) Identification**

The extracts containing amino acids were seperated on Whatmann No.1 Chromatographic filter paper(23x28 cm)


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employing two-dimensional ascending technique using the solvent system:

1) Sec. butanol : Formic acid : Water(75:13:12v/v/v)-1st direction.

2) Buffer saturated phenol (1:2v/v)-2nd direction(6.3 g of Sodium citrate and 3.7g of Potassium dihydrogen phosphate were dissolved in 100ml of distilled water. To this 200ml of distilled phenol was added)

The amino acids were identified based on comparision of $R_f$ values, colours and with those of authentic samples by co-chromatographic studies.

**C) Chromogenic spray reagents**

**Ninhydrin:**It was prepared by dissolving 200 mg of Ninhydrin in 98ml of n-butanol with 2ml of glacial acetic acid.

**Table 3a:** Amino acids

| Compoud | *Terminalia pallida* | |
|---|---|---|
| | Stem Bark | Fruit |
| Aspartic acid | + | + |
| Arginine | + | + |
| Asparagine | + | - |
| α-Alanine | + | - |
| β-Alanine | + | + |
| 2-Aminobutyric acid | - | + |
| Cystaine | + | + |
| Cystine | + | + |
| Glutamic acid | - | - |
| Glutamine | + | + |
| Glycine | + | + |
| Histidine | + | + |
| Isoleucine | + | + |
| Leucine | + | + |
| Lycine | - | - |
| γ-Methylene glutamic acid | + | + |
| γ-Methylene glutamine | + | + |
| Norleucine | + | - |
| Ornithine | + | + |
| Phenylalanine | - | - |
| Proline | + | + |
| Serine | + | - |
| Threonine | + | - |
| Tryptophan | + | - |
| Valine | + | + |
| Tyrosine | - | - |

**Table 3b:** $R_f$ values and colour reactions of Amino acids on Paper Chromatograms

| Compound | $R_f$ values in solvent | | Colour with Ninhydrin |
|---|---|---|---|
| L-Aspartic acid | 0.05 | 0.10 | Light violet |
| DL-Arginine | 0.10 | 0.60 | Violet |
| DLAsparagine | 0.19 | 0.41 | Violet |
| α-Alanine | 0.26 | 0.28 | Light violet |
| β-Alanine | 0.42 | 0.77 | Deep violet |
| DL-2-Aminobutyric acid | 0.55 | 0.70 | Light violet |
| L-Cystaine | 0.38 | 0.61 | Deep violet |
| L-Cystine | 0.23 | 0.53 | Violet |
| L-Glutamic acid | 0.17 | 0.20 | Violet |
| L-Glutamine | 0.14 | 0.82 | Violet |
| L-Glycine | 0.09 | 0.38 | Violet |
| L-Histidine | 0.08 | 0.52 | Violet |
| DL-Isoleucine | 0.68 | 0.82 | Violet |
| L-Leucine | 0.79 | 0.83 | Deep violet |
| L-Lycine | 0.79 | 0.83 | Deep violet |
| γ-Methylene glutamic acid | 0.20 | 0.68 | Violet |
| γ-Methylene glutamine | 0.30 | 0.71 | Violet |
| DL-Norleucine | 0.96 | 0.68 | Violet |
| DL-Ornithine | 0.04 | 0.27 | Light violet |
| DL-Phenylalanine | 0.60 | 0.90 | Light violet |
| L-Proline | 0.39 | 0.89 | Yellow |
| DL-Serine | 0.20 | 0.23 | Deep violet |
| DL-Threonine | 0.28 | 0.35 | Deep violet |
| DL-Tryptophan | 0.50 | 0.76 | Violet |
| DL-Valine | 0.59 | 0.77 | Deep violet |
| L-tyrosine | 0.52 | 0.65 | Light violet |

**Solvents:** 1. Sec. butanol : Formic acid :Water(75:13:12)
2. Buffer: Phenol(1:2)

**E. Anthocyanidins**

**a) Extractive procedure**

The anthocyanidin constituents were extracted according to the method described by Harborne (1973).

About 5g of plant material was immersed in 20ml of 2N HCl in a boiling test tube and heated for 30-40 minutes at6 $100^0$c. The extract was cooled and filtered. The filtrate was washed twice with 20 ml of ethyl acetate to remove flavones. The remaining aqueous extract was further heated at $80^0$c for 3 minutes to remove the last traces of ethyl acetate. The pigment was re-extracted again with a small volume of Iso-amyl alcohol. The Ethyl acetate extract was evaporated to dryness on a boiling water bath. The anthocyanidin in the residue was diluted with 1ml of 1% Methanolic HCl and preserved at low temperature in dark for future use.

**b) Identification**

The extracts containing anthocyanidins was separated on 23 x 29 cm Whatmann No.1 Chromatographic filter paper. Uni-dimensional Chromatographic ascending technique was employed with Conc. Hydrochloric acid, Formic acid, Water (2:5:3 v/w/v) and n-butanol : Acetic acid : water (4:1:5). The Chromatograms developed from the said solvent systems were taken out from the glass chambers and dried at room temperature. The fluorescent regions of dried papers were marked under UV light. The $R_f$ values and colours of the spots were determined by comparing with those of the authentic markers on the Chromatograms.

| Compoud | *Terminalia pallida* | |
|---|---|---|
| | Stem Bark | Fruit |
| Cyanidin | + | - |
| Petunidin | - | - |
| Delphinidin | + | + |

**Table 4b:** $R_f$ Values and Colours of Anthocyanidins on Paper Chromatograms

| Compound | $R_f$ values in solvent | | Visible colour | U.V. fluorescence | |
|---|---|---|---|---|---|
| | 1 | 2 | | without $NH_3$ | with $NH_3$ |
| 1 | 0.38 | 0.68 | Magenta | pink | blue green |
| 2 | 0.26 | 0.50 | Purple | mauve | Mauve |
| 3 | 0.15 | 0.40 | Purple | mauve | blue green |

**Solvents :** 1. Conc. Hydrochloric acid : Formic acid : Water(2:5:3)
2. n-butanol : Acetic acid : Water(4:1:5).


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**F. Lipids**

**a) Extractive procedure**

Lipids were extracted following the method adopted by Hoppe and Heitefuss (1974).

A solvent mixture consisting of 30ml Chloroform, 60ml of Methanol and 20 ml Water(1:2:0.8 v/v/v) was taken and allowed to boil. About 5g of plant material was homogenized in the above solvent mixture. The contents were filtered and taken separately. The residual mixture was treated with 70ml Methanol and the filtrate taken. The residue was again washed with 100ml Chloroform. All the above filtrate mixtures were taken in a separating funnel and 90ml of water added. The mixture now contains Chloroform**:** Methanol**:** Water in the ratio of 2**:**2**:**1.8 respectively and the mixture were allowed to settle. The lower lipid layer containing chloroform was separated and transferred into a breaker. The upper water layer was treated with 50ml of Chloroform successively for three times. All the extracted Chloroform layers were evaporated to dryness in a vacuum by rotary evaporation maintained at $40^0$C. The residue was treated with 2ml of Benzene to remove the traces of chlorophyll if present. Now the final lipid residue was dissolved in 2 ml of Chloroform and stored at low temperature in dark until use.

**b) Identification**

Thin layer plates were prepared by spreading a slurry of silicagel-G (50g in 100ml distilled water) to 105 mm thickness over thin glass plates. The glass plates were air dried and stored at room temperature. Before using, the plates were heated at $110^0$c for 30 minutes in a hot air oven for activation.

Using micropipette, one gram equivalent of lipid extract was taken and potted on TLC plates. The spotted areas were allowed for immediate dryness with the help of a drier. The dried plates were run in uni dimensional ascending Chromatography by using TLC glass chambers. The chambers were saturated with developing solvents one day before the plates were developed.

**Solvent systems**

1) Chloroform: Methanol: Acetic acid: Water (170:25:25:3 v/v/v/v)
2) Acetone: Benzene: Water(91:30:8 v/v/v).

The plates were placed in airtight tanks. The developed plates were removed and dried at room temperature and exposed to Iodine vapours to visualize all the lipid compounds.

The TLC plates were sprayed with 25% Sulphuric acid reagent with the help of an automizer for the clear detection of various lipid layers. The lipids were identified by comparision of $R_f$ values, color and with those of authentic samples by Co-Chromatographic studies.

**c) Chromogenic spray reagent**

The TLC plates were sprayed with 25% Sulphuric acid and heated to $230^0$c for 15 minutes, and the colour observed. Glycolipids gave red brown while phospholipids gave bright, red and other lipids gave pale brown colour spots on white background.

**Table 5 a:** Lipids

| Compoud | *Terminalia pallida* | |
|---|---|---|
| | Stem Bark | Fruit |
| Phosphatidyl serine | + | + |
| Phosphatidyl inositol | + | + |
| Phosphatidyl Clioline | + | + |
| Phosphatidyl ethanolamine | + | - |
| Digalactosyl diglyceride | - | - |
| Phosphatidyl glycerol | - | + |
| Sulphoquinovosyl diglyceride | + | + |
| Monogalactosyl diglyceride | + | + |
| Steryl glycoside | + | + |

**Table 5b:** Rf values and colour reaction of lipids on thin layer Chromatograms

| Compound | $R_f$ values in solvent | Colour with iodine vapours | Colour with $H_2SO_4$ (25%) |
|---|---|---|---|
| Phosphatidyl serine | 0.09 | + | + |
| Phosphatidyl inositol | 0.13 | + | + |
| Phosphatidyl Clioline | 0.18 | + | + |
| Phosphatidyl ethanolamine | 0.23 | + | + |
| Digalactosyl diglyceride | 0.33 | + | + |
| Phosphatidyl glycerol | 0.41 | + | + |
| Sulphoquinovosyl diglyceride | 0.57 | + | + |
| Monogalactosyl diglyceride | 0.81 | + | + |
| Steryl glycoside | 0.87 | + | + |

Solvent : $CHCl_3$ : MeOH : HOAc : $H_2O$ (170:25:25.3).

**Physicochemical studies:**

For several years, the crude drugs were identified by comparison only with the standard descriptions available. But recently, due to advancement in the field of Pharmacognosy, various techniques are followed to the standardization of crude drugs. Among such techniques, ash and extractive values are considered very important in promoting the quality and in establishing the Pharmacopeial standards of the drug.

Substandard quality of many drugs is due to either faulty collection or incorrect storage. When the constituents of a drug cannot be readily estimated by any other means, ash and extractive values are very useful especially for their evaluation. To prove its acceptability as a drug, studies of ash and extractive values are basically required in determining the quality and purity of selected crude drug.

## 5. Materials and Methods

The physical constants like ash and extractive values were determined by standard methods (Anonymous, 1985 and Kokate, 1991).

## 6. Experimental Studies

**A. Determination of ash values**

The object of ashing crude drugs is to remove all traces of organic matter which may otherwise interfere in an analytical determination. The inorganic salts naturally occurring in drug or adhering to it or deliberately added to as


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a form of adulteration are removed by gradual incineration of the drug. Thus the residue remaining after incineration of the powdered drug is known as ash content. The ash values are a criterion to judge the identity or purity and quality of the crude drug.

**a) Determination of total ash**

Total ash usually consists of Phosphates, Silicates and Carbonates of Potassium, Calcium and Magnesium. About 2 gm of the air dried powdered drug was accurately weighed and taken in a tared silica crucible, which was previously ignited and weighed. The powdered drug was spread as a fine even layer at the bottom of the crucible. The crucible containing the drug was gradually incinerated in a muffle furnace by increasing the temperature. It was heat dull red hot until free from carbon or converted into ash. Later the crucible was allowed to cool and kept in desiccators. The residue was weighed the percentage of total ash calculated with reference to the air dried sample. The residue was weighed the percentage of total ash calculated with reference to the air dried sample. The procedure was repeated till constant result was obtained.

**b) Determination of acid insoluble ash**

Acid insoluble ash is a part of total ash insoluble in dilute Hydrochloric acid. The acid insoluble ash content is determined and recommended for certain drugs may be coated with dirt and sand. The total ash obtained as described above was treated with 25ml of 10% Hydrochloric acid and boiled for 5 minutes. The insoluble matter was filtered and collected on ashless filter paper (Whatman No.42) and the paper washed with hot water. The insoluble ash was ignited and weighed in a tared silica crucible. The acid insoluble ash of the drug was repeated to get constant results.

**c) Determination of water soluble ash**

The total ash obtained from the above process was boiled with 25 ml of distilled water for 5 minutes. The insoluble ash was filtered through ash less filter paper (Whatman No.42). The residue was once again washed with water and ignited up to temperature not exceeding 450$^{o}$c and converted into ash. The difference between the weight of total ash and insoluble matter represent the weight of water soluble ash. The percentage of water soluble ash was calculated with reference to the air dried drug.

**B. Determination of extractive values**

Extractive values indicate the nature of the constituents present in a crude drug. Based on the diversity in chemical nature and properties of the contents of the drug, various solvents were used for the determination of extractives. The solvents used for extraction dissolve appreciable quantity of substances desired. The methods used to find out the extractive values were as follows.

**a) Determination of alcohol soluble extract**

Alcohol is an ideal solvent frequently employed to determine various chemical contents like Tannins, Resins etc. Generally, Ethyl alcohol is used for determination of alcohol-soluble extractive. Dilute Alcohol a may also be used in some cases, depending upon solubility of constituents in a crude drug. In the present work, the author used 100 ml of 90% Alcohol for determining crude drug was macerated with 100 ml of 90% Alcohol in a stoppered flask for 24 hours. It was shaken frequently every 6 hours and allowed to stand to 18 hours. Then the extract was filtered rapidly through filter paper, taking precaution against loss of alcohol, about 25 ml of the filtrate was evaporated to dryness in a tared flat bottomed shallow dish, transferred to the oven and dried at 105$^{o}$C and weighed. The percentage of alcohol soluble extract was calculated with reference to the air dried drug.

**Table 6:** Ash value of various parts of *Terminalia pallida*

| S.No. | Plant species | Plant Parts | Total ash (%) | Acid insoluble ash (%) | Water insoluble ash (%) |
|---|---|---|---|---|---|
| 1. | ***Terminalia pallida*** | Stem bark | 8.65 | 0.15 | 0.4 |
| | | Fruit | 4.00 | 0.35 | 2.4 |

**Table 7:** Extractive value of the stem bark and fruit of *Terminalia pallida*

| S.No. | Species | Plant Parts | 90% alcohol soluble extract (% w/w) | Water soluble extract (%w/w) | Chloroform soluble extract (%w/w) | Pet.Ether soluble extract (%w/w) |
|---|---|---|---|---|---|---|
| 1 | ***Terminalia pallida*** | Stem bark | 28.8 | 32 | 1.2 | 1.6 |
| | | Fruit | 18 | 4.8 | 0.4 | 0.8 |

**Antibacterial Activity**

The presence of antimicrobial substances in the higher plants provide a source of inspiration for novel drug compounds as plants derived medicines have made significant contribution towards human health. The antimicrobial compounds from plants may inhibit microbial growth by different mechanism than those presently used antimicrobials and may have a significant clinical value in treatment of resistant microbial strains. Therefore, random screening of plants for active chemicals is as important as the screening of ethnobotanically targeted species (Principle, 1989).

## 7. Materials and Methods

**Collection of medicinal plants**: Selected medicinal plant, *Terminalia pallida*, has been used in the present study and it was collected from Veligonda hill range, Eastern Ghats, Nellore Dt, Andhra Pradesh, India.

**Bacterial Cultures:** The bacterial cultures were procured from the Department of Microbiology, Sri Venkateswara Institute of medical Sciences (SVIMS), Tirupati. Pathogenic Gram positive bacteria such as *Bacillus subtilis*, *Klebsiella pneumoniae*, and Gram negative bacteria *Proteus vulgaris*, *Pseudomonas aeruginosa*, were maintained on nutrient agar slants at 4$^{0}$C until further used for experimental studies**.**


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**Preparation of the medium**

**Nutrient Agar media (P.H 7.0)**
For the preparation of 1 lt of Nutrient Agar media ingredients like 1.5 g of beef extract, 1.5 g of yeast extract, 5 g of peptic digest of animal tissue and 5 g of sodium chloride were weighed and added in 500 ml of distilled water and heated with agitation to dissolve the constituents. Finally, the volumes were made upto 1 lt. Before the addition of agar (15 g) the pH of the medium was adjusted to 7.0 by adding few drops of 0.1 N NaOH or HCl using digital pH meter ( Elico Pvt. Ltd., Hyderabad). These were then sterilized by autoclaving at 15 lbs pressure at $120^0$ C for 15 min; cooled to $40^0$ C and approximately 20 ml of medium was poured to each 90mm sterilized petridish.

**Preparation of inoculum:**
**Bacteria:** 18 hrs old bacterial broth cultures were used as inoculae after adjusting its population to $10^6$ CFU/ ml (Colony Forming Units) using 0.9% (w/v) sterile saline by the method described by Forbes *et al*.,(1990).

**Preparation of plant extract:** The methanolic extracts of the four selected medicinal plants were prepared by dissolving 10gm of fine powder of each medicinal plants separately in 100 ml of methanol solvent. The contents were kept in orbitary shaker for 48 h. Then the extract was filtered and it is dried in hot air oven at $40^0$ C. Then the extract was stored under refrigeration at $4^0$ C for further studies**.**

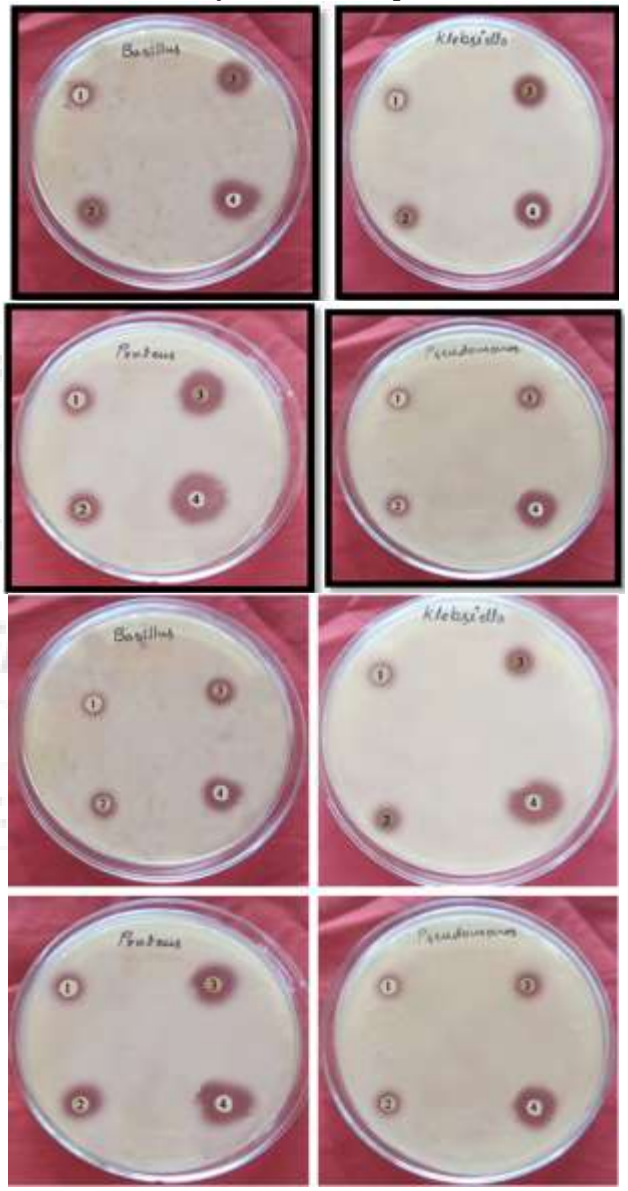
**Preparation of sterile disc:** Whatman's No.3 filter paper was punched into 5 mm disc form and they sterilized, each sterile disc was incorporated individually with 20 – 60 mg/ml of extracts using micropipette. Precautions were taken to prevent the flow of the solvent extract from the discs to the outer surface. The condensed extracts were applied in small quantities on discs and they were allowed to dry in air. Then they were stored at $4^0$ C.

**Assay of antimicrobial activity using Disc diffusion method :**The antimicrobial activity was performed by employing the disc diffusion method adopted by Bauer *et al.,* (1966) and Cruickshank (1968). The 20 ml of sterilized Muller Hinton Agar was poured into sterile petriplates, after solidification, 100 µl of fresh culture of human pathogens were swabbed on the respective plates. Sterile discs of Whatman No. 1 filter paper of about 6 mm were prepared. The discs were kept over the agar plates using sterile forceps at various concentrations (20, 40, and 60 mg/ml). Streptomycin 10mg/ml containing disc used as standard control. The plates were incubated for 24 h at $37^0$ C and the diameter of the inhibition zones was recorded. The assessment of antimicrobial activity was based on measurement of inhibition zones formed around discs. A zone of inhibition around the disc indicates that the compounds, which diffused into the agar from the disc, inhibited the growth of the organism.

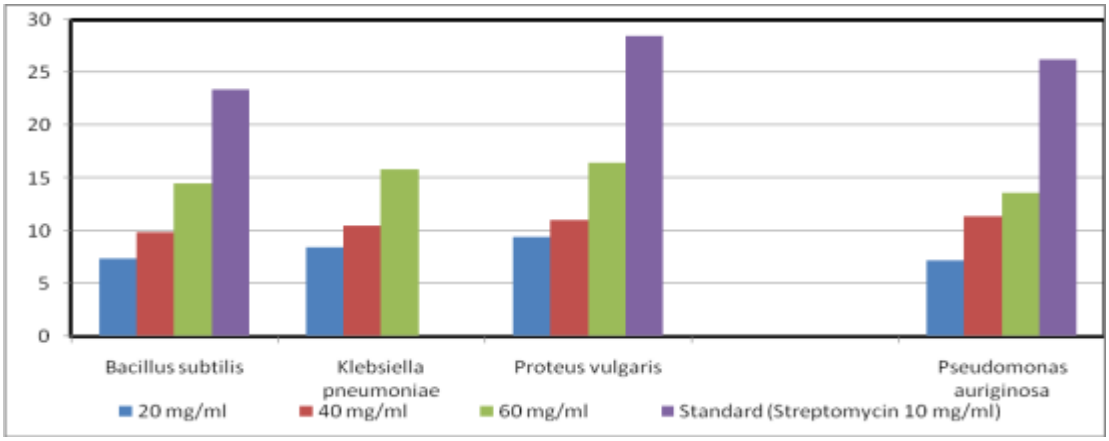
## 8. Results

Present investigation, antibacterial activity of *Terminalia pallida* on pathogenic bacterial strains, the plant exhibited significant antibacterial activity. For the Methanol extract of *Terminalia pallida* at the concentration 60 mg/ml *P. vulgaris* (16.5mm) was more susceptible, followed by *K. pneumonia* (15.8mm), *B.subtilis* (15.4mm) and *P. aeruginosa* (13mm).

**Antibacterial activity of *Terminalia pallida*:**




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| S. No | Name of the microorganism | 20 mg/ml | 40 mg/ml | 60 mg/ml | Standard (Streptomycin 10 mg/ml) |
|---|---|---|---|---|---|
| 1. | *Bacillus subtilis* | 7.4 ± 0.44mm | 9.84 ± 0.63mm | 14.5 ± 0.28mm | 23.45 ± 0.65mm |
| 2. | *Klebsiella pneumoniae* | 8.5 ± 1.2mm | 10.5 ± 0.6mm | 15.82 ± 0.24mm | 24. 4 ± 0.53mm |
| 3. | *Proteus vulgaris* | 9.4 ± 0.39mm | 11.04 ± 0.56mm | 16.5 ± 0.35mm | 28.53 ± 0.74mm |
| 4. | *Pseudomonas auriginosa* | 7.2 ± 0.68mm | 11.4 ± 0.57mm | 13.65 ± 0.56mm | 26.25 ± 0.36 mm |

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# Studies on Antibacterial Activity of Boswellia Ovalifoliolata and Syzygium Alternifolium Against Bacillus Subtilis and Pseudomonas Auriginosa

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***Abstract:*** **- Medicinal plants have been used for centuries as remedies for human diseases because they contain components of therapeutic value. The two selected medicinal plants exhibited significant antibacterial activity on pathogenic bacterial strains. Methanol stem extract of *Boswellia ovalifoliolata* and *Syzigium alternifolium* showed potent antibacterial activity on *P. auriginosa* and *B. subtilis*.**

***Keywords: Boswellia ovalifoliolata, Syzigium alternifolium, Pseudomonas auriginosa, Bacillus subtilis*.**

## I. INTRODUCTION

Recently, the acceptance of traditional medicine as an alternative form of health care and the development of microbial resistance to the available antibiotics has led authors to investigate the antimicrobial activity of medicinal plants (Maoz and Neeman 1998; Hammer *et al.* 1999). During the last ten years the pace of development of new antimicrobial drugs has slowed down while the prevalence of resistance has increased astronomically (Hugo and Russell, 1984). In addition to this problem, antibiotics are sometimes associated with adverse effects on the host, including hypersensitivity, immunosuppression and allergic reactions (Ahmad *et al*, 1998). This situation forced scientists to search for new antimicrobial substances. Given the alarming incidence of antibiotic resistance in bacteria of medical importance (Monroe and Polk, 2000), there is a constant need for new and effective therapeutic agents (Bhavnani and Ballow, 2000). Therefore, there is a need to develop alternative antimicrobial drugs for the treatment of infectious diseases from medicinal plants (Cordell, 2000).

Literature reports and ethnobotanical records suggest that plants are sleeping giants of pharmaceutical industry (Hostettmann and Hamburger, 1991).They may provide natural source of antimicrobial drugs that will provide novel compounds that may be employed in controlling some infection globally. According to World Health Organization medicinal plants would be the best source to obtain a variety of drugs. About 80% of individuals from developed countries use traditional medicine, which has compounds derived from medicinal plants.

The use of plant extracts and phytochemicals, both with known antimicrobial properties, can be of great significance in therapeutic treatments. In the last few years, a number of studies have been conducted in different countries to prove such efficiency (Ikram and Inamul, 1984). The beneficial medicinal effects of plant materials typically result from the combinations of secondary products present in the plant. In plants, these compounds are mostly secondary metabolites such as alkaloids, steroids, tannins, and phenol compounds, which are synthesized and deposited in specific parts or in all parts of the plant. These compounds are more complex and specific and are found in certain taxa such as family, genus and species, but heterogeneity of secondary compounds is found in wild species (Balandrin *et al*, 1985). The medicinal actions of plants are unique to a particular plant species or group, consistent with the concept that the combination of secondary products in a particular plant is taxonomically distinct (Wink, 1999).

The plant's secondary products may exert their action by resembling endogenous metabolites, hormones, signal transduction molecules or neurotransmitters and thus have beneficial medicinal effects on humans due to similarities in their potential target sites. The presence of antimicrobial substances in the higher plants provide a source of inspiration for novel drug compounds as plants derived medicines have made significant contribution towards human health. The antimicrobial compounds from plants may inhibit microbial growth by different mechanism than those presently used antimicrobials and may have a significant clinical value in treatment of resistant microbial strains. Therefore, random screening of plants for active chemicals is as important as the screening of ethnobotanically targeted species (Principle, 1989).


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## II MATERIALS AND METHODS

Collection of medicinal plants: Selected medicinal plants, *Boswellia ovalifoliolata and Syzigium alternifolium*, have been used in the present study and they were collected from Veligonda hills, Nellore district, Andhra Pradesh, India.

Bacterial Cultures: The bacterial cultures were procured from the Department of Microbiology, Sri Venkateswara Institute of medical Sciences (SVIMS), Tirupati.Pathogenic Gram positive bacteria such as *Bacillus subtilis*, and Gram negative bacteria *Pseudmonas aeruginosa*, were maintained on nutrient agar slants at $4^0$C until further used for experimental studies.

*Bacillus subtilis* : Bacillus subtilis was a gram positive, rod shaped, endospore forming catalase-positive bacterium commonly found in soil ( Madigan and Mortinnko, 2005). *Bacillus subtilis contaminate* food and causes food poisoning ( Ryan and Ray, 2004). It causes conjunctivitis followed by irridocheroiditis (Green wood *et al.*, 1997).

*Pseudomonas auriginosa* : *Pseudomonas auriginosa* is a gram negative rod shaped, non-encapsulated, aerobic ansd non-spore forming bacterium with unipolar motility occuring as an oppurtunistic pathogen of plants and human, which typically infects the pulmonary tract, burns, wounds and causes blood infections .The most common cause of burn infections was *P.auriginosa* and post- operative infection in radical keratotomy surgery patients.

1. PREPARATION OF THE MEDIUM:

*Nutrient Agar media (pH 7. 0)*

For the preparation of 1 litre of Nutrient Agar media ingredients like 1.5 g of beef extract, 1.5 g of yeast extract, 5 g of peptic digest of animal tissue and 5 g of sodium chloride were weighed and added in 500 ml of distilled water and heated with agitation to dissolve the constituents. Finally, the volumes were made up to 1 liter. Before the addition of agar (15 g) the pH of the medium was adjusted to 7.0 by adding few drops of 0.1 N NaOH or HCl using digital pH meter (Elico Pvt. Ltd., Hyderabad). These were then sterilized by autoclaving at 15 lbs pressure at 1200 C for 15 min; cooled to 400 C and approximately 20 ml of medium was poured to each 90mm sterilized petridish.

2. *Preparation of inoculum:*
Bacteria: 18 hrs old bacterial broth cultures were used as inocula after adjusting its population to $10^6$ CFU/ ml (Colony Formong Units) using 0.9% (w/v) sterile saline by the method described by Forbes *et al*.,(1990).

3. *Preparation of plant extract:* The methanolic extracts of the four selected medicinal plants were prepared by dissolving 10gm of fine powder of each medicinal plant separately in 100 ml of methanol solvent. The contents were kept in arbitrary shaker for 48 h. Then the extract was filtered and it is dried in hot air oven at $40^0$ C. Then the extract was stored under refrigeration at $4^0$ C for further studies.

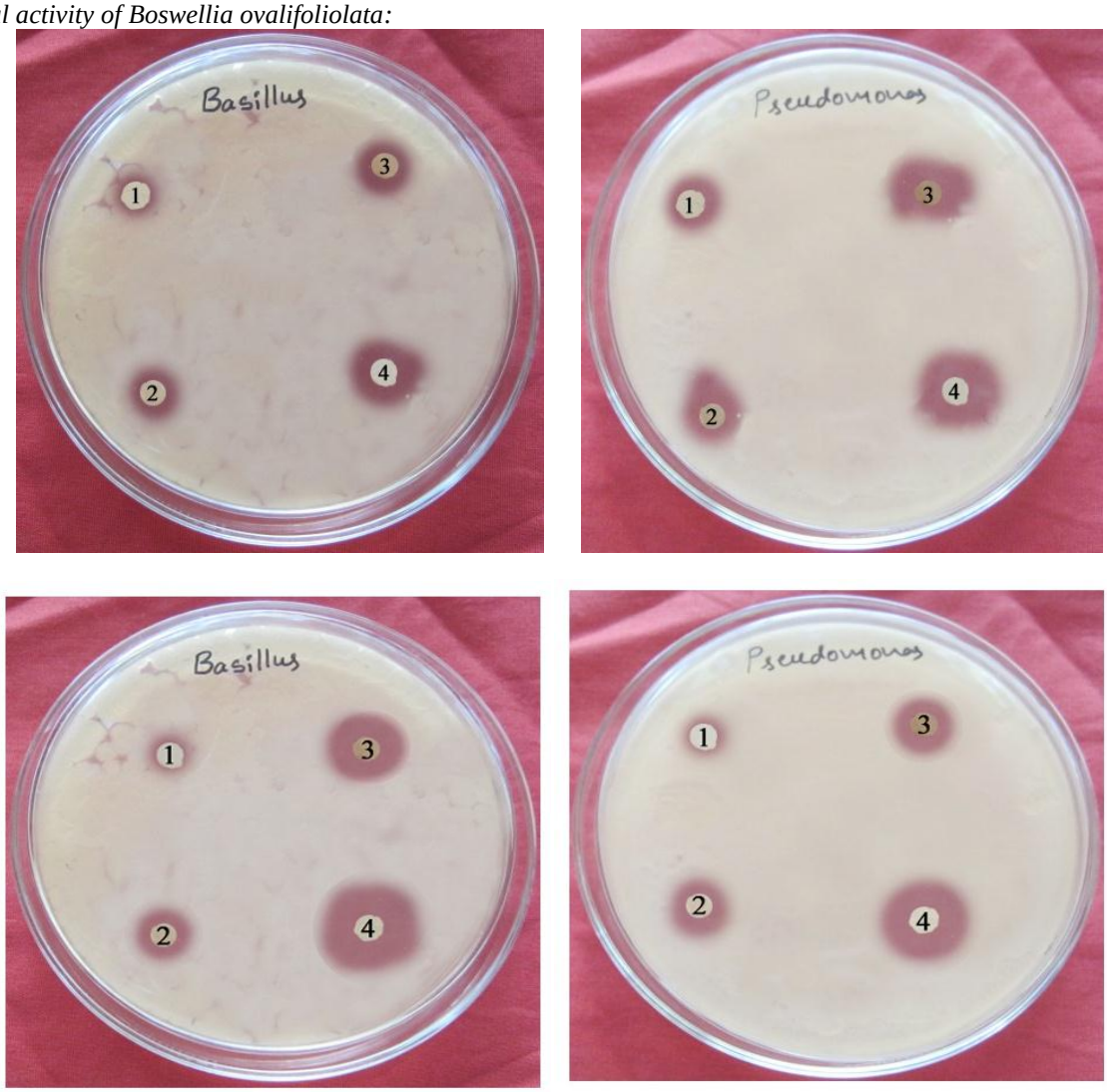
4. *Preparation of sterile disc:* Whatman's No.3 filter paper was punched into 5 mm disc form and they sterilized, each sterile disc was incorporated individually with 20 – 60 mg/ml of extracts using micropipette. Precautions were taken to prevent the flow of the solvent extract from the discs to the outer surface. The condensed extracts were applied in small quantities on discs and they were allowed to dry in air. Then they were stored at $4^0$ C.

5. *Assay of antimicrobial activity using Disc diffusion method:* The antimicrobial activity was performed by employing the disc diffusion method adopted by Bauer *et al.*, (1966) and Cruickshank (1968). The 20 ml of sterilized Muller Hinton Agar was poured into sterile Petri-plates, after solidification, 100 µl of fresh culture of human pathogens were swabbed on the respective plates. Sterile discs of Whatman No. 1 filter paper of about 6 mm were prepared. The discs were kept over the agar plates using sterile forceps at various concentrations (20, 40, and 60 mg/ml). Streptomycin 10mg/ml containing disc used as standard control. The plates were incubated for 24 h at $37^0$ C and the diameter of the inhibition zones was recorded. The assessment of antimicrobial activity was based on measurement of inhibition zones formed around discs. A zone of inhibition around the disc indicates that the compounds, which diffused into the agar from the disc, inhibited the growth of the organism.


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*Antibacterial activity of Boswellia ovalifoliolata:*



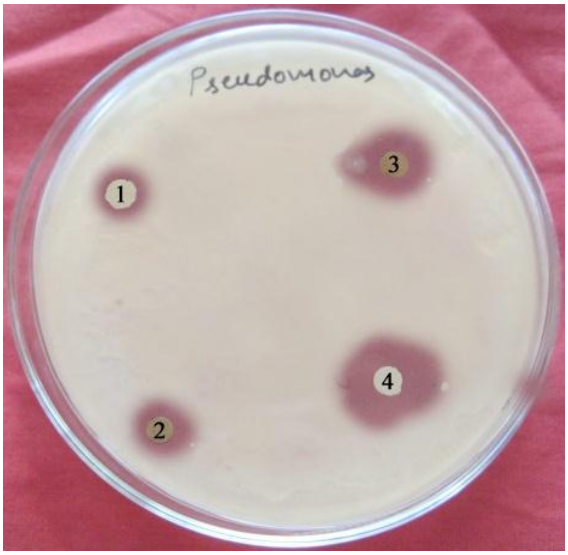

| S. No | Name of the microorganism | 20 mg/ml | 40 mg/ml | 60 mg/ml | Standard (Streptomycin 10 mg/ml) |
|---|---|---|---|---|---|
| 1 | *Bacillus subtilis* | 8.14± 0.24mm | 10.32 ±0.61mm | 14.35 ± 0.34mm | 23.45 ± 0.65mm |
| 2 | *Pseudomonas auriginosa* | 7.54 ± 0.23 mm | 10.3 ± 0.45mm | 16.32 ± 0.29mm | 26.25 ± 0.36 mm |

*Antibacterial activity of Syzigium alternifolium:*


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| S. No | Name of the microorganism | 20 mg/ml | 40 mg/ml | 60 mg/ml | Standard (Streptomycin 10 mg/ml) |
|---|---|---|---|---|---|
| 1 | *Bacillus subtilis* | 7.21 ± 0.39mm | 10.42 ± 0.56 mm | 13.54 ± 0.49mm | 23.45 ± 0.65mm |
| 4 | *Pseudomonas auriginosa* | 7.5 ± 0.28mm | 10.7 ± 0.88mm | 15.5± 0.57mm | 26.25 ± 0.36 mm |

## RESULTS

Present investigation, anti bacterial activity of two selected medicinal plants, on pathogenic bacterial strains, all exhibited significant antibacterial activity. Methanol stem extract of *Boswellia ovalifoliolata* at the concentration 60 mg/ml showed potent antibacterial activity. *Pseudomonas auriginosa* (16mm) was more susceptible followed by *B. subtilis* (14mm). Methanol stem extract of *Syzigium alternifolium* at the concentration 60 mg/ml, *Pseudomonas auriginosa* (15.2mm) was more susceptible, followed by *B. subtilis* (13.5mm).

## III CONCLUSION

Among the two selected medicinal plants Methanol stem extract of *Boswellia ovalifoliolata* showed potent antibacterial activity, followed by *Syzigium alternifolium. Boswellia ovalifoliolata*, showed highest antibacterial activity and *Syzigium alternifolium* showed moderate antibacterial activity against the selected bacterial strains.


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# Spectrophotometric Methods for the Estimation of Third and Fourth Generation Cephalosporins In Dosage Form

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***Abstract:*** ***The proposed spectrophotometric methods are rapid, sensitive and reproducible for the analysis of cefdinir(A), and cefepime(B) in pharmaceutical dosage forms with short analysis time. The authors developed reagent for the estimation of cefdinir and cefepime, third and fourth generation cephalosporins respectively using catechol ( or p amino aceto phenone-AAP ) and sodium meta periodate at a λmax of 460 nm. The Beers law range, molar absorptivity and Sandell sensitivity will be 50-250 µg/mL,4.5X10$^3$ and 0.03 for cefdinir respectively. In case of cefepime the Beers law range, molar absorptivity and Sandell sensitivity will be 20-250µg/mL,6.05x10$^3$ and 0.02 respectively.***

***Keywords- Catechol , p-Amino aceto phenone and Sodium meta per iodate,cefdinir,cefepime***

## I. INTRODUCTION

*A. Cefdinir*

is chemically known as 8-[2-(2-amino-1,3-thiazol-4- yl)-1-hydroxy-2- nitroso-ethenyl] amino- 4-ethenyl-7-oxo- 2-thia-6- azabicyclo [4.2.0]oct-4-ene-5-carboxylic acid, a semi-synthetic, broad- spectrum antibiotic in the third generation of the cephalosporin class. It is used to control for common bacterial infections of the ear, sinus, throat, and skin. Therapeutic uses of cefdinir include otitis media, soft tissue infections, and respiratory tract infections, including sinusitis, strep throat, community-acquired pneumonia and acute exacerbations of bronchitis.

*B. Cefepime*

is chemically known as (6R,7R,Z)-7-(2-(2-aminothiozyl-4-yl)-2-(methoxyimino)acetamido)-3-((1-ethylpyrrolidinium1-yl)methyl)-8-oxo-5-thia-1-aza-bicyclo(4,2,0) oct-2-ene-2- carboxylate (Fig-1.2.1) is a fourth generation cephalosporin used to control both gram positive and gram negative bacteria. Cefepime is usually reserved to treat severe nosocomialpneumonia, infections caused by multi-resistant microorganisms (e.g. pseudomonas aeruginosa) and empirical treatment of febril eneutropenia. Cefepime has good activity against important pathogens including pseudomonas aeruginosa, Staphylococcus aureus, and multiple drug resistant Streptococcus pneumoniae. It acts against enterobacteriaceae, whereas other cephalosporins are degraded by many plasmid- and chromosome-mediated beta-lactamases.
Side effects of cefepime are mild pain, redness, or swelling at the injection site.

## II. EXPERIMENTAL

*A. Preparation of Solutions*

Catechol : 0.1% solution was prepared by dissolving 0.1 g of catechol sample (A.R .grade SDFCL Mumbai) in 100 mL of distilled water.

Sodium meta per iodate, $NaIO_4$ : 2.1392 g of NaIO4 (AR grade Hi Media laboratories Mumbai-66) was dissolved in distilled water and the total volume was brought to 1 Lt (0.01M) in a standard volumetric flask.

Standard solution of cefdinir and cefepime (in dosage form): Drug (RTIST – DT for Cefdinir or Novapime for cefepime – Lupin laboratories, Mumbai) solution was prepared by dissolving 100 mg of drug sample in 100mL of distilled water. Working solutions of drug sample (100mg / mL) were prepared by diluting aliquots of the stock solutions with distilled water.

*B. Instrumentation*

Spectral measurements and absorbance readings were made on Elico SL 177 double beam Spectrophotometer. pH measurements



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were carried out using Elico pH meter model LI 615.

*C. Establishment of Optimum Conditions*

The optimum conditions were established in each case basing on the development of maximum color and its stability and results are presented inTable – I. Among the various oxidizing agents tried, IO4- is the best one, followed by $H_2O_2$. The other oxidizing agents such as $IO_3^-$, Fe(III), $MnO_4^-$, $Ocl^-$ $Fe(CN)_6^{3-}$, were found not suitable. The efficiency of the oxidizing agent depends upon its relative reactive tendency towards reactants, (drug, catechol) products (indo-dyes) and also on the behavior of its reduced form. The formation of colored species of same λmax in the case of cefdinir (cefepime) with each pair of reagents, (Catechol – $IO_4^-$ and AAP-$IO_4^-$) suggests that the indo dye formed with both compounds is the same.

Table-I Experimental Conditions

| S.No | Drug | $P^H$ | Catechol | $NaIO_4$ | Maximum Colour development | Stability | λmax |
|---|---|---|---|---|---|---|---|
| 1 | Cefdinir | 4±0.4 | 1 mL | 1mL | 5 min. | 120 min. | 460 nm |
| 2 | Cefepime | 4±0.4 | 1 mL | 1mL | 5 min. | 180 min. | 460 nm |

*D. Assay Procedure*

1) *For Cefdinir (or Cefepime) using Catechol- $IO_4^-$*: 15 mL of buffer solution, 0.4 –5mL of aliquots of cefdinir (Cefepime) solution,1mLof $IO_4^-$, 1mLof catechol(or AAP)were successively placed in a 25 ml volumetric flask, so as to make total volume of 25 mL.The absorbance of colored species was measured at 460 nm between 5—70 min. against corresponding reagent blank prepared in a similar manner. The amount of cefdinir (or cefepime ) was read from calibration curve prepared with the standard solution under identical conditions.

*E. Optical Characteristics*

1) *Adherence to Beer's law.*: In order to test whether the cefdinir-catechol-$IO_4^-$(or AAP- $IO_4^-$ ) or cefepime- catechol-$IO_4^-$ (or AAP- $IO_4^-$) systems adhere to Beer's law, the absorbance at λmax of a set of solutions (25mL) containing varying amounts of cefdinir (cefepime),15 mL of buffer solutions, specified concentrations of catechol, (or AAP) and oxidizing agent (Table-II) were measured against blank on spectrophotometer. The linearity of the plot between absorbance and the concentration range specified in Table-II shows that the color system obeys Beer's law, Fig's 1.1 and 1.2. Beer's limits, molar absorptivity, optimum photometric range and Sandal's sensitivity values of the method in the case of cefdinir were calculated and results are incorporated in Table-II

Table-II Optical Characteristics

| Reagent | Beers Law Range µg/mL | Molar Absorptivity Lt/mol/cm | Sandell's sensitivity µg/cm2/0.001 absorbance units | Optimum photometric range µg/25 ml |
|---|---|---|---|---|
| Catechol-$IO_4^-$ and cefdinir | 50 – 250 | $4.5 \times 10^3$ | 0.03 | 100—257 |
| Catechol-$IO_4^-$ and cefepime | 20 - 250 | $6.05 \times 10^3$ | 0.02 | 80 – 316 |


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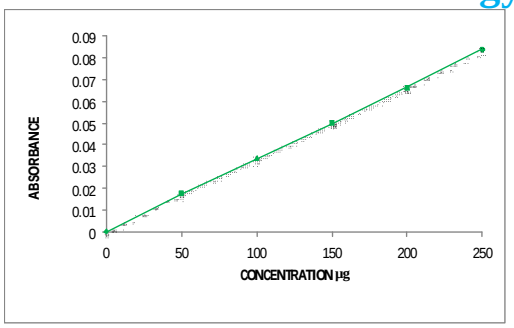
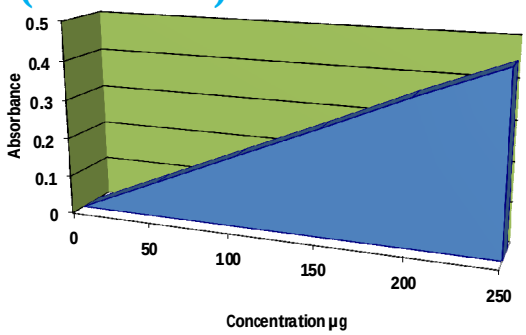



Fig.1.1 Linearity of Cefepime




(3D) Fig.1.2 Linearity of Cefdinir

*F. Precision and Accuracy*

The precision and accuracy of the methods in the determination of cefdinir and cefepime were tested by measuring the absorbance of six replicates each containing approximately 3/4 th of the Beer's law limit concentrations. The percentage of relative standard deviations and confidence limits (0.05 and 0.01 levels) in the methods are presented below.

Table. III. Precision and Accuracy

| Cefdinir | Amount of Drug * | | % Error | % R.S.D | % Range of Error | |
|---|---|---|---|---|---|---|
| | Taken mg | Found mg | | | 95% Confidence Limit | 99% Confidence Limit |
| Catechol IO4- reagent and cefdiir | 0.25 | 0.247 | 1.174 | 2.657 | ±1.6 | ±2.92 |
| | 0.15 | 0.148 | 1.3 | 1.26 | ±1.32 | ±2.92 |
| Catechol-$IO_4^-$reagent cefipime | 0.20 | 0.197 | 1.172 | 1.27 | ±1.3 | ±1.98 |
| | 0.25 | 0.247 | 1.174 | 2.655 | ±1.6 | ±2.92 |

To justify the suitability of the proposed methods, known amounts of Cefdinir ( or cefepime ) was added to the quantities of previously analyzed samples (in dry form) and then analyzed again. The results are incorporated in Table-IV.

Table-IV. Results of analysis of formulations and Recovery experiments

| Sample | Labeled Amount | Amount found | %Recovery |
|---|---|---|---|
| Ciplacef | 125 mg | 124.86 mg | 99.88 |
| Cefast | 125 mg | 124.55 mg | 99.64 |
| Cepime | 500 mg | 499.6 mg | 99.92 |
| Megapime | 500 mg | 495.75 mg | 99.15 |

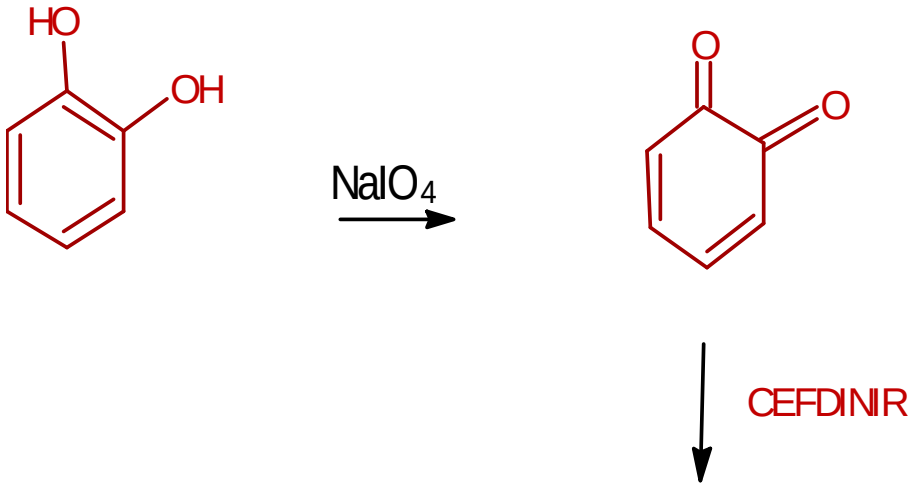

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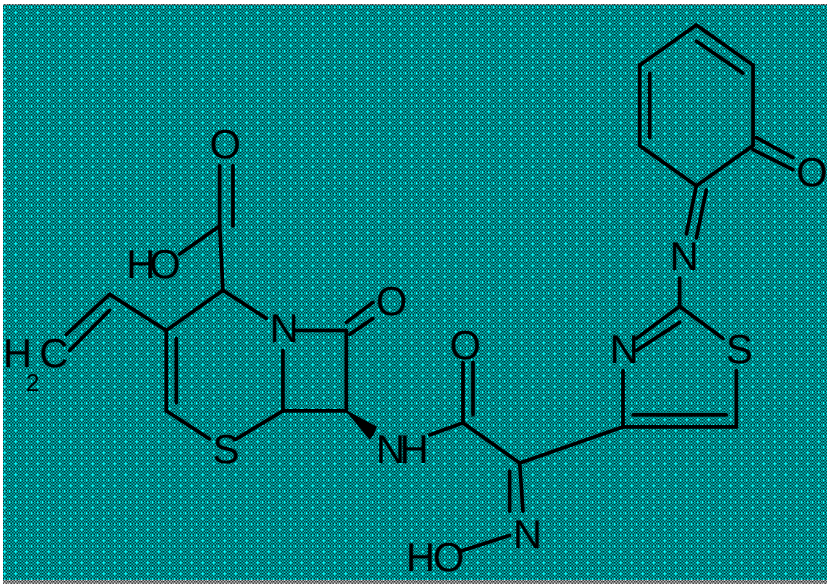
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## III. RESULTS AND DISCUSSION

Based on the results furnished in Tables I. –IV it can be inferred that the method proposed for the spectrophotometric determination of cefdinir ( cefepime) is simple, rapid, sensitive and specific with reasonable precision and accuracy. The methods have been extended to determine cefdinir (or cefepime) different pharmaceutical preparations.

The proposed method appears to be superior to many of the reported methods7-9 and so they can be employed in routine determinations. Catechol is readily oxidisable by sodium meta per iodate to form o-benzoquinone. Cefdinir ( cefepime ) by virtue of its strong electron donating group, (-$NH_2$) oxidative coupling reaction takes place with electron deficient o-benzo quinone to form indo dye.




## IV. CONCLUSION

Hence the authors conclude that the proposed spectrophotometric methods are sensitive and reproducible for the analysis of cefdinir ( cefepime) in pharmaceutical dosage forms with short analysis time.

## V. ACKNOWLEDGEMENTS

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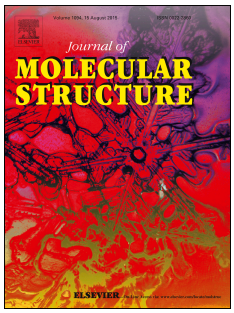

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# Accepted Manuscript




Supramolecular architecture of 5-bromo-7-methoxy-1-methyl-1*H*-benzoimidazole.3$H_2O$: Synthesis, spectroscopic investigations, DFT computation, MD simulations and docking studies

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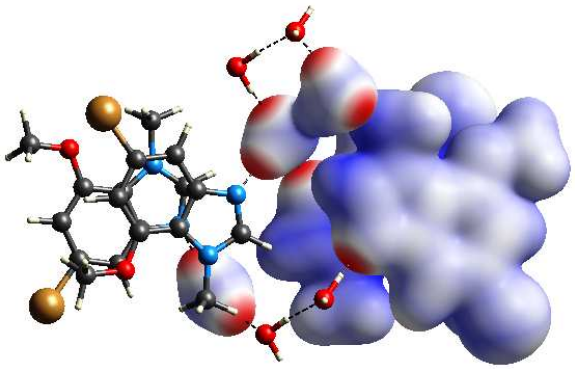
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# Supramolecular architecture of 5-bromo-7-methoxy-1-methyl-1*H*-benzoimidazole.3$H_2O$: Synthesis, spectroscopic investigations, DFT computation, MD simulations and Docking studies

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**Abstract**

Crystal and molecular structure of newly synthesized compound 5-bromo-7-methoxy-1-methyl-1*H*-benzoimidazole (BMMBI) has been authenticated by single crystal X-ray diffraction, FT-IR, FT-Raman, $^{1}$H-NMR, $^{13}$C-NMR and UV-Visible spectroscopic techniques; compile both experimental and theoretical results which are performed by DFT/B3LYP/6-311++G(d,p) method at ground state in gas phase. Visualize nature and type of intermolecular interactions and crucial role of these interactions in supra-molecular architecture has been investigated by use of a set of graphical tools 3D-Hirshfeld surfaces and 2D-fingerprint plots analysis. The title compound stabilized by strong intermolecular

hydrogen bonds N...H-O and O...H-O, which are envisaged by dark red spots on $d_{norm}$ mapped surfaces and weak Br...Br contacts envisaged by red spot on $d_{norm}$ mapped surface. The detailed fundamental vibrational assignments of wavenumbers were aid by with help of Potential Energy distribution (PED) analysis by using GAR2PED program and shows good agreement with experimental values. Besides frontier orbitals analysis, global reactivity descriptors, natural bond orbitals and Mullikan charges analysis were performed by same basic set at ground state in gas phase. Potential reactive sites of the title compound have been identified by ALIE, Fukui functions and MEP, which are mapped to the electron density surfaces. Stability of BMMBI have been investigated from autoxidation process and pronounced interaction with water (hydrolysis) by using bond dissociation energies (BDE) and radial distribution functions (RDF), respectively after MD simulations. In order to identify molecule's most important reactive spots we have used a combination of DFT calculations and MD simulations. Reactivity study encompassed calculations of a set of quantities such as: HOMO-LUMO gap, MEP and ALIE surfaces, Fukui functions, bond dissociation energies and radial distribution functions. To confirm the potential of title molecule in the area of pharmaceutics, we have also calculated a series of drug likeness parameters. Possibly important biological activity of BMMBI molecule was also confirmed by molecular docking study.

**Keywords:** Benzoimidazole; Supra-molecular architecture; BDE; RDF; molecular docking.

## 1. Introduction

Benzimidazole is a fused heterocyclic compound formed by the merger of benzene and imidazole, occupied a remarkable place among various heterocycles by virtue of their greater use in medicinal chemistry, drug discovery, structurally related to purine bases and is found in a variety of natural products, such as vitamin B12. Benzimidazole nucleus is termed "master key" as it is an important core in many bioactive compounds, key building block prevalently present of numerous compounds DNA intercalator [1], anticancer [2], cytotoxic, antitumor [3], Hv1 proton channel inhibitor [4], agonist neurotransmitter serotonin receptors, antiulcer [5], antifungal [6], analgesic and anti-amoebic [7]. At the same time, owing to the coordination ability of azoles, the benzimidazole chelating ligands have been extensively studied in the modelling biological systems [8]. In addition, these compounds have been used as organic ligands [9], liquid crystals [10], OLED's [11], chemo sensing [12] and in corrosion science [13]. Sundaraganesan et al. [14] have been investigated the vibrational spectra and DFT studies of benzimidazole. Miranda et al. [15] reported bis-(1*H*-Benzimidazol-2- yl)-methanone: new preparation method, crystal structure, and vibrational spectroscopy and DFT

calculations. Sudha et al. [16] investigated molecular structure, vibrational spectroscopic, first-order hyperpolarizability and HOMO, LUMO studies of 2-aminobenzimidazole. Most recently, Sundaraganesan et al. [17] carried out investigation of FT-IR, FT-Raman, dispersive Raman, NMR spectroscopic studies and NBO analysis of 2-Bromo-1*H*-Benzimidazol by density functional method. To our knowledge, crystal structural analysis, computational studies, MD simulations have no testimony till now. In this present study, we report synthesis, supra-molecular architecture of BMMBI along with detailed spectral investigation by FT-IR, FT-Raman and NMR, correlate these results with computational results and they shows good agreement. New molecular structures with great potential to be practically applied in the area of materials science, medicine, pharmacology are being proposed every day. An inexpensive and widely used tool for investigation of these structures is based on computational molecular modelling, mostly on DFT calculations and MD simulations. Thanks to these approaches various important reactive properties can be obtained for molecular structures that haven't been synthetized yet [18, 19]. Beside determination of molecule's "hot spots", the strength of molecular modelling lies in the fact that various spectra can be simulated with very high precision, if the proper levels of theory are used. This helps not only for characterization of compounds, but also to the structure confirmation of new and not synthetized molecules. In this particular work we have simulated IR and NMR spectral information in order to determine specificities of this newly synthetized molecule. Beside spectral investigation of the title molecule, in this work we have applied DFT calculations in order to determine global and local reactive properties [20]. Reactive properties predicted by this study were used in order to draw certain conclusions about the degradation properties of BMMBI molecule, because, as other pharmaceutical molecules, it could end up in various water resources [21]. Thanks to the fact that pharmaceutical molecules are highly stable and that natural conditions and conventional degradation pathways are not efficient enough for their removal, great attention of the scientific community is focused to the solving of this problem [21-23], especially by means of advanced oxidation processes [22, 24-28]. For these tasks computational molecular modelling turned out to be particularly useful [29-32].

## 2. Material and methods

### 2.1. General remarks

The reagents and solvents used for synthesis were of Analar grade and used without further purification. The synthesis was carried out under anaerobic condition (oxygen free inert atmosphere). $^{1}$H-NMR and $^{13}$C-NMR spectra were recorded on Bucker 400MHz

spectrometer operating at room temperature in DMSO-$d_6$ as solvent. The chemical shifts values (δ) are reported in parts per million (ppm) using TMS as an internal standard. FT-IR spectrum (Fig.S1-supporting material) was recorded in the range 4000-400 $cm^{-1}$ region with an ATR module ALPHA-T Bruker FT-IR spectrophotometer. FT-Raman spectrum (Fig.S2-supporting material) of the solid compound was recorded on a Bruker RFS 100/s (Germany) using 1064 nm line of Nd:YAG laser as excitation wavelength 1064nm in the region 4000-0 $cm^{-1}$.

**2.2. Synthesis of 5-bromo-7-methoxy-1-methyl-1H-benzoimidazole (BMMBI)**

Take a mixture of 4-bromo-6-methoxy-N1-methylbenzene-1,2-diamine (800 mg, 3.461 mmol), trimethylorthoformate (417.6 μL, 3.80 mmol) and para-toluene sulfonic acid (catalytic amount) in toluene (13 mL) and then the reaction mixture was refluxed for 2 hours at 105°C. Reaction was monitor by TLC. After, completion of reaction by TLC, the crude products purified by column chromatography to give 5-bromo-7-methoxy-1-methyl-1H-benzoimidazole as beige solid (amount 820 mg, yield 78.8%) [33]. (Scheme-1 supporting information-Fig.S3).

**2.3. X-ray crystallography**

A colourless, needle shaped single crystal of the title compound, with dimensions of 0.5 mm × 0.4 mm × 0.3 mm was selected and mounted on a Bruker APEX-II CCD diffractometer with monochromated MoKα radiation (λ = 0.71073 Å) at 273(2) K. The data was processed with SAINT and corrected for absorption using SADABS [34]. The crystal structure solved by direct method using the program SHELXL [35] and was refined by full-matrix least squares technique on $F^2$ using anisotropic displacement parameters for all non-hydrogen atoms.

**2.4. Computational details**

The optimized geometry of title compound have been obtained by performing DFT calculations at B3LYP/6-311++G(d,p) using Gaussian09 software [36] with X-ray crystallography Cartesian coordinates as the starting geometry without any structural constraints were applied. The optimized geometry parameters were used for calculation of vibrational wavenumbers, isotropic chemical shifts, electronic properties and surface/counter studies. The assignments of the calculated wavenumbers are assisted by the animation option of GAUSSVIEW program, which gives a visual presentation of the vibrational modes [37] and the potential energy distribution values were calculated with the help of GAR2PED software package [38].

Two main programs of the Schrödinger Materials Science Suite 2017-1 (SMSS), Jaguar 9.4 [39] and Desmond [40-43], have been used as well for DFT calculations and MD simulations, respectively. B3LYP exchange-correlation functional [44] with 6-311++G(d,p), 6-31+G(d,p), and 6-311G(d,p) basis sets for obtaining ALIE, Fukui functions and BDEs, have been used respectively. For MD simulation an OPLS 3 force field [40, 45-47] was used. MD parameters also include: simulation time set to 10 ns, temperature set to 300 K, pressure set to 1.0325 bar, and cut off radius set to 12 Å, within isothermal–isobaric (NPT) ensemble class. Solvent was treated by simple point charge (SPC) model [48] was used. For MD simulation one BMMBI molecule was placed into the cubic box with ~3000 water molecules. Noncovalent interactions have been detected also by Jaguar program, relying to the method of Johnson et al. [49, 50] Maestro GUI [51] was used in the cases of activities with Schrödinger Materials Science Suite 2017-1. In order to investigate the charge transfer due to the excitation, a Multiwfn [52-55] program was used. Electron density variation and $C_{+/-}$ functions were visualized with the VMD program [56-62]. A Tachyon [63] ray tracing library, as implemented in VMD, was used for the rendering of figures.

### 2.5. Hirshfeld surface and finger print surface analysis

Hirshfeld surfaces [64] and the allied 2D fingerprint plots [65] are unique for any crystal structure, which are proposed as an effective way to discern intermolecular interactions between molecules that are responsible for the molecular arrangement in the crystalline state and the nature of packing of molecules in their solid-state are calculated by using Crystal Explorer [66] and which accepts a structure input file in the CIF format. The Hirshfeld surface fingerprint plots were generated using two distances, $d_e$, the distance from the point to the nearest nucleus exterior to the surface, and $d_i$, the distance to the nearest nucleus interior to the surface. Graphical plots of the molecular Hirshfeld surfaces mapped with a fixed colour scheme red-white-blue, where red highlights shorter contacts which is denoted as $d_{norm}$ values with negative sign, white is used for contacts around the vdW separation represented as $d_{norm}$ equal to zero and blue is for longer contacts which is denoted as $d_{norm}$ values with positive sign.

## 3. Results and discussion

### 3.1. Crystal structural analysis

The title compound crystallizes in triclinic *P*-1 with $a$ = 7.147(5) Å, $b$ = 9.327(6) Å, $c$ =18.214(11) Å, V = 1147.4(13) Å$^3$ and Z = 4.The crystallographic data and structure refinement parameters are summarized in Table S1 (supporting material) and geometric parameters for hydrogen bonds and other intermolecular contacts (Å, º) operating in the

crystal structure of BMMBI in Table S2 (supporting material). The ORTEP diagram of the molecule is shown in Fig.S4 (supporting material). The compound crystallizes with two independent molecules (A and B) in the asymmetric unit in addition to the three water molecules. The benzimidazole rings of both the molecules A and B are planar, the root mean squared deviations of two rings being 0.008 Å in molecule A and 0.005 Å in B. The crystal structure analysis revealed that, in the crystal, the water molecules self assemble to form ribbons along (100) with alternating tetrameric and hexameric clusters (Fig.S5a-supporting material) of water molecules. The hexameric cluster comprises of three water molecules (O1, O2 and O3) linked by six O-H…O hydrogen bonds (Table S2), while the O1 and O2 water molecules form an additional tetrameric cluster, the two adjacent alternating clusters being fused with O1 and O2 water molecules common to both. Two A molecules of the compound are linked into the O3 water molecules of the hexameric cluster via O-H…N hydrogen bonds (Table S2), while two B molecules are linked into the O2 water molecules of the tetrameric cluster (Fig.S5b-supporting material). Thus, in the absence of any direct structure directing interactions between the molecules, the self assembly of water molecules which in turn links with the molecules A and B is very crucial in deciding the supra-molecular architecture (Fig.S5b). The A molecules are further interconnected via short Br…Br contacts (3.592(3) Å) along the crystallographic b axis forming a two dimensional architecture (Fig.S5c). Several $\pi_{aryl}\ldots\pi_{aryl}$ interactions are also observed in the crystal structure which give additional stability to the crystal structure (Fig.S5d, Table S2).

### 3.2. Geometrical parameters

The optimized geometrical parameters with XRD data are given in Table S3 (supporting material) and atom labelling is given in Fig.1**.** In the present case the experimental C-C bond lengths are in the range of 1.4104-1.3785 Å and the calculated C-C bond lengths are in the range of 1.4057-1.3727 Å and the literature data for similar derivatives are, 1.389-1.413 Å [14] and 1.391-1.416 Å [16]. For the title compound, the C-Br bond length is 1.9237 Å (DFT) and 1.9055 Å (XRD) which is in agreement with literature [67]. For the title compound, the bond length C21-N9 = 1.3081/1.3277 Å (DFT/XRD) shows double bond character, while, the bond lengths (DFT/XRD), C11-N9 = 1.3831/1.3866 Å, C10-N16 = 1.3855/1.3816 Å, C21-N16 = 1.3729/1.3397 Å, C1-N6 = 1.4567/1.4627 Å are less than the normal single C-N bond length of about 1.48 Å [68] and the corresponding reported values of C-N bond lengths of similar derivatives are, 1.3211 Å, 1.3855 Å, 1.3853 Å, 1.4071 Å, 1.4596 Å [68]. At C17 position, the bond angles (/DFTXRD) are C19-C17-C6 = 123.5/123.7°, C19-C17-Br5 =119.1/119.2° and C6-C17-Br5 = 117.3/117.1° and the asymmetry in angles is due

to the electronegative bromine atom. The influence of the methoxy group and methyl group are revealed from the bond angles (DFT/XRD) around C18 (C6-C18-C10 = 117.4/117.9°, C6-C18-O8 = 125.2/124.8°, C10-C18-O8 = (17.4/117.3°) and N16 (C1-N16-C10 = 128.4/128.3°, C1-N16-C21 = 126.1/125.2°, C10-N16-C21 = 105.6/106.5°). The interactions between the two rings is evident from the bond angles (DFT/XRD) at C10 and C11, which are respectively, C11-C10-C18 = 121.1/121.7°, C11-C10-N16 = 105.5/104.9°, C18-C10-N16 = 132.9/133.4° and N9-C11-C10 = 110.0/110.5°, N9-C11-C19 = 129.0/128.8°, C10-C11-C19 = 121.0/120.7°.

### 3.3 Hirshfeld surface analysis

The Hirshfeld surfaces of title compound (Fig.S6-supporting material) mapped over $d_{norm}$ range of (A), shape index (B) and curvedness (C) -0.678 to 1.611 Å, 1.0 to 1.0 Å and -4.0 to 0.4 Å. The information present in Table S2 is summarized effectively, the large deep red spots visible on the $d_{norm}$ mapped surfaces indicative of hydrogen bonding contacts and light red spot on the surface indicates weaker and longer contact other than hydrogen bonds. The title compound predominantly exhibits two strong intermolecular hydrogen bonds, one is N---H-O (which is denoted as a and b on $d_{norm}$) while another is O---H-O (which is denoted as c, d, e, f, g, h, i and j on $d_{norm}$ mapped surface), due to the self-assembly of water molecules and former one is H-atom of water link with the nitrogen of imidazole ring (Fig.S6). The appearance of two distinct spikes of almost equal lengths in the 2D fingerprint plots of title compound, which is due to the dominant imidazole/water molecule interactions. The O---H-O (10.8%) and N---H-O (8.4%) intermolecular interactions appear as two distinct spikes of almost equal lengths in the 2D fingerprint plots labelled as A and B, respectively. The H---O/ O---H interactions are represented by a spike in the lower left (donor) and upper right (acceptor) area of the fingerprint plot (mark as A), indicating that H-atom of water interacting with O-atom of water and as well as O-atom of water interacting with H-atom of water leads to the self-assembly of water molecules. The H---N/ N---H interactions are represented by a spike in the upper left (donor) and lower right (acceptor) area of the fingerprint plot (mark as B), indicating that H-atom of water interacting with N-atom of imidazole ring and as well as N-atom of imidazole ring interacting with H-atom of water (Fig.S7-supporting material). The wings marked with black circles in Fig.S7 represent the H···Br interactions and the sharpness of central spike marked with red circles in Fig.S7 is due to H···H contacts title compound. The relative contribution of the different interactions to the Hirshfeld surface was calculated for title compound. It is evident that the H---H contacts can account for about 48.9% of the Hirshfeld surface area; The remaining contribution was mostly due to H---O

10.8%, H---N 8.4%, H---Br 17.9%, C---C 4.2% and C---H 3.0% interactions, with only minor contribution from C---N, C---O, N---N and Br---Br (maximum 5.8%).

### 3.4. IR and Raman Spectra

The rings C10-C11-C19-C17-C6-C18 and N16-C21-N9-C11-C10 are designated as PhI and PhII in the following discussion and the vibrational assignments are presented in Table 1. In the present case, for the title compound, the phenyl CH stretching modes are assigned at 3078 $cm^{-1}$ in the Raman spectrum and at 3103, 3095 $cm^{-1}$ theoretically [69]. For the title compound, the phenyl ring C-C stretching modes are assigned at 1584, 1542, 1423, 1331, 1248 $cm^{-1}$ (IR), 1584, 1549, 1441, 1249 $cm^{-1}$ (Raman), in the range 1586-1251 $cm^{-1}$ (DFT) with PEDs in the range 62-42%. The PED analysis gives ring breathing mode of PhI at 1052 $cm^{-1}$ as expected [69,70] with a PED of 47% and low IR activity. According to literature [71], the ring breathing mode of a poly-substituted phenyl ring is assigned at 1025 $cm^{-1}$ in IR, 1027 $cm^{-1}$ in Raman and 1032 $cm^{-1}$ theoretically. The CH in-plane deformation modes of PhI are assigned at 1185, 1073 $cm^{-1}$ (IR), 1192, 1079 $cm^{1}$ (Raman) and the theoretical values are at 1190 $cm^{-1}$ and 1079 $cm^{-1}$ as expected [69]. The out-of-plane C-H modes are assigned at 830 $cm^{-1}$ and 783 $cm^{-1}$ (DFT) for PhI. According to literature, the C-O-C stretching modes are expected in the range 1200-850 $cm^{-1}$ [69] and for the title compound, the C-O-C vibrations are assigned at 1103 and 959 $cm^{-1}$ theoretically with PEDs 48 and 61%. Experimentally bands are observed at 955 $cm^{-1}$ in the IR spectrum and at 1107, 960 $cm^{-1}$ in the Raman spectrum. In the present case, the methyl $CH_3$ stretching modes are observed at 3050, 3002, 2954, 2925, 2895 $cm^{-1}$ in the IR spectrum, 3054, 3002, 2958, 2931, 2902 $cm^{-1}$ in the Raman spectrum and in the range 3016-2897 $cm^{-1}$ theoretically [69]. The methyl $CH_3$ deformation modes of the title compound are observed at 1456, 1437, 1423, 1408, 1372, 1163, 1125 $cm^{-1}$ (IR), 1444, 1410, 1360, 1027 $cm^{-1}$ (Raman) and in the range 1458-1025 $cm^{-1}$ theoretically [69]. The C-N stretching modes of the title compound are assigned at 1287, 1073 $cm^{-1}$ in IR spectrum, 1288, 1079, 1027 $cm^{-1}$ in Raman spectrum and at 1328, 1295, 1079, 1025 $cm^{-1}$ (DFT) which are in agreement with literature [69]. The C=N stretching mode is observed at 1475 $cm^{-1}$ in IR, 1475 $cm^{-1}$ in Raman and at 1468 $cm^{-1}$ theoretically [69]. The CN stretching modes have PEDs ranging from 35 to 55% with moderate IR intensities and Raman activities. Bromine compounds [69] absorb strongly in the region of 635 ± 85 $cm^{-1}$ due to C-Br stretching vibration and in the present case, band at 618 $cm^{-1}$ (IR), 620 $cm^{-1}$ (Raman) and 620 $cm^{-1}$ (DFT) is as assigned as this mode.

### 3.5. Frontier molecular orbital analysis

HOMO means the ability of the molecule to donate an electron and is directly related to ionization potential, while LUMO means the ability to accept an electron and is directly

related to electron affinity, the energy gap between FMO's calculated by DFT/B3LYP/6-311++G(d,p) method and the pictorial representation shown in Fig.S8 (supporting material). HOMO (MO 60) of π nature is delocalized the entire molecule and LUMO (MO 61) also π-nature, delocalized full molecule except methyl groups, bromine atom. The energy gap between HOMO and LUMO molecular orbitals plays very crucial role in determining properties such as chemical behaviour (reactivity, kinetic stability), spectroscopic properties (optical, electronic, vibrational), the theoretical reactivity indices defined by Par and Pearson [72] (ionization potential (I), electron affinity (A), chemical potential (μ), electronegativity (χ) global hardness (η), global softness (ν) and global electrophilicity index (ω)) and biological activity. The $E_{HOMO}$ and $E_{LUMO}$ energy value, their difference ($\Delta E$=$E_{HOMO}$-$E_{LUMO}$) along with the global reactivity indices are given in Table S4 (supporting material) and the results indicates that the chemical potential of the title compound is negative and it means that the compound is stable.

### 3.6. Molecular Electrostatic Potential

The molecular electrostatic potential (MEP) is an effective tool to predict physiochemical property relationship, study of biological recognition processes and hydrogen bonding interactions. The MEP surfaces of title compound are generated from optimized geometry by DFT/B3LYP/6-311++G(d,p) method and mapped a rainbow colour scheme with red (representing the electron rich region) while blue (represents electron poor region). The molecular electrostatic potentials are mapped over in the range between – 6.424 a.u. (deepest red) through 0 (white) to 6.424 a.u. (deepest blue) (Fig.S9-supporting material). From the MEP plot (Fig.S9), the negative region (red) localized over imidazole nitrogen (C=N) groups are possible sites for electrophilic attack and the positive region (blue) is covers all hydrogen atoms, as possible sites for nucleophilic attack. Also, the pictorial representation electrostatic potential mapped over the $d_{norm}$ surface of the neighbouring molecules shown in Fig.S10 (supporting material) neatly indicates that the electrode potential on the hydrogen bond donors and acceptors in the neighbouring molecules are complementary to one another (red spots close to H-bond acceptors and blue spots close to H-acceptors) thus providing further evidence to the formation O-H---O hydrogen bonds by self assemble of water molecules leads to formation of alternating tetrameric and hexameric clusters and N---H-O hydrogen bonds by interaction of water molecules with nitrogen atom of imidazole ring.

### 3.7. ALIE surfaces, Fukui functions and non-covalent interactions

In order to locate molecule's "hot spots" from the aspect of sensitivity towards electrophilic attacks, besides using the MEP surfaces, it is also possible to employ the concept of ALIE

surfaces, Fig.2. This descriptor is defined as a sum of orbital energies weighted by the orbital densities [73, 74]. The following equation is valid in the case of ALIE surfaces according to the following equation:

$$I(r)=\sum_i \frac{\rho_i(\vec{r})|\varepsilon_i|}{\rho(\vec{r})}, \quad (1)$$

$\rho_i(\vec{r})$ is electronic density of the i-th molecular orbital at the point $\vec{r}$, $\varepsilon_i$ is orbital energy, while $\rho(\vec{r})$ is total electronic density function[75, 76]. Representative ALIE surface is provided in Fig.2.

ALIE surface of the BMMBI molecule indicate three molecule hot spots possibly sensitive towards the act of electrophilic attacks. These molecule sites where electrons are least tightly bound can be seen in the near vicinities of bromine atom Br5 and nitrogen atom N9, characterized by the ALIE values of 190 kcal/mol. Fig.2 also indicates that only one intra-molecular noncovalent bond is formed, between the oxygen atom O8 and carbon atom C1, with corresponding strength of –0.008 electron/bohr$^3$. Further detection of molecule's hot spots has been performed by mapping of the Fukui functions to the electron density surface. In the case of Fukui functions in the finite difference approach, the following equations are valid:

$$f^+ = \frac{\left(\rho^{N+\delta}(r)-\rho^N(r)\right)}{\delta}, \quad (2)$$

$$f^- = \frac{\left(\rho^{N-\delta}(r)-\rho^N(r)\right)}{\delta}$$

where $N$ is number of electrons in reference state of the molecule, while $\delta$ is the fraction of electron which default value is set to be 0.01 [77]. In general, Fukui functions serve to track the changes of electron density as a consequence of charge addition or removal. If the charge is added then the locations where electron density increased (coloured by purple colour in Fig.3a), indicate electrophilic parts of the molecule, while the whole Fukui function is regarded as $f^+$ function. Similarly, if the charge is removed then the locations where electron density decreased (coloured by the red colour), indicate nucleuophilic parts of molecule, while the whole Fukui functions is regarded as $f^-$ function. Fukui functions mapped to the electron density surface in the case of BMMBI molecule are presented in Fig.3. According to the position of purple colour in the case of Fukui $f^+$ function represented in Fig.3a, it can be concluded that near vicinities of atoms C21 and H22 are of electrophilic character. This is in very good agreement with the results related to ALIE surface, according to which its adjacent

nitrogen atom has the lowest ALIE values. Thus, the five member ring of the BMMBI molecule could be sensitive towards electrophilic attacks. According to the Fig.3b, it can be seen that certain portions of red coloured surface are located around methyl groups, designating them as nucleophilic in case of the charge removal.

### 3.8. Nonlinear optical properties

Nonlinear optical (NLO) effect arise from the interactions of electromagnetic fields in various media to produce new fields altered in phase, frequency, amplitude or other propagation characteristics from the incident fields. NLO properties like the dipole moment, polarizability, first and second order hyperpolarizabilities are calculated using B3LYP/6-311++G(d) (5D, 7F). The total molecular dipole moment of the title compound is 5.8031 Debye, polarizability is $2.1686 \times 10^{-23}$ esu, and the first and second order hyperpolarizabilities are $1.5286 \times 10^{-30}$ and $-7.03 \times 10^{-37}$ esu. Here, the first hyperpolarizability of the title compound is 11.76 times that of the standard NLO material urea [77]. The larger component of second order hyperpolarizability is associated with the larger ground state polarization which leads to strong electronic coupling between the ground and the low lying excited state. The NLO properties are also related to the energy gap between HOMO and LUMO. The energy gap of the investigated compound is 4.332 eV which is lower than that of urea (6.7 eV) [77]. Therefore, the investigated molecule is considered good candidate for nonlinear optical applications.

### 3.9. Natural bonding orbital analysis

Natural bond orbital (NBO) calculations were performed using NBO 3.1 program [78] as executed in the Gaussian09 package at the DFT/B3LYP/6-311++G(d,p) method in order to understand various second-order interactions presented in Tables S5 and S6 (supporting material). The important inter-molecular hyper-conjugative interactions are: N9-C21 from N16 of n1(N16)→π*(N9-C21), C10-C11 from N16 of n1(N16)→π*( C10-C11) and C6-C18 from O8 of n2(O8)→π*( C6-C18), with electron densities, 0.34171, 0.47308, 0.38200 e and stabilization energies, 47.61, 32.84, 29.08 kJ/mol. Almost 100% p-character was observed in π-bonding orbitals of N9-C21 (99.82), C10-C11 (99.97), C6-C18 (99.95) and the lone pairs of n1N16(99.99) and n2O18(99.96).

### 3.10. Mulliken atomic charges

The calculation and analysis of Mulliken atomic charges plays crucial role in the application of quantum mechanical calculations to the molecular systems [79]. The Mulliken atomic charges of title compound calculated in gaseous phase by using DFT/B3LYP/6-311++G(d,p) basic set are given in Table S7(supporting material). From the Table S7, all

nitrogen atoms have negative charge and all hydrogen have positive charge. It is worthy to mention that the C21(0.389) atom shows positive sign, it is due to substitution highly electronegative atoms like nitrogen. In imidazole ring azonitrogen (C=N) shows more negative charge when comparative other nitrogen, it may suggest the formation of intermolecular hydrogen bond with water molecules in solid state.

### 3.12. $^{1}$H and $^{13}$C NMR chemical shift analysis

After performing geometry optimization of title compound (BMMBI), then SCF GIAO Magnetic shielding ($^{1}$H and $^{13}$C) calculations has been made by using DFT/B3LYP/6-311++G(d,p) method. The experimental $^{1}$H and $^{13}$C NMR spectra are given in Figs.S11 and S12 (supporting information).The experimental and calculated chemical shift values in ppm relative to TMS of title compound are given in Table S8 **(**supporting material**)**.The signals of the proton spectra were observed in two regions; the first one is around 6.92-8.08/6.55-7.62 and second is one around 3.93-3.97/3.82-3.83 experimental/theoretical chemical shift values (in ppm), respectively. The first group is due to the protons in the aromatic region (imidazole proton (H22) 7.41/7.30, benzene ring protons (H20, H7) 8.08/7.62, 6.92/6.55, the second group is due to methyl group on O (H13, H14, H15) and N(H2, H3, H4) 3.93/3.83 and 3.97/3.82 (experimental/theoretical), respectively. The experimentally and theoretically calculated chemical shift values of $^{13}$C-NMR for aromatic carbons were observed in the range 107.08-147.79/108.68-154.63. The experimentally/calculated chemical shift value of C18, C11 and C21 are also found significantly high due to the impact of electronegative oxygen atom and nitrogen atom, are observed at 147.79/153.03, 145.69/154.63 and 146.17/147.29 (experimental/theoretical), respectively. The upfield signal observed at 33.46 and 56.28 ppm and calculated at 34.75 and 55.14 ppm was assigned to methyl carbon on nitrogen and oxygen at C1 and C12. According to these results, the theoretical chemical shifts are in compliance with the experimental findings.

### 3.12. Reactive properties based on autoxidation and hydrolysis

Computational molecular modelling based on the DFT calculations and MD simulations is very important for the environmental studies [80-83], especially when it comes to the oxidation reactions, which are essential for the degradation and removal of the pharmaceutical pollutants from water resources [84-86]. In order to evaluate sensitivity of molecule towards the autoxidation mechanism, calculations of bond dissociation energies for hydrogen abstraction (H-BDE) could be particularly useful. Fig.4 contains bond dissociation energies for all single acyclic bonds of BMMBI molecule. According to the results in Fig.4, BMMBI molecule cannot be regarded as a molecule sensitive to autoxidation mechanism,

since there are no H-BDE values ranging from 70 to 85 kcal/mol [29, 87-89]. H-BDE values in the range between 85 and 90 kcal/mol [88] are also not present, thus it can be stated that BMMBI is highly stable in the open air or in the presence of oxygen. This also emphasizes the fact that its stability is high and that degradation of this molecule could be hardly initiated by natural conditions. On the other side, the lowest bond dissociation energy (~57 kcal/mol) was calculated for the bond denoted with number 8, indicating that degradation pathway could start by detachment of the methyl group. Stability of BMMBI molecule in water was also evaluated, by means of MD simulation and by calculation of radial distribution functions (RDF). RDF, g(*r*), are useful indicators of the probability for finding a particle in the distance *r* from another particle [90]. Significant RDFs of the BMMBI molecule's atoms have been presented in Fig.5. According to the distance of the maximal g(r) values, the most important atoms are oxygen atom O8 and nitrogen atom N9, located at around 2.7 Å. Also, RDFs of these atoms are characterized by two solvation spheres. The highest maximal g(r) values have been calculated for bromine Br5 and carbon atoms C1 and C12. However, distances of their maximal g(r) values are located at more than 3.5 Å. Nitrogen atom N16 also has significantly high maximal g(r) value, however, it is located at distance of more than 4.5 Å, indicating not so significant interactions with water molecules. In general, the lack of hydrogen atoms with significant RDFs indicates high stability of BMMBI molecule in water.

**3.13. Drug likeness**

In order to initially assess to what extent BMMBI molecule could be considered as orally active, we have calculated a set of parameters recommended by Lipinski, Table 2 [91, 92]. Firstly, it can be seen in Table 2 that AlogP parameter has very competitive value of 2.24. Perspective drug candidate molecules should have less than 5 and 10 HBD and HBA, respectively, which is definitely fulfilled by BMMBI molecule. The mass criterion under 500 is also fulfilled by far in the case of BMMBI. According to the work of Ghose et al. [93], molar refractivity should take values between 40 and 130, while number of atoms should be in the range between 20 and 70. These conditions also go in favour of BMMBI molecule. PSA shouldn't take values above 140 $Å^2$, which is easily accomplished by the BMMBI molecule, due to its size. Veber et al. [94] has also commented that a good oral bioavailability is reflected by less than 10 rotatable bonds, which is also true for BMMBI molecule. Along with Lipinski's rule of five, Congreeveet al. [95] introduced the "rule of three". By Congreeve's hardened criteria, logP value shouldn't take values above 3, molecule mass shouldn't take values above 300, while HBD, HBA and number of rotatable bonds must not take values above 3. Drug likeness parameters provided in Table 2 clearly indicate that

BMMBI molecule fulfils conditions of Congreeve's rule of three, thanks to which title molecule could be considered as lead compound for new drugs.

### 3.14. TDDFT calculations and UV spectra

In this work we have used TD-DFT calculations in order to simulate UV spectra and to investigate the charge transfer within the BMMBI molecule, arising from the lowest energy excitation. UV spectrum of the BMMBI molecule has been presented in Fig.S13 (supporting material), while information regarding the first ten excitations have been provided in Table S9 (supporting material). According to the results provided in Fig.S13 there is only one pronounced absorption peak located at wavelength of 196 nm. Results provided in Table S9 indicate that two most important excitations from the aspect of light absorption are excitations 6 and 7, with corresponding oscillator strengths of 0.9 and 0.3, respectively. Due to the size and structure of BMMBI molecule it can be concluded that the most important part of the molecule, with respect to UV absorption, is benzene ring, which is also confirmed by visualization of natural transition orbitals (NTO), Fig.S14 (supporting material). Results presented in Fig.S14 indicate that hole and particle of NTO 1 match to the frontier molecular orbitals, indicating that the lowest energy excitation is principally depending on the HOMO to LUMO transition. In order to further identify the nature of the lowest energy excitation we will refer to the analysis of *C* functions, Fig.S15 (supporting material), according to the procedure incorporated within the Multiwfn program. Classifications of the excitations can be done by measuring the distance between the barycenters of $C_+$ and $C_-$ functions, provided in Fig.S15. Green coloured surface in the Fig.S15 corresponds to the $C_+$ function, while blue coloured surface corresponds to the $C_-$ function. This distance is also called CT length and besides this quantity it is also useful to measure the $\Delta r$ parameter, whose value also indicates the type of the excitation. Appropriate definitions on CT length and $\Delta r$ parameter can be found can be found in papers [96, 97]. Visualization presented in Fig.S15 indicates that in the case of the first excitation of the BMMBI molecule, CT length has the value of 0.91 Å, while $\Delta r$ parameter has the value of just 0.673 Å. These results indicate that the first excitation is of the local excitation (LE) type, localized within benzene ring.

### 3.15. Molecular docking

PASS [98] is an online tool to predict the biological activity spectrum of a compound. PASS analysis of the compounds predicts the title ligands to be Antineurotic agents with $P_a$ score of 0.68. To further establish their Antineurotic activity, we decided to carry out molecular docking studies of the compound against human acetylcholinesterase [PDB ID: 5HF5]. The PDB structure 5HF5 [99] was selected for docking as the reported structure has

been established from X-ray Crystallographic data with a good resolution of 2.15 Å. Further the enzyme has an attached co-crystallized inhibitor so has a well defined binding site which could be targeted. All docking calculations were performed on AutoDock-Vina software [100]. The 3D crystal structure of PfDHFR-TS was obtained from Protein Data Bank. Before docking the ligands, the protein was prepared by removing co-crystallized waters, ligands and co-factors. The AutoDockTools graphical user interface was used to calculate Geisteger charges, add polar hydrogen and partial charges using Kollman united charges. The active site of the enzyme was defined to include residues of the active site within the grid size of 50 x 50 x 50 Å. The ligand was prepared for docking by minimizing its energy at B3LYP/6-311++G(d,p)(5D, 7F) level of theory. The most popular algorithm, Lamarckian Genetic Algorithm (LGA) available in Autodock was employed for docking. The docking protocol was tested by docking the co-crystallized inhibitor onto the enzyme catalytic site which showed perfect synergy with the co crystallised ligand with RMSD close to zero. Amongst the docked conformations the best scored conformation predicted by AutoDock scoring function was visualized in DSV, LigPlot and Pymol softwares for ligand–protein interactions. The molecule binds at the catalytic site of the substrate by weak non-covalent interactions (Fig.6). Amino acid SER125, ASP74, TYR337, GLY121, TRP86 and TYR124 are the main interacting residues. TRP86 forms H-bond with N atom of the title molecule (Fig.S16-supporting material). TYR124 forms a strong π-π interaction (Fig.S17-supporting material). Docking scores of -6.2 kcal/mol is predicted for the title compound. These results reveal that the ligands bind at the active site of the macromolecule and could restrict or block the functioning of Acetylcholinesterase, thereby acting as antineurotic agents.

## 4. Conclusion

A novel bezoimidazole derivative was synthesized and characterized by XRD, FT-IR, CT-Raman and NMR spectra and MD simulations and DFT calculations were used to predict stability and reactive properties. The predicted geometrical parameters were in good agreement with the experimental geometrical parameters. The theoretically predicted wavenumbers are in agreement with the experimentally observed wavenumbers. From the MEP plot the negative region localized over imidazole nitrogen groups are possible sites for electrophilic attack and the positive region is covers all hydrogen atoms, as possible sites for nucleophilic attack.The first hyperpolarisability of the title compound is 11.76 times that of the standard NLO material urea. ALIE surface and Fukui functions indicate that five member ring could be sensitive towards the electrophilic attacks. According to the distribution of ALIE values on electron density surface, near vicinity of bromine atom could also be

sensitive towards the electrophilic attacks. BMMBI molecule is highly stable, when it comes to the sensitivity towards the autoxidation mechanism, as all H-BDE values are much higher than 90 kcal/mol. MD simulations and RDFs of significant atoms indicate that title molecule is highly stable in water as well. Drug likeness parameters indicate that BMMBI molecule could be considered as one of the lead compounds for the development of new drugs. Study of the first excitation within the BMMBI molecule indicates that the charge transfer is of LE type. Molecular docking studies reveal that the ligands bind at the active site of the macromolecule and could restrict or block the functioning of Acetylcholinesterase, thereby acting as anti-neurotic agents.

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**Supplementary Material**

The cif file of the title compound have been assigned CCDC number 1478268 and can be obtained free of cost on application to CCDC 12 Union Road, Cambridge CB21 EZ, UK. (Fax: (+44) 1223 336-033: e-mail: data_request@ccdc.cam.ac.uk).

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**Figure captions**

Fig.1 Optimized geometry of 5-bromo-7-methoxy-1-methyl-1H-benzoimidazole

Fig.2 ALIE surface of the BMMBI molecule

Fig.3 Fukui functions a) $f^{+}$ and b) $f^{-}$ of the BMMBI molecule

Fig.4 Bond dissociation energies of all single acyclic bonds of BMMBI molecule

Fig.5 RDFs of atoms of BMMBI molecule with significant interactions with water molecules

Fig.6 Surface representation of the binding of title compound with 5hf5 shows that it binds at the active site

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**Table captions**

Table 1. Calculated scaled wave numbers, observed IR, Raman bands and assignments of 5-bromo-7-methoxy-1-methyl-1*H*-benzoimidazole(BMMBI).

Table 2 Drug likeness parameters of 5-bromo-7-methoxy-1-methyl-1H-benzoimidazole molecule

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Table 1

Vibrational assignments of title compound

| B3LYP/ B3LYP/6-311++G(d,p) | | | IR | Raman | Assignments[a] |
|---|---|---|---|---|---|
| υ($cm^{-1}$) | $IR_I$ | $R_A$ | υ($cm^{-1}$) | υ($cm^{-1}$) | - |
| 3103 | 2.22 | 50.65 | - | - | υCHI(99) |
| 3100 | 1.75 | 129.83 | 3103 | 3098 | υCH(99) |
| 3095 | 0.27 | 75.38 | - | 3078 | υCHI(99) |
| 3016 | 18.09 | 108.65 | 3050 | 3054 | $\upsilon CH_3$(90) |
| 3011 | 9.87 | 70.24 | - | - | $\upsilon CH_3$(99) |
| 2997 | 12.12 | 64.22 | 3002 | 3002 | $\upsilon CH_3$(99) |
| 2956 | 29.32 | 52.66 | 2954 | 2958 | $\upsilon CH_3$(100) |
| 2933 | 44.41 | 207.08 | 2925 | 2931 | $\upsilon CH_3$(99) |
| 2897 | 49.57 | 162.42 | 2895 | 2902 | $\upsilon CH_3$(99) |
| 1586 | 63.46 | 2.50 | 1584 | 1584 | υPhI(50), υCN(10) |
| 1546 | 120.87 | 44.12 | 1542 | 1549 | υPhI(62), δCH(14) |
| 1468 | 80.25 | 31.22 | 1475 | 1475 | υCN(52), δCH(17) |
| 1458 | 36.98 | 13.88 | 1456 | - | $\delta CH_3$(88) |
| 1450 | 16.98 | 10.46 | - | - | $\delta CH_3$(54), υPhI(11) |
| 1446 | 96.52 | 4.92 | - | 1444 | $\delta CH_3$(37), υPhI(42) |
| 1435 | 9.22 | 11.75 | 1437 | - | $\delta CH_3$(92) |
| 1424 | 11.00 | 12.17 | 1423 | - | $\delta CH_3$(100) |
| 1422 | 11.84 | 9.45 | 1423 | - | υPhI(50), $\delta CH_3$(19) |
| 1409 | 47.05 | 4.38 | 1408 | 1410 | $\delta CH_3$(68) |
| 1379 | 38.46 | 22.36 | 1372 | 1360 | $\delta CH_3$(48), υCN(16), υPhI(17) |
| 1333 | 17.05 | 43.16 | 1331 | - | υPhI(61), δCHI(10) |
| 1328 | 14.26 | 29.81 | - | - | υCN(55), δCHI(11), υPhI(10) |
| 1295 | 26.77 | 73.75 | 1287 | 1288 | υCN(35), υCN(11), υPhI(22) |
| 1251 | 146.71 | 10.72 | 1248 | 1249 | υCO(19), υCN(17), υPhI(49) |
| 1213 | 25.14 | 5.10 | 1213 | 1214 | δCH(35), υCO(11), δCHI(17), υCN(10) |
| 1190 | 12.13 | 3.10 | 1185 | 1192 | δCHI(45), δCH(14), υCN(10) |
| 1162 | 4.02 | 3.36 | 1163 | - | $\delta CH_3$(75) |
| 1124 | 0.85 | 2.34 | 1125 | - | $\delta CH_3$(94) |

| | | | | | |
|---|---|---|---|---|---|
| 1103 | 164.11 | 2.59 | - | 1107 | υCO(48), υCN(18) |
| 1102 | 0.11 | 0.79 | - | - | $\delta CH_3$(96) |
| 1079 | 9.15 | 7.45 | 1073 | 1079 | υCN(42), δCHI(38) |
| 1052 | 0.74 | 22.05 | - | - | υPhI(47), δCHI(16) |
| 1025 | 16.29 | 3.19 | - | 1027 | $\delta CH_3$(40), υCN(35) |
| 959 | 8.02 | 1.92 | 955 | 960 | υCO(61), υCN(10) |
| 836 | 38.31 | 7.16 | 833 | 838 | δPhI(47), δPhII(18) |
| 830 | 20.22 | 0.47 | - | - | γCHI(63), γCH(18), τPhI(10) |
| 820 | 0.55 | 0.26 | - | 818 | γCH(65), γCHI(18), τPhII(12) |
| 783 | 28.57 | 0.47 | 781 | 782 | γCHI(69), τPhI(14), γCO(10) |
| 756 | 73.31 | 0.39 | 753 | 750 | υCBr(11), δPhII(30), δPhI(10) |
| 731 | 1.26 | 0.04 | 735 | - | τPhI(43), τPhII(33), γCO(11) |
| 689 | 3.60 | 12.88 | 690 | 687 | δCO(26), δPhII(39) |
| 621 | 4.04 | 8.04 | 625 | - | δPhII(36), δCO(10), δPhI(18) |
| 620 | 10.39 | 0.59 | 618 | 620 | τPhII(23), τPhI(10) υCBr(39) |
| 561 | 0.10 | 0.16 | - | 565 | τPhII(20), τPhI(42) |
| 547 | 8.52 | 0.58 | - | 538 | τPhI(36), γCO(25), γCBr(20), τPhII(11) |
| 502 | 3.61 | 1.98 | - | 505 | δPhI(50), δCN(13) |
| 495 | 3.64 | 1.13 | - | - | δPhI(48), δCO(15) |
| 366 | 0.21 | 8.03 | - | 362 | δCO(36), δCN(22) |
| 330 | 0.30 | 0.14 | - | 331 | τPhII(39), τPhI(24), γCBr(11), γCN(10) |
| 322 | 0.72 | 0.10 | - | - | δCN(30), δCO(34), δCBr(15) |
| 255 | 0.28 | 0.03 | - | 252 | τCO(59), τPhI(18), γCBr(10) |
| 237 | 1.53 | 8.35 | - | - | δPhI(37), δCN(11) |
| 223 | 0.01 | 0.07 | - | - | τPhII(28), τPhI(30), γCN(14), τCO(16) |
| 196 | 0.02 | 1.80 | - | 202 | τCO(27), τPhI(39), γCN(18) |
| 179 | 3.33 | 0.10 | - | - | δCO(24), δCBr(15), δCN(15), δPhI(10) |
| 146 | 1.86 | 1.12 | - | 152 | γCBr(23), γCN(13), $\tau CH_3$(12), τCO(12) |
| 141 | 0.96 | 1.37 | - | 139 | δCBr(56), δCO(32) |

| | | | | | |
|---|---|---|---|---|---|
| 89 | 0.99 | 0.07 | - | - | $\tau CH_3(51)$, $\tau PhII(10)$, $\gamma CN(10)$ |
| 82 | 3.83 | 0.45 | - | - | $\tau CO(70)$, $\tau CH_3(12)$, $\gamma CN(10)$ |
| 59 | 1.06 | 0.87 | - | - | $\gamma CN(39)$, $\tau CH_3(21)$, $\tau PhI(18)$, $\tau CO(10)$ |

[a]υ-stretching; δ-in-plane deformation; γ-out-of-plane deformation; τ-torsion; PhI-C10-C11-C19-C17-C6-C18; PhII-N16-C21-N9-C11-C10.

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Table 2

Table 2 Drug likeness parameters of 5-bromo-7-methoxy-1-methyl-1H-benzoimidazole molecule

| Descriptor | Value |
|---|---|
| Hydrogen Bond Donor (HBD) | 0 |
| Hydrogen Bond Acceptor (HBA) | 2 |
| Mass | 241.09 |
| AlogP | 2.24 |
| Polar surface area (PSA) [Å$^2$] | 27.05 |
| Molar refractivity | 52.77 |
| Number of atoms | 22 |
| Number of rotatable bonds | 1 |

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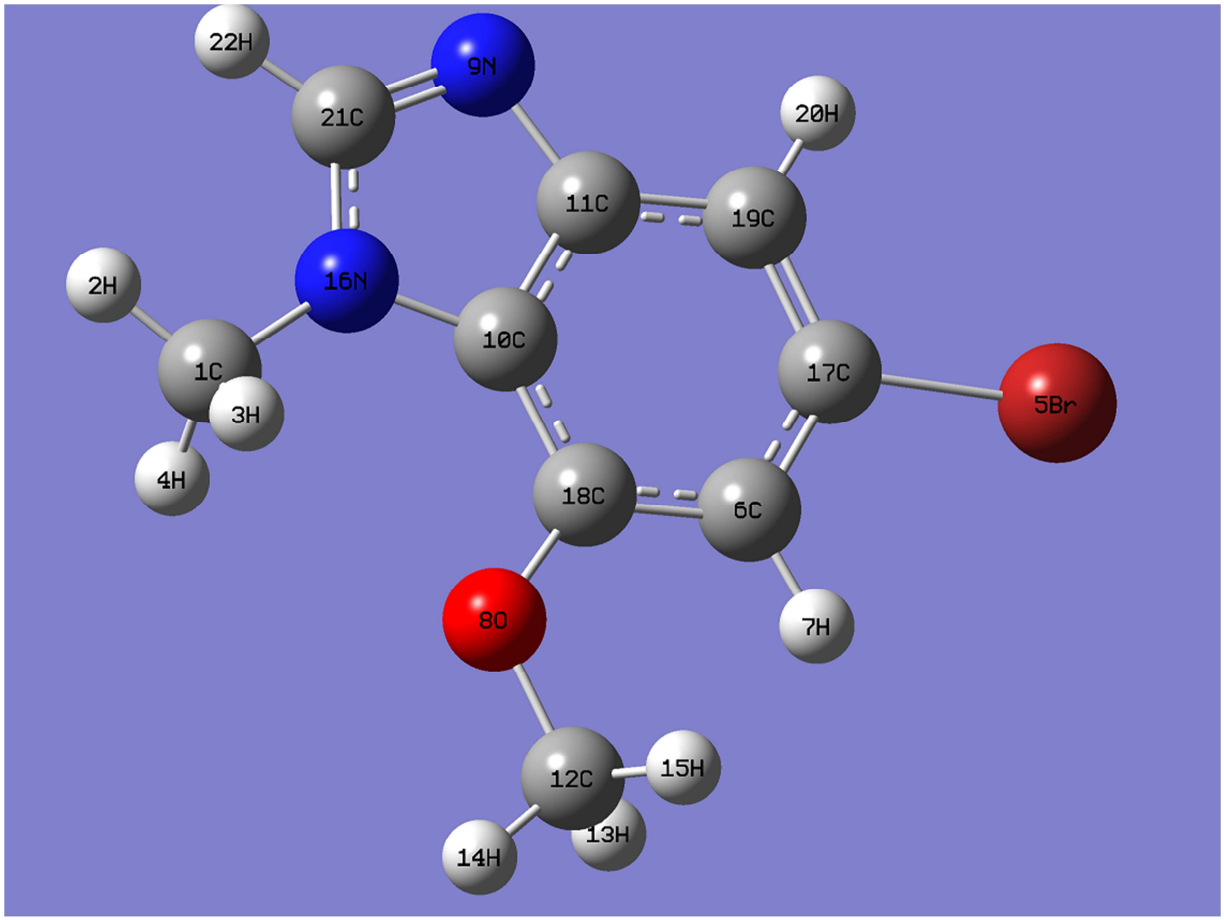



**Fig.1 Optimized geometry of 5-bromo-7-methoxy-1-methyl-1H-benzoimidazole**

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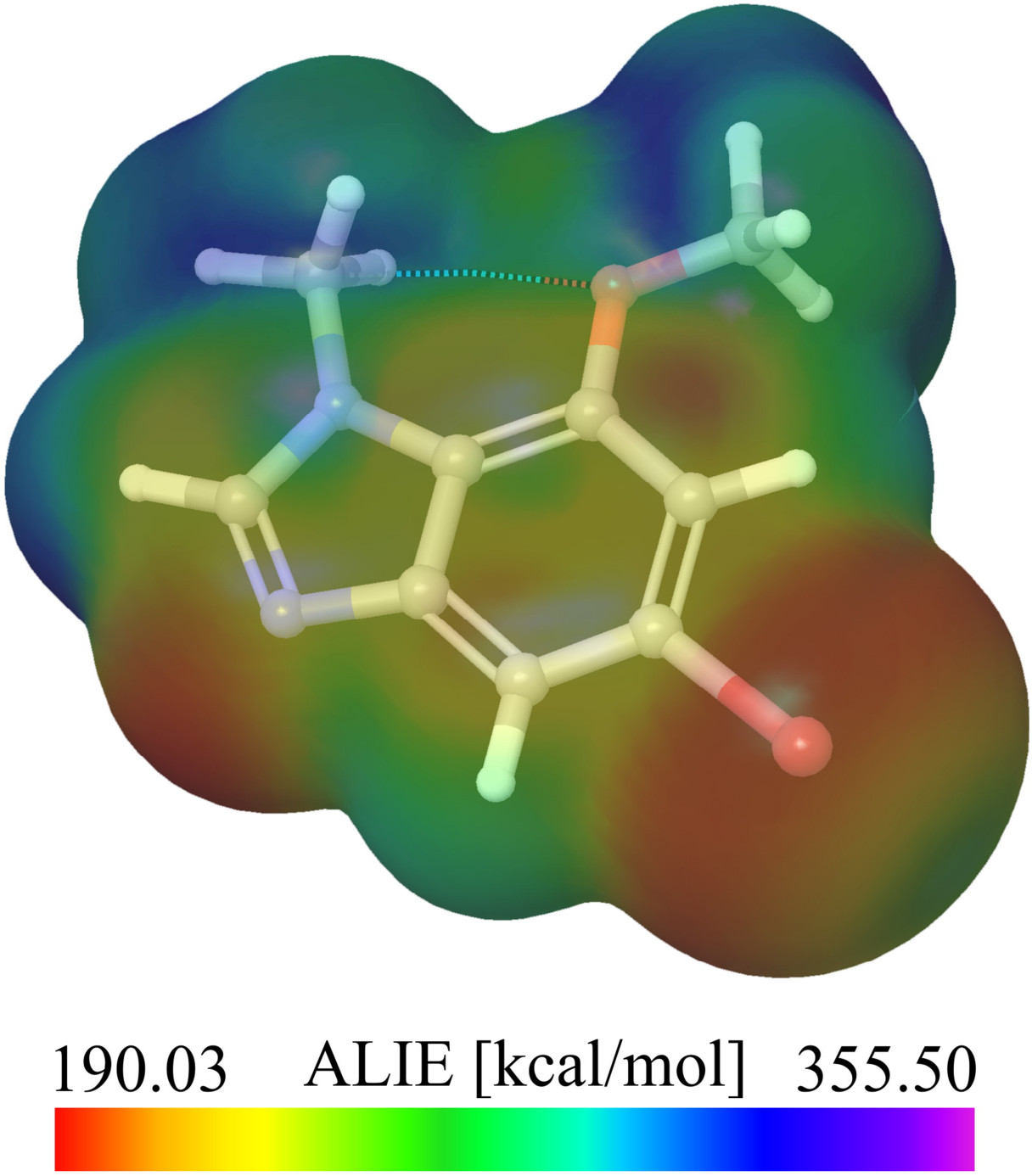



**Fig.2 ALIE surface of the BMMBI molecule**

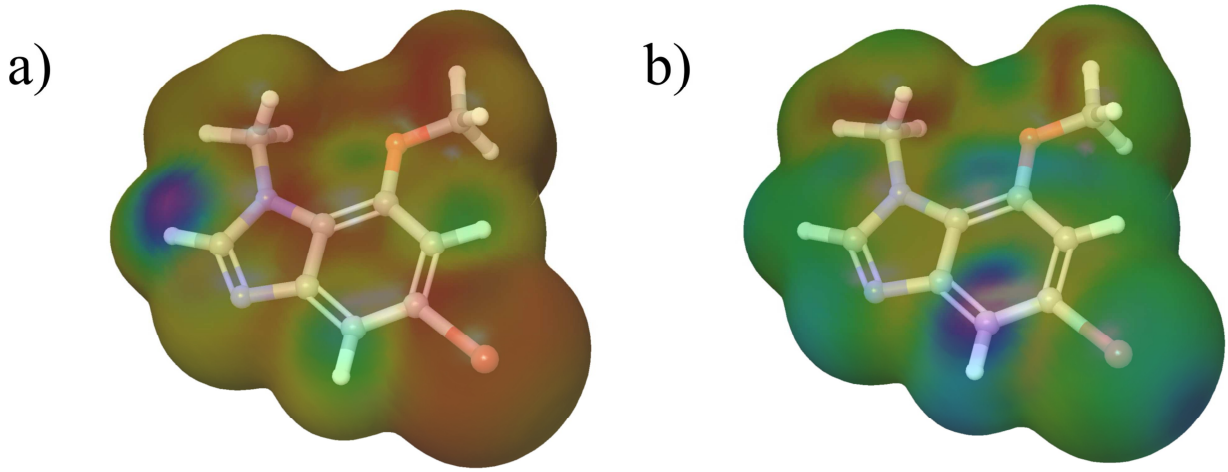
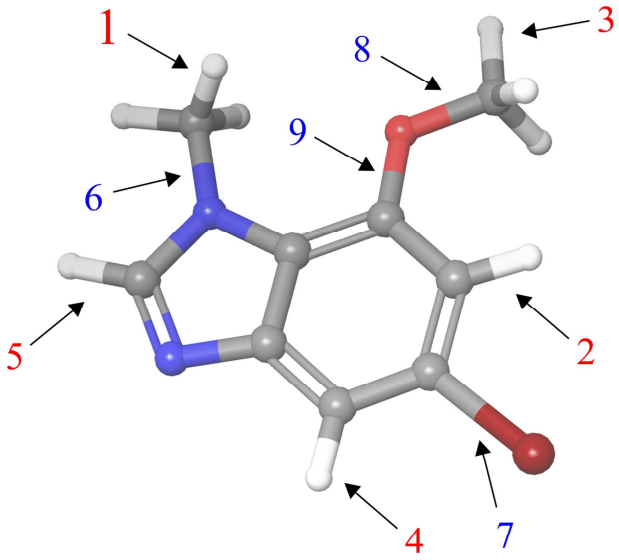



**Fig.3 Fukui functions a) $f^+$ and b) $f^-$ of the BMMBI molecule**

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| Bond | BDE [kcal/mol] |
|---|---|
| 1 | 99.23 |
| 2 | 118.38 |
| 3 | 102.85 |
| 4 | 120.81 |
| 5 | 120.20 |
| 6 | 81.18 |
| 7 | 72.40 |
| 8 | 56.74 |
| 9 | 97.41 |

**Fig.4 Bond dissociation energies of all single acyclic bonds of BMMBI molecule**

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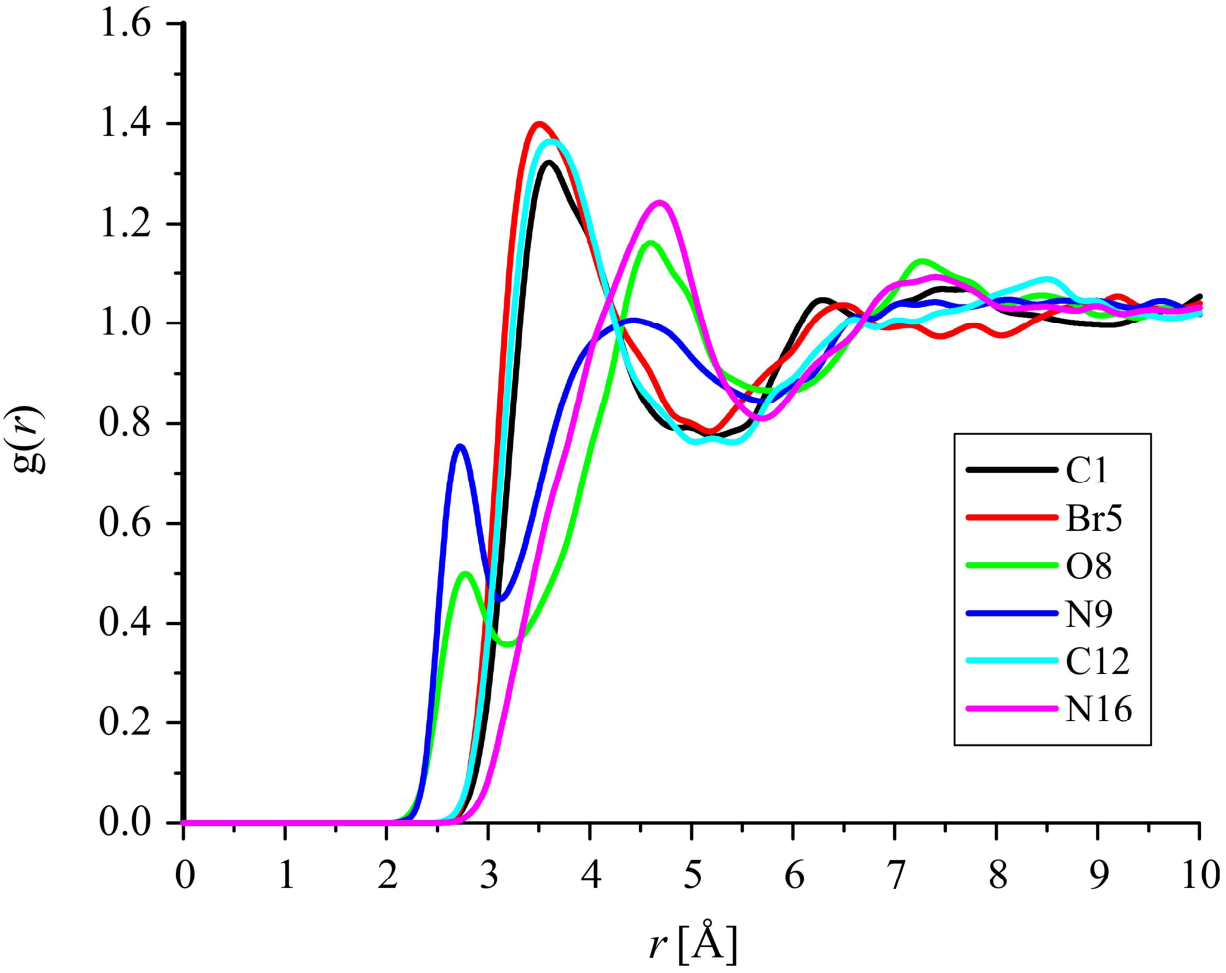



**Fig.5 RDFs of atoms of BMMBI molecule with significant interactions with water molecules**

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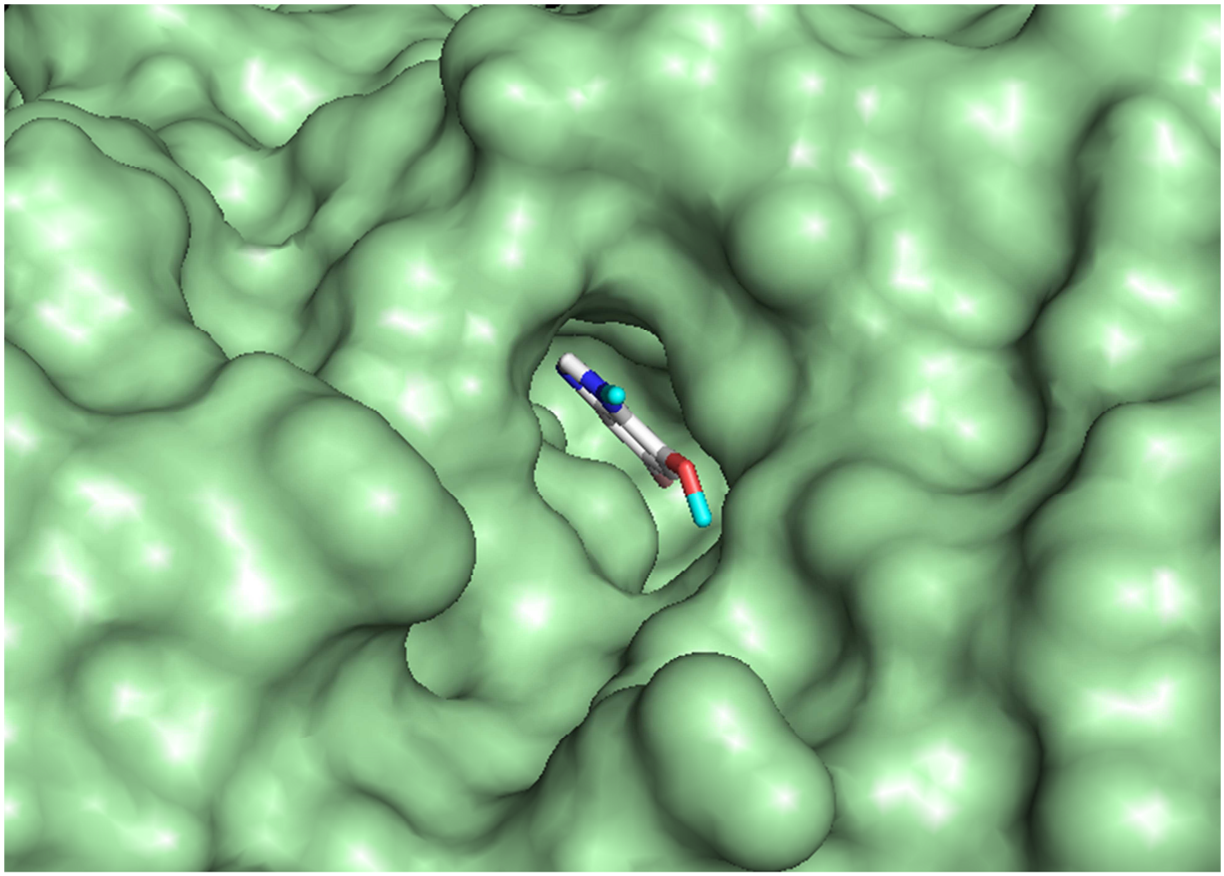


**Fig.6 Surface representation of the binding of title compound with 5hf5 shows that it binds at the active site**

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Highlights

- A novel benzoimidazole derivate is synthesized and characterized by XRD
- The FT-IR and FT-Raman spectra were interpreted
- Local reactivity properties are investigated
- Possible degradation properties are predicted
- Molecular docking study is also done

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IUCrData

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# 3,5-Dibromo-6-methylpyridin-2-amine

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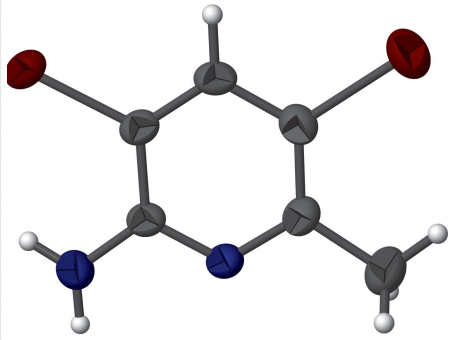
**Keywords:** crystal structure; halogenated compounds; N—H···N hydrogen bonds; $R_2^2(8)$ dimers.

**CCDC reference**: 1532242

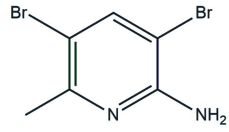
**Structural data**: full structural data are available from iucrdata.iucr.org

The title molecule, $C_6H_6Br_2N_2$, is almost planar (r.m.s. deviation for the non-H atoms = 0.012 Å). In the crystal, inversion dimers linked by pairs of N—H···N hydrogen bonds generate $R_2^2(8)$ loops.

**3D view**



**Chemical scheme**




## Structure description

Halogenated organic compounds are known to exhibit diverse biological activities showing anticancer (Nussbaumer *et al.*, 2011), antiviral (De Clercq, 2013), anti-tuberculosis (Beena & Rawat, 2013), anti-malarial (Biamonte *et al.*, 2013), antifungal and anti-diabetic (Hector, 2005) properties. As part of our studies in this area, the crystal structure of the commercially available title compound was determined.

The molecule is almost planar (Fig. 1) with the r.m.s. deviation for the non-H atoms being 0.012 Å. An intramolecular N—H···Br interaction occurs. In the crystal, inversion dimers linked by pairs of N2—H2···N1 hydrogen bonds generate $R_2^2(8)$ loops (Fig. 2, Table 1). The crystal structure does not feature any other interactions, and thus, the supramolecular architecture displayed is zero dimensional.

## Synthesis and crystallization

The title compound was purchased from Avra Synthesis Pvt. Ltd, India, and was used as such. Colourless blocks were grown by recrystallization from methanol solution at room temperature.

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**Table 1**
Hydrogen-bond geometry (Å, °).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N2—H1···Br1 | 0.87 (5) | 2.68 (5) | 3.128 (4) | 114 (4) |
| N2—H2···N1$^{i}$ | 0.88 (4) | 2.19 (4) | 3.070 (6) | 173 (3) |

Symmetry code: (i) $-x+1, -y+1, -z+1$.

## Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

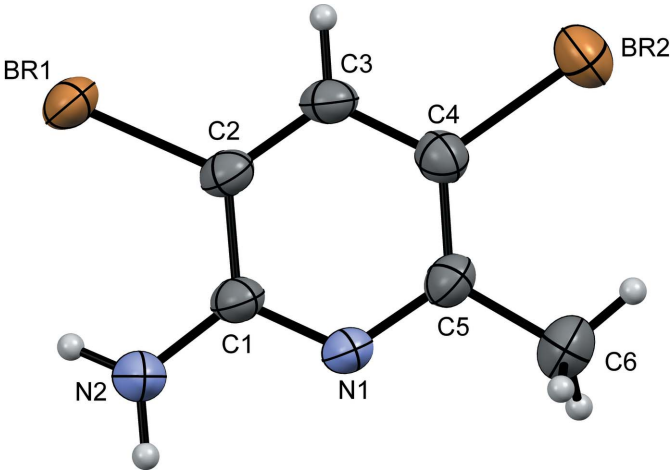



**Figure 1**
A view of the molecular structure of the title compound, showing displacement ellipsoids drawn at the 50% probability level.

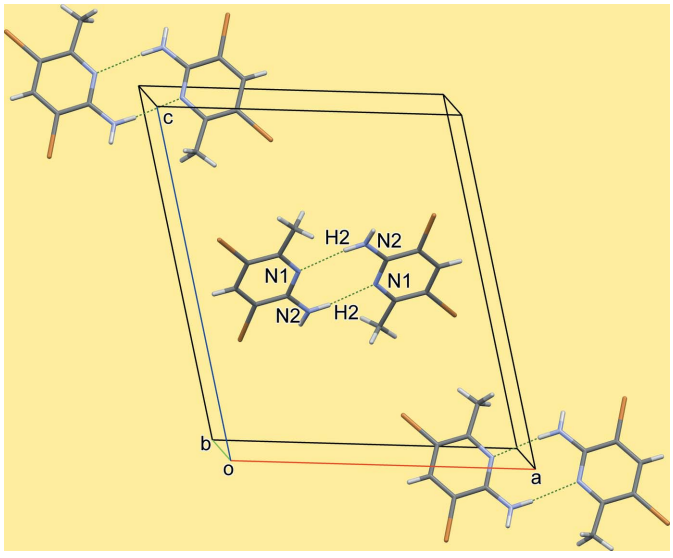



**Figure 2**
Crystal packing of the title compound, displaying N—H···N hydrogen-bonded $R_2^2(8)$ loops.

**Table 2**
Experimental details.

| | |
|---|---|
| Crystal data | |
| Chemical formula | $C_6H_6Br_2N_2$ |
| $M_r$ | 265.95 |
| Crystal system, space group | Monoclinic, $P2_1/n$ |
| Temperature (K) | 296 |
| $a, b, c$ (Å) | 13.1047 (16), 4.0310 (4), 15.7631 (18) |
| $\beta$ (°) | 105.720 (4) |
| $V$ (Å$^3$) | 801.54 (16) |
| $Z$ | 4 |
| Radiation type | Mo $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 10.04 |
| Crystal size (mm) | 0.26 × 0.22 × 0.20 |
| | |
| Data collection | |
| Diffractometer | Bruker APEXII CCD |
| Absorption correction | Multi-scan (*SADABS*; Bruker, 2009) |
| $T_{min}$, $T_{max}$ | 0.085, 0.134 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 10577, 1670, 1461 |
| $R_{int}$ | 0.050 |
| (sin $\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.631 |
| | |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.038, 0.108, 1.09 |
| No. of reflections | 1670 |
| No. of parameters | 101 |
| No. of restraints | 2 |
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 1.03, −0.86 |

Computer programs: *APEX2*, *SAINT-Plus* and *XPREP* (Bruker, 2009), *SHELXT2016* (Sheldrick, 2015a), *SHELXL2016* (Sheldrick, 2015b) and *Mercury* (Macrae *et al.*, 2008).

## Acknowledgements

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# full crystallographic data

*IUCrData* (2017). **2**, x170728 [https://doi.org/10.1107/S2414314617007283]

## 3,5-Dibromo-6-methylpyridin-2-amine

**P. Krishna Murthy, R. Sreenivasa Rao, V. Suneetha, L. Giri and P. A. Suchetan**

### 3,5-Dibromo-6-methylpyridin-2-amine

*Crystal data*

$C_6H_6Br_2N_2$
$M_r$ = 265.95
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
$a$ = 13.1047 (16) Å
$b$ = 4.0310 (4) Å
$c$ = 15.7631 (18) Å
$\beta$ = 105.720 (4)°
$V$ = 801.54 (16) Å$^3$
$Z$ = 4
$F(000)$ = 504
Prism
$D_x$ = 2.204 Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 133 reflections
$\theta$ = 2.4–26.7°
$\mu$ = 10.04 mm$^{-1}$
$T$ = 296 K
Block, colourless
0.26 × 0.22 × 0.20 mm

*Data collection*

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
phi and $\varphi$ scans
Absorption correction: multi-scan (SADABS; Bruker, 2009)
$T_{min}$ = 0.085, $T_{max}$ = 0.134
10577 measured reflections
1670 independent reflections
1461 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.050
$\theta_{max}$ = 26.7°, $\theta_{min}$ = 2.4°
$h$ = −16→16
$k$ = −5→4
$l$ = −19→19

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.108
$S$ = 1.09
1670 reflections
101 parameters
2 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0701P)^2 + 0.463P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 1.03 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.86 e Å$^{-3}$
Extinction correction: SHELXL2016 (Sheldrick, 2015b), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.064 (4)

*Special details*

**Geometry**. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| C1 | 0.3237 (3) | 0.5000 (10) | 0.4445 (2) | 0.0352 (8) |
| C2 | 0.2125 (3) | 0.5194 (10) | 0.4153 (2) | 0.0343 (8) |
| C3 | 0.1522 (3) | 0.3994 (10) | 0.4668 (2) | 0.0360 (8) |
| H3 | 0.078637 | 0.410750 | 0.448303 | 0.043* |
| C4 | 0.2038 (3) | 0.2597 (9) | 0.5477 (3) | 0.0366 (9) |
| C5 | 0.3126 (3) | 0.2404 (10) | 0.5746 (3) | 0.0377 (9) |
| C6 | 0.3748 (4) | 0.0910 (15) | 0.6593 (3) | 0.0566 (12) |
| H6A | 0.417884 | −0.086130 | 0.647437 | 0.085* |
| H6B | 0.327119 | 0.005584 | 0.690749 | 0.085* |
| H6C | 0.419361 | 0.257416 | 0.694366 | 0.085* |
| N1 | 0.3710 (3) | 0.3633 (9) | 0.5226 (2) | 0.0385 (8) |
| N2 | 0.3883 (3) | 0.6093 (13) | 0.3955 (3) | 0.0517 (10) |
| BR1 | 0.14692 (3) | 0.70991 (12) | 0.30385 (3) | 0.0436 (2) |
| BR2 | 0.11914 (4) | 0.10117 (13) | 0.61976 (3) | 0.0544 (3) |
| H1 | 0.359 (4) | 0.736 (12) | 0.351 (3) | 0.056 (16)* |
| H2 | 0.458 (3) | 0.609 (15) | 0.415 (3) | 0.063 (16)* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| C1 | 0.026 (2) | 0.046 (2) | 0.0313 (18) | −0.0019 (16) | 0.0032 (15) | −0.0038 (16) |
| C2 | 0.029 (2) | 0.040 (2) | 0.0304 (18) | 0.0003 (16) | 0.0019 (15) | −0.0044 (15) |
| C3 | 0.0243 (19) | 0.044 (2) | 0.038 (2) | −0.0019 (15) | 0.0046 (16) | −0.0047 (17) |
| C4 | 0.037 (2) | 0.040 (2) | 0.035 (2) | −0.0040 (16) | 0.0123 (17) | −0.0031 (15) |
| C5 | 0.036 (2) | 0.045 (2) | 0.0288 (19) | 0.0000 (16) | 0.0029 (16) | −0.0006 (15) |
| C6 | 0.052 (3) | 0.074 (3) | 0.040 (2) | −0.001 (2) | 0.004 (2) | 0.011 (2) |
| N1 | 0.0260 (17) | 0.056 (2) | 0.0308 (16) | −0.0020 (15) | 0.0031 (13) | 0.0018 (15) |
| N2 | 0.032 (2) | 0.085 (3) | 0.037 (2) | −0.0064 (19) | 0.0073 (17) | 0.0091 (19) |
| BR1 | 0.0351 (3) | 0.0561 (3) | 0.0337 (3) | 0.00406 (17) | −0.00072 (19) | 0.00301 (17) |
| BR2 | 0.0524 (4) | 0.0647 (4) | 0.0525 (3) | −0.0082 (2) | 0.0248 (2) | 0.0056 (2) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| C1—N1 | 1.338 (5) | C4—BR2 | 1.900 (4) |
| C1—N2 | 1.364 (5) | C5—N1 | 1.358 (5) |
| C1—C2 | 1.407 (5) | C5—C6 | 1.491 (6) |
| C2—C3 | 1.366 (6) | C6—H6A | 0.9600 |
| C2—BR1 | 1.896 (4) | C6—H6B | 0.9600 |
| C3—C4 | 1.390 (6) | C6—H6C | 0.9600 |
| C3—H3 | 0.9300 | N2—H1 | 0.87 (3) |
| C4—C5 | 1.375 (6) | N2—H2 | 0.88 (3) |
| | | | |
| N1—C1—N2 | 116.7 (4) | N1—C5—C6 | 115.3 (4) |
| N1—C1—C2 | 120.3 (3) | C4—C5—C6 | 124.6 (4) |
| N2—C1—C2 | 123.0 (4) | C5—C6—H6A | 109.5 |

| | | | |
|---|---|---|---|
| C3—C2—C1 | 120.1 (3) | C5—C6—H6B | 109.5 |
| C3—C2—BR1 | 120.3 (3) | H6A—C6—H6B | 109.5 |
| C1—C2—BR1 | 119.7 (3) | C5—C6—H6C | 109.5 |
| C2—C3—C4 | 118.2 (4) | H6A—C6—H6C | 109.5 |
| C2—C3—H3 | 120.9 | H6B—C6—H6C | 109.5 |
| C4—C3—H3 | 120.9 | C1—N1—C5 | 120.6 (3) |
| C5—C4—C3 | 120.7 (4) | C1—N2—H1 | 117 (4) |
| C5—C4—BR2 | 121.5 (3) | C1—N2—H2 | 123 (4) |
| C3—C4—BR2 | 117.8 (3) | H1—N2—H2 | 118 (5) |
| N1—C5—C4 | 120.1 (4) | | |

| | | | |
|---|---|---|---|
| N1—C1—C2—C3 | 0.2 (6) | C3—C4—C5—N1 | 1.1 (6) |
| N2—C1—C2—C3 | 178.7 (4) | BR2—C4—C5—N1 | −178.4 (3) |
| N1—C1—C2—BR1 | −179.4 (3) | C3—C4—C5—C6 | −179.1 (4) |
| N2—C1—C2—BR1 | −0.8 (6) | BR2—C4—C5—C6 | 1.4 (6) |
| C1—C2—C3—C4 | 0.0 (6) | N2—C1—N1—C5 | −178.3 (4) |
| BR1—C2—C3—C4 | 179.5 (3) | C2—C1—N1—C5 | 0.3 (6) |
| C2—C3—C4—C5 | −0.6 (6) | C4—C5—N1—C1 | −0.9 (6) |
| C2—C3—C4—BR2 | 178.9 (3) | C6—C5—N1—C1 | 179.3 (4) |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N2—H1···Br1 | 0.87 (5) | 2.68 (5) | 3.128 (4) | 114 (4) |
| N2—H2···N1$^{i}$ | 0.88 (4) | 2.19 (4) | 3.070 (6) | 173 (3) |

Symmetry code: (i) −*x*+1, −*y*+1, −*z*+1.

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# Synthesis, Crystal structure, Hirshfeld surface studies and frontier orbitals analysis of 4-(1-benzofuran-2-yl)-2-methyl-6-phenylpyrimidine

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**Abstract**

*4-(benzofuran-2-yl)-2-methyl-6-phenylpyrimidine(BFMPP) has been synthesized and characterized by FT-IR, $^{1}H$ &$^{13}CNMR$ and Mass spectrometry techniques. Single crystals of title compound were grown by slow evaporation solution growth technique at room temperature and crystal structure has been determined by single crystal X-ray diffraction technique. The title compound(BFMPP) crystallizes in monoclinic space group $P2_1$, with cell dimensions a = 4.803(3) Å, b = 9.498(5) Å, c = 15.557(9) Å, β= 93.25 (4)$^{o}$ and Z = 2. The crystal structure is stabilized by weak C-H…N intermolecular interactions generating a one dimensional C(4) network propagating along the [100] direction and two pi…pi interactions. Further, a detailed analysis of the Hirshfeld surfaces facilitating an understanding of the type and nature of intermolecular interactions in the supramolecular structure is made. The calculated HOMO-LUMO energy gap discloses that charge transfer occurs within the molecule.*

**Keywords:** BFMPP, Crystal structure, X-ray diffraction, Hirshfeld analysis, HOMO-LUMO plots.

**Specifications Table**

| | |
|---|---|
| Subject area | *X-ray crystallography* |
| Compounds | *4-(benzofuran-2-yl)-2-methyl-6-phenylpyrimidine* |
| Data category | *Crystallographic data* |
| Data acquisition format | *CIF for crystallography* |
| Data type | *Analyzed* |
| Procedure | *The unit cell parameters and the intensity data at 298K for the title compound was obtained on an Oxford Diffraction Xcalibur Gemini single crystal X-ray diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The CrysAlisPro software was used for data collection, reduction and absorption correction.* |
| Data accessibility | *CCDC:1411045 URL:https://www.ccdc.cam.ac.uk/conts/retrieving.html* |

## 1. Rationale

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Heterocycles hold a key point in organic and medicinal chemistry as they act as a bridge between life sciences and biochemical investigations. A significant amount of contemporary investigation is being currently pursued on these compounds worldwide. The pyrimidine rings are nitrogen rich heterocycles, key constituent of many natural, synthetic compounds and shows very interesting pharmacological activity [1-4]. In recent years, pyrimidine derivatives have received significant attention owing to their diverse biological properties, particularly as cytostatic [5-8], immune modulating [9], antitubercular, calcium channel blockers [10], antimicrobial properties [11], herbicides [12] and pesticides [13].

The biological importance of pyrimidine derivatives has motivated significant interest towards the synthesis of 4-(benzofuran-2-yl)-2-methyl-6-phenylpyrimidine(BFMPP) and the structure was characterized well as it would be more useful. Further, various intermolecular interactions are well supported by Hirshfeld surface and fingerprint plots analysis.

## 2. Experimental

### 2.1. General remarks

The reagents and solvents used for synthesis were procured from Spectrochem, Sigma Aldrich and used as such received. Reactions were monitor by analytical thin layer chromatography (TLC) and TLC plates were visualized by exposing UV light, KMnO4 solution or by iodine vapors. The FT-IR spectrum was recorded in KBr pellets using JASCO FTIR-4100 spectrometer in the range of 4000 – 400 $cm^{-1}$ at resolution of ± 2 $cm^{-1}$.$^{1}$H &$^{13}$C-NMR spectrum was recorded on JEOL-400 MHz NMR instrument using $CDCl_3$ as solvent. The chemical shifts values (δ) are reported in parts per million (ppm) using TMS as an internal standard. Mass spectrum was recorded on Shimadzu-2010EV with APCI and ESI probes.

### 2.2. Synthesis of 4-(1-benzofuran-2-yl)-2-methyl-6-phenylpyrimidine

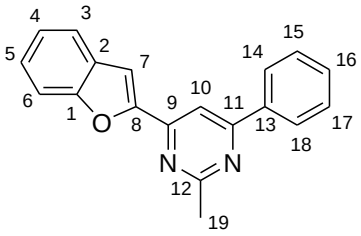
To a stirred solution of (1-benzofuran-2-yl)-3-phenylprop-2-en-1-one (0.5g, 2.06mmol) in mixture of ethanol: water (4:1, 5 mL), acetamidine hydrochloride (0.11g, 2.06 mmol), KOH (0.12g, 2.2mmol) was added and the reaction mixture refluxed for 6 hours. After completion of reaction indicated by TLC, the reaction mixture was poured into ice cold water and extracted to ethyl acetate (3 x 20 mL). The organic layer washed with water, brine and dried over anhydrous $Na_2SO_4$. Evaporate the organic layer under reduced pressure to get crude product. The crude product was purified by column chromatography using silica 60-120 mesh and ethyl acetate: petroleum ether (1:9) as eluent to get desire product (0.39g, yield: 68.4%, M.p: 130-133$^{o}$C).

### Method of crystallization

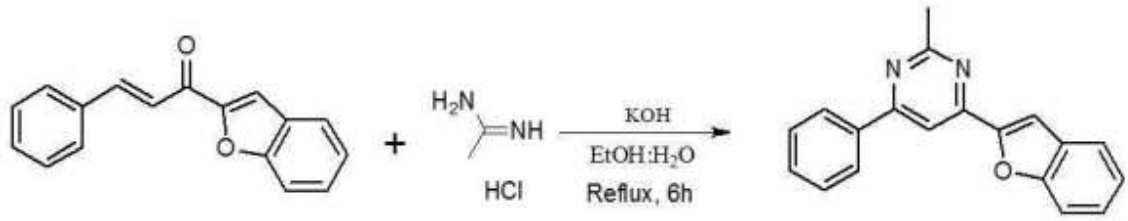
100mg of compound was dissolved in 15mL of ethyl acetate and warmed for 5 minutes. The solution was filtered through Whatmann filter paper and resulting solution was kept at room temperature in conical flask with stopper slightly open. After 5 days, the crystals of BFPP were developed; filtered and suitable crystals for single crystal analysis were selected (**Scheme-1**).

**$^{1}$H NMR (400MHz, $CDCl_3$):** δ 8.20-8.17 (2H, m, Ar-H), 8.05 (1H, s, Py-H), 7.71-7.69 (2H, dd,Ar-H), 7.62-7.53 (4H, m, Ar-H), 7.43-7.39 (1H, m, Ar-H), 7.32 (1H, m, Ar-H), 2.86 (3H, s, Py-CH3).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 168.576 (C12), 165.217 (C9), 156.213 (C11), 155.642 (C1), 153.310 (C8), 136.973 (C13), 130.901 (C14 & C18), 128.915 (C15 & C17), 128.295 (C16), 127.278 (C5), 126.313 (C4), 123.510 (C2), 122.248 (C3), 111.670 (C6), 108.906(C7), 108.124 (C10), 26.204 (C19).




**Mass (m/z):** Calculated: 286.32, Found: 287.59 (M+1)




**Scheme.** Synthesis of 4-(1-benzofuran-2-yl)-2-methyl-6-phenylpyrimidine

**2.3. X-Ray Crystallography**

A suitable colourless, needle shaped single crystal of the title compound with dimensions of0.36mm x 0.20mm x 0.16mm was selected and data was collected on an Oxford diffraction X caliber Gemini diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at 293 K. The CrysAlisProsoftware [14] was used for data collection, reduction and absorption correction. The structure was solved by direct method and refined by full-matrix least-squares methods on $F^2$ using SHELX-97 [15] available in the WinGX package [16]. All the non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in the structure factor calculations and treated using a riding model. Molecular graphics and crystal packing were created using *ORTEP* [17] and *MERCURY* [18] packages. The parameter for data collection and structure refinement of compound BFMPP are listed in Table 1.

**2.4. Hirshfeld surfaces**

The Hirshfeld surface analyses were carried out and fingerprint plots were plotted using Crystal Explorer 3.0 [19-25]. When the CIF files were uploaded into the Crystal-Explorer software, all bond lengths to hydrogen were automatically modified to standard neutron diffraction values, i.e. C–H = 1.083 Å.

**3. Data, value and validation**

**3.1. Crystal and molecular structure description of BFMPP**

The molecular structure of BFMPP determined by X-ray diffraction is depicted in **Figure 1**. BFMPP crystallizes in the monoclinic space group $P2_1$with cell dimensions *a* = 4.803(3) Å, *b* = 9.498(5) Å, *c* = 15.557(9) Å, β= 93.25 (4)$^o$ and Z = 2.The molecule is almost planar with root mean squared deviation (considering non-H atoms) being 0.101 Å. The dihedral angle between the benzene (A), the pyrimidine

ring (B) and the benzofuran ring (C) are 4.79 (A/B), 10.76 (A/C) and 8.42(1)°(B/C) respectively. The crystal structure is stabilized by weak C-H…N intermolecular interactions (Table 2 and **Figure 2**) running into C(4) chains along [100] and two pi…pi interactions. Hence, the supra molecular architecture exhibited is one dimensional.

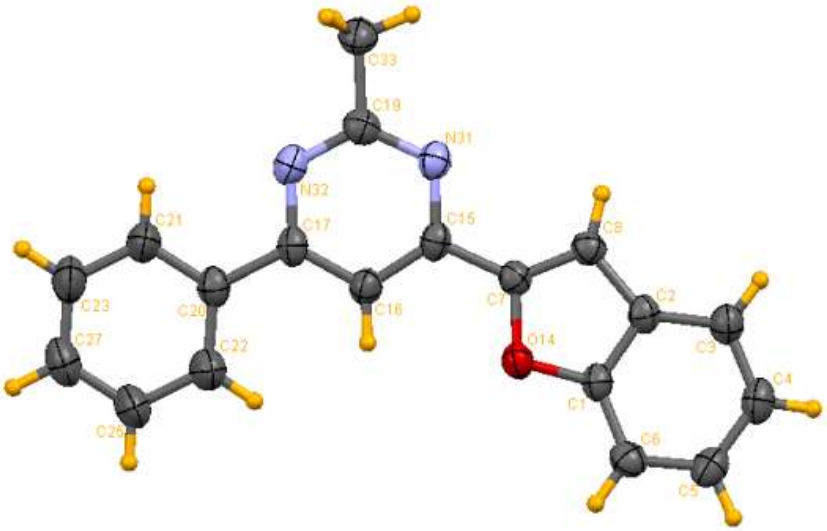



**Figure 1.** *ORTEP* view of the molecule with atom numbering scheme for non-hydrogen atoms

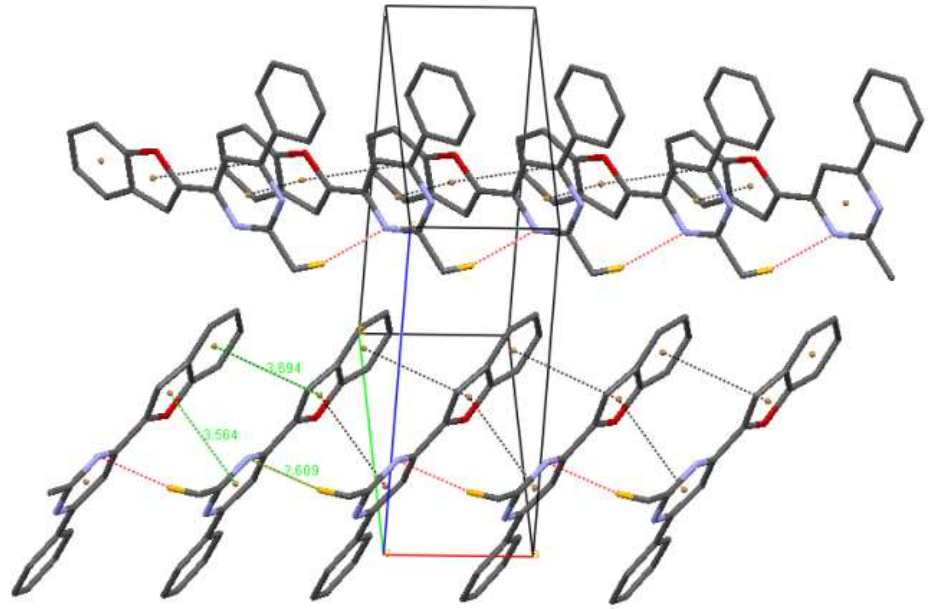



**Figure 2.** Crystal packing of BFMPP

### 3.2. Hirshfeld surface analysis

The Hirshfeld surfaces of title compound illustrated in **Figure 3**, showing surfaces that have been mapped over a $d_{norm}$(A), shape index (B) and curvedness (C) range of -0.111 to 1.143 Å, -1.0 to 1.0 Å and -4.0 to 0.4 Å, respectively. The predominant interactions between the methyl hydrogen of pyrimidine ring and the nitrogen of pyrimidine ring, which can be seen in the Hirshfeld surfaces as the bright red spot marked as A in **Figure 3** and clearly seen in **Figure 4**. In the 2D fingerprint plots (**Figure 5**), the C-

H···N intermolecular interactions appear as two distinct spikes circled with green color. Prominent pairs of sharp spikes of almost equal lengths in the fingerprint plots (**Figure 5**) are characteristics of nearly equal C(donor)···N(acceptor) distances and generate a one dimensional C(4) network propagating along the [100] direction. The upper spike (**Figure 5**) corresponds to the donor spike (H atom of methyl group interacting with N-atoms of the pyrimidine ring), with the lower spike being an acceptor spike (N-atomsof the pyrimidine ring interacting with H- atom of methyl group). The wings marked in Figure 5 (circled with black) are due to the C···H contacts. A significant difference in terms of H···H contacts appears asspikes (marked as red circles in **Figure 5**). The relative contribution of the different interactions to the Hirshfeld surface was calculated for title compound. It is evident that the H···H contacts can account forabout 50.5% of the Hirshfeld surface area; the remaining contribution was mostly due to C···H 28.2%,N···H 6.5%, O···H 3.3% and C···C 6.0% interactions, with only minor contribution from C···N, O···C and O···N (maximum 5.5%).

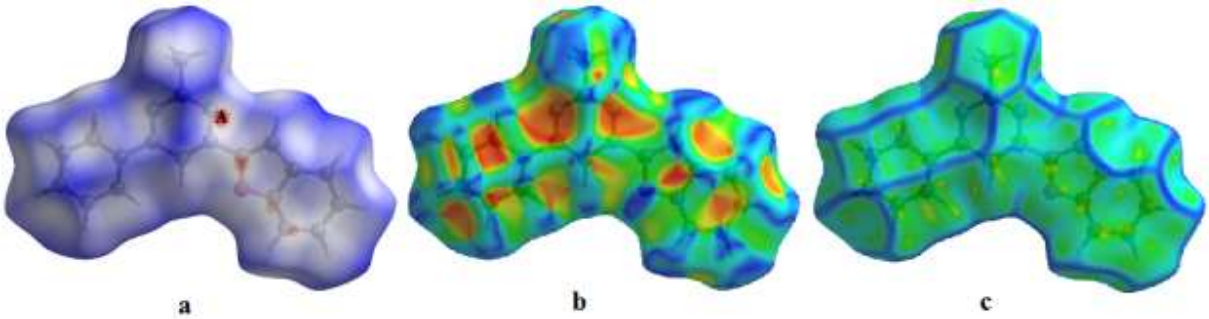



**Figure 3.** Hirshfeld surfaces of BFMPP.

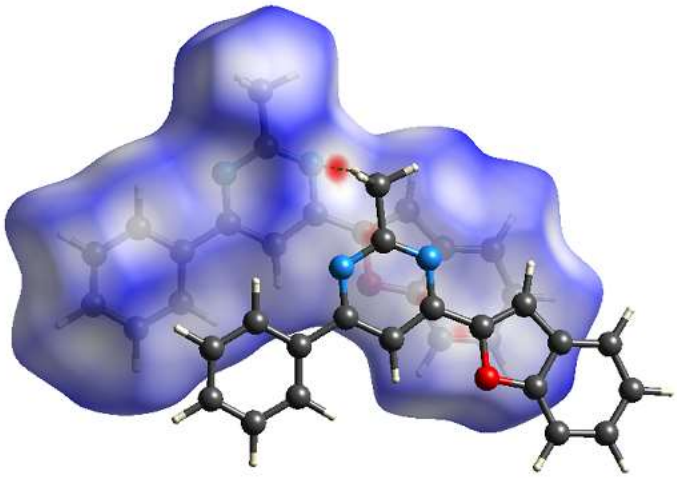


**Figure 4.** C-H…N intermolecular interactions mapped on $d_{norm}$ surface.

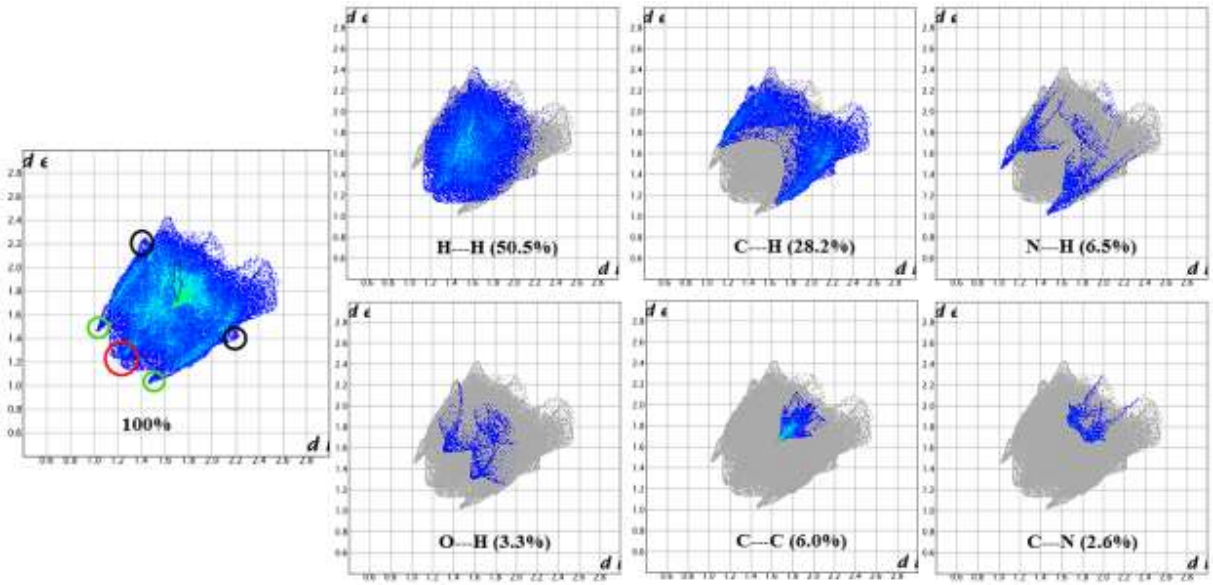



**Figure 5.** 2D Fingerprint plots of BFMPP.

### 3.3.Frontier molecular orbital analysis

The HOMO-LUMO energy plots of BFMPP has been obtained from Crystal Explorer with Tonto program using DFT/Becke88LYP/6-31G(d) method and the pictorial representation shown in **Figure 6**. The HOMO (MO 75) lies at -6.28 eV and whereas the LUMO (MO 76) is located at -2.2 eV. In the title compound, the HOMO of π nature is delocalized all over the molecule except phenyl ring, methyl group and LUMO in addition to this on the phenyl ring except methyl group. Accordingly, the HOMO-LUMO transition implies an electron density transfer from the benzofuran ring to phenyl ring through the pyrimidine ring, and that the frontier orbital energy gap is 4.08 eV. The global chemical descriptors associated with a molecular system are: ionization potential (I) = $-E_{HOMO}$= 6.28, electron affinity (A) = $-E_{LUMO}$= 2.2, chemical potential (μ) = - (I+A)/2 = -4.24, the global hardness (η) = (I-A)/2 = 2.04 ,softness (ν)= 1/ η = 0.49, electronegativity (χ) = (I+A)/2 = 4.24 and electrophilicity index (ω) = $\mu^2/2\eta$ = 4.406 [26,27]. It is seen that the chemical potential of the title compound is negative and it implies that the molecular system is stable. They do not decompose spontaneously into the elements they are made up of. The hardness signifies the resistance towards the deformation of electron cloud of chemical system under small perturbation encountered during the chemical process.

### 3.4. UV-Visible spectral analysis

The electronic spectra of title compound calculated at TD-DFT/B3LYP/SDD method using optimized geometry and the calculation are performed in methanol. The electronic spectra of title compound shows an electronic absorption band with maxima 344 nm (**Figure S5**)and this transition mainly due to the transition HOMO-LUMO that is the π-π transition predicted. The excitation transitions, CI coefficient, excitation energies, oscillator strengths and wavelength can be seen in Table S1.

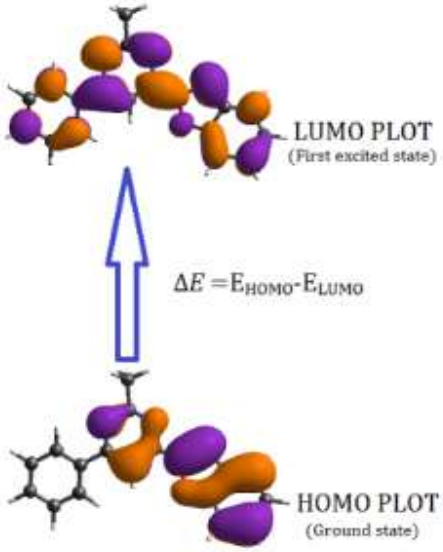



**Figure 6.** HOMO plot and LUMO plot of the title compound (BFMPP).

### 3.5. FT-IR spectral analysis

FT-IR spectrum of title compound is shown in **Figure S1**. Vibrational frequencies of title compound calculated at ground state by using B3LYP/DFT/SDD basic set in gas phase(Table S2).The CH stretching frequency of aromatic rings are theoretically assigned at 3181, 3117, 3090 $cm^{-1}$ for benzofuran ring and 3150 $cm^{-1}$ for pyrimidine ring. For mono-substituted phenyl ring, the CH stretching modes are expected above 3000 $cm^{-1}$[28, 29] and DFT calculations give these modes in the range 3120, 3106, 3094 $cm^{-1}$ and experimentally bands are observed at 3051 $cm^{-1}$. The $CH_3$ stretching modes are expected in the region 2900-3050 $cm^{-1}$[28]. The bands observed at 2925 $cm^{-1}$ and in the range 3060-2939 $cm^{-1}$ (DFT) are assigned as stretching modes of the methyl group. The aromatic ring stretching modes are observed in the range 1585, 1558$cm^{-1}$ and 1598, 1569 $cm^{-1}$ theoretically expected. The C=N stretching modes is observed at1528$cm^{-1}$experimentally and computed 1528 $cm^{-1}$. In present case in-plane and out-of-plane CH deformation observed at above and below 1000 $cm^{-1}$ and good agreement literature values.

### 4. Conclusion

4-(1-benzofuran-2-yl)-2-methyl-6-phenylpyrimidine(BFMPP)has been synthesized and characterized by single crystal X-ray diffraction, FT-IR, $^{1}H$ & $^{13}C$NMR and Mass spectrometry. The X-ray diffraction studies showed that the title BFMPP crystallized in monoclinic space group $P2_1$, with cell dimensions $a$ = 4.803(3) Å, $b$ = 9.498(5) Å, $c$ = 15.557(9) Å, β= 93.25 (4)$^{o}$ and Z = 2.The difference in HOMO and LUMO energies supports the charge transfer interaction within the molecule. The calculated HOMO and LUMO energies were used to semi-quantitatively estimate the ionization potential, electron affinity, electronegativity, electrophilicity index, hardness and chemical potential. The crystal surface analysis carried out by Hirshfeld surface studies and fingerprint plots analysis, which facilitates to understanding the type and nature of intermolecular interactions and as well as packing in the solid-state.

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**Table 1.** Crystallographic data and structure refinement of BFMPP

| | |
|---|---|
| Formula | $C_{19}H_{14}N_2O$ |
| Formula weight | 286.32 |
| Wavelength(Å) | 0.71073 |
| Crystal system | Monoclinic |
| *a* (Å) | 4.803(3) |
| *b* (Å) | 9.498(5) |
| *c* (Å) | 15.557(9) |
| *β* (°) | 93.25(4) |
| V (Å$^3$) | 708.6(6) |
| Space group | $P2_1$ |
| *Z* | 2 |
| T(K) | 293(2) |
| Crystal size (mm$^3$) | 0.36 x 0.20 x 0.16 |
| $\rho_{calcd}$ (g cm$^{-3}$) | 1.342 |
| $\mu$ (mm$^{-1}$) | 0.084 |
| $\vartheta$ range (°) | 2.62 to 61.5 |
| *h* / *k* / *l* indices | -6 ≤ h ≤ 6, -12 ≤ k ≤ 13, -22 ≤ l ≤ 22 |
| Reflections collected | 14129 |
| Unique reflection, $R_{int}$ | 4208 |
| GooF | 0.937 |
| *R*1[*I* > 2σ(*I*)] | $R_1$ = 0.0609, w$R_2$ = 0.1518 |
| *wR*2[all data] | $R_1$ = 0.1665, w$R_2$ = 0.1719 |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.15/-0.22 |

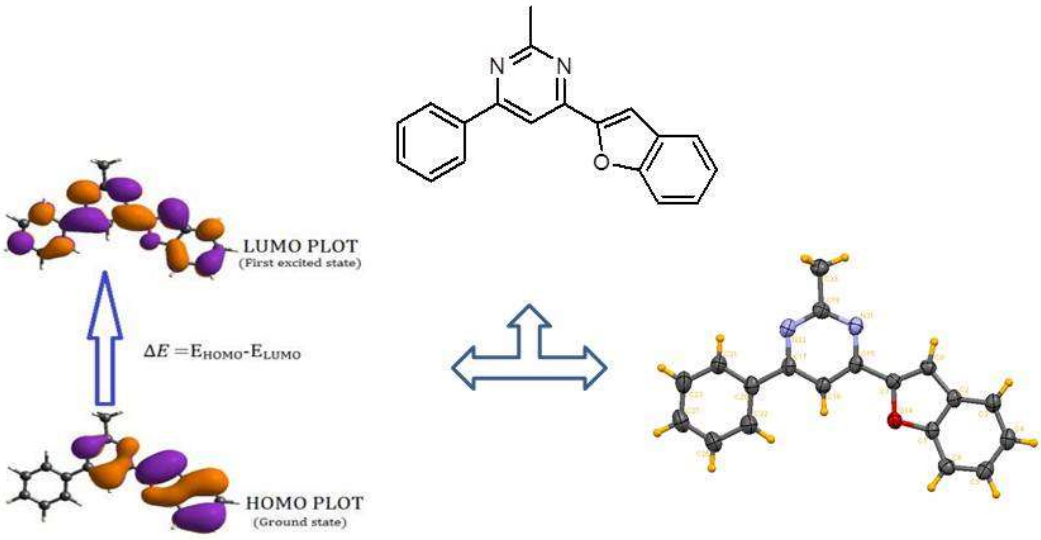
**Table 2.** Hydrogen bond geometry (°, Å) in the BFMPP.

| **D–H···A** | **D–H (Å)** | **H...A (Å)** | **D...A (Å)** | **D–H...A (°)** |
|---|---|---|---|---|
| C33-H33B-N31$^{i}$ | 0.96 | 2.61(1) | 3.5355(1) | 162(1) |
| Cg1...Cg2$^{ii}$ | - | - | 3.5644(1) | - |
| Cg1...Cg3$^{i}$ | - | - | 3.6945(1) | - |
| Cg1, Cg2 and Cg3 are the centroid of the furan ring, pyrimidine and the benzene ring of benzofuran ring respectively. | | | | |

Symmetry codes: (i) -1+x, y, z; (ii) 1+x, y, z;

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Graphical abstract




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# Influence of Nano Materials in Medicine for next generation

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**ABSTRACT**

Nano particles, because of their special properties attracted researchers from both theoretical and practical point of view. Many efforts have been made in the past two decades using novel nanotechnology and nanoscience knowledge to get nanomaterials with determined functionality. Nanomaterials are objects with the three external dimensions at the nanoscale. The main type of nanomaterial used in medicinal application are semiconductor nanomaterials, metal nanoparticles, magnetic nanomaterials, hydro gel nanocomposites, carbon nanomaterials, dendrimers, liposomes, , polymer nanocomposites, and biodegradable polymers. In this article, we have provided a concise review of the most common and popular nanomaterials viz., titania, carbon nanotubes (CNTs), zero-valent iron, zirconia (zirconium oxide), dendrimers, gold and silver nanomaterials which are currently used in medical field. Although expectations are too high but safety of nanomedicine is not yet completely proved. Over the next coming years, it is predicted that nanotechnology going to evolve and expand in different fields of life sciences and its achievements being applied in medicine like diagnostics, tissue engineering and patient improvement which play crucial role in treatment of human diseases and also in improving human physiology.

**KEY WORDS:** Nanomaterials, nanotechnology, carbon nanotubes, nanomedicine.

## 1. INTRODUCTION

Nanotechnology is the "science and technology where dimensions and tolerances are in the range of 0.1 nanometer (nm) to 100 nm play a critical role." Nanotechnology in medicine currently focuses on applications of nanoparticles as well as longer term research that involves the use of manufactured nano-robots to make treatment at the cellular level. Nanotechnology is considered an emerging technology because of its special properties to create new products with totally new characteristics and functions with enormous potential in a wide range of applications. The existing health care system is focused on treating disease rather than preventing disease. Patients are generally not tested until physiological re taken and sent to laboratories for analysis, the results often symptoms are present and they meet with their physicians. When samples of tissue or blood fluid an take several days and can be inconclusive if the disease is at an early stage. Consequently, many diseases are not detected until long after taking root in the body. In addition to various industrial uses, great innovations are foreseen in biotechnology, biology, in metrology, medicine, medical technology, information and communication technology, etc. It is anticipated that nanotechnology will have a huge positive influence on human health. Basically, internal processes of living organisms occur at nanometre scale. Proteins or cell membranes and elementary biological units like DNA are of this dimension. With nanotechnology, these biological units are going to be better guided. Increasing the precision to nanometre scale, makes it an essential feature of procedures and biomedical products in post genomic era. Nanoscale devices are similar in size to large biomolecules such as receptors and enzymes. Nanoscale devices which are smaller than 20 nm can move in and out of blood vessels as they circulate through the human body. Applications of nanotechnology in the field of biomedicine present an opportunity to fight against many dreadful diseases. An area with near-term potential is detecting molecules associated with diseases such as diabetes, cancer, neurodegenerative diseases, mellitus, as well as detecting microorganisms and viruses associated with infections, such as pathogenic bacteria, fungi, and HIV viruses. For example, in the field of cancer therapy, promising novel nanoparticles will respond to externally applied physical stimuli in ways that make them suitable therapeutics or therapeutic delivery systems. Nano technology is even used in biomaterials. For example in orthopedic implants or as scaffolds for tissue engineered products. Nanotechnology prevents non-specific protein adsorption by nano-structured surfaces. By gaining the control over the surface properties at nanolevel, biocompatibility of the materials can be increased.

**Nanomaterials and nanoparticles in medicine: A new approach:** In future, nanotechnology will enable a shift to preventive medicine and the use of "point of care" diagnostics to quickly identify diseases. In contrasts to the laboratory analysis, "point of care" testing is performed closed to the patient, at the time that care is required. Just as kits are available today for women to obtain instant information about pregnancy, portable diagnostic kits will become available to test whether a person is genetically predisposed to a specific disease, or have the earliest symptoms of a disease. Long before any physiological symptoms of the disease are present, a doctor (or even a patient in the comfort of her own home) will be able to take a sample of blood or saliva and insert the sample into a small chip. The chip consists of nanoscale sensors which will detect particular molecules associated with certain diseases, and will quickly provide feedback to the doctor or patient. "Point of care" diagnostics present a significant



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arket opportunity for companies that can move disease detection out of complex laboratories and into clinics, nursing homes, pharmacies and workplaces. Many companies are now focusing on making diagnostics simpler, smaller and more widely available in the many places patients receive treatment.

**Nanomaterials and Nanoparticles in Biomedical Applications:** The advanced applications of micro- and nanotechnology in medicine are the microchip-based drug delivery systems, which are devices incorporating micrometer-scale pumps, valves and flow channels. They allow controlled release of single or multiple drugs on demand. Micro- and nanotechnology-based methods (e.g. UV-photolithography, chemical vapour deposition, electron beam evaporation, reactive ion etching) can be used for the fabrication of these silicon-based chips. A lot of studies are going, on the applications of micro and nanotechnologies in chips for medical molecular diagnostics. For example protein microarrays (protein chips), DNA microarrays (gene chips), cell chips and lab-on-a-chip devices. These devices or systems are constructed by using micro/nanoscale fabrication methods. They are used for processing, manipulation, delivery, analysis or construction of biological and chemical entities. Inkjet printing methods are used in DNA microarrays for human genomics and in protein microarrays (or protein chips), which are useful for molecular diagnostics. For the detection of diseases either radionuclide-based markers or fluorescence- or surface Plasmon resonance spectroscopy can be applied.

**Carbon nanotubes:** Carbon nanotubes are of diameter of 1-20 nm. Gold-coated silica nanoshells, magnetic iron oxide nanoparticles and carbon nanotubes can transform electro-magnetic energy into heat. By increasing irradiation with an external laser source of near infra-red light or increasing magnetic field causing an increase in temperature which is lethal to cancer cells the very location where these nanoparticles are bound to or internalised within tumour cells, there by blasting them without causing any damage to healthy cells.

**Quantum dots (2-10 nm):** Due to their relatively inexpensive and simple synthesis, quantum dots have already entered the market for experimental biomedical imaging applications. Quantum dots can emit light at any wavelength in the visible and infrared ranges, and can be inserted anywhere, including liquid solution, dyes etc. Quantum dots can be inserted into a variety of organisms through surface ligands for in-vivo research.

**Dendrimers:** Dendrimers are hyper branched, tree-like structures. It contains three different regions: core moiety, branching units, and closely packed surface. It has globular structure and encloses internal cavities. Its size is less than 10 nm. These are used for long circulatory, controlled delivery of bioactive material, targeted delivery of bioactive particles to macrophages and liver targeted delivery. Anionic dendrimers have been shown to have antiviral activity. Having approximately the size of a virus, dendrimers are designed to bind multivalent either to the viral components or to the host cell surface through electrostatic forces, causing inhibition of infection at the stage of entry of virus to the cell. Dendrimer not only inhibit entry of virus but also inhibit its replication. (Gong, 2002). Activity has been shown against HSV, RSV and HIV while Starpharma's Vivage ITM, a vaginal dendrimeric formulation against HIV is currently entering clinical trials phase II (Gong, 2005). Dendrimers have also been shown to exhibit antimicrobial activity. Typically these dendrimers have cationic surface groups, usually lysine.

**Nanotechnology and Nanomedicine: New Medical concept:**

**Nanomedicine:** The use of nanobiotechnology in medicine is termed nanomedicine. Thus, nanomedicine is an offshoot of nanotechnology, referring to highly specific medical treatment at the molecular scale for therapeutic purposes (involving repairing damaged tissues or curing diseases), and for the development of diagnostics for rapid monitoring, targeted cancer therapies, localized drug delivery, improved cell material interactions, scaffolds for tissue engineering and genetics. Nanomedicine can focus on several topics, such as Engineering Topics including, for example, peptide nanoparticles for medical applications, the transition from semiconductors to biochemistry in lithography industry; Clinical Applications (like nanomedicine and protein misfiling diseases); Topics in genetics (e.g. nano structured probes for gene detection in living cells, detecting UV damage to individual DNA molecules with AFM, etc.); Topics in Diagnostics, with its main focus on early diagnosis in vitro and in vivo; Policy Commercialization Topics, including initiative in nano medicine to focus efforts in research, development and applied nanotechnology for improving the diagnostics, therapeutics and treatment of cancer; Experimental Research topics, which are an important basis for preclinical study, like nanodiagnostic imaging; Topics on Basic nanomedicine, Pharmacology Topics and Topics on Oncology and on Toxicology.

**Nanorobots and Nanodevices:** Imagine going to the doctor to get treatment for a persistent fever. Instead of a tablet pill, the doctor sends you to a special medical team which introduces a nano robot into your bloodstream. The robot travels to the appropriate system, detects the cause of your fever and provides medication directly to the affected area. Actually, we are not that far from using such nanodevices in medical procedures. Engineering teams working hard to design nanorobots that will eventually be used to treat everything from hemophilia to cancer. Preliminary design is for the following specific applications:

**Tumours:** Tumours are cells grouped in a clumped mass. The treatment is not to replace them but to destroy timorous cells to minimize the risk of reoccurrence. The technique is intended to be able to treat tumours that cannot be treated via conventional surgery such as [illegible]

nd much less debilitating than conventional surgery, it should be used, if possible, as a replacement for conventional surgery in this application.

**Arteriosclerosis:** This is caused by fatty deposits on the walls of arteries. The device should be able to remove these deposits from the artery walls. This will allow for both improving the blood flow through them and the flexibility of the walls of the arteries. Removing these accumulated fatty acids and leaving these particles into blood stream should allow the body's natural processes to remove the overwhelming preponderance of material.

**Blood clots:** They (fatty acids) cause damage when they travel through the bloodstream where they can block the flow of blood to a vital area of the body. This can result in damage to vital organs in very short order. In most of the cases, these blood clots are only detected when they cause a blockage and damage the organ in question, often but not always the brain. By introducing a nanorobot into the body to blast such clots into smaller pieces before they have a chance to break free and move on their own, the chances of damage can be greatly reduced.

**Nanotechnology in Orthopaedic Implants:** Biomaterials is one of the most important applications of nanotechnology in medicine. Example: in orthopaedic implants or in tissue engineered products. Next generation of orthopaedic implant depends completely on Nanostructured materials.

They create a surface environment more conducive for osteoblast. An important field of application for nanotechnology in medicine is the biomaterials. Example: in orthopaedic implants or in tissue engineered products. Next generation of orthopaedic implant depends completely on Nanostructured function. The nanoscale composition of bone substitute materials emulates the hierarchic organization of natural bone, shows initiation of the desirable formation of an appetite layer. Nanotechnology also improved the quality of surgical blades and cutting performance. Nanofibrous membrane wound dressings containing antibacterial properties reduces postoperative infection rates. Drug delivery, including nanotherapeutics for treating bone cancer and arthritis are the most notable applications of nanotechnology in orthopaedics. Nanotechnology is used in orthopaedics, and likely will play a valuable role in future developments.

**Nanotechnology in Cardiology:** Nanotechnology has various applications in the field of cardiology research not only for diagnostic but also for therapeutical purposes. Recently, University of Michigan researchers developed a nanoparticle that could be the key to a targeted therapy for cardiac arrhythmia, a condition that causes the heart to beat erratically and can lead to heart attack or heart stroke. The cells that cause cardiac arrhythmia are precisely targeted and destroyed within the heart by nanotechnology. The U-M team in their studies conducted on rodents and sheep, found that the treatment successfully kills the cells that cause cardiac arrhythmia while leaving surrounding cells unharmed. In the journal, Science Translational Medicine, they published their findings.

**Nanotechnology against Cancer:** The use of nanotechnology in cancer treatment gives a new hope of fighting this dreadful disease. This technology has the capability to destroy cancer tumours with a minimum effect on healthy organs and tissues. Nano robots can detect and eliminate cancer cells before they form tumours. Cancer treatment through nanotechnology is at research or development stage. National Cancer Institute, The Alliance for Nanotechnology in Cancer in U.S., is promoting innovation and collaboration among researchers to resolve some of the major challenges in the application of nanotechnology to cancer. In addition, there are many universities and companies worldwide working in this area. In a decade or so, cancer can be eliminated completely by these efforts. (Similar to smallpox elimination by vaccines).

**Nanotechnology against antibacterial activity:** Nano $TiO_2$ is excellent photo catalyst used in antiseptic which can not only inhibit reproduction ability of bacterium, but also decompose its structure of cell membrane which will degrade microorganisms completely and thus avoid a second time pollution caused by creatoxin.

Titanium Oxide Nanoparticle is a non-dissolved material which does not dissolve itself when degrades organic contaminant and kills germs. It kills germs and degrades organic contaminants. $TiO_2$ nanoparticle is widely used as UV-resistant material and in the field of producing chemical fibre, printing ink ,plastics, coating, self-cleaning ceramics, self-cleaning glass, air purification, antibacterial material, , chemical industry and sewage treatment, cosmetics- natural white moisture protection cream ,sunscreen cream, beauty and whitening cream, moistening refresher, morning and night cream, skin protecting cream , vanishing cream and face washing milk. They are also used in powders in make-up and foods packing material.

Coating for paper-making industry: $TiO_2$ nano particles are used for improving the opacity and impressionability of the paper. Ferrotitanium alloy, carbide alloy, Titanium etc. can be produced from these nanoparticles, in the metallurgical industry, astronautics industry. It is also used in manufacture of moisture sensor, gas sensor and conducting materials.

## 2. CONCLUSION

Nanotechnology in modern medicine and nanomedicine is in infancy, having the potential to change medical research dramatically in the 21st century. Due to their small sizes, surface area modification capacity and unique biological properties, nanomaterials have a broad scope of application in analytical, imaging, detection, diagnostic and therapeutic purposes and procedures, such as targeting cancer, gene delivery systems, improving cell-material

interactions, scaffolds for tissue engineering, and drug delivery and provide innovative opportunities in the fight against incurable diseases. Thanks to nanotechnology tools and techniques, there has been a huge progress on understanding the function of biological structures and their interaction and integration with several non-living systems, but there are still open issues to be answered, mainly related to biocompatibility of the materials and devices which are introduced into the body. The vision is to improve health by enhancing the efficacy and safety of nanosystems and nanodevices. In addition, early diagnosis of cancer causing tumour, blood clot which might lead to a heart attack or diabetes helps to cure them with a minimum treatment. In the coming years, nanotechnology will play a key role in the medicine of tomorrow providing revolutionary opportunities for early disease detection, therapeutic procedures and diagnostics to improving health and enhancing human physical abilities, and enabling precise and effective therapy tailored to the patient.

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# Stress Degradation Studies of Almotriptan Tablets by a Validated Stability-Indicating Liquid Chromatographic Method

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## ABSTRACT

*Almotriptan is an anti-migrain drug prescribed to treat severe migraine headaches and vascular headaches and for acute treatment of migraine attacks with or without aura. In the present study, degradation behavior of almotriptan was studied by subjecting the drug to various International Conference on Harmonization-recommended stress conditions. Also, a stability indicating high-performance liquid chromatography method was established for analysis of the drug in the presence of various degradation products. An acceptable separation of the drug and its degradation products was achieved on a C-18 column at 40°C using a mobile phase comprised of methanol, acetonitrile and acetic acid in the ratio of 75:20:5 (v/v/v) at a flow rate of 1 mL/min. The detection wavelength was 231 nm. The method was validated for linearity, precision, accuracy, selectivity, specificity, and robustness. The method was found to be linear over a concentration range of 20–120 - µg/mL (n = 6). The value of slope was found to be 3933.6x ppm with correlation coefficient of 0.9996 and relative standard deviation (RSD) of 0.5673%. RSD values ranged from 1.651% to 0.5670% in the case of intra-day precision studies, whereas the values ranged from 1.0470% to 0.3843% in the case of inter-day precision. Validation parameters were evaluated according to the International Conference on Harmonization (ICH) Q2R1 guidelines. Using HCl, NaOH, $H_2O_2$, thermal, UV radiation and water performed the forced degradation studies. Almotriptan is more sensitive towards oxidative degradation condition. The developed method was successfully applied for the quantification and hyphenated instrumental analysis. The results obtained from the stress testing reveal that almotriptan drug substance is particularly unstable under acidic, alkaline and thermal degradation conditions. Therefore, care should be taken in the manufacturing process and storage of this product in order to avoid degradation, since if the drug is degraded it could result in decrease of therapeutic activity and safety.*

**Keywords:** Almotriptan, HPLC, Stress testing, Stability-indicating, Acidic, Neutral, Alkaline, Oxidation, Photolysis, Tablets, Forced degradation

## INTRODUCTION

A forced degradation or stress testing studies are the intentional degradation of the API and/or DP to an appropriate extent by means of various stress conditions include acidic, alkaline, neutral hydrolysis conditions, pH, temperature, light, oxidizing agents, and mechanical stress [1-3]. Forced degradation studies are designed to generate product-related variants and develop analytical methods to determine the degradation products formed during accelerated pharmaceutical studies and long-term stability studies. Any significant degradation product should be evaluated for potential hazard and the need for characterization and quantitation [4,5].

Almotriptan is a selective agonist of 5-HT1B/D receptors (Figure 1) [6]. The therapeutic activity of almotriptan for the treatment of migraine headache can most likely be attributed to the agonist effects at the 5-$HT_{1B/D}$ receptors on intracranial blood vessels and sensory nerves of the trigeminal system, which result in cranial vessel constriction, and inhibition of pro- inflammatory neuropeptide release. Due to presence of the indole moiety it is susceptible to undergo degradation. Almotriptan binds with high affinity to 5-HT1D, 5-HT1Band 5-HT1F receptors and has weak affinity for 5-HT1A and 5-HT7 receptors, with no significant affinity or pharmacological activity at 5-HT2, 5-HT3, 5-HT4, 5-HT6, alpha or beta adrenergic, adenosine (A1 and A2), angiotensin - (AT1 and AT2), dopamine (D1 and D2), endothelia (ETA and ETB) or tachykinin (NK1, NK and NK3) binding sites. The IUPAC name is 1[[[3-[2-(Dimethyl amine) ethyl]-1Hindol5yl] methyl] sulfonyl] pyrrolidine hydroxybutanedioate (1:1). The empirical formula is $C_{17}H_{25}N_3O_2S.C_4H_6O_5$, representing a molecular weight of 469.56.

In the literature, various analytical methods analytical methods such as RP-HPLC and spectrometry methods have been reported for the determination of almotriptan in formulations. A stability-indicating assay method helps in establishing the inherent stability of a drug, providing assurance on detection changes in identity, purity, and potency of the product. To date, no report is available on the stability studies of almotriptan in bulk under the various stress conditions (acidic, neutral, alkaline, oxidative, thermal, and photolytic stress) specified in the ICH guidelines for stress testing of a drug substance. Using the reversed-phase high performance liquid chromatography (RP-HPLC) method, degradation studies were performed on the drug after exposing the drug to various stress conditions [7-11].

### Experimental Procedure

Almotriptan was obtained as a gift sample from Natco Pharma Ltd, Hyderabad, India. The branded formulation of almotriptan was procured from the local market. Analytical reagent (AR) NaOH and $H_2O_2$ were purchased from S.D. Fine-Chem. Ltd., Mumbai, India. HCl, acetonitrile, methanol, and orthophosphoric acid (HPLC grade) was from Merk India (Mumbai). All other chemicals were of analytical grade.

***Almotriptan stock standard solution***

Accurately weighed 100 mg of almotriptan powder was transferred to a 100-mL volumetric flask; to this, 30 mL of water was added, then the mixture was sonicated for 40 s. The final volume was made up with water, and the resulting solution was vortexed for 1 min (1 mg/mL).

***Instrumentation and chromatographic conditions***

Chromatography was performed by using a LC-10 ATVP Shimadzu pump (Japan) equipped with a SPD-10 A VP UV-visible detector. The data was processed using Spinchrom Software. The separations were carried out using a C-8 RP column (Thermo Hypersil, BDS, 150 Å~ 4.6 mm, S-5 µ), which was operated at 40°C. The mobile phase comprised of methanol, acetonitrile and acetic acid in the ratio of 75:20:5 (v/v/v). The flow rate was adjusted at 1 mL/min, and the wavelength of detection was 231 nm. Specificity testing was done on a Waters (Milford, MA) Delta 600 HPLC equipped with a 600 controller pump, 2996 photodiode array (PDA) detector, and a degasser module. Empower 2 Software was used for data acquisition and processing. For the investigation of photo stability of the drug, a stability chamber (KBF 240, WTB Binder, Tuttlingen, Germany) equipped with light sources was used, as defined under option 2 of the ICH guideline Q1B. In this chamber, the combination of two black lights OSRAM L73 lamps and four white fluorescent OSRAM L20 lamps formed the light bank. The spectral distribution of black light lamps was between 345 and 410 nm with a maximum output set at 365 nm, whereas the output of white fluorescent lamps was similar to that specified in ISO 10977 (1993). Both UV and visible lamps were put on simultaneously. The chamber was maintained at 40°C and 75% relative humidity (RH). The samples were exposed for a total period of 10 days. Thermal degradation of the drug was investigated using a hot air oven maintained at 60°C for 15 days.

***Mobile phase selection***

In order to select a suitable mobile phase for the analysis of almotriptan, various combinational ratios of various solvents were tried on the basis of trial and error. Considering the system suitability parameters viz., tailing factor, number of theoretical plates, retention time etc. and the mobile phase found to be most suitable for analysis was acetonitrile, methanol and acetic acid in the ratio of 20:75:05 (v/v/v). The mobile phase was filtered through 0.45 µ filter paper to remove particulate matter and then degassed by sonication. Flow rate employed for analysis was 1.0 mL/min and the concentration was detected at 231 nm.

***Preparation of standard solution***

Ten tablets of almotriptan 2.5 mg were weighed and powdered. A portion equivalent to 10 mg of almotriptan was accurately weighed and transferred to a 10 ml volumetric flask, sufficient amount of mobile phase was added to dissolve it and volume was made upto to 10 mL. Aliquots of stock solution were further diluted with mobile phase up to 10 mL to get concentration of 20, 40, 60, 80, 100, and 120 - µg/ml for the linearity study [12-16].

***Forced decomposition (stress) studies***

Forced decomposition studies were performed under different conditions as mentioned in ICH QIA (R2) [17,18].

***Acid hydrolysis***

Forced degradation in acid media was performed by adding an aliquot of stock solution (1 mg/ml) of almotriptan to 10 ml each of methanol and 0.1 M HCl and refluxing the mixture at 60°C for approximately six hours. The solution was then left to reach room temperature, neutralized to pH 7 by the addition of 0.1 M NaOH, and diluted to 100 ml with the mobile phase so as to get a final concentration of 10 µg/ml.

***Alkaline hydrolysis***

Alkali - induced, forced degradation was performed by adding an aliquot of stock solution (1 mg/ml) of almotriptan to 10 ml each of methanol and 0.1 M NaOH, and refluxing the mixture at 60°C for approximately six hours. The solution was then left to reach room temperature, neutralized to pH 7 by addition of 0.1 M HCl, and diluted to 100 ml with the mobile phase, so as to get a final concentration of 10 µg/ml.

***Oxidative degradation***

To study the effect of oxidizing conditions, an aliquot of stock solution (1 mg/ml) of almotriptan was added to 10 ml of 30% $H_2O_2$ solution and the mixture was refluxed at 60°C for approximately six hours. The solution was left to reach room temperature and diluted to 100 ml with the mobile phase, so as to get a final concentration of 10µg/ml.

***Thermal degradation***

To study the effect of temperature, approximately 50 mg almotriptan was stored at 100°C in a hot air oven for 24 hours. It was then dissolved in 10 ml of methanol and the volume was adjusted to 50 ml with the mobile phase. The above solution was further diluted with the mobile phase, to give a solution of final concentration equivalent to 10 µg/ml of almotriptan

***Photolysis***

To study the effect of UV light, approximately 50 mg of almotriptan was exposed to short and long wavelength UV light (254 nm and 366 nm, respectively) for 24 hours, and then dissolved in 10 ml of methanol. The volume was made up by the mobile phase in a 50 ml volumetric flask, and then 1 ml of stock solution was further diluted with the mobile phase to give a solution of final concentration equivalent to 10 µg/ml of almotriptan.

Twenty microliters of the resulting almotriptan solution was injected into the HPLC system and the chromatograms were recorded. The stability samples were analyzed using a PDA detector to determine the peak purity.

***Method validation***

**Linearity and range:** A calibration curve of almotriptan was prepared in water for the establishment of linearity. For the same, a stock solution of the drug (1 mg/mL) was prepared in water. The concentrations ranging from (20–120 µg/mL) were prepared after suitable dilution (n = 6). The samples were filtered through a 0.45-µ-membrane filter prior to HPLC analysis. All

the determinations were done in triplicate. The linearity plots were constructed, and linear regression was applied on the data [19,20].

**Precision:** To determine the repeatability (intra-day precision) and intermediate precision (inter-day precision) of the method, the almotriptan solution at nominal standard concentration (100 µgmL-1) and sample solution (100 µgmL-1) were analyzed in six replicates on the same day (intra-day precision) and daily for six times over a period of three days (inter-day precision). The results were expressed as % RSD of the measurements [21].

**Accuracy:** Accuracy of the proposed method was determined using recovery studies. The recovery studies were carried out by adding different amounts (20%, 40%, and 60%) of the pure drug to the pre-analyzed formulation. The solutions were prepared in triplicates and the % recovery was calculated.

**Specificity and selectivity:** The specificity of the method was established through the study of resolution factors of the drug peak from the nearest resolving peak and also among all other peaks [22].

**LOD and LOQ:** The LOD and LOQ were determined at signal-to-noise ratios of 3:1 and 10:1, respectively, by injecting a series of dilute solutions with known concentrations.

**Robustness:** Robustness of the method was investigated by varying the chromatographic conditions, such as, change of flow rate (± 10%), organic content in the mobile phase (± 2%), wavelength of detection (± 5%), and pH of the buffer in the mobile phase (± 0.2%). Robustness of the developed method was indicated by the overall % RSD between the data, at each variable condition.

**Solution stability:** The solution stability was carried out by storing standard solutions of almotriptan in tightly capped volumetric flasks at -20°C for seven days. These solutions were assayed after seven days against fresh samples.

## RESULT AND DISCUSSION

Forced degradation study was carried out by subjecting the drug to acid and alkaline hydrolysis, chemical oxidation and photolytic conditions and it chromatograms were showed in Figure 2. The forced degradation studies of almotriptan tablet formulation was done on stress degradation by using 0.1N HCl and product degradation was found to be 21.84% for 8hrs, stress degradation by hydrolysis under alkaline conditions by using 0.1 N NaOH was found to be 27.84% for 8hrs, Dry heat induced degradation was done by using 90 ºC temperature was found to be 27.18% for 48 hours. Using hydrogen peroxide 30% did oxidative degradation and product degradation was found to be 20.62% for 6hrs. Photolytic degradation was found to be Photolytic degradation (VIS) 71.57% for 48 hrs and Photolytic degradation (UV) 33.3% for 48 hours [23-27].

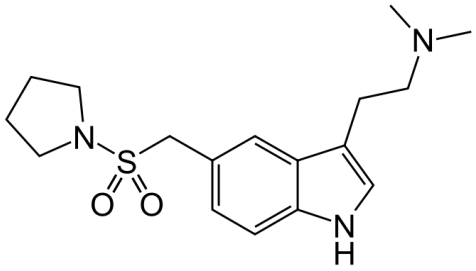
Maximum degradation of almotriptan was observed in Photolytic degradation (VIS), followed by decomposition under Photolytic degradation (UV), alkaline and thermal photolysis. Minimum degradation of drug was observed in acid hydrolysis and oxidative conditions. Percent degradation of drug under all stressed conditions is included in Table 1.

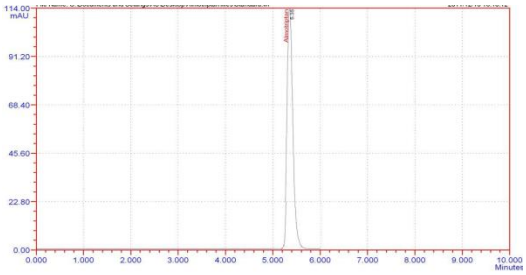
| Stress conditions | Degradation studies (Hrs.) | AM | |
|---|---|---|---|
| | | % Assay | % Degradation |
| Control | | 99.9 | ----- |
| Acid hydrolysis | 8 | 78.06 | 21.84 |
| Base hydrolysis | 8 | 72.06 | 27.84 |
| Hydrolytic | 8 | 78.50 | 21.4 |
| Oxidative | 6 | 79.28 | 20.62 |
| Thermal | 48 | 72.72 | 27.18 |
| Photolytic(VIS Light) | 48 | 80.5 | 19.5 |
| Photolytic (UV Light) | 48 | 66.6 | 33.3 |

**Table 1:** Forced degradation study results.

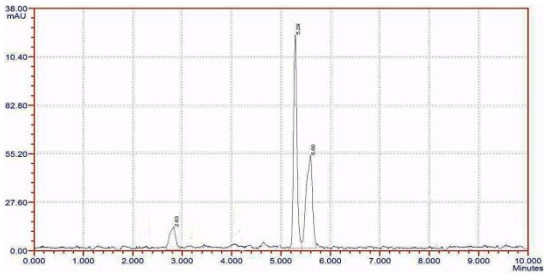
### *Method validation*

The method was validated with respect to parameters like linearity, precision, accuracy, specificity and robustness (Figure 1).

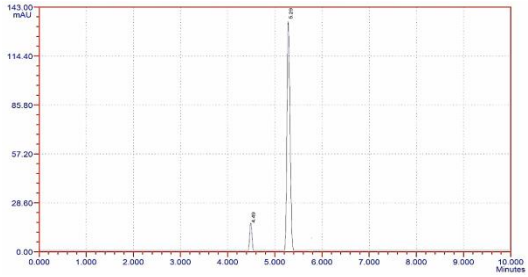


Standard chromatogram



Base degradation



Oxidative degradation

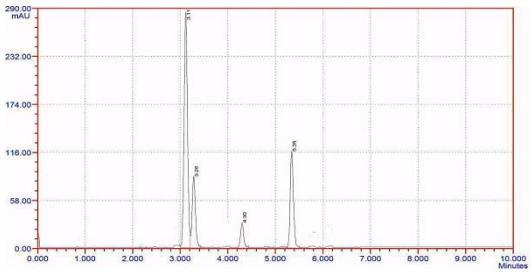
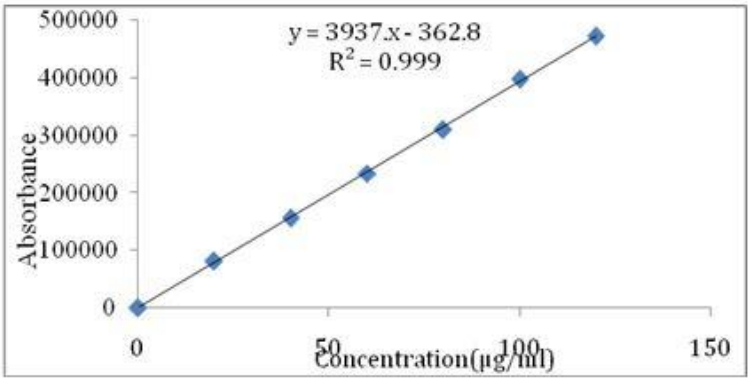


Photo stability (VIS light)

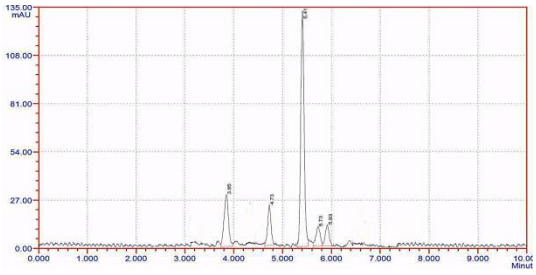
**Figure 1:** Structure of Almotriptan

***Linearity***

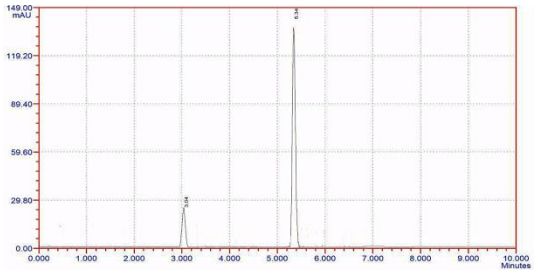
The response for this drug was strictly linear in the concentration range between 20–120 µg/mL. The equation of the line was y = 3933. × -221.9. A very high correlation of 0.9996 was obtained with RSD of 0.5673% was shown in Tables 2 and 3 (Figure 2).



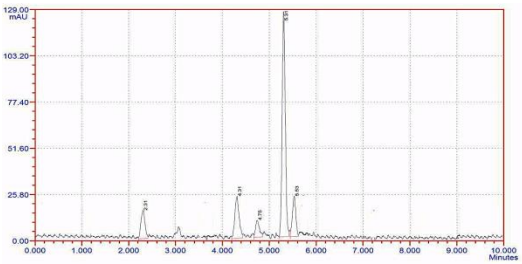

Linearity graph of Almotriptan.



Acid degradation



Hydrolytic degradation



Thermal degradation

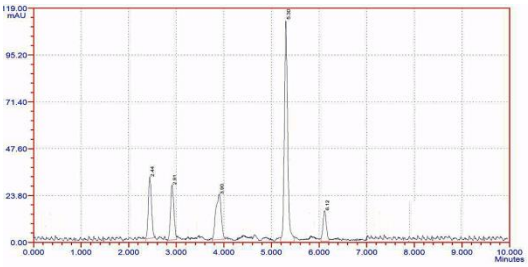


Photo stability (UV light) degradation

**Figure 2:** Degradation of Almotriptan.

**Table 2:** Forced degradation study results.

| Stress conditions | Degradation studies (Hrs.) | AM | |
|---|---|---|---|
| | | % Assay | % Degradation |
| Control | ----- | 99.9 | ----- |
| Acid hydrolysis | 8 | 78.06 | 21.84 |
| Base hydrolysis | 8 | 72.06 | 27.84 |
| Hydrolytic | 8 | 78.50 | 21.4 |
| Oxidative | 6 | 79.28 | 20.62 |
| Thermal | 48 | 72.72 | 27.18 |
| Photolytic(VIS Light) | 48 | 80.5 | 19.5 |
| Photolytic (UV Light) | 48 | 66.6 | 33.3 |

**Table 3:** Linearity.

| S. No | Concentrations µg/ml | Area of the peak |
|---|---|---|
| 1 | 20 | 80521.4 |
| 2 | 40 | 156326 |
| 3 | 60 | 234462 |
| 4 | 80 | 310114 |
| 5 | 100 | 397319 |
| 6 | 120 | 472596 |

***Precision***

Table 4 shows the results of intra and inters –day precision studies. From the intra and day studies, the % RSD value was found to be in the range of 1.6510% to 0.5670%: whereas, in the case of inter-day studies, the values ranged from 1.0470% to 0.3843%.

**Table 4:** Intra and Inter day precisions.

| S.NO | Concentration (µg/ml) | Intra-day precision mean n = 3 | % Amount calculated | % RSD | Inter-day precision mean n = 3 | % Amount calculated | % RSD |
|---|---|---|---|---|---|---|---|
| 1 | 15 | 14.83 | 98.87 | 1.651 | 15.03 | 100.2 | 1.047 |
| 2 | 30 | 29.96 | 99.87 | 0.408 | 30.03 | 100.1 | 0.4078 |
| 3 | 45 | 44.93 | 99.84 | 0.567 | 45.06 | 100.1 | 0.3843 |

***Accuracy***

The data obtained from the recovery studies is represented in Table 5. The recovery was in the range of 97.65% to 101.67%.

**Table 5:** Data recovery studies.

| Time | AM | |
|---|---|---|
| | % Assay | % Difference |
| Initial | 99.29 | --- |
| 12 $^{th}$ hr | 98.71 | 0.58 |
| 18 $^{th}$ hr | 98.89 | 0.4 |
| 24 $^{th}$ hr | 98.68 | 0.61 |

***Robustness***

The method was found to be robust by varying the temperature of column as shown in Table 6.

**Table 6:** Robust to vary the temperature of column.

| S. No | Variations | Chromatographic parameters | |
|---|---|---|---|
| | | Tailing factor | Theoretical plates |
| 1 | 34% of methanol in the mobile phase | 1.14 | 9638 |

| | | | |
|---|---|---|---|
| 2 | 24% of methanol in the mobile phase | 1.88 | 8854 |
| 3 | Flow rate at 0.9ml/min | 0.96 | 6240 |
| 4 | Flow rate at 1.1ml /min | 1.11 | 9685 |
| 5 | pH change of mobile phase | 1.16 | 9677 |
| 6 | pH change of mobile phase | 1.39 | 9942 |

## CONCLUSION

The proposed method described a new RP-HPLC were developed and validated as per ICH guidelines, the standard deviation and % RSD calculated for the proposed method are low, indicating high degree of precision of the method. The recovery study performed show the high degree of accuracy and has the use of inexpensive solvent where it has the ability to separate these drugs from their degradation products, related substance; excipients found in tablet dosage forms and can be applied, for the routine analysis in quality control laboratory.

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# Bio-inspired green synthesis of RGO/$Fe_3O_4$ magnetic nanoparticles using *Murrayakoenigii* leaves extract and its application for removal of Pb(II) from aqueous solution

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†These authors contributed equally

## Abstract

We have report a facile, ecofriendly and cost-effective approach to remove toxic heavy metal ions of Pb(II) by magnetically separable reduced graphene oxide/iron oxide (RGO/$Fe_3O_4$) nanocomposite synthesized via green method utilizing *Murrayakoenigii* (Mk) leaves extract as reducing and capping agent. The synthesized RGO/$Fe_3O_4$ nanocomposite were characterized using Fourier transform infrared spectroscopy (FTIR), powder X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), nitrogen adsorption-desorption (BET), vibrating sample magnetometer (VSM) and Raman spectroscopy measurements. RGO/$Fe_3O_4$ nanocomposite was used for the removal of Pb(II) from aqueous solution by batch adsorption experiments. The results show that adsorption was followed the pseudo-second-order kinetic model. The adsorption isotherm data fitted well with Freundlich model and Langmuir isotherm, the monolayer adsorption capacity was found to be 48 mg/g at 301K. The results show that the as synthesized RGO/$Fe_3O_4$ nanocomposite acts an efficient

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adsorbent for removal of Pb(II) from aqueous solutions. The overall results of the study indicate that this newly synthesized magnetically separable RGO/$Fe_3O_4$ nanocomposite may be potentially utilized for many environmental remediation applications.

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**Keywords**: RGO/$Fe_3O_4$, XRD, XPS, BET, VSM

## 1. Introduction

Fast industrialization has led to an increased release of wastewater including heavy metals (Hg, Cr, Cd, As and Pb), which have dangerous effects on the environment. Among these, Pb(II) was one of the most toxic heavy that causes major environmental health disorders [1,2]. The Pb(II) and their compounds were frequently used in modern society, such as fuels, printing inks and storage battery industries [3]. The Pb(II) revelation may cause damage to organs including liver, kidneys, heart and also cause edema to the immune system [4]. Thus efficient removal of Pb(II) from aqueous system is very important and has become a challenging assignment for scientists. There were numerous processes that have been developed to restrict heavy metal pollution like chemical precipitation, ion-exchange, membrane filtration, electrode deposition, solvent extraction, and bio adsorption [5-10]. Among these methods, adsorption is one of the most assure and extensively used methods because it is straightforward and relatively low-cost. Many researchers have tried to find easily and low-cost obtainable adsorbents to remove hazardous metal ions, such as zeolites, clays and plant waste materials [11-13]. Recently, the application based on graphene/$Fe_3O_4$nanocomposite in sample preparation to sorb trace analytes has gained significant importance [14]. In this process, iron nanoparticles were homogeneously secured onto the surface of the sheets with the support of –COOH on GO, which disallowed the

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agglomeration of $Fe_3O_4$ nanoparticles and inhibited their growth. These magnetite/reduced graphene oxide nanocomposite exhibited excellent removal efficiency and fast separation from water by an external magnetic field. It is evident from the available literature that the synthesis of magnetic reduced graphene oxide shows excellent applications [15-21]. On the other hand, the oxygen containing functional groups on RGO have strong complexation capacities with metal ions and therefore, it is apt to remove radionuclides and heavy metal ions from wastewater.

Using organic solvents like $C_6H_6$, $NaBH_4$, $N_2H_4$, and $CO_2$ is highly reactive and potentially hazardous to the environment. Hence, the accessible synthesis methods were environmentally unfriendly, complex, expensive and time consuming. Therefore, it is still a great challenge to develop eco-friendly synthesis methods. To the best of our knowledge, no reports on green synthesis of magnetite reduced graphene oxide (RGO/$Fe_3O_4$) composite using Murraya*konenigii* leaves extract. In this article, firstly RGO/$Fe_3O_4$ nanocomposite was fabricated via reduction of $Fe^{3+}$ ion and GO by *Murrayakonenigii* leaves extract as a reducing and stabilizing agent. The RGO/$Fe_3O_4$ nanocomposite was employed as magnetically recycled adsorbent for the removal of Pb(II) from aqueous solution.

## 2. Materials and Methods

### 2.1 Materials

Graphite powder and $FeCl_3$ $6H_2O$ were purchased from Sigma Aldrich and used as received without further purification. All solutions were prepared in double distilled water.

### 2.2. Preparation of the extract

Fresh *Murrayakoenigii* leaves were collected and thoroughly washed with deionized water, then chopped into small pieces. 20 g of *Murrayakoenigii* leaves was heated with 100 mL distilled

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water at 60 ºC for 2 h. Subsequently, the mixture was permitted to cool to room temperature and aqueous extract centrifuged at 8000 rpm then was easily obtained by filtration.

### 2.3. Preparation of the RGO using the aqueous extract of *Murrayakoenigii* leaves

The GO was prepared from natural graphite powder by a modified Hummers method [22]. The RGO was prepared through phytochemical reduction of a colloidal suspension of GO. For the preparation of RGO, 60 mg of GO was dispersed in 50 mL Milli-Q water by ultrasonication for 35 min. The suspension was thoroughly mixed with an appropriate volume of *Murrayakoenigii* leaves extract and magnetically stirred under reflux conditions for 5 h at 60 °C. The obtained product was centrifuged at 10,000 rpm and then dried at 100 °C. The mechanism of reduction is due to the complex phytochemical constituents. The phytochemicals such as Apigenin, Luteolin and ascorbic acid present in the leave extracts helps in the reduction of GO. The detailed reduction mechanism of GO to RGO was well established and explained by Thakur et al. [23].

### 2.4 Preparation of $Fe_3O_4$ magnetic nanoparticles

An aqueous solution of 50 mL of 1 mM iron (III) chloride was prepared and subsequently 10 mL of *Murrayakoenigii* leaves extract was added with continuous stirring. Further, 1.0 M NaOH solution was added to the above mixture and continued stirring for another 3 h. After 3 h the formation of $Fe_3O_4$ magnetic nanoparticles (MNPs) are marked by the appearance of the intense black precipitate. The resulting solution was cooled to room temperature and the obtained black product was isolated by applying an external magnetic field and washed with ethanol and dried in a vacuum oven at 80 °C for 12 h that results nano $Fe_3O_4$.

### 2.5 Preparation of RGO/$Fe_3O_4$ nanocomposite

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The RGO/$Fe_3O_4$ nanocomposite was synthesized by phytochemical method and the procedure is as follows. First, 0.1 g of GO was mixed with double distilled water and dispersed using ultrasonication. To this dispersed GO solution, 0.2 M 100 mL of $FeCl_3.6H_2O$ solution was added drop wise. Then, the aqueous extract of *Murrayakoenigii* leaves was added to the above mixture with continuous stirring and the resulting solution was stirred magnetically for 1 h. Further, the resulting reaction mixture was refluxed for 5 h at 80 °C. The obtained RGO/$Fe_3O_4$ nanocomposite was separated and washed with deionized water and absolute ethanol and then dried in vacuum oven at 100 °C for 2 h. The $Fe_3O_4$: RGO (2 wt%) nanoadsorbent was obtained and used for further studies.

**2.6 Characterization techniques**

FTIR measurements of *Murrayakoenigii* leaves extract, the as-synthesized RGO/$Fe_3O_4$ nanocomposite were made with Thermo Nicolet FTIR-200 thermoelectron corporations at room temperature. The powder X-ray diffraction (XRD) patterns were obtained RGO/$Fe_3O_4$ sample using Bruker AXS D8 advanced diffractometer at room temperature using Cu Kα (λ= 0.15406 nm) radiation generated at 40 kV and 30mA with scan rate of 0.02° per min from 5 to 80°. Morphology and size of the as synthesized RGO@$Fe_3O_4$ nanocomposite were investigated by transmission electron microscopy (JEOL JEM-3010) machine operated at 200 kV. A For the magnetization measurement, a vibrational sample magnetometer (VSM, Lakeshore 7410) was used at room temperature.

**2.7 Point of Zero charge**

The $pH_{PZC}$ (point of zero charge) is the pH when the charge on the surface of RGO/$Fe_3O_4$ nanocomposite is zero. The procedure of $pH_{PZC}$ drift method [24] could be described as follows: To a series of 250 mL conical flasks, 50 mL of 0.01 N NaCl was added. Then, the initial solution

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pH values (say pH initial) were adjusted in range between 2 and 9 with intervals of one using 0.01 N HCl solutions and 0.01 N NaOH. After constant value of $pH_{initial}$ had been reached, 0.010 g of RGO/$Fe_3O_4$ nanocomposite was added into each conical flask and caped them immediately. These solutions were stirred for 12 h to reach equilibrium. After 12 h, pH of solution was measured noted as $pH_{final}$. The $pH_{PZC}$ of RGO/$Fe_3O_4$ nanocomposite is the point when $pH_{initial}$ = $pH_{final}$.

**2.8 Batch adsorption experiments**

The adsorption of Pb(II) ion on to the RGO/$Fe_3O_4$ nanocomposite was studied in aqueous solution by batch adsorption experiments with pH range (Initial pH of the solution) varied from 2 to 7 at 301K. Pb(II) stock solution was prepared with different concentrations and then 3.5 mg of magnetic nanoadsorbent was added to 25 mL of each Pb(II) ion solution. The initial pH of Pb(II) ion was adjusted by using 0.1 M NaOH/HCl solution. The solution mixture was ultrasonicated at room temperature for 15min and transferred to 100mL Erlenmeyer flask was shaken in a thermostatic incubator (200 rpm) at 300K. Following that the magnetic nanoadsorbent was removed magnetically from the solution. The concentration of Pb(II) ions was determined using AAS(ShimadzuAA-6300). The amount of Pb(II) adsorbed by the RGO/$Fe_3O_4$ nanocomposite at equilibrium was obtained using the following equation.

$$q_e = \frac{(C_i - C_e)V}{M} \qquad (1)$$

where, $q_e$ (mg/g) is the equilibrium adsorption capacity of Pb(II), $C_i$ and $C_e$ are the initial and equilibrium concentrations (mg/L) of Pb(II), M is the adsorbent dosage (mg) and V is the volume of the solution (L). The percentage removal (%R) of Pb(II) from aqueous solution was calculated using the following equation:

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$$Adsorption(\%) = \frac{(C_i - C_e)}{C_i} \times 100 \qquad (2)$$

## 3. Results and discussion

### 3.1. FT-IR analysis

The FT-IR analysis was carried out to identify the possible functional groups and the formation the RGO/$Fe_3O_4$nano composite. Fig. 1 shows the FT-IR spectra of *Murrayakoenigii* leaves extract RGO/$Fe_3O_4$ nanocomposite respectively. FT-IR spectra of leaves extract show peaks at 3328, 2952, 1658, 1449 and 1122 $cm^{-1}$. The sharp and intense band at ~3328 is ascribed to the O-H stretching vibration corresponding to the polyphenol groups. The band at 2952 $cm^{-1}$ can be assigned to methyl C-H stretching vibrations and the one at 1642 $cm^{-1}$ is due to the C=O stretching of aldehydes in the leave extract. The other peaks observed are due to stretching C=C aromatic ring and C-OH stretching vibrations. In contrast to leave extract FT-IR spectra of RGO/$Fe_3O_4$ show slight shift in these peaks along with a few new peaks Fig. 1B. It is worth noticing that the intense and relatively sharp –O-H stretching vibration observed ~ 3328 $cm^{-1}$ in leave extract has become broad and weak in RGO/$Fe_3O_4$ composite. This shows that polyphenol groups present in leave extract has significant contribution for the formation of $Fe_3O_4$. In addition to other bands a sharp peak ~585 $cm^{-1}$ appears in RGO/$Fe_3O_4$ composite sue to the characteristic Fe-O stretching. It is worth mentioning that the slight shift in FT-IR bands in composite compared to pure leave extract might be due to the binding nature of these functional groups with the metal oxide RGO composite.

### 3.2 Powder XRD analysis

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The powder XRD patterns of GO, RGO and RGO/$Fe_3O_4$ composite are shown in Fig. 2. As can be seen that the graphene oxide (GO) shows a diffraction peak at 2θ of 10.1° corresponds to the (001) plane [25]. The reduced graphene oxide prepared after the reduction of GO with *Murrayakoenigii* leaves extract showed a broad diffraction peak at 2θ of 24.3° (002). Moreover, the XRD analysis of RGO/$Fe_3O_4$ nanocomposite exhibit major diffraction peaks at 30.2°, 35.5°, 43.2°, 53.5° and 62.6° which can be indexed to(220), (311), (400), (422) and (440) planes of the cubic phase $Fe_3O_4$ (JCPDS card no. 19-0629) with a face centered cubic structure [26].

### 3.3. TEM and SEM analysis

The morphology and structure of RGO/$Fe_3O_4$ nanocomposite were studied by TEM and SEM. From Fig. 3(A) TEM image of RGO/$Fe_3O_4$ nanocomposite exhibited significant changes in the surface morphology and roughness, visually demonstrating the presence of $Fe_3O_4$ nanoparticles. The $Fe_3O_4$ nanoparticles with an average size of ~12 nm were homogeneously assembled on the surface of RGO sheets, and no big agglomeration of $Fe_3O_4$ particles or large vacancy on RGO is observed. Nevertheless, it can be observed that the $Fe_3O_4$ nanoparticles are still strongly deposited on the surface of RGO sheets due to, the strong interaction between $Fe_3O_4$ nanoparticles and RGO sheets. The SEM measurement (Fig. 3B) explored that the nanocomposite obsessed a hierarchy dimensional morphology. The large RGO flakes showed slightly wrinkled surface and the $Fe_3O_4$ nanoparticles appeared a bright dots, densely and evenly deposited on both sides of RGO sheets.

### 3.4 BET isotherms

The BET specific surface area and porosity of GO, RGO/$Fe_3O_4$ nanocomposite samples are determined by $N_2$ adsorption-desorption isotherms at 77 K using liquid nitrogen as an adsorbent. Fig. 4 shows BET isotherms of GO and RGO/$Fe_3O_4$ samples, which characterize

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"type IV" isotherms with H3 hysteresis loops representing the mesoporous nature of the respective samples. The BET specific surface area for RGO/$Fe_3O_4$ nanocomposite sample is 58 $m^2$ $g^{-1}$. However, the modified Hummers method route obtained GO nanostructure specific surface area shows 76 $m^2$ $g^{-1}$ (Fig. 4), this is relatively higher than the RGO/$Fe_3O_4$ nanocomposite [27]. The decreased surface area in the RGO/$Fe_3O_4$ nanocomposite is sowed to the preferential blocking of the pores by the large size nanocrystalline $Fe_3O_4$ MNPs.

### 3.5. Raman spectra

The Raman spectrum of graphene oxide is generally described by two specific features such as G and D modes which are indicated to the $E_{2g}$ phonon of $sp^2$ carbon atom and breathing mode of kpoint photons of $A_{1g}$symmetry, respectively [28-31]. The prepared graphene oxide exhibited D and G modes at 1342 and 1610 $cm^{-1}$ Fig. 5 (a) and the reduced graphene oxide (RGO) was blue shifted to 1334 and 1600 $cm^{-1}$ Fig. 5 (b). Moreover, to the after mentioned carbon peaks, the characteristics $A_{1g}$ mode of $Fe_3O_4$ was found at 670 $cm^{-1}$ [32-34] confirming the hybrid structure of RGO/$Fe_3O_4$ nanocomposite Fig. 5C.

### 3.6. Magnetic behavior of RGO/$Fe_3O_4$ nanocomposite

Studying the magnetic behavior of the synthesized magnetically separable RGO/$Fe_3O_4$ nanocomposites is essential. In this respect, VSM analysis was carried out at room temperature for both the bare $Fe_3O_4$ nanoparticles and the RGO/$Fe_3O_4$ nanocomposites, and the results are shown in Fig. 6. The bare $Fe_3O_4$ nanoparticles and RGO/$Fe_3O_4$ nanocomposites showed typical S-like curve magnetization hysteresis loops with no coercivity, inferring that they exhibit super-paramagnetism, while their magnetization behaviors were removed in the absence of the applied magnetic field. The saturated magnetization value observed for the pristine $Fe_3O_4$and RGO/$Fe_3O_4$ nanocomposites were 15.3 emu $g^{-1}$, 12.6 emu $g^{-1}$, which was higher than that of the

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magnetic RGO/$Fe_3O_4$ nanocomposites. This can be ascribed to the presence of graphene in the nanocomposites. The advantage of the RGO/$Fe_3O_4$ nanocomposite is it can be easily separable by an external magnetic from the mixture reaction after the catalytic reaction.

### 3.7 Influence of pH value

The pH of solution is one of the most significant variables, influence of the pH value on the removal of Pb(II) ion by RGO/$Fe_3O_4$ nanocomposite was studied at pH 2-7, 301K and different Pb(II) initial concentrations of 30, 40 and 50 mg/L. As shown in Fig. 7A, the percentage removal of Pb(II) increased with an increase in pH from 2 to 5 and decreased with an increased pH 6-7 and the nanocomposite showed a maximum removal of 96% at pH 5.0, initial concentration of 30 mg/L. According to speciation diagram [35] at pH $\leq$5, lead predominately exists as $Pb^{2+}$, between pH 5-8 as $Pb(OH)^{+}$ and beyond pH 8 as $Pb(OH)_2$. Hence, the decrease in Pb(II) removal at higher pH is due to the formation of Pb(II) as Pb $(OH)^{+}$, and $Pb(OH)_2^0$ and $Pb(OH)_3^-$ at different pH values [36]. As less effect was observed when the initial concentration of Pb(II) was as 40 or 50 mg/L and the adsorption capacity of RGO/$Fe_3O_4$ nanocomposite was below 60%. The pH value of the solution can affect the surface charge of RGO/$Fe_3O_4$ nanocomposite this impacts the adsorption of metal ions on the magnetic adsorbent. At lower pH Pb(II) removal was inhibited due to the $H^{+}$ competed with Pb(II) for adsorption sites[37], which significantly affected Pb(II) adsorption at low pH medium. This is also supported from the pH PZC results. The pH PZC of RGO/$Fe_3O_4$ nanocomposite was found to be 4.5 (see Fig. 8). When the solution pH was below pH PZC the Pb(II) removal was low due to increased concentration of positive charges. In the pH range of ~4-5.5 due to the electrostatic attraction between positively charged Pb(II) and negative surface of RGO/$Fe_3O_4$ nanocomposite there is increased removal of Pb (II).

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### 3.8 Adsorption kinetic studies

Fig. 7(B) shows the adsorption behavior of Pb(II) on the RGO/$Fe_3O_4$ nanocomposite at an initial concentration of 30 mg/L, pH at 5.0 and 301K as a function of contact time. The adsorption rate of Pb(II) on RGO/$Fe_3O_4$ nanocomposite was almost finished within 35 min and then gradually reached equilibrium in 80 min. The pseudo first order and pseudo second order kinetic models were used to examine the kinetics of exclusion on the RGO/$Fe_3O_4$ nanocomposite [38-40]. The linear form of pseudo first order kinetic model is explained by the equation:

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right) t \qquad (3)$$

where $k_1$ ($min^{-1}$) is the pseudo first order rate constant of adsorption, $q_e$ and $q_t$ are the amount of the Pb(II) removal per unit mass of biosorbent (mg/g) at equilibrium and at time t (min). The pseudo first order kinetic constant was found out from the slope of the plot of log ($q_e$-$q_t$) vs. t. The $R^2$ value is very less indicative of that the adsorption of Pb(II) ions does not pursue pseudo first order kinetic model (Table 1). The kinetic data were further investigated using pseudo second order kinetic model. The linear form of pseudo second order kinetic model is elucidated by the equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right) t \qquad (4)$$

where$k_2$ (g/mg $min^{-1}$) is the pseudo second order rate constant of adsorption, qe and qt are the amount of the Pb(II) removal per unit mass of biosorbent (mg/g) at equilibrium and at time t (min). The values of $K_2$ and qe can be calculated from the slope intercept of t/$q_t$ vs. t (Table 1). From the removal kinetics shown in Fig. 9 the slope explained good linearity with the correlation coefficient value ($R^2$) 0.999, indicating that the removal kinetic follow the pseudo second order

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rate model. The adsorption system obeyed the pseudo second order kinetic model for the entire adsorption period.

### 3.9 Adsorption isotherms

To quantify the sorption capacity of Pb(II) ions onto RGO/$Fe_3O_4$ nanocomposite was understand by, two parameter equations namely Langmuir [41] and Freundlich [42] isotherm models. The freundlich isotherm is another form of approach for the adsorption isotherm on heterogeneous surfaces. The freundlich model is considered as multisite adsorption, when the adsorbate surface has heterogeneity (Fig. 10A). The linearized form of the freundlich isotherm model is represented as below;

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \qquad (5)$$

Where $k_f$ (mg/g) is a constant relating the sorption capacity and 1/n is an empirical parameter relating the sorption intensity. The values of Freundlich constants $k_f$ and 1/n obtained from plots of log $C_e$ vs. log $q_e$ (Table. 2).

Langmuir isotherm assumes that there is monolayer coverage on adsorbent surface and no subsequent interaction among adsorbed molecules (Fig. 10B). The linearized form of the Langmuir isotherm is represented as follows:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m b} \qquad (6)$$

where $q_e$ is the equilibrium metal ion concentration on the sorbent (mg/g), $q_m$ is the monolayer sorption capacity of the sorbent (mg/g), $C_e$ is the equilibrium metal ion concentration in the solution (mg/L) and b is the Langmuir constant related to the free energy of sorption. The values of $q_m$ (mg/g), and b were calculated from the slope and intercept of $C_e/q_e$ versus $C_e$ (Table 2).

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The maximum monolayer sorption capacity was found to be 48.26 mg/g of Pb(II) onto RGO/$Fe_3O_4$ nanocomposite. Another parameter in the Langmuir isotherm a dimension less separation factor (RL) is defined as follows.

$$RL = \frac{1}{1 + bC_i} \qquad (7)$$

where $C_i$ (mg/g) is the initial metal concentration, b is the Langmuir constant. For favorable sorption, RL must lie within 0 to 1, where RL >1, RL=1 and RL<0 indicate the unfavorable linear and irreversible sorption. In this study, the RL is 0.0785 which lies between 0 and 1. This indicates a highly favorable adsorption and increasing adsorption efficiency at higher Pb(II) concentrations. For all cases, the Langmuir equation fits the experimental data better than the Freundlich isotherm. It is clear that the Freundlich model could not fit all the experimental data well, as $R^2$ values are generally lower than the Langmuir model. The adsorption capacity of the present RGO/$Fe_3O_4$ nanocomposite is compared with that reported for other materials in Table 3. It should be noted that the prepared material showed a better Pb(II) adsorption capacity than other organic-molecule-capped nanoparticles and a value similar to the best adsorption capacity among the reported materials.

**3.10 Desorption and reusability**

It is desirable for any adsorbent to retain the adsorption capacity when regenerated to be reused further that makes the adsorbent economically viable. Therefore the regeneration of the adsorbent was carried out using 0.2 M HCl that leads to the desorption of the Pb(II) from the adsorbent surface. The acidic pH favours the desorption of Pb(II) from the RGO/$Fe_3O_4$ adsorbent. This is due to the fact that higher concentration of hydrogen ion makes the surface positively charge due to higher protonated groups that helps in desorption of positively charged

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Pb(II) ions. It is also evident from our pH studies that at low pH the adsorption capacity of RGO/$Fe_3O_4$ was found to be lesser due to competition between protonated groups and Pb(II) ions. This result also supports the greater desorption of Pb(II) at acidic pH. Further, the regenerated RGO/$Fe_3O_4$ adsorbent was further tested for adsorption of Pb(II) to check the feasible reusability of the adsorbent. The results showed that the regenerated adsorbent shows 95, 89 and 81% removal for first, second and third cycle respectively. This result indicates that RGO/$Fe_3O_4$ is a promising adsorbent that can be regenerated and be reused.

## 4. Conclusion

In this work, we studied a novel and environmentally benign route for the synthesis of RGO/$Fe_3O_4$ nanocomposite. The particles in synthesized nanocomposite showed spherical shape and was explored by transmission electron microscope. The powder XRD and FT-IR results confirm the formation of RGO/$Fe_3O_4$ nanocomposite. The super paramagnetic property of the nanocomposite was confirmed by vibrating sample magnetometer at room temperature. A strong electrostatic attraction present between RGO/ $Fe_3O_4$ nanocomposite and Pb(II) at different pH and plays a vital role in the adsorption. The maximum adsorption capacity was found to be 48 mg/g at pH 5 and temperature 301 K. The adsorption data best fits Langmuir isotherms model and adsorption follows second order kinetics. We also have demonstrated that the adsorbent can be easily removed by magnetic separation with external magnet. These features of magnetically separable RGO/$Fe_3O_4$ nanocomposite make it a promising and recyclable adsorbent for many environmental remediation applications.

## Acknowledgements

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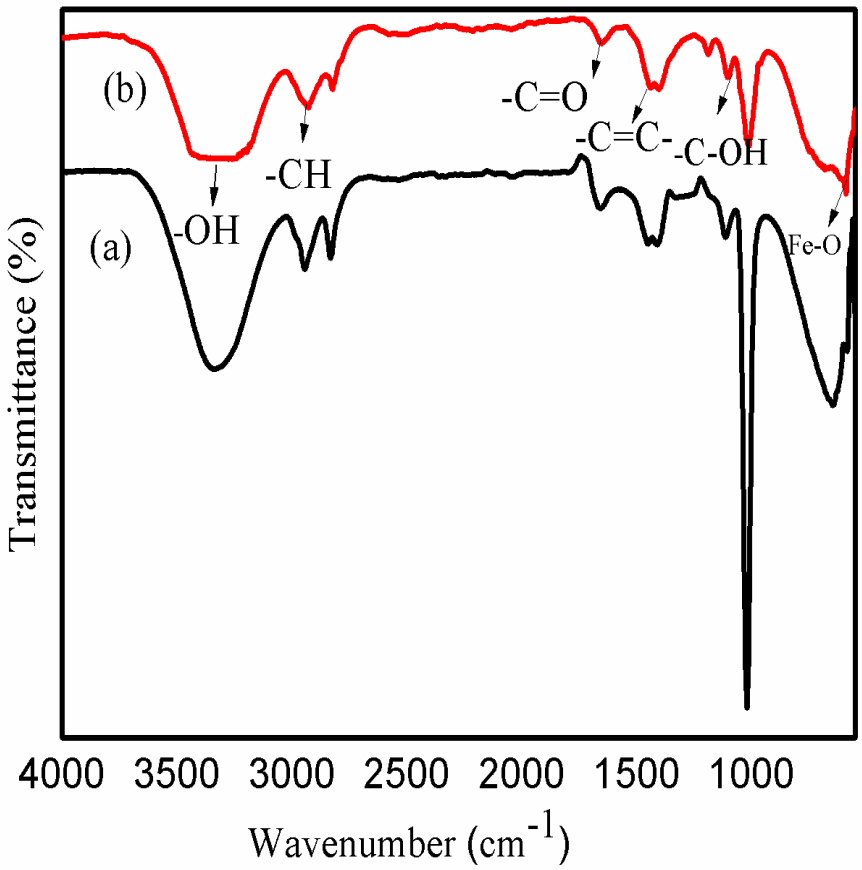



**Fig. 1** FT-IR spectrum of (a) *Murraya koenigii* leaves extract and (b) synthesized RGO/$Fe_3O_4$ nanocomposite.

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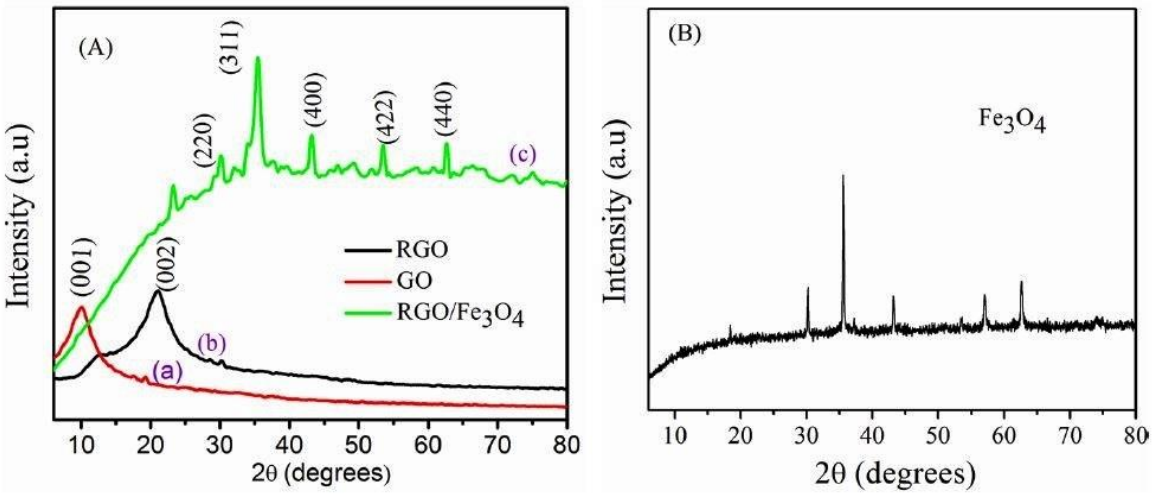



**Fig. 2** (A) the powder XRD pattern of the GO (b) RGO (c) RGO/ $Fe_3O_4$ nanocomposite; (B) bare Fe3O4 sample synthesized with RGO addition

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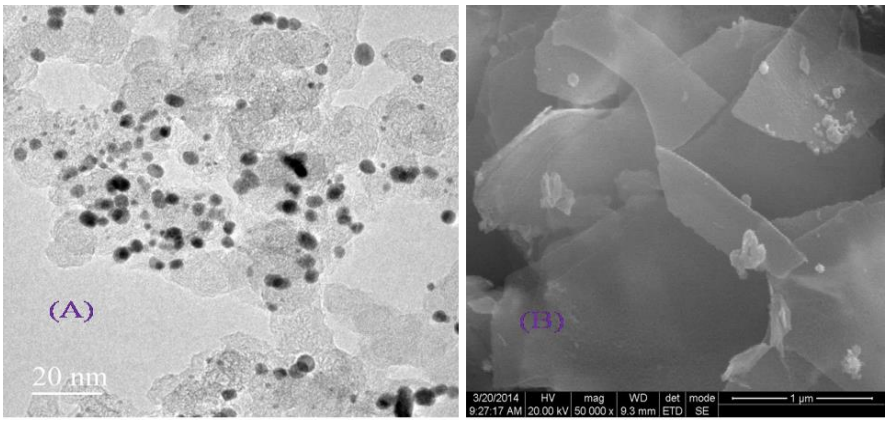



**Fig. 3** (A) TEM (B) SEM images of RGO/$Fe_3O_4$ nanocomposite

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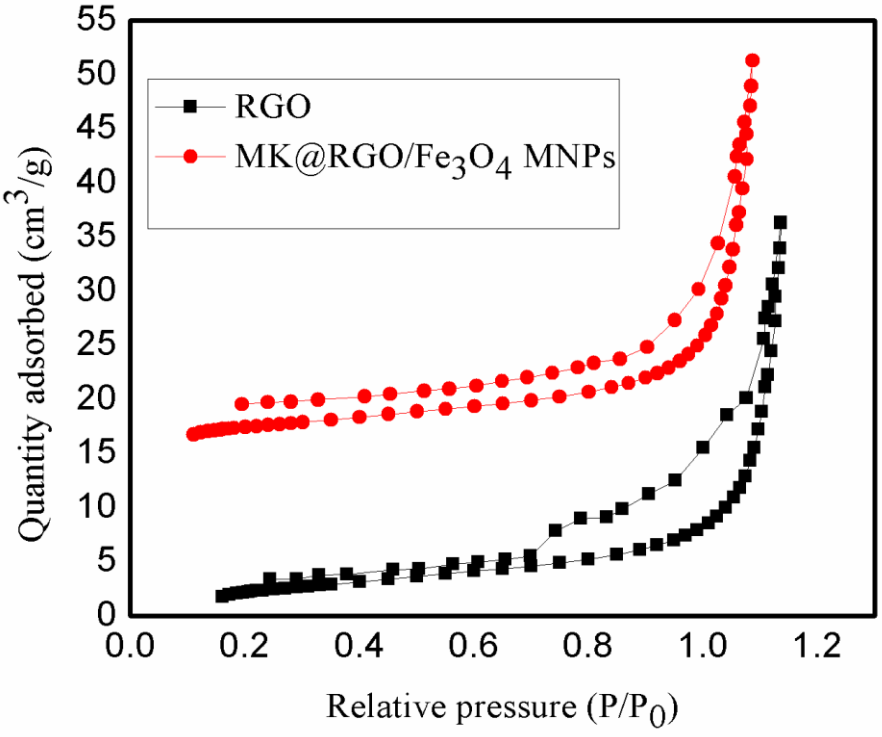



**Fig. 4** $N_2$ adsorption-desorption isotherm of RGO and RGO/$Fe_3O_4$ nanocomposite sample.

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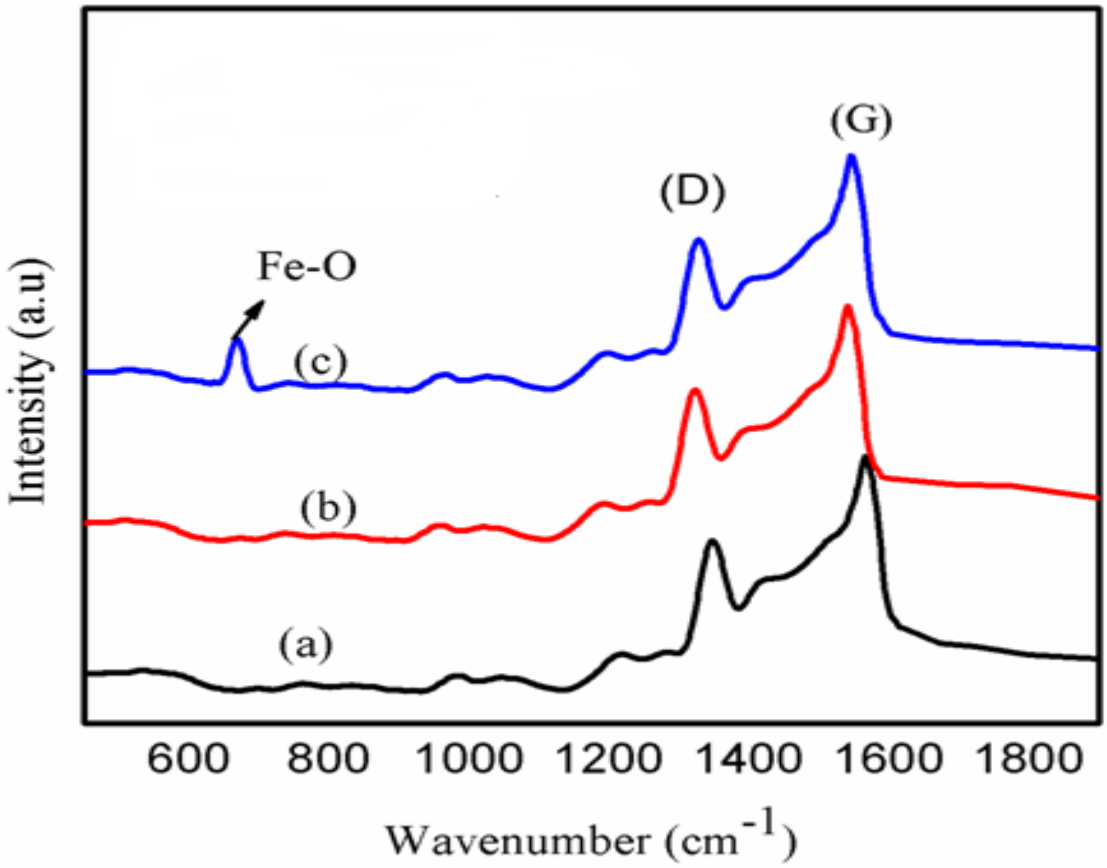



**Fig. 5**(a) Raman spectra of GO (b) RGO and (c) RGO/$Fe_3O_4$ nanocomposite samples.

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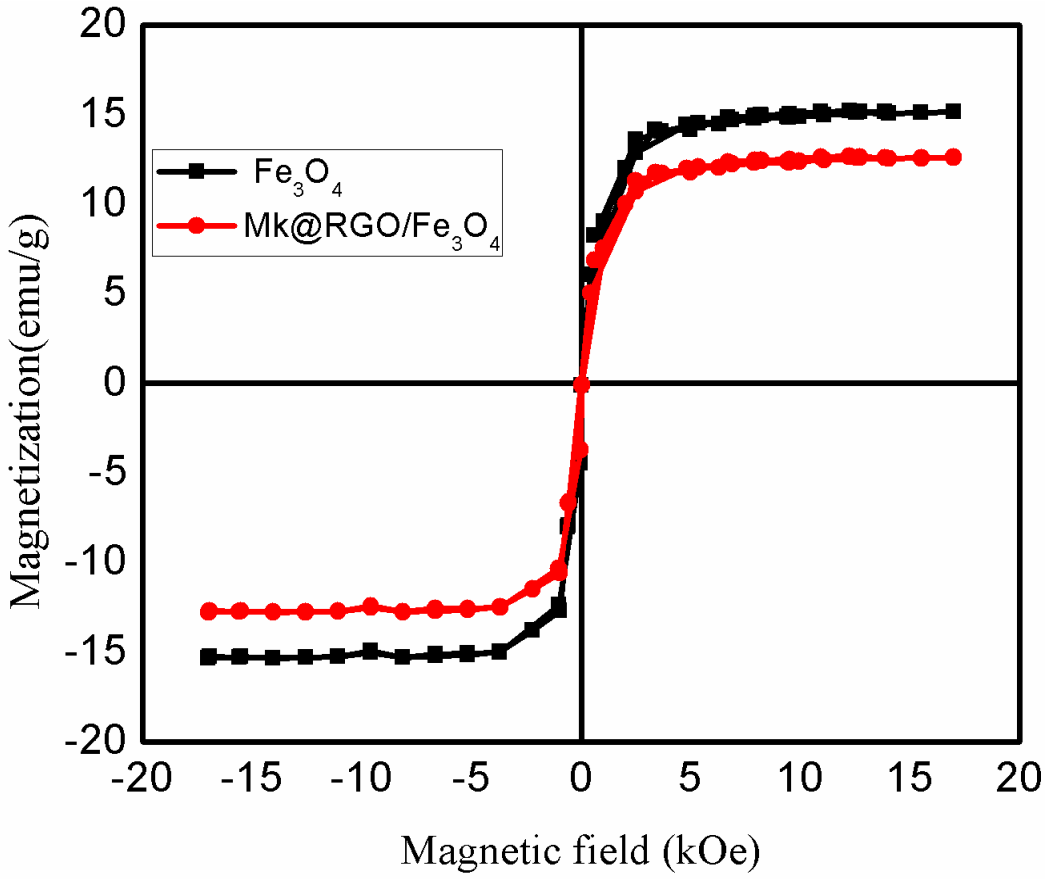



**Fig. 6** M-H hysteresis curve of $Fe_3O_4$, RGO/$Fe_3O_4$ nanocomposite sample measures at 300 K

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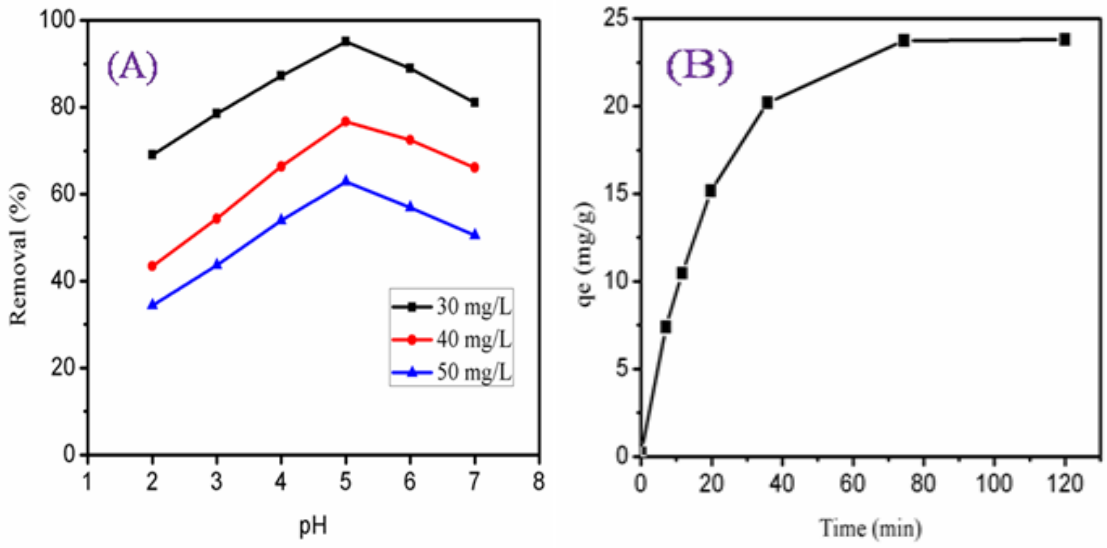



**Fig. 7** (A) effect of pH value on the adsorption of Pb(II) by RGO/$Fe_3O_4$MNPs at different initial concentration of Pb(II): 30, 40, 50 mg/L, solution volume: 25 mL, time: 120 min, temperature: (301K) (B) effect of contact time on the extraction of Pb(II) by RGO/$Fe_3O_4$ nanocomposite.

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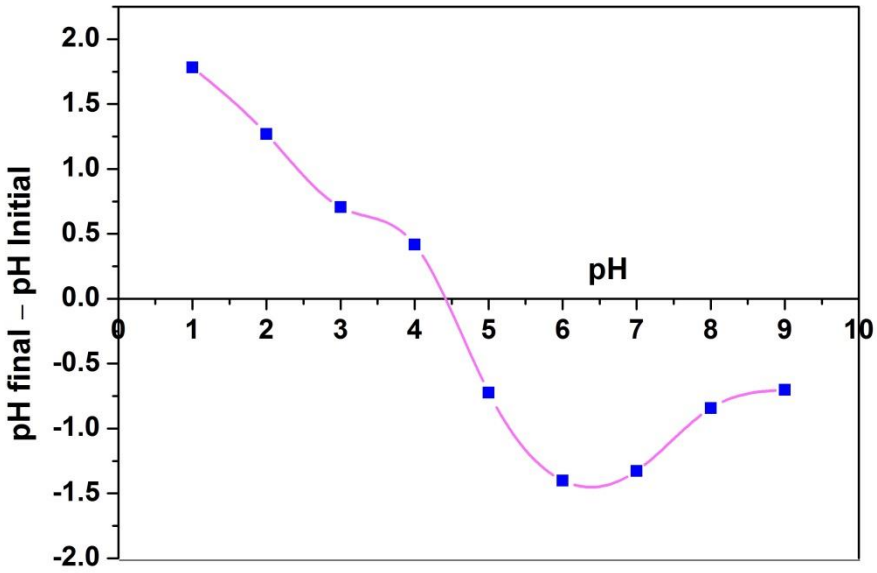



**Fig. 8** pH PZC of the RGO/ $Fe_3O_4$ nanocomposite determined by drift method

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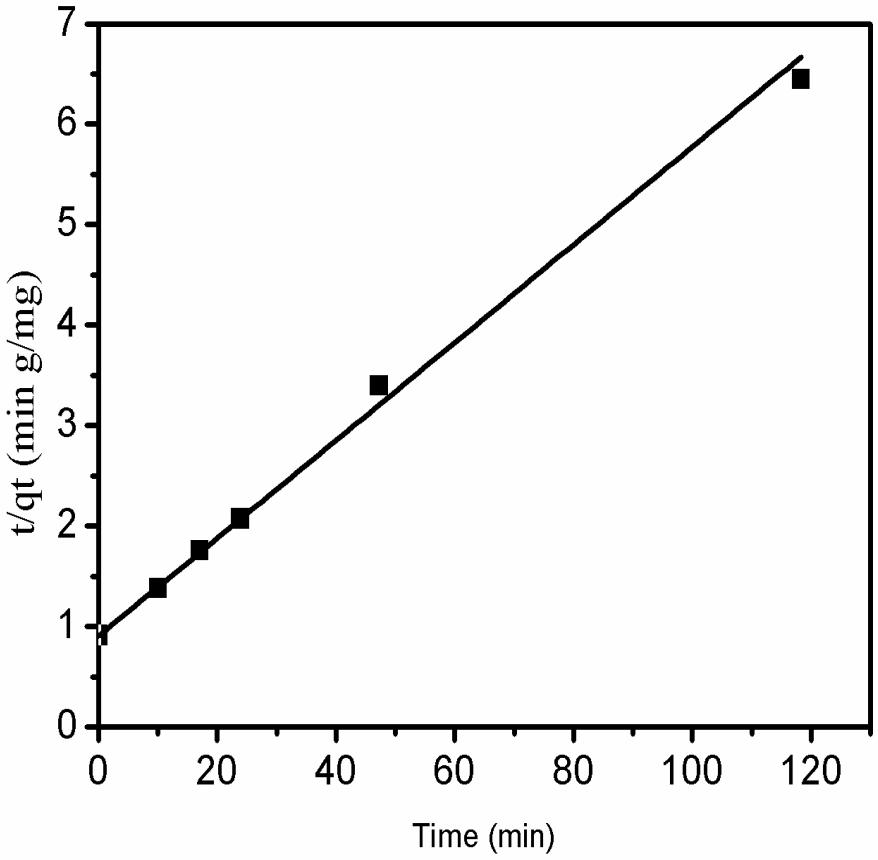



**Fig. 9** Pseudo second order adsorption kinetics of Pb(II) on RGO/ $Fe_3O_4$ nanocomposite

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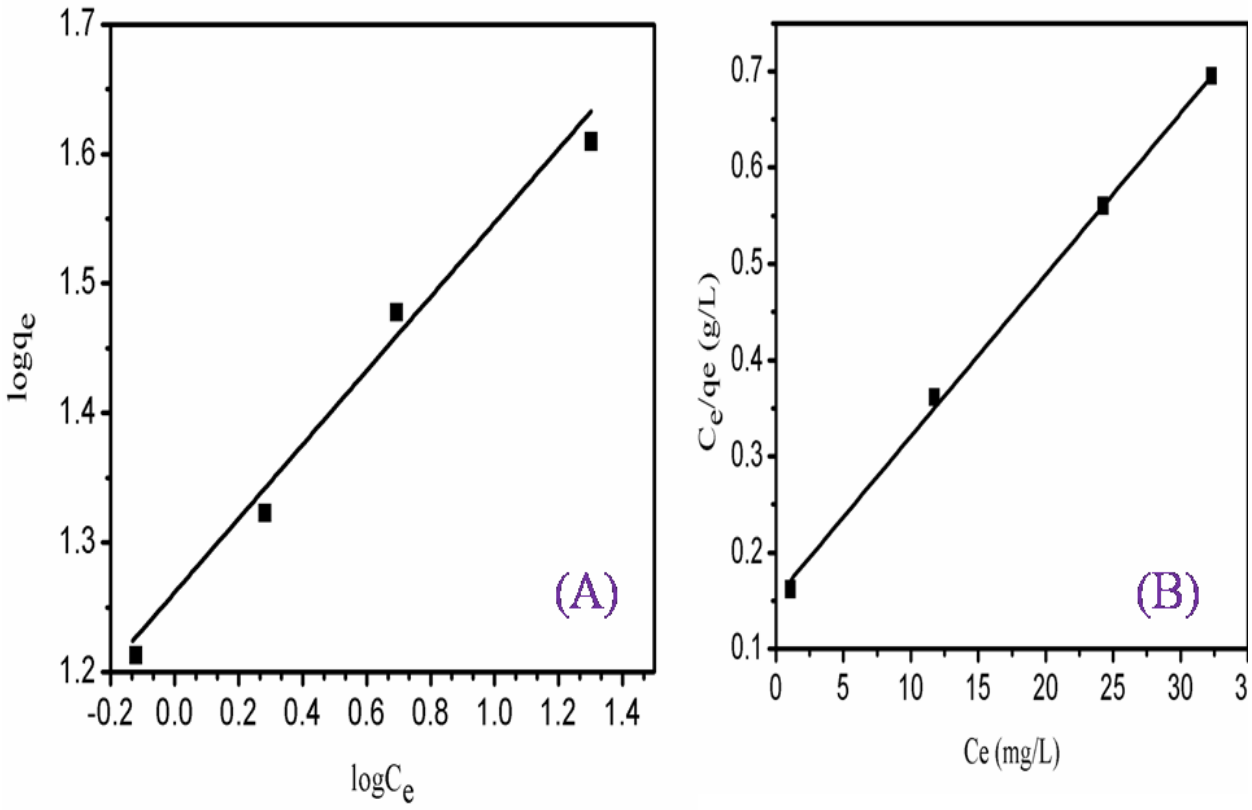



**Fig. 10** (A) Linear plot of Freundlich isotherm of Pb(II) on RGO/$Fe_3O_4$ MNPs (B) Linear plot of Langmuir of Pb(II) on RGO/$Fe_3O_4$ nanocomposite.

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**Table 1:** Kinetic parameters for the adsorption of Pb(II) onto RGO/$Fe_3O_4$ nanocomposite at different metal ion concentrations.

| Pb(II) Conc. (ppm) | Lagergren first order | | | Pseudo-second-order | | |
|---|---|---|---|---|---|---|
| | $K_1$ (1/min) | $R^2$ | SSE | $K_2$n) | $R^2$ | SSE |
| 30 | 0.023 | 0.985 | 0.903 | 0.014 | 0.999 | 0.0160 |
| 40 | 0.028 | 0.979 | 0.907 | 0.018 | 0.999 | 0.0054 |
| 50 | 0.034 | 0.976 | 0.910 | 0.022 | 0.998 | 0.0062 |

**Table 2:** Langmuir and Freundlich isotherm constants and correlation coefficients for Pb(II) adsorption onto RGO/$Fe_3O_4$ nanocomposite at constant temperatures.

| Temp. | Langmuir | | | | Freundlich | | | |
|---|---|---|---|---|---|---|---|---|
| (K) | $q_m$ (mg/g) | $K_L$ (L/mg) | $R^2$ | $\chi^2$ | $K_f$ (mg/g) | 1/n | $R^2$ | $\chi^2$ |
| 301 | 48.26 | 9.67 | 0.999 | 10.67 | 12.28 | 0.567 | 0.985 | 58.53 |

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**Table 3.** Comparison of adsorption capacity of various sorbents with RGO@$Fe_3O_4$ nanocomposite onto Pb(II) ions.

| **Adsorbent** | **$q_{max}$ (mg/g)** | **Reference** |
|---|---|---|
| $Fe_3O_4$@C | 71.42 | 43 |
| $Fe_3O_4$/$SiO_2$nano composite | 17.65 | 44 |
| $Fe_3O_4$nanospheres | 18.47 | 45 |
| chitosan-tripolyphosphate beads | 57.33 | 46 |
| chitosan immobilized on bentonite | 32.55 | 47 |
| RGO@$Fe_3O_4$ MNPs | 49.00 | Present study |

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# Synthesis, Crystal structure, Hirshfeld surface studies and frontier orbitals analysis of 4-(1-benzofuran-2-yl)-2-methyl-6-phenylpyrimidine

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**Abstract**

*4-(benzofuran-2-yl)-2-methyl-6-phenylpyrimidine(BFMPP) has been synthesized and characterized by FT-IR, $^{1}H$ &$^{13}CNMR$ and Mass spectrometry techniques. Single crystals of title compound were grown by slow evaporation solution growth technique at room temperature and crystal structure has been determined by single crystal X-ray diffraction technique. The title compound(BFMPP) crystallizes in monoclinic space group $P2_1$, with cell dimensions a = 4.803(3) Å, b = 9.498(5) Å, c = 15.557(9) Å, β= 93.25 (4)$^{o}$ and Z = 2. The crystal structure is stabilized by weak C-H…N intermolecular interactions generating a one dimensional C(4) network propagating along the [100] direction and two pi…pi interactions. Further, a detailed analysis of the Hirshfeld surfaces facilitating an understanding of the type and nature of intermolecular interactions in the supramolecular structure is made. The calculated HOMO-LUMO energy gap discloses that charge transfer occurs within the molecule.*

**Keywords:** BFMPP, Crystal structure, X-ray diffraction, Hirshfeld analysis, HOMO-LUMO plots.

**Specifications Table**

| | |
|---|---|
| Subject area | *X-ray crystallography* |
| Compounds | *4-(benzofuran-2-yl)-2-methyl-6-phenylpyrimidine* |
| Data category | *Crystallographic data* |
| Data acquisition format | *CIF for crystallography* |
| Data type | *Analyzed* |
| Procedure | *The unit cell parameters and the intensity data at 298K for the title compound was obtained on an Oxford Diffraction Xcalibur Gemini single crystal X-ray diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The CrysAlisPro software was used for data collection, reduction and absorption correction.* |
| Data accessibility | *CCDC:1411045 URL:https://www.ccdc.cam.ac.uk/conts/retrieving.html* |

## 1. Rationale

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Heterocycles hold a key point in organic and medicinal chemistry as they act as a bridge between life sciences and biochemical investigations. A significant amount of contemporary investigation is being currently pursued on these compounds worldwide. The pyrimidine rings are nitrogen rich heterocycles, key constituent of many natural, synthetic compounds and shows very interesting pharmacological activity [1-4]. In recent years, pyrimidine derivatives have received significant attention owing to their diverse biological properties, particularly as cytostatic [5-8], immune modulating [9], antitubercular, calcium channel blockers [10], antimicrobial properties [11], herbicides [12] and pesticides [13].

The biological importance of pyrimidine derivatives has motivated significant interest towards the synthesis of 4-(benzofuran-2-yl)-2-methyl-6-phenylpyrimidine(BFMPP) and the structure was characterized well as it would be more useful. Further, various intermolecular interactions are well supported by Hirshfeld surface and fingerprint plots analysis.

## 2. Experimental

### 2.1. General remarks

The reagents and solvents used for synthesis were procured from Spectrochem, Sigma Aldrich and used as such received. Reactions were monitor by analytical thin layer chromatography (TLC) and TLC plates were visualized by exposing UV light, KMnO4 solution or by iodine vapors. The FT-IR spectrum was recorded in KBr pellets using JASCO FTIR-4100 spectrometer in the range of 4000 – 400 $cm^{-1}$ at resolution of ± 2 $cm^{-1}$.$^{1}$H &$^{13}$C-NMR spectrum was recorded on JEOL-400 MHz NMR instrument using $CDCl_3$ as solvent. The chemical shifts values (δ) are reported in parts per million (ppm) using TMS as an internal standard. Mass spectrum was recorded on Shimadzu-2010EV with APCI and ESI probes.

### 2.2. Synthesis of 4-(1-benzofuran-2-yl)-2-methyl-6-phenylpyrimidine

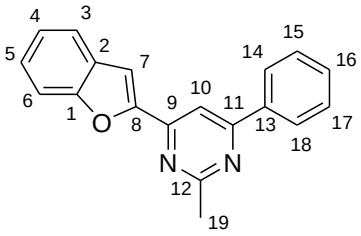
To a stirred solution of (1-benzofuran-2-yl)-3-phenylprop-2-en-1-one (0.5g, 2.06mmol) in mixture of ethanol: water (4:1, 5 mL), acetamidine hydrochloride (0.11g, 2.06 mmol), KOH (0.12g, 2.2mmol) was added and the reaction mixture refluxed for 6 hours. After completion of reaction indicated by TLC, the reaction mixture was poured into ice cold water and extracted to ethyl acetate (3 x 20 mL). The organic layer washed with water, brine and dried over anhydrous $Na_2SO_4$. Evaporate the organic layer under reduced pressure to get crude product. The crude product was purified by column chromatography using silica 60-120 mesh and ethyl acetate: petroleum ether (1:9) as eluent to get desire product (0.39g, yield: 68.4%, M.p: 130-133$^{o}$C).

### Method of crystallization

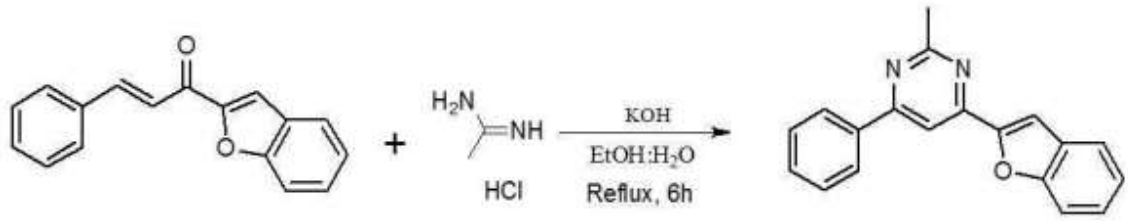
100mg of compound was dissolved in 15mL of ethyl acetate and warmed for 5 minutes. The solution was filtered through Whatmann filter paper and resulting solution was kept at room temperature in conical flask with stopper slightly open. After 5 days, the crystals of BFPP were developed; filtered and suitable crystals for single crystal analysis were selected (**Scheme-1**).

**$^{1}$H NMR (400MHz, $CDCl_3$):** δ 8.20-8.17 (2H, m, Ar-H), 8.05 (1H, s, Py-H), 7.71-7.69 (2H, dd,Ar-H), 7.62-7.53 (4H, m, Ar-H), 7.43-7.39 (1H, m, Ar-H), 7.32 (1H, m, Ar-H), 2.86 (3H, s, Py-CH3).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 168.576 (C12), 165.217 (C9), 156.213 (C11), 155.642 (C1), 153.310 (C8), 136.973 (C13), 130.901 (C14 & C18), 128.915 (C15 & C17), 128.295 (C16), 127.278 (C5), 126.313 (C4), 123.510 (C2), 122.248 (C3), 111.670 (C6), 108.906(C7), 108.124 (C10), 26.204 (C19).




**Mass (m/z):** Calculated: 286.32, Found: 287.59 (M+1)




**Scheme.** Synthesis of 4-(1-benzofuran-2-yl)-2-methyl-6-phenylpyrimidine

**2.3. X-Ray Crystallography**

A suitable colourless, needle shaped single crystal of the title compound with dimensions of0.36mm x 0.20mm x 0.16mm was selected and data was collected on an Oxford diffraction X caliber Gemini diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at 293 K. The CrysAlisProsoftware [14] was used for data collection, reduction and absorption correction. The structure was solved by direct method and refined by full-matrix least-squares methods on $F^2$ using SHELX-97 [15] available in the WinGX package [16]. All the non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in the structure factor calculations and treated using a riding model. Molecular graphics and crystal packing were created using *ORTEP* [17] and *MERCURY* [18] packages. The parameter for data collection and structure refinement of compound BFMPP are listed in Table 1.

**2.4. Hirshfeld surfaces**

The Hirshfeld surface analyses were carried out and fingerprint plots were plotted using Crystal Explorer 3.0 [19-25]. When the CIF files were uploaded into the Crystal-Explorer software, all bond lengths to hydrogen were automatically modified to standard neutron diffraction values, i.e. C–H = 1.083 Å.

**3. Data, value and validation**

**3.1. Crystal and molecular structure description of BFMPP**

The molecular structure of BFMPP determined by X-ray diffraction is depicted in **Figure 1**. BFMPP crystallizes in the monoclinic space group $P2_1$with cell dimensions *a* = 4.803(3) Å, *b* = 9.498(5) Å, *c* = 15.557(9) Å, β= 93.25 (4)$^o$ and Z = 2.The molecule is almost planar with root mean squared deviation (considering non-H atoms) being 0.101 Å. The dihedral angle between the benzene (A), the pyrimidine

ring (B) and the benzofuran ring (C) are 4.79 (A/B), 10.76 (A/C) and 8.42(1)°(B/C) respectively. The crystal structure is stabilized by weak C-H…N intermolecular interactions (Table 2 and **Figure 2**) running into C(4) chains along [100] and two pi…pi interactions. Hence, the supra molecular architecture exhibited is one dimensional.

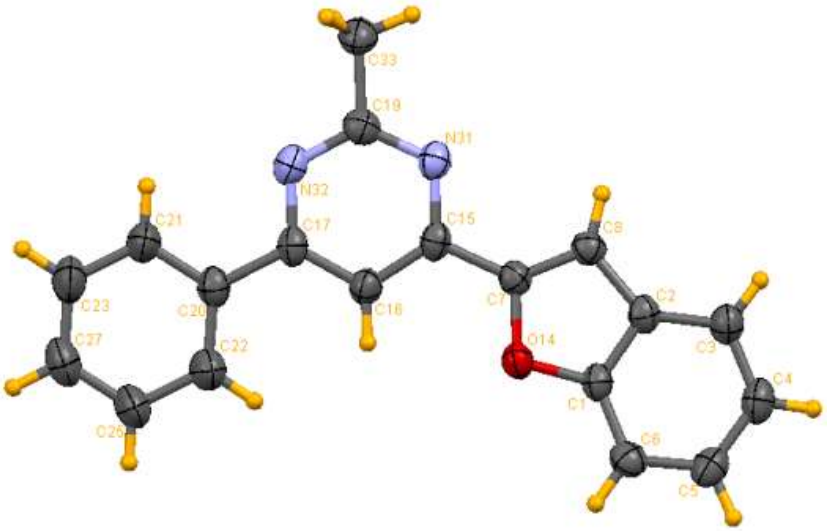



**Figure 1.** *ORTEP* view of the molecule with atom numbering scheme for non-hydrogen atoms

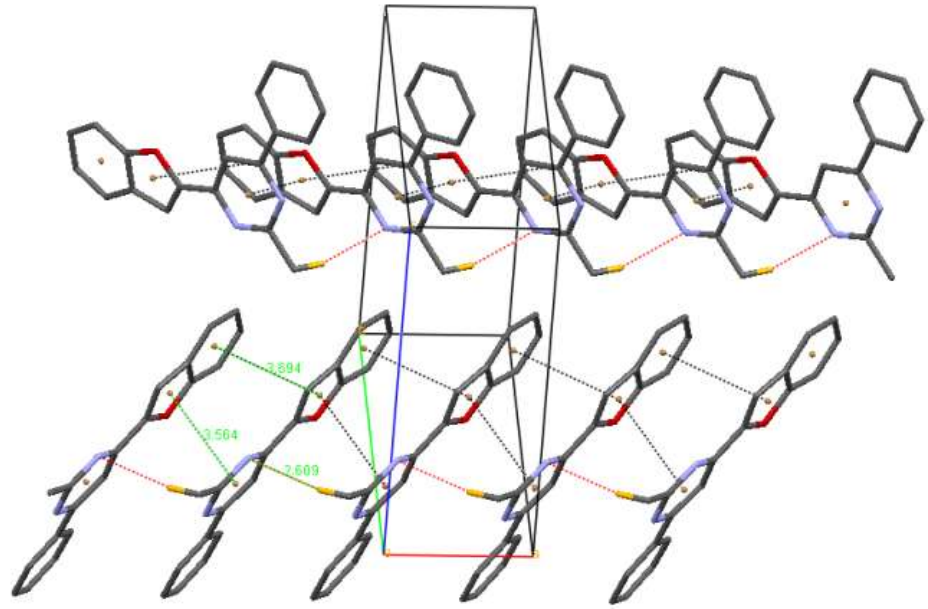



**Figure 2.** Crystal packing of BFMPP

### 3.2. Hirshfeld surface analysis

The Hirshfeld surfaces of title compound illustrated in **Figure 3**, showing surfaces that have been mapped over a $d_{norm}$(A), shape index (B) and curvedness (C) range of -0.111 to 1.143 Å, -1.0 to 1.0 Å and -4.0 to 0.4 Å, respectively. The predominant interactions between the methyl hydrogen of pyrimidine ring and the nitrogen of pyrimidine ring, which can be seen in the Hirshfeld surfaces as the bright red spot marked as A in **Figure 3** and clearly seen in **Figure 4**. In the 2D fingerprint plots (**Figure 5**), the C-

H···N intermolecular interactions appear as two distinct spikes circled with green color. Prominent pairs of sharp spikes of almost equal lengths in the fingerprint plots (**Figure 5**) are characteristics of nearly equal C(donor)···N(acceptor) distances and generate a one dimensional C(4) network propagating along the [100] direction. The upper spike (**Figure 5**) corresponds to the donor spike (H atom of methyl group interacting with N-atoms of the pyrimidine ring), with the lower spike being an acceptor spike (N-atomsof the pyrimidine ring interacting with H- atom of methyl group). The wings marked in Figure 5 (circled with black) are due to the C···H contacts. A significant difference in terms of H···H contacts appears asspikes (marked as red circles in **Figure 5**). The relative contribution of the different interactions to the Hirshfeld surface was calculated for title compound. It is evident that the H···H contacts can account forabout 50.5% of the Hirshfeld surface area; the remaining contribution was mostly due to C···H 28.2%,N···H 6.5%, O···H 3.3% and C···C 6.0% interactions, with only minor contribution from C···N, O···C and O···N (maximum 5.5%).

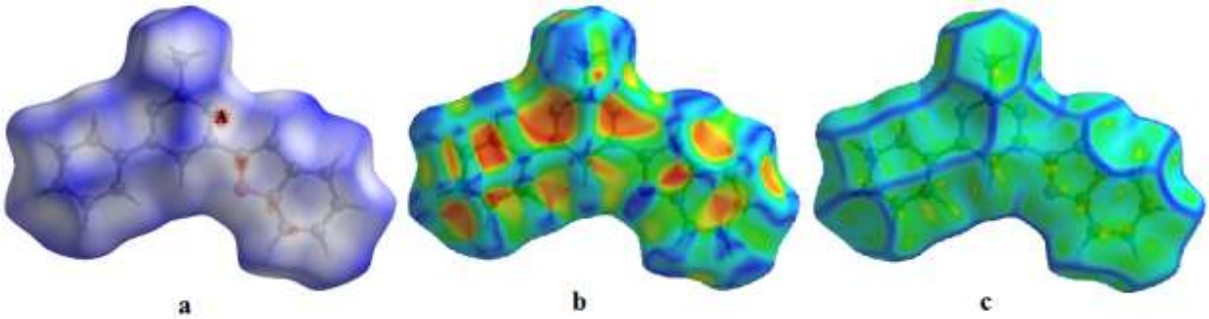



**Figure 3.** Hirshfeld surfaces of BFMPP.

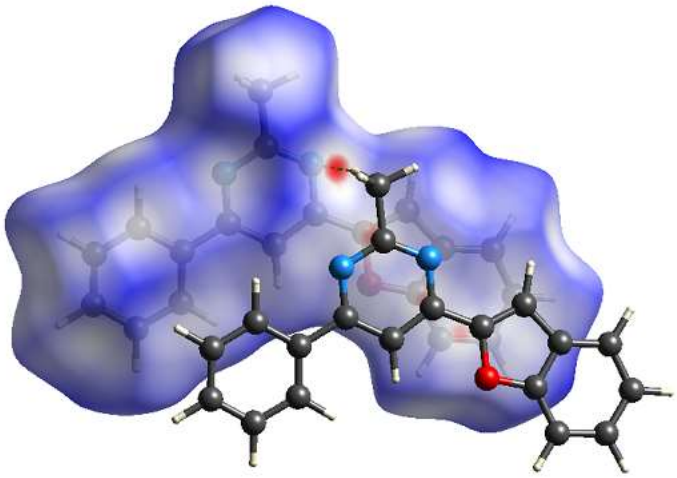


**Figure 4.** C-H…N intermolecular interactions mapped on $d_{norm}$ surface.

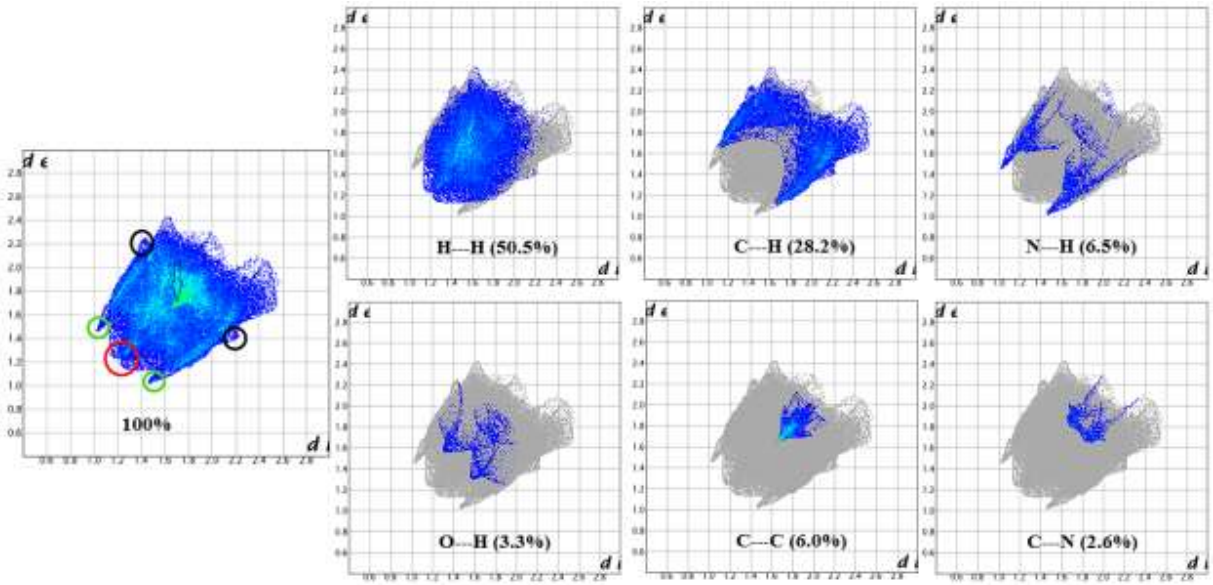



**Figure 5.** 2D Fingerprint plots of BFMPP.

### 3.3.Frontier molecular orbital analysis

The HOMO-LUMO energy plots of BFMPP has been obtained from Crystal Explorer with Tonto program using DFT/Becke88LYP/6-31G(d) method and the pictorial representation shown in **Figure 6**. The HOMO (MO 75) lies at -6.28 eV and whereas the LUMO (MO 76) is located at -2.2 eV. In the title compound, the HOMO of π nature is delocalized all over the molecule except phenyl ring, methyl group and LUMO in addition to this on the phenyl ring except methyl group. Accordingly, the HOMO-LUMO transition implies an electron density transfer from the benzofuran ring to phenyl ring through the pyrimidine ring, and that the frontier orbital energy gap is 4.08 eV. The global chemical descriptors associated with a molecular system are: ionization potential (I) = $-E_{HOMO}$= 6.28, electron affinity (A) = $-E_{LUMO}$= 2.2, chemical potential (μ) = - (I+A)/2 = -4.24, the global hardness (η) = (I-A)/2 = 2.04 ,softness (ν)= 1/ η = 0.49, electronegativity (χ) = (I+A)/2 = 4.24 and electrophilicity index (ω) = $\mu^2/2\eta$ = 4.406 [26,27]. It is seen that the chemical potential of the title compound is negative and it implies that the molecular system is stable. They do not decompose spontaneously into the elements they are made up of. The hardness signifies the resistance towards the deformation of electron cloud of chemical system under small perturbation encountered during the chemical process.

### 3.4. UV-Visible spectral analysis

The electronic spectra of title compound calculated at TD-DFT/B3LYP/SDD method using optimized geometry and the calculation are performed in methanol. The electronic spectra of title compound shows an electronic absorption band with maxima 344 nm (**Figure S5**)and this transition mainly due to the transition HOMO-LUMO that is the π-π transition predicted. The excitation transitions, CI coefficient, excitation energies, oscillator strengths and wavelength can be seen in Table S1.

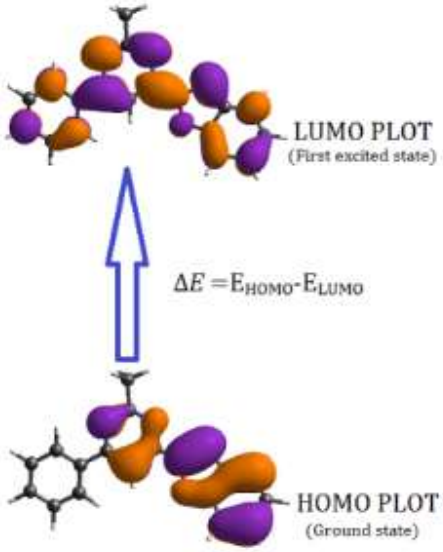



**Figure 6.** HOMO plot and LUMO plot of the title compound (BFMPP).

### 3.5. FT-IR spectral analysis

FT-IR spectrum of title compound is shown in **Figure S1**. Vibrational frequencies of title compound calculated at ground state by using B3LYP/DFT/SDD basic set in gas phase(Table S2).The CH stretching frequency of aromatic rings are theoretically assigned at 3181, 3117, 3090 $cm^{-1}$ for benzofuran ring and 3150 $cm^{-1}$ for pyrimidine ring. For mono-substituted phenyl ring, the CH stretching modes are expected above 3000 $cm^{-1}$[28, 29] and DFT calculations give these modes in the range 3120, 3106, 3094 $cm^{-1}$ and experimentally bands are observed at 3051 $cm^{-1}$. The $CH_3$ stretching modes are expected in the region 2900-3050 $cm^{-1}$[28]. The bands observed at 2925 $cm^{-1}$ and in the range 3060-2939 $cm^{-1}$ (DFT) are assigned as stretching modes of the methyl group. The aromatic ring stretching modes are observed in the range 1585, 1558$cm^{-1}$ and 1598, 1569 $cm^{-1}$ theoretically expected. The C=N stretching modes is observed at1528$cm^{-1}$experimentally and computed 1528 $cm^{-1}$. In present case in-plane and out-of-plane CH deformation observed at above and below 1000 $cm^{-1}$ and good agreement literature values.

### 4. Conclusion

4-(1-benzofuran-2-yl)-2-methyl-6-phenylpyrimidine(BFMPP)has been synthesized and characterized by single crystal X-ray diffraction, FT-IR, $^{1}H$ & $^{13}C$NMR and Mass spectrometry. The X-ray diffraction studies showed that the title BFMPP crystallized in monoclinic space group $P2_1$, with cell dimensions $a$ = 4.803(3) Å, $b$ = 9.498(5) Å, $c$ = 15.557(9) Å, β= 93.25 (4)$^{o}$ and Z = 2.The difference in HOMO and LUMO energies supports the charge transfer interaction within the molecule. The calculated HOMO and LUMO energies were used to semi-quantitatively estimate the ionization potential, electron affinity, electronegativity, electrophilicity index, hardness and chemical potential. The crystal surface analysis carried out by Hirshfeld surface studies and fingerprint plots analysis, which facilitates to understanding the type and nature of intermolecular interactions and as well as packing in the solid-state.

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**Table 1.** Crystallographic data and structure refinement of BFMPP

| | |
|---|---|
| Formula | $C_{19}H_{14}N_2O$ |
| Formula weight | 286.32 |
| Wavelength(Å) | 0.71073 |
| Crystal system | Monoclinic |
| *a* (Å) | 4.803(3) |
| *b* (Å) | 9.498(5) |
| *c* (Å) | 15.557(9) |
| *β* (°) | 93.25(4) |
| V (Å$^3$) | 708.6(6) |
| Space group | $P2_1$ |
| *Z* | 2 |
| T(K) | 293(2) |
| Crystal size (mm$^3$) | 0.36 x 0.20 x 0.16 |
| $\rho_{calcd}$ (g cm$^{-3}$) | 1.342 |
| $\mu$ (mm$^{-1}$) | 0.084 |
| $\vartheta$ range (°) | 2.62 to 61.5 |
| *h* / *k* / *l* indices | -6 ≤ h ≤ 6, -12 ≤ k ≤ 13, -22 ≤ l ≤ 22 |
| Reflections collected | 14129 |
| Unique reflection, $R_{int}$ | 4208 |
| GooF | 0.937 |
| *R*1[*I* > 2σ(*I*)] | $R_1$ = 0.0609, w$R_2$ = 0.1518 |
| *wR*2[all data] | $R_1$ = 0.1665, w$R_2$ = 0.1719 |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.15/-0.22 |

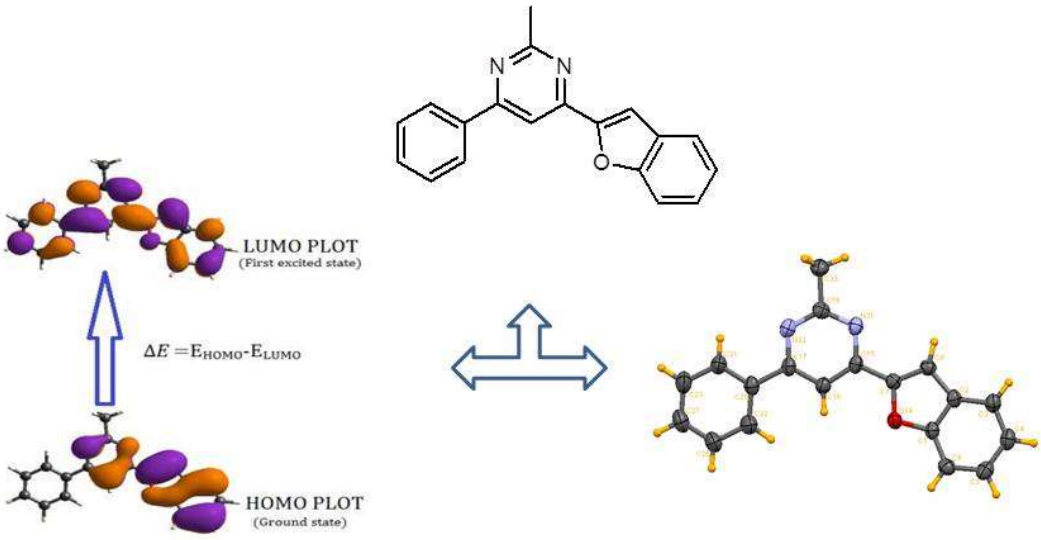
**Table 2.** Hydrogen bond geometry (°, Å) in the BFMPP.

| **D–H···A** | **D–H (Å)** | **H...A (Å)** | **D...A (Å)** | **D–H...A (°)** |
|---|---|---|---|---|
| C33-H33B-N31$^{i}$ | 0.96 | 2.61(1) | 3.5355(1) | 162(1) |
| Cg1...Cg2$^{ii}$ | - | - | 3.5644(1) | - |
| Cg1...Cg3$^{i}$ | - | - | 3.6945(1) | - |
| Cg1, Cg2 and Cg3 are the centroid of the furan ring, pyrimidine and the benzene ring of benzofuran ring respectively. | | | | |

Symmetry codes: (i) -1+x, y, z; (ii) 1+x, y, z;

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Graphical abstract




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# A COMPARATIVE STUDY OF HUMAN DEVELOPMENT INDEX OF SELECTED INDIAN STATES USING STATISTICAL TOOLS

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***ABSTRACT***

***This paper tried to find out major factor of Human Development Index like health index, Education index and income index. The objective of this study is found out the trend of human development of Indian states and to suggest measures for improving human development. The Human Development Index is a statistical tool used to measure countries overall achievements in its social and economic dimensions.***

***Key words:*** ***Human Development Index; Health Index; Education Index; Income Index.***

## INTRODUCTION

Human development is concerned with what I take to be the basic development idea: namely, advancing the richness of human life, rather than the richness of the economy in which human beings live. In 1990 Human Development Index was developed and launched by Pakistani economist Mahbub-ul-Haq, followed by Amartya Sen, an Indian economist. Human Development Index (HDI), is a comprehensive tool devised by the United Nations for measuring the levels of social and economic developments of the different countries and ranking them accordingly. It is a comparative measure of life expectancy, education, literacy and standard of living. Essentially, Human Development Index, makes use of four parameters for measuring and ranking countries according to their social and economic development which includes the Life Expectancy at Birth, Expected Years of Schooling, Mean Years of Schooling and Gross National Income per Capita. There are six basic pillars of human development: equity, sustainability, productivity, cooperation and security. Now a day's several recent model of development have given lot of importance to human development. It can take place through education, health and family welfare and also influenced by legal, political and social environments in the society. It's very much required for economic, social and cultural developments in society.

In 2004 Gustav Ranis in his study to define the important Interrelations between human development (HD) and economic growth (EG). Region of India. In 2005 Rajarshi Majumder in his study entitled that Human Development in India. In 2009 Purusottam Nayak in his study entitled that Human Development in North-eastern . In 2010 Santanu Ray and Purusottam Nayak in his study entitled that Human Development in North East India. The development goal is to create conditions where people can live a long and healthy life and benefit in knowledge. The Human Resource Development Index is one of the important indicators of economic development for each country and is considered to have an effective role in economic development. The importance of the Human Development Index is put to review on the Indian economy. Trends change each of the three human resource development indexes during the 30-year period from 1980 to 2010. In this article, we consider the relationship between GDP and three indicators of human resources in India. In addition, we will evaluate the relationship and mutual effects of each of the three indicators of human resource development in the Indian economy using the latest (2010) formula provided by the United Nations. In this study, GDP or income act as the dependent Variables and the three indicators of long life, health and education act as independent variables.

## OBJECTIVES OF THE STUDY

1. To suggest measures for improving the human development
2. To analyze the trend of human development of Indian states

## RESEARCH DESIGN AND METHODOLOGY &HYPOTHESIS

| | |
|---|---|
| **Data:** | Secondary |
| **Data source:** | Research papers, Books, Periodicals, Journals and Government websites etc. |
| **Period of study:** | 2001 to 2012 |
| **Type of Research:** | Combination of descriptive and explorative research |
| **Tools:** | Simple statistical tools such as time series cross section analysis etc. |
| **Universe size:** | East zone, West zone, South zone, North zone, north east zone ,Central zone |

| | |
|---|---|
| **Sample size:** | 20 States (Andhra Pradesh, Assam, Bihar, Gujarat, Karnataka, Kerala, M.P, Maharashtra, Orissa, Punjab, Rajasthan, Tamil Nadu, U.P, West Bengal, Himanchal Pradesh, Goa, Jharkhand, Chattisgardh, Uttaarakhand, Arunachal Pradesh) |
| **Parameters:** | Human Development Indicators ( education, income, health ) |

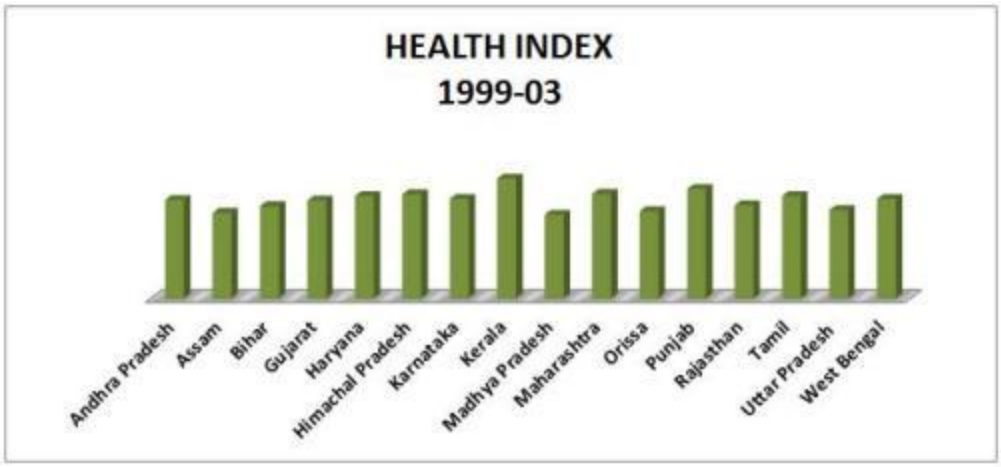
Analysis

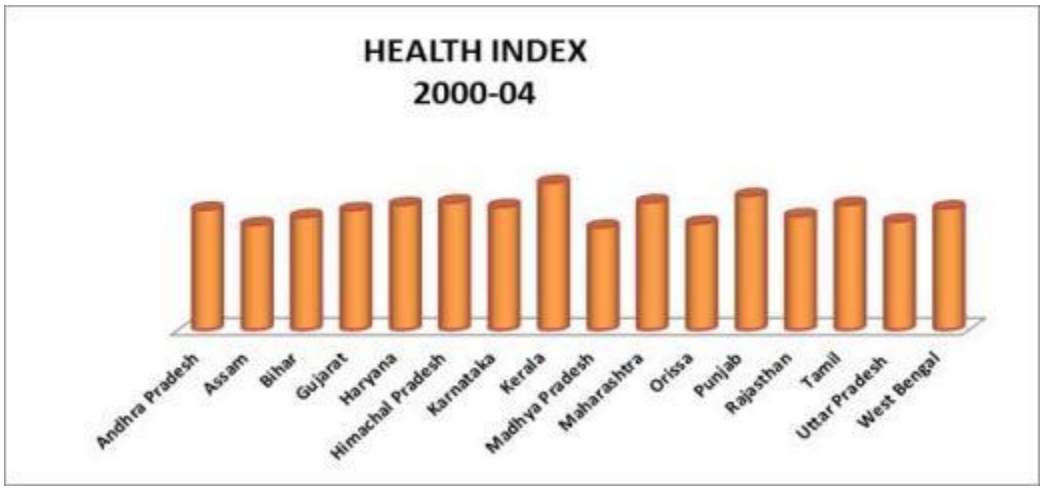
**Human Development Index are Health Index, Education Index, Income Index**

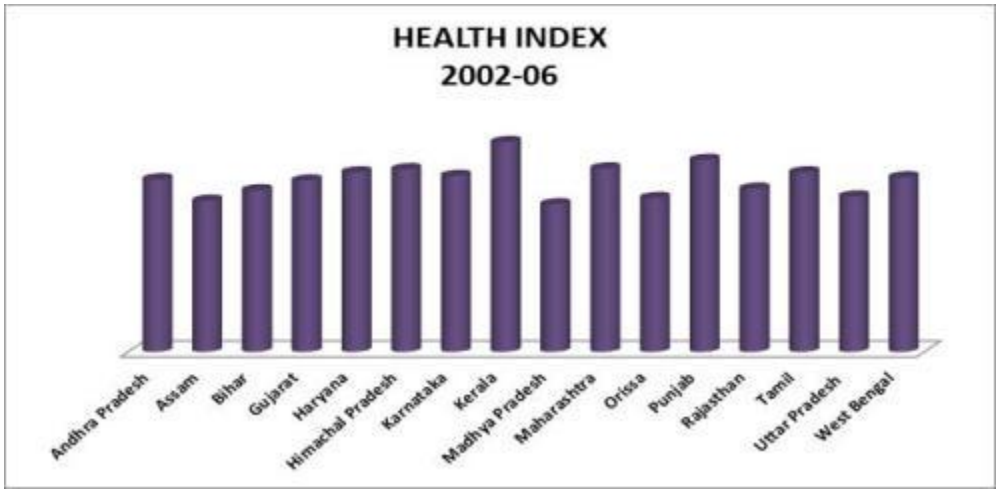
**Table 1.** Health Index

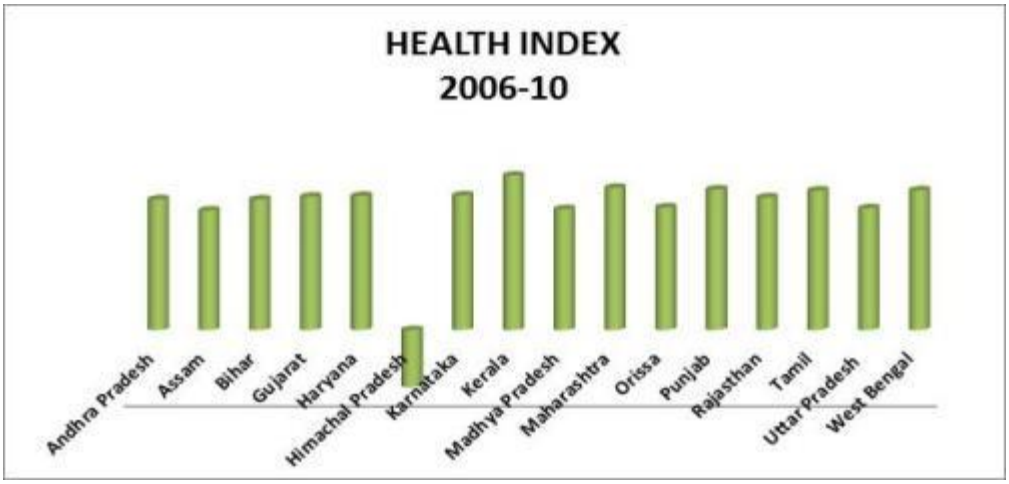
| **Indian States** | **HEAITH INDEX** | | | |
|---|---|---|---|---|
| | **1999-03** | **2000-04** | **2002-06** | **2006-10** |
| Andhra Pradesh | 0.691455696 | 0.694620253 | 0.702531646 | 0.724684 |
| Assam | 0.601265823 | 0.606012658 | 0.615506329 | 0.662975 |
| Bihar | 0.648734177 | 0.651898734 | 0.658227848 | 0.724684 |
| Gujarat | 0.688291139 | 0.691455696 | 0.69778481 | 0.740506 |
| Haryana | 0.71835443 | 0.721518987 | 0.731012658 | 0.743671 |
| Himachal Pradesh | 0.731012658 | 0.735759494 | 0.743670886 | -0.31646 |
| Karnataka | 0.699367089 | 0.710443038 | 0.716772152 | 0.746835 |
| Kerala | 0.841772152 | 0.849683544 | 0.85443038 | 0.857595 |
| Madhya Pradesh | 0.588607595 | 0.591772152 | 0.601265823 | 0.670886 |
| Maharashtra | 0.734177215 | 0.737341772 | 0.746835443 | 0.789557 |
| Orissa | 0.612341772 | 0.615506329 | 0.626582278 | 0.68038 |
| Punjab | 0.768987342 | 0.773734177 | 0.78164557 | 0.780063 |
| Rajasthan | 0.653481013 | 0.65664557 | 0.664556962 | 0.735759 |
| Tamil | 0.71835443 | 0.723101266 | 0.731012658 | 0.773734 |
| Uttar Pradesh | 0.621835443 | 0.626582278 | 0.632911392 | 0.675633 |
| West Bengal | 0.69778481 | 0.702531646 | 0.710443038 | 0.775316 |

**Source:** National Health Profile 2009


HEALTH INDEX
1999-03
Andhra Pradesh
Assam
Bihar
Gujarat
Haryana
Himachal Pradesh
Karnataka
Kerala
Madhya Pradesh
Maharashtra
Orissa
Punjab
Rajasthan
Tamil
Uttar Pradesh
West Bengal


HEALTH INDEX
2000-04
Andhra Pradesh
Assam
Bihar
Gujarat
Haryana
Himachal Pradesh
Karnataka
Kerala
Madhya Pradesh
Maharashtra
Orissa
Punjab
Rajasthan
Tamil
Uttar Pradesh
West Bengal


HEALTH INDEX
2002-06
Andhra Pradesh
Assam
Bihar
Gujarat
Haryana
Himachal Pradesh
Karnataka
Kerala
Madhya Pradesh
Maharashtra
Orissa
Punjab
Rajasthan
Tamil
Uttar Pradesh
West Bengal




**Interpretation**

In this study using the data of life expectancy at birth researchers prepare the health index and providing the ranking on the basis of health index. Kerala has taken highest rank following Punjab, Maharashtra, then and Madhya Pradesh, Andhra Pradesh, Assam and Bihar. But the Karnataka, Tamil Nadu has obtained moderate rank.

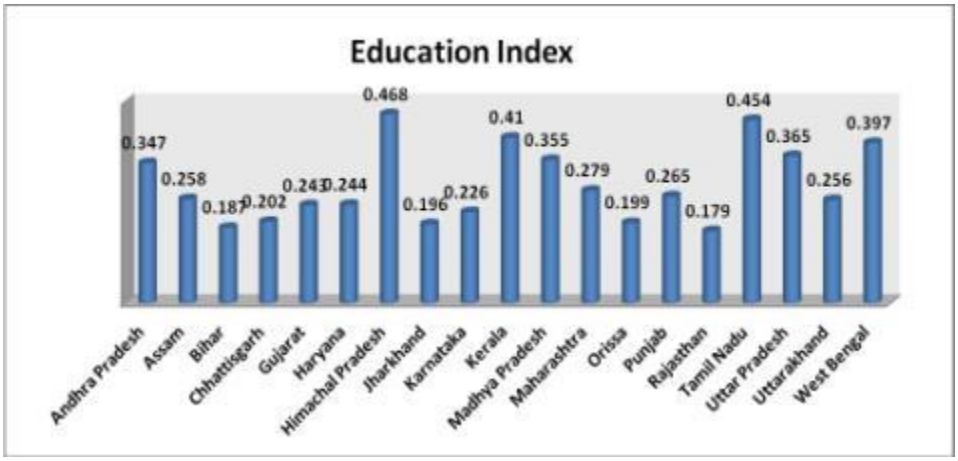
**Education Index**

**Table 3.** Education Index

| State | Mean Years Of Schooling (Years) (2004/05) | School Life Expectancy (Years) (2007/08) | Education Index | Rank |
|---|---|---|---|---|
| Andhra Pradesh | 3.06 | 9.66 | 0.347 | 7 |
| Assam | 3.96 | 9.54 | 0.258 | 10 |
| Bihar | 2.97 | 9.58 | 0.187 | 18 |
| Chhattisgarh | 3.39 | 9.31 | 0.202 | 15 |
| Gujarat | 4.54 | 8.79 | 0.243 | 13 |
| Haryana | 4.74 | 9.68 | 0.244 | 12 |
| Himachal Pradesh | 4.88 | 11.05 | 0.468 | 1 |
| Jharkhand | 3.32 | 9.68 | 0.196 | 17 |
| Karnataka | 3.95 | 9.75 | 0.226 | 14 |
| Kerala | 6.19 | 11.33 | 0.41 | 3 |
| Madhya Pradesh | 3.47 | 8.95 | 0.355 | 6 |
| Maharashtra | 5.12 | 9.86 | 0.279 | 8 |
| Orissa | 3.34 | 8.74 | 0.199 | 16 |
| Punjab | 5.12 | 9.8 | 0.265 | 9 |
| | | | | |

| | | | | |
|---|---|---|---|---|
| Rajasthan | 2.96 | 9.19 | 0.179 | 19 |
| Tamil Nadu | 4.79 | 10.57 | 0.454 | 2 |
| Uttar Pradesh | 3.56 | 9.19 | 0.365 | 5 |
| Uttarakhand | 4.97 | 10.23 | 0.256 | 11 |
| West Bengal | 4.36 | 8.87 | 0.397 | 4 |

**Source:** UNDP Report 2011



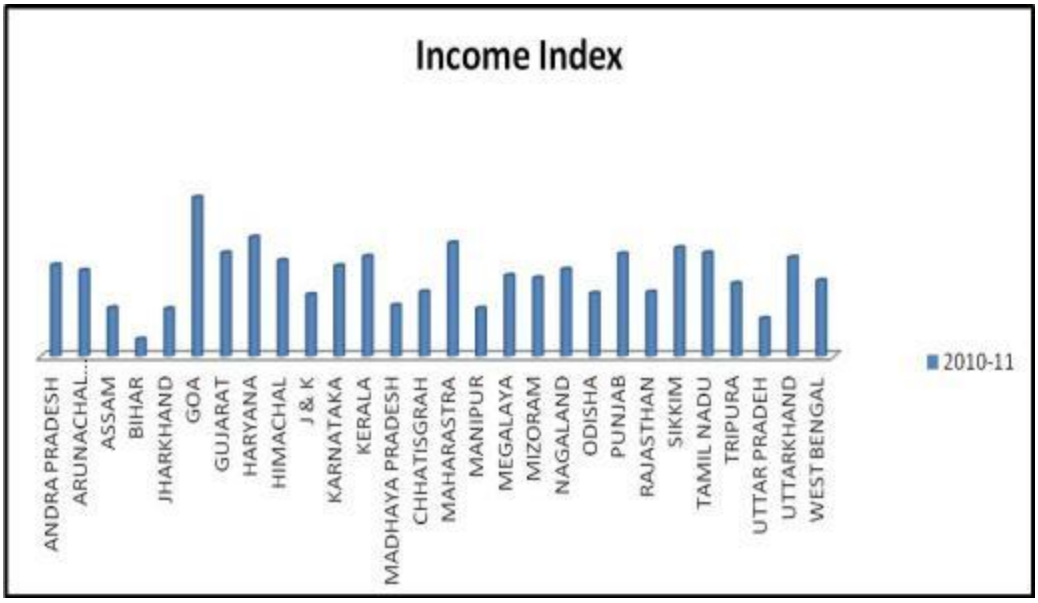

**Interpretation**

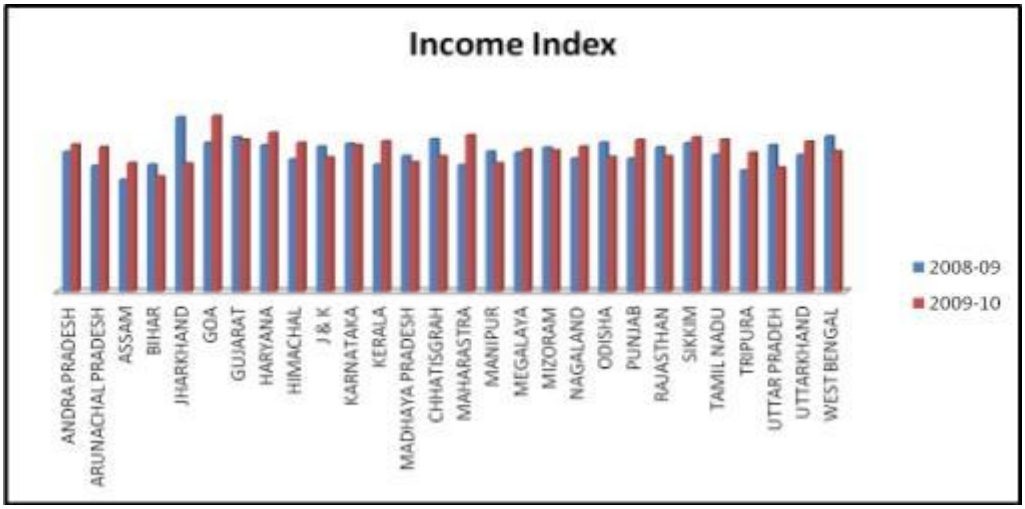
After perusal of the data obtained from UNDP report of HDI 2011 on education index, it is clear that Himachal Pradesh has taken highest rank followed by Tamil Nadu and Kerala. Assam, Jharkhand, Bihar and Rajasthan have taken consistently lowest rank. Whereas Punjab, Orissa, Uttarakhand then Maharashtra has a moderate rank in education Index.

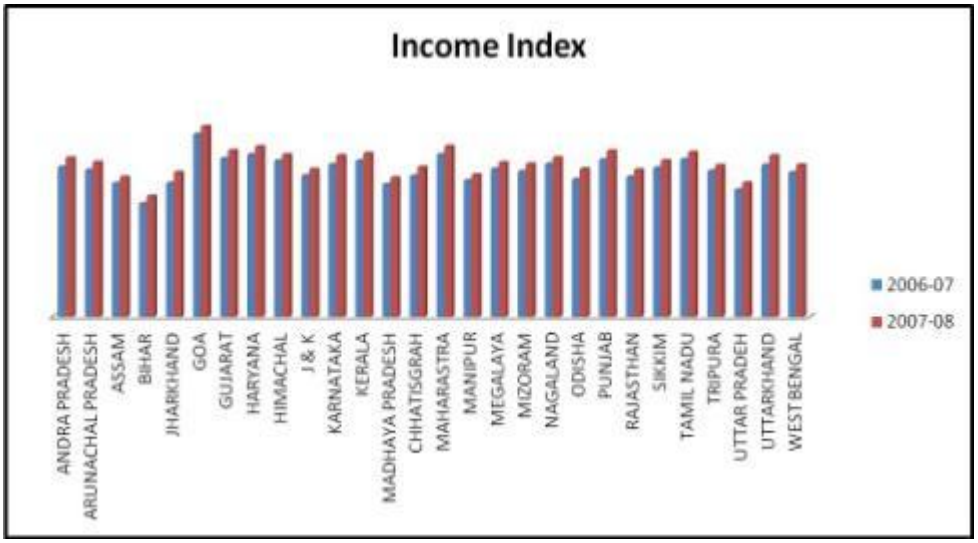
**INCOME INDEX**

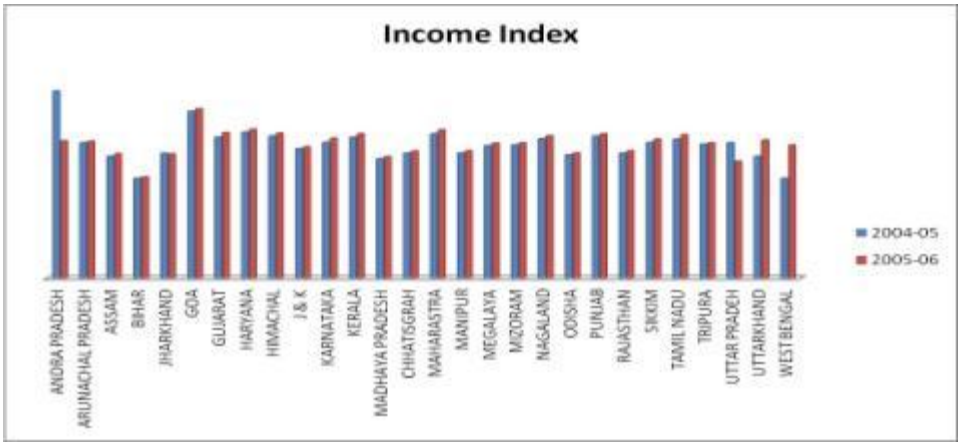
| STATE | 2004-05 | 2005-06 | 2006-07 | 2007-08 | 2008-09 | 2009-10 | 2010-11 |
|---|---|---|---|---|---|---|---|
| Andra Pradesh | 2.761 | 2.025 | 2.08 | 2.21 | 2.152 | 2.263 | 0.605 |
| Arunachal Pradesh | 1.998 | 2.018 | 2.037 | 2.147 | 1.936 | 2.227 | 0.569 |
| Assam | 1.798 | 1.835 | 1.855 | 1.94 | 1.722 | 1.979 | 0.321 |
| Bihar | 1.472 | 1.492 | 1.572 | 1.676 | 1.953 | 1.772 | 0.114 |
| Jharkhand | 1.841 | 1.833 | 1.857 | 2.006 | 2.688 | 1.974 | 0.315 |
| Goa | 2.46 | 2.498 | 2.537 | 2.648 | 2.295 | 2.711 | 1.052 |
| Gujarat | 2.079 | 2.147 | 2.198 | 2.311 | 2.383 | 2.343 | 0.685 |
| Haryana | 2.153 | 2.196 | 2.253 | 2.367 | 2.252 | 2.447 | 0.789 |
| Himachal Pradesh | 2.096 | 2.138 | 2.166 | 2.255 | 2.034 | 2.294 | 0.635 |
| J & K | 1.91 | 1.936 | 1.959 | 2.05 | 2.236 | 2.067 | 0.409 |

**Source:** Central Statistics Office (CSO)


Income Index
ANDRA PRADESH
ARUNACHAL...
ASSAM
BIHAR
JHARKHAND
GOA
GUJARAT
HARYANA
HIMACHAL
J & K
KARNATAKA
KERALA
MADHAYA PRADESH
CHHATISGRAH
MAHARASTRA
MANIPUR
MEGALAYA
MIZORAM
NAGALAND
ODISHA
PUNJAB
RAJASTHAN
SIKKIM
TAMIL NADU
TRIPURA
UTTAR PRADEH
UTTARKHAND
WEST BENGAL
2010-11


Income Index
ANDRA PRADESH
ARUNACHAL PRADESH
ASSAM
BIHAR
JHARKHAND
GOA
GUJARAT
HARYANA
HIMACHAL
J & K
KARNATAKA
KERALA
MADHAYA PRADESH
CHHATISGRAH
MAHARASTRA
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ODISHA
PUNJAB
RAJASTHAN
SIKKIM
TAMIL NADU
TRIPURA
UTTAR PRADEH
UTTARKHAND
WEST BENGAL
2008-09
2009-10


Income Index
ANDRA PRADESH
ARUNACHAL PRADESH
ASSAM
BIHAR
JHARKHAND
GOA
GUJARAT
HARYANA
HIMACHAL
J & K
KARNATAKA
KERALA
MADHAYA PRADESH
CHHATISGRAH
MAHARASTRA
MANIPUR
MEGALAYA
MIZORAM
NAGALAND
ODISHA
PUNJAB
RAJASTHAN
SIKKIM
TAMIL NADU
TRIPURA
UTTAR PRADEH
UTTARKHAND
WEST BENGAL
2006-07
2007-08




**RANKING**

| State | 2004-05 | 2005-06 | 2006-07 | 2007-08 | 2008-09 | 2009-10 | 2010-11 |
|---|---|---|---|---|---|---|---|
| Andra Pradesh | 1 | 13 | 12 | 12 | 15 | 11 | 11 |
| Arunachal Pradesh | 14 | 14 | 15 | 14 | 26 | 14 | 14 |
| Assam | 24.5 | 24 | 25 | 25 | 28 | 24 | 24 |
| Bihar | 27.5 | 27 | 28 | 28 | 24 | 28 | 28 |
| Jharkhand | 22 | 25 | 24 | 23 | 1 | 26 | 26 |
| Goa | 2 | 1 | 1 | 1 | 6 | 1 | 1 |
| Gujarat | 7 | 4 | 4 | 4 | 3 | 5 | 5.5 |
| Haryana | 3 | 2 | 3 | 3 | 10 | 2 | 2 |
| Himachal Pradesh | 5 | 5 | 8 | 8 | 22 | 10 | 10 |
| J & K | 18 | 19 | 19 | 21 | 11 | 22 | 22 |
| Karnataka | 11 | 10 | 10 | 10 | 8 | 12 | 12 |
| Kerala | 8 | 6 | 7 | 7 | 23 | 8 | 8 |
| Madhya Pradesh | 26 | 26 | 26 | 26 | 19 | 23 | 23 |
| Chhattisgarh | 20.5 | 22 | 20 | 19 | 4 | 19 | 19 |
| Maharashtra | 4 | 3 | 2 | 2 | 25 | 3 | 3 |
| Manipur | 19 | 20 | 23 | 24 | 14 | 25 | 25 |
| Meghalaya | 17 | 17 | 14 | 15 | 16 | 15 | 15 |
| Mizoram | 16 | 15.5 | 17 | 16 | 13 | 16 | 16 |
| Nagaland | 9 | 9 | 9 | 11 | 20 | 13 | 13 |
| Odisha | 23 | 23 | 22 | 20 | 5 | 21 | 21 |
| Punjab | 6 | 7 | 6 | 5 | 21 | 7 | 7 |
| Rajasthan | 20.5 | 21 | 21 | 22 | 12 | 20 | 20 |
| Sikkim | 12 | 11 | 13 | 13 | 7 | 4 | 4 |
| Tamil Nadu | 10 | 8 | 5 | 6 | 17 | 6 | 5.5 |
| Tripura | 15 | 15.5 | 16 | 18 | 27 | 18 | 18 |
| Uttar Pradesh | 14 | 26 | 27 | 27 | 9 | 27 | 27 |
| Uttarakhand | 24.5 | 12 | 11 | 9 | 18 | 9 | 9 |
| West Bengal | 27.5 | 18 | 18 | 17 | 2 | 17 | 17 |

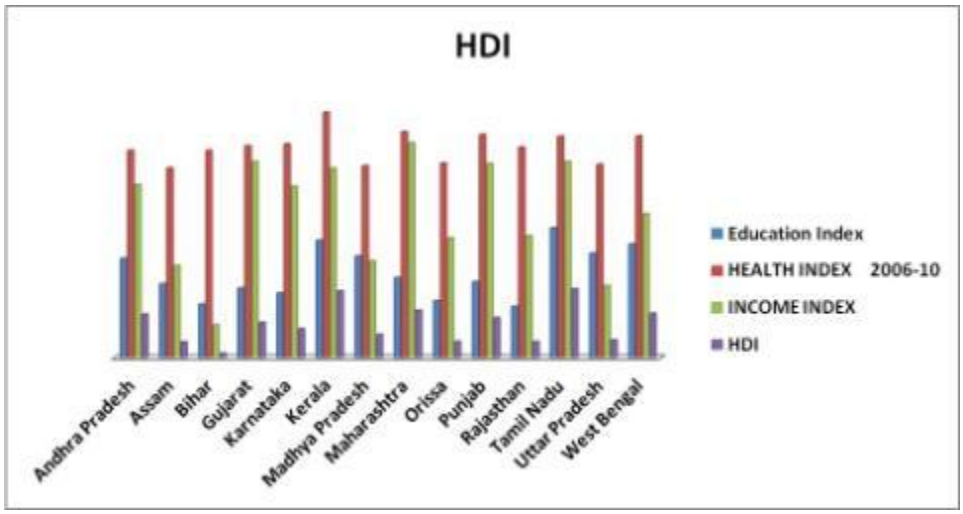
**Interpretation**

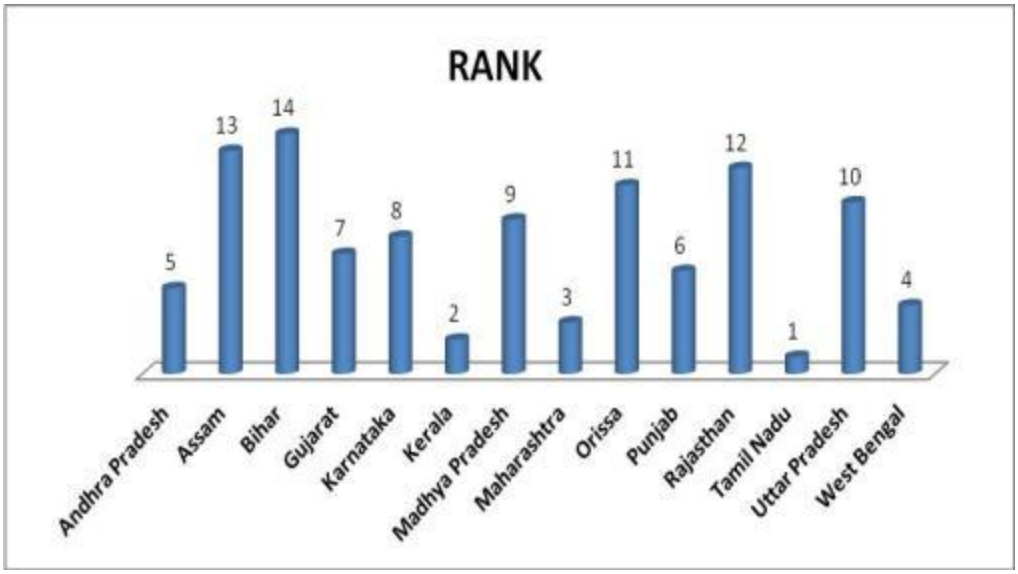
On study the income index data obtained from planning commission, it is clear that GOA has obtained top rank following Haryana and Maharashtra whereas Gujarat, Madhya Pradesh, Jharkhand, Assam and Bihar have taken consistently lowest rank. Karnataka, Tamil Nadu and Andhra Pradesh has taken moderate ranking in income index

**Human Development Index**

**Human Development Index**

| State | Education Index | Health Index 2006-10 | Income Index 2010-11 | HDI | Rank |
|---|---|---|---|---|---|
| Andhra Pradesh | 0.347 | 0.724684 | 0.605 | 0.152137 | 5 |
| Assam | 0.258 | 0.662975 | 0.321 | 0.054906 | 13 |
| Bihar | 0.187 | 0.724684 | 0.114 | 0.015449 | 14 |
| Gujarat | 0.243 | 0.740506 | 0.685 | 0.123261 | 7 |
| Karnataka | 0.226 | 0.746835 | 0.599 | 0.101102 | 8 |
| Kerala | 0.41 | 0.857595 | 0.662 | 0.232768 | 2 |
| Madhya Pradesh | 0.355 | 0.670886 | 0.338 | 0.0805 | 9 |
| Maharashtra | 0.279 | 0.789557 | 0.751 | 0.165435 | 3 |
| Orissa | 0.199 | 0.68038 | 0.418 | 0.056595 | 11 |
| Punjab | 0.265 | 0.780063 | 0.678 | 0.140154 | 6 |
| Rajasthan | 0.179 | 0.735759 | 0.426 | 0.056105 | 12 |
| Tamil Nadu | 0.454 | 0.773734 | 0.685 | 0.240624 | 1 |
| Uttar Pradesh | 0.365 | 0.675633 | 0.251 | 0.061898 | 10 |
| West Bengal | 0.397 | 0.775316 | 0.503 | 0.154824 | 4 |






**Interpretation**

On the basis of the health index, education index and income index researcher came on conclusion Tamil Nadu has taken highest rank followed by Kerala whereas Bihar, Assam is at lowest rank. The state like Punjab, Gujarat and Karnataka obtained moderate rank.

## FINDINGS

- In this study researcher construct the health index and find the trend of health index from different states during different period of time.
- Researcher found that the Kerala has taken highest rank Punjab, Maharashtra, Madhya Pradesh, Andhra Pradesh, Assam and Bihar has taken a consistency lowest rank. Karnataka, Tamil Nadu has obtained moderate rank in health index.
- According to UNDP report regarding education index Himachal Pradesh has taken highest rank, Tamil Nadu then Kerala. Rajasthan, Bihar, Jharkhand, Assam and Bihar have taken a consistency lowest rank. Punjab, Orissa, Uttarakhand, Maharashtra have obtained moderate rank.
- In this study researcher construct the income index and find the trend of income of different states from different period of time. And also scattered trend of states of India. Goa has taken highest rank then Haryana, Maharashtra and Gujarat. Madhya Jharkhand, Assam and Bihar has taken a consistency lowest rank. Karnataka, Tamil Nadu, Andhra Pradesh have taken moderate rank.
- According to the HDI Tamil Nadu has taken a highest rank followed by Kerala and lowest rank is taken by Bihar and Assam. Punjab, Gujarat, and Karnataka have taken moderate rank.

## SUGGESTION

In this study researcher obtained that some states facing backward situation facing in major area like: education, health facility, low income etc. This study provide help to state government create an awareness activities regarding vocational skills, development for income generation, focus on education system and also providing medical facility and health insurance etc. it is compulsory for every people.

## CONCLUSION

In this study researcher obtained that several states have good health index and highest ranked like Kerala then Punjab, Maharashtra. Some states have good education index and highest ranked like Himachal Pradesh has taken highest rank, Tamil Nadu then Kerala. Some states have good income index and highest ranking like Haryana, Maharashtra, and then Gujarat. But some states have lowest health index and lowest ranked Madhya Pradesh, Andhra Pradesh, Assam then Bihar. Some states have lowest education index and lowest ranked Rajasthan, Bihar, Jharkhand, Assam then Bihar. Some states have lowest income index and lowest ranked Madhya Jharkhand, Assam then Bihar.

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# Non-differentiable multi objective fractional minimax programming problem under $[F, \alpha, \rho, d]$-convex functions

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**Abstract**
In this paper, we derive some theorems and duality theorems on non-differentiable Multiobject Fractional Minimax Programming Under $[F, \alpha, \rho, d]$ convex function.

**Keywords:** $[F, \alpha, \rho, d]$ convex function and Duality

## 1. Introduction

Minimax fractional problems appear in the formulation of discrete and continous rational approximation problems with respect to the Chebyshev Norm [3], in continuous rational games [12], in multiobjective programming [15], in engineering design as well as in some portfolio selection problems discussed by Bajona-Xandri and Martinez legaz [2].

Minimax mathematical programming has been of much interest in the recent past [1, 4, 5, 11, 13, 17, 18, 19]. Schmitendorf [11] established necessary and sufficient optimality conditions for minimax problem. Tanimoto [14] applied these optimality conditions to define a dual problem and derived duality theorms, which were extended for the fractional analogue of generalized minimax problem by Yadav and Mukherjee [18].

Motivated by various concepts of generalized convexity, Liang *et al*. [8, 9] introduced a unified formulation of generalized convexity, which was called $[F, \alpha, \rho, d]$- convexity and obtained some corresponding optimality conditions and duality results for the single objective practional problems and multiobjective problems. Recently, Liang and Shi [10] obtained sufficient conditions and duality theorems for minimax fractional problem under $[F, \alpha, \rho, d]$-convexity. Lia *et al*. [7] derived necessary and sufficient conditions for nondifferentiable minimax fractional problem with generalized convexity and applied these optimality conditions to construct one parametric dual model and also discussed duality theorems, Lai and Lee [6] obtained duality theorems for two parametric-free dual models of non-differentiable minimax fractional problem involving generalized convexity assumptions. Recently, Mishra *et al*. [12] established duality results for one parametric and two parametric-free dual models of nondifferentiable minimax fractional programming problem under generalized univexity.

But no serious attempt in utilizing multiobjective fractional minimiax under $[F, \alpha, \rho, d]$-convexity. Hence in this Paper an attempt is made to fill the gap in the aim of research by developing some theorems based on $[F, \alpha, \rho, d]$ convex function.

## 2. Formulation

We now consider the following non-differentiable minimax fractional programming problem.

### 2.1. Primal Problem

$$(FP)\quad \min_{x \in R^n} \sup_{y \in Y} \frac{f_i(x, y) + (x^t, Bx)^{\frac{1}{2}}}{h_i(x, y) - (x^t, Dx)^{\frac{1}{2}}},$$

$$\text{Subject to } g_j(x) \leq 0,\ x \in X,$$

Where Y is a compact subset of $R^m, f_i, h_i : R^n \times R^m \to R$ are $C^1$ on $R^n \times R^m$ and $g_j : R^n \to R^p$ is $C^1$ on $R^n$. B and D are nxn positive semidefinite matrices.

Let $S = \{x \in X : g(x) \leq 0\}$ denote the set of all feasible solutions of $(FP)$. For each $(x, y) \in R^n \times R^m$, we define

$$\phi(x, y) = \frac{f_i(x, y) + (x^t, Bx)^{\frac{1}{2}}}{h_i(x, y) - (x^t, Dx)^{\frac{1}{2}}},$$

Such that for each $(x, y) \in s \times Y, f_i(x, y) + (x^t, Bx)^{\frac{1}{2}} \geq 0$ and $h_i(x, y) - (x^t, Dx)^{\frac{1}{2}} > 0$. For each $x \in s,$ we define

$$J(x) = \left\{ j \in J \quad g_j(x) = 0 \right\}. \text{ where } J = \{1, 2, ..... p\}$$

$$Y(x) = \left\{ y \in Y : \frac{f_i(x, y) + (x^t, Bx)^{\frac{1}{2}}}{h_i(x, y) - (x^t, Dx)^{\frac{1}{2}}} = \sup_{z \in Y} \frac{f_i(x, z) + (x^t, Bx)^{\frac{1}{2}}}{h_i(x, z) - (x^t, Dx)^{\frac{1}{2}}} \right\},$$

$$k(x) = \left(s, t_i, \bar{y}\right) \in N \times R_+^s \times R^{ms} : 1 \leq s \leq n+1, t = (t_1, t_2 ..... t_s) \in R_+^s$$

$$\text{with } \sum_{i=1}^{s} t_i = 1, \ \bar{y} = (\bar{y}_1, \bar{y}_2 ..... \bar{y}_s) \text{ with } \bar{y}_i \in Y(x) \ (i = 1, 2, .... s)$$

Since f and h are continuously differentiable and Y is compact in $R^m$, it follows that for each $x^* \in s, y(x^*) \neq \phi$, and for any $\bar{y}_i \in Y(x^*)$, we have a positive constant

$$k_0 = \phi(x^*, \bar{y}_i) = \frac{f_i(x^*, \bar{y}_i) + (x^{*t}, Bx^*)^{\frac{1}{2}}}{h_i(x^*, \bar{y}_i) - (x^{*t}, Dx^*)^{\frac{1}{2}}}$$

We shall need the following generalized Schwartz inequality.
Let B be a positive semidefinite matrix of order n. Then for all $x, w \in R^n,$

$$x^t Bw \leq (x^t Bx)^{\frac{1}{2}} (w^t Bw)^{\frac{1}{2}} \tag{21.1.1}$$

We observe that equality holds if $Bx = \lambda Bw$ for some $\lambda \geq 0$. Evidently, if $(w^t Bw)^{\frac{1}{2}} \leq 1,$ we have $x^t Bw \leq \left(x^t Bw\right)^{\frac{1}{2}}$.

If the functions $f_i$, $g_i$ and $h_i$ in problem $(FP)$ are continuously differentiable with respect to $x \in R^n$.

**2.2. Dual Formulation**

$$(D) \qquad \max_{(s, t^*, \bar{y}) \in K(z)} \ \sup_{(z, \mu, v, w) \in H(s, t_i^*, \bar{y})} \frac{\sum_{i=1}^{s} t_i^* \left\{ f_i(z, \bar{y}_i) + z^t Bw \right\} + \sum_{j=1}^{p} \mu_j g_j(z)}{\sum_{i=1}^{s} t_i^* \left\{ h_i(z, \bar{y}_i) - z^t DV \right\}}$$

Where $H(s, t_i^*, \bar{y})$ denote the set of all $(z, \mu, v, w) \in R^n \times R_+^p \times R^n \times R^n$
Satisfying

$$\nabla \left( \frac{\sum_{i=1}^{s} t_i^* \left\{ f_i(z, \bar{y}_i) + z^t Bw \right\} + \sum_{j=1}^{p} \mu_j g_j(z)}{\sum_{i=1}^{s} t_i^* \left\{ h_i(z, \bar{y}_i) - z^t DV \right\}} \right) = 0$$

$$\begin{cases} w^t\, Bw \le 1, \quad (z^t\, Bz)^{\frac{1}{2}} = z^t\, Bw, \\ v^t\, Dv \le 1, \quad (z^t\, Dz)^{\frac{1}{2}} = z^t\, Dv \end{cases}$$

If the set $H(s, t^*, \bar{y})$ is empty, we define supremum over it to be $-\infty$. For convenience, we use the notation:

$$\psi(\square) = \left[\sum_{i=1}^{s} t_i^* \left\{h_i(z, \bar{y}_i) - z^t Dv\right\}\right]\left[\sum_{i=1}^{s} t_i^* \left\{f_i(\cdot, \bar{Y}_i) + (\cdot)^t, Bw\right\} + \sum_{j=1}^{p} \mu_j g_j(\cdot)\right]$$

$$-\left[\sum_{i=1}^{s} t_i^* \left\{f_i(z, \bar{y}_i) + z^t, Bw)\right\} + \sum_{j=1}^{p} \mu_j g_j(z)\right]\left[\sum_{i=1}^{s} t_i^* \left\{h_i(\cdot, \bar{Y}_i) - (\cdot)^t\, Dv\right\}\right]$$

Suppose that

$$\sum_{i=1}^{s} t_i^* \left\{f_i(z, \bar{y}_i) + z^t Bw\right\} + \sum_{j=1}^{p} \mu_j g_j(z) \ge 0 \quad \text{and} \quad \sum_{i=1}^{s} t_i^* \left\{h_i(z, \bar{y}_i) - z^t Dv\right\} > 0, \quad \text{For all } (s, t^*, \bar{y}) \in k(z),$$

$(z, \mu, w, v) \in H(s, t^*, \bar{y})$.

**3. Definition**

Let $R^n$ be the n-dimensional Euclidean space and X and open set in $R^n$.

**Definition (3.1):** A functional $F: X \times X \times R^n \to R$ is said to be sublinear if $\forall x, \bar{x} \in X$

(i) $F(x, \bar{x}; a_1 + a_2) \le F(x, \bar{x}; a_1) + F(x, \bar{x}; a_2)\ \forall\, a_1, a_2 \in R^n$

(ii) $F(x, \bar{x}; \beta a) = \beta F(x, \bar{x}; a)\ \forall \beta \in R_+$ And $\forall a \in R^n$.

By (ii) it is clear that $F(x, \bar{x}, 0) = 0$.

**Definition (3.2)**

[8, 9] given an open set $x \subset R^n$, a number $\rho \in R$, and two functions $\alpha: X \times X \times \to R_+ \setminus \{0\}$ and $d\left(\cdot, \cdot\right) X \times X \to R$, a differentiable function $\zeta$ over x is said to be $(F, \alpha, \rho, d)$ - convex at $\bar{x}$, if for any $x \in X$, $F: X \times X \times \to R^n \to R$ is sublinear, and $\zeta$ (x) satisfies the following condition.

$$\zeta(x) - \zeta(\bar{x}) \ge F\left(x, \bar{x}; \alpha(x, \bar{x}) \nabla \zeta(\bar{x})\right) + \rho d^2(x, \bar{x})$$

**Definition (3.3)**

Given an open set $x \subset R^n$, a number $\rho \in R$, and two functions $\alpha: X \times X \times \to R_+ \setminus \{0\}$ and $d\left(\cdot, \cdot\right) X \times X \to R$, a differentiable function $\zeta$ over x is said to be $(F, \alpha, \rho, d)$ -Pseudo convex at $\bar{x}$, if for any $x \in X$, there exists a sublinear functional $F: X \times X \times R^n \to R$ such that $\mu(x) < \mu(\bar{x}) \Rightarrow F\left(x, \bar{x}; \alpha(x, \bar{x}) \nabla G(\bar{x})\right) - \rho^2 d^2(x, \bar{x})$

Further $\mu$ is said to be strictly $F(\alpha, \rho, d)$ -Pseudo convext at $\bar{x}$ if for any $x \in X$, there exists a sublinear functional $FiX \times X \times R^n \to R$

Such that

$F\left(x, \bar{x}; \alpha(x, \bar{x}) \nabla \zeta(\bar{x})\right) \ge -\rho d^2(x, \bar{x}) \Rightarrow \zeta(x) > \zeta(\bar{x})$.

**4. Necessary optimality condition**

If $x^*$ is a solution of problem $(FP)$. Assuming $z_{\bar{y}}(x^*)$ to be empty, there exist $(s, t^*, \bar{y}) \in k(x^*)$, $w, v \in R^n$ and $\mu^* \in R_+^p$ satisfying

$$\nabla\left(\frac{\sum_{i=1}^{s} t_i^*\left\{f(x^*, \bar{y}_i)+x^{*t}Bw\right\}+\sum_{j=1}^{p}\mu_j^* g_j(x^*)}{\sum_{i=1}^{s} t_i^*\left\{h(x^*, \bar{y}_i)-x^{*t}DV\right\}}\right)=0$$

$$\sum_{j=1}^{p}\mu_j^* g_j(x^*)=0$$

$$t_i^* \in R_+^s \ (i=1, 2, ..... s), \ \sum_{i=1}^{s} t_i^* = 1$$

$$w^t\ Bw \le 1, \quad (x^{*t}\ Bx^*)^{\frac{1}{2}} = x^{*t}\ Bw,$$

$$v^t\ Dv \le 1, \quad (x^{*t}\ Dx^*)^{\frac{1}{2}} = x^{*t}\ Dv$$

**5. Duality Theorems**

**5.1. Theorem (Weak Duality):** Suppose that x and $(z, \mu, v, w, s, t, \bar{y})$ are respectively the feasible solution for $(FP)$ and (D). Also assume that $\psi(\square)$ is $[F, \alpha, \rho, d]$-Pseudo Convex at z and the inequality $\frac{\rho}{\alpha(x, z)} \ge 0$. Holds, then

$$\sup_{y\in Y} \frac{f_i\ (x, y)+(x^t, Bx)^{\frac{1}{2}}}{h_i\ (x, y_i)-(x^*, Dx)^{\frac{1}{2}}} \ge \frac{\sum_{i=1}^{s} t_i^*\left\{f_i\ (z, \bar{y}_i)+z^tBw\right\}+\sum_{j=1}^{p}\mu_j g_j(z)}{\sum_{i=1}^{s} t_i^*\left\{h_i\ (z, \bar{y}_i)-z^tDV\right\}}$$

**Proof:** By means of a contradiction, suppose that

$$\sup_{y\in Y} \frac{f_i\ (x, y)+(x^t\ Bx)^{\frac{1}{2}}}{h_i\ (x, y)-(x^t\ Dx)^{\frac{1}{2}}} < \frac{\sum_{i=1}^{s} t_i\left\{f_i\ (z, \bar{y}_i)+z^tBw\right\}+\sum_{j=1}^{p}\mu_j g_j(z)}{\sum_{i=1}^{s} t_i\left\{h_i\ (z, \bar{y}_i)-z^tDv\right\}}$$

For $y \in Y$. If we replace y by $\bar{y}_i$ in the above in equality and sum up after multiplying by $t_i$, then we have

$$\left[\sum_{i=1}^{s} t_i\left\{f_i\ (x, \bar{y}_i)+(x^t\ Bx)^{\frac{1}{2}}\right\}\right]\left[\sum_{i=1}^{s} t_i\left\{h_i\ (z, \bar{y}_i)-z^tDv\right\}\right]$$

$$<\left[\sum_{i=1}^{s} t_i\left\{f_i\ (z, \bar{y}_i)+z^tBw\right\}+\sum_{j=1}^{p}\mu_j g_i(z)\right]\left[\sum_{i=1}^{s} t_i\left\{h_i\ (x, \bar{y}_i)-(x^t\ Dx)^{\frac{1}{2}}\right\}\right]$$

Using the generalized Schwartz inequality and (2.2.2) we get

$$\phi(x) \le \left[\sum_{i=1}^{s} t_i\left\{h_i\ (z, \bar{y}_i)-z^tDv\right\}\right]\left[\sum_{i=1}^{s} t_i\left\{f_i\ (x, \bar{y}_i)+(x^t\ Bx)^{\frac{1}{2}}+\sum_{j=1}^{p}\mu_j g_j(x)\right\}\right]$$

$$-\left[\sum_{i=1}^{s} t_i\left\{f_i\ (z, \bar{y}_i)+z^tBw\right\}+\sum_{j=1}^{p}\mu_j g_j(x)\right]\left[\sum_{i=1}^{s} t_i\left\{h_i\ (x, \bar{y}_i)-(x^t\ Dx)^{\frac{1}{2}}\right\}\right]$$

$$<\sum_{j=1}^{p}\mu_j g_j(x)\sum_{i=1}^{s} t_i\left\{h_i\ (z, \bar{y}_i)-z^tDv\right\}$$

Since $\sum_{i=1}^{s} t_i \left\{ h_i(z, \bar{y}_i) - z^t Dv \right\} > 0 \ \sum_{j=1}^{p} \mu_j g_j(x) \le 0,$

It follows that $\psi(x) < 0 = \psi(z)$

As $\psi$ (.) is $(F, \alpha, \rho, d)$ - Pseudo Convex at z. Therefore $F\left(x, z; \alpha(x, z)\nabla\psi(z)\right) < -\rho d^2(x, z),$ that is

$$F(x, z; \alpha(x, z)\left[\sum_{i=1}^{s} t_i \left\{ h_i(z, \bar{y}_i) - z^t Dv \right\}\right] \nabla \left[\sum_{i=1}^{s} t_i \left\{ f_i(z, \bar{y}_i) + z^t Bw + \sum_{j=1}^{p} \mu_j g_j(z) \right\}\right]$$

$$-\left[\sum_{i=1}^{s} t_i \left\{ f_i(z, \bar{y}_i) \times z^t Bw \right\} + \sum_{j=1}^{p} \mu_j g_j(z)\right] \nabla \left[\sum_{i=1}^{s} t_i \left\{ h_i(z, \bar{y}_i) - z^t Dv \right\}\right] < -\rho d^2(x, z)$$

On multiplying the above inequality by

$$\frac{1}{\alpha(x, z)\left[\sum_{i=1}^{s} t_i \left\{ h_i(z, \bar{y}_i) - z^t\, Dv \right\}\right]^2}$$ and using the sublinearity of F, we have

$$F(x, z; \nabla \left( \frac{\sum_{i=1}^{s} t_i \left\{ f_i(z, \bar{y}_i) + z^t\, Bw \right\} + \sum_{j=1}^{p} \mu_j g_j(z)}{\sum_{i=1}^{s} t_i \left\{ h_i(z, \bar{y}_i) - z^t\, Dv \right\}} \right) < \frac{-\rho d^2(x, z)}{\alpha(x, z)\left[\sum_{i=1}^{s} t_i \left\{ h_i(z, \bar{y}_i) - z^t\, Dv \right\}\right]^2}$$

Using the fact that $\frac{\rho}{\alpha(x, z)} \ge 0,$

We have

$$F\left( x, z; \nabla \left( \frac{\sum_{i=1}^{s} t_i \left\{ f_i(z, \bar{y}_i) + z^t\, Bw \right\} + \sum_{j=1}^{p} \mu_j g_j(z)}{\sum_{i=1}^{s} t_i \left\{ h_i(z, \bar{y}_i) - z^t\, Dv \right\}} \right) \right) < 0 \qquad (5.1.1)$$

In the right of (2.2.1) in equality (5.1.1) contradicts F(x, z; 0) =0.

**Theorem (5.2) (Strong Duality)**

Suppose that $\bar{x}$ is optimal for $(FP)$ and $\nabla g_j(\bar{x}),\ j \in J(\bar{x})$ is linearly independent. Then there exist $(\bar{s}, \bar{t}, \bar{y}^*) \in k(\bar{x})$ and $(\bar{x}, \bar{\mu}, \bar{v}, \bar{w}) \in H(\bar{s}, \bar{t}, \bar{y}^*)$ such that $(\bar{x}, \bar{\mu}, \bar{v}, \bar{w}, \bar{s}, \bar{t}, \bar{y}^*)$ is feasible for (D).

Further, if the weak duality (theorem 5.1) holds for all feasible $(z, \mu, v, w, s, t, \bar{y})$ of (D), then $(\bar{x}, \bar{\mu}, \bar{v}, \bar{w}, \bar{s}, \bar{t}, \bar{y}^*)$ is optimal for (D) and the two objectives have the same extreme values.

**Proof:** Since $\bar{x}$ is optimal for $(FP)$ and $\nabla g_j(\bar{x}),\ j \in J(\bar{x})$ is linearly independent. Then by necessary condition there exist $(\bar{s}, \bar{t}, \bar{y}^*) \in k(\bar{x})$ and $(\bar{x}, \bar{\mu}, \bar{v}, \bar{w}) \in H(\bar{s}, \bar{t}, \bar{y}^*)$ such that $(\bar{x}, \bar{\mu}, \bar{v}, \bar{w}, \bar{s}, \bar{t}, \bar{y}^*)$ is feasible for (D) and the two objective values are equal. The optimality of $(\bar{x}, \bar{\mu}, \bar{v}, \bar{w}, \bar{s}, \bar{t}, \bar{y}^*)$ for $(FP)$ thus follows from weak duality (Theorem 5.1).

**Theorem (5.3) (Strict Converse Duality)**

Let $\bar{x}$ and $(\bar{z}, \bar{\mu}, \bar{v}, \bar{w}, \bar{s}, \bar{t}, \bar{y}^*)$ be optimal solutions for $(FP)$ and (D) respectively. Also suppose that $\psi$ (.) is strictly $[F, \alpha, \rho, d]$-Pseudo Convex at $\sum$, for all $(\bar{s}, \bar{t}, \bar{y}^*) \in k(\bar{x})$, $(\bar{z}, \bar{\mu}, \bar{w}, \bar{v}) \in H(\bar{s}, \bar{t}, \bar{y}^*)$, and the inequality $\frac{\rho}{\alpha(x, z)} \ge 0$ holds, and $\nabla g_j(\bar{x}),\ j \in J(\bar{x})$ is linearly independent. Then $\bar{z} = \bar{x};$ that is, $\bar{z}$ is optimal for $(FP)$.

**Proof:** We shall assume that $\bar{z} \neq \bar{x};$ and exhibit a contradiction. Since $(\bar{z}, \bar{\mu}, \bar{v}, \bar{w}, \bar{s}, \bar{t}, \bar{y}^*)$ is feasible for (D), it follows that

$$\nabla\left(\frac{\sum_{i=1}^{\bar{s}} \bar{t}_i \left\{f_i(\bar{z}, \bar{y}_i^*) + \bar{z}^t B\bar{w}\right\} + \sum_{j=1}^{p} \bar{\mu}_j g_j(\bar{z})}{\sum_{i=1}^{s} \bar{t}_i \left\{h_i(\bar{z}, \bar{y}_i^*) - \bar{z}^t D\bar{v}\right\}}\right) = 0$$

The above inequality along with the sublinearity of F and $\frac{\rho}{\alpha(\bar{x}, \bar{z})} \geq 0$

$$F(\bar{x}, \bar{z}; \nabla\left[\frac{\sum_{i=1}^{\bar{s}} \bar{t}_i \left\{f_i(\bar{z}, \bar{y}_i^*) + \bar{z}^t B\bar{w}\right\} + \sum_{j=1}^{p} \bar{\mu}_j g_j(\bar{z})}{\sum_{i=1}^{\bar{s}} \bar{t}_i \left\{h_i(\bar{z}, \bar{y}_i^*) - \bar{z}^t D\bar{v}\right\}}\right] = 0$$

$$\geq \frac{-\rho d^2(\bar{x}, \bar{z})}{\alpha(\bar{x}, \bar{z})}$$

Which together with the sublinearity of F and $\alpha(\bar{x}, \bar{z}) > 0$ yields

$$F\left(\bar{x}, \bar{z}; \alpha(\bar{x}, \bar{z})\right) \nabla \left[\frac{\sum_{i=1}^{\bar{s}} \bar{t}_i \left\{f_i(\bar{z}, \bar{y}_i^*) + \bar{z}^t B\bar{w}\right\} + \sum_{j=1}^{p} \bar{\mu}_j g_j(\bar{z})}{\sum_{i=1}^{\bar{s}} \bar{t}_i \left\{h_i(\bar{z}, \bar{y}_i^*) - \bar{z}^t D\bar{v}\right\}}\right] \geq -\rho d^2(\bar{x}, \bar{z})$$

Using strict $[F, \alpha, \rho, d]$- Pseudo convexity of $\psi(.)$, we obtain $\psi(\bar{x}) > \psi(\bar{z})$

Since $\psi(\bar{z})$ =0, then we have $\psi(\bar{x}) > 0,$ that is

$$\left[\sum_{i=1}^{\bar{s}} \bar{t}_i \left\{h_i(\bar{z}, \bar{y}_i^*) - \bar{z}^t D\bar{v}\right\}\right] \left[\sum_{i=1}^{\bar{s}} \bar{t}_i \left\{f_i(\bar{x}, \bar{y}_i^*) + (\bar{x}^t B\bar{w})\right\} + \sum_{j=1}^{p} \bar{\mu}_j g_j(\bar{x})\right]$$

$$> \left[\sum_{i=1}^{\bar{s}} \bar{t}_i \left\{f_i(\bar{z}, \bar{y}_i^*) + \bar{z}^t B\bar{w}\right\} + \sum_{j=1}^{p} \bar{\mu}_j g_j(\bar{z})\right] \left[\sum_{i=1}^{\bar{s}} \bar{t}_i \left\{f_i(\bar{z}, \bar{y}_i^*) + (\bar{z}^t B\bar{w})\right\} + \sum_{j=1}^{p} \bar{\mu}_j g_j(\bar{z})\right]$$

$$\left[\sum_{i=1}^{\bar{s}} \bar{t}_i \left\{h_i(\bar{x}, \bar{y}_i^*) - (\bar{x}^t D\bar{v})\right\}\right] \qquad (5.3.1)$$

The relations (2.1), (2.2.2), (5.3.1) and

$\sum_{j=1}^{p} \bar{\mu}_j g_j(\bar{x}) \leq 0$ Imply

$$\sup_{y \in Y} \frac{f_i(\bar{x}, y) + (\bar{x}^t \bar{B}x)^{\frac{1}{2}}}{h_i(\bar{x}, y) - (\bar{x}^t D\bar{x})^{\frac{1}{2}}} > \frac{\sum_{i=1}^{\bar{s}} \bar{t}_i \left\{f_i(\bar{z}, \bar{y}_i^*) + \bar{z}^t B\bar{w}\right\} + \sum_{j=1}^{p} \mu_j g_j(\bar{z})}{\sum_{i=1}^{s} \bar{t}_i \left\{h_i(\bar{z}, \bar{y}_i^*) - \bar{z}^t D\bar{v}\right\}} \qquad (5.3.2)$$

Since $\bar{x}$ is optimal for $(FP)$ and $g_j(\bar{x}), j \in J(\bar{x})$ is linearly independent, by strong duality (Theorem 5.2), there exist $(\bar{s}, \bar{t}, \bar{y}^*) \in k(\bar{x})$ and $(\bar{x}, \bar{\mu}, \bar{v}, \bar{w}) \in H(\bar{s}, \bar{t}, \bar{y}^*)$ such that $(\bar{x}, \bar{\mu}, \bar{v}, \bar{w}, \bar{s}, \bar{t}, \bar{y}^*)$ turns to be an optimal solution of (D) and

$$\sup_{y\in Y} \frac{f_i(\bar{x}, y) + (\bar{x}^t \bar{B}x)^{\frac{1}{2}}}{h_i(\bar{x}, y) - (\bar{x}^t D\bar{x})^{\frac{1}{2}}} = \frac{\sum_{i=1}^{\bar{s}} \bar{t}_i \left\{f_i(\bar{z}, \bar{y}_i^*) + \bar{z}^t B\bar{w}\right\} + \sum_{j=1}^{p} \bar{\mu}_j g_j(\bar{z})}{\sum_{i=1}^{\bar{s}} \bar{t}_i \left\{h_i(\bar{z}, \bar{y}_i^*) - \bar{z}^t D\bar{v}\right\}}$$

Which contradicts the fact of (5.3.2). Hence $\bar{x} = \bar{z}$.

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Research Article

# Report on Antidiabetic, Diuretic and Analgesic Activities of Methanolic Extract of Leaves of *Strychnos colubrina L.*an Endangered Medicinal Plant

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**ABSTRACT**

*Strychnos colubrina* L. belongs to family Loganiaceae was known as snake wood tree.The methanolic extracts from Strychnos colubrina L. leave collected from different provinces in Penchalakona of Nellore district were prepared by decoction and maceration with methanol and evaluated for their antidiabetic, diuretic and analgesic activities. Methanolic extracts from *Strychnos colubrina* L. leaves (SCM) were evaluated for anti diabetic effect in Streptozocin (STZ) induced diabetes in rats. The blood sugar levels were analysed as indices of diabetes. 200 mg/kg b.w. of the extract showed a greater reduction in blood glucose level which was comparable to glibenclamide. To find out diuretic efficacy, SCM of leaves were administered to experimental rats orally at doses of 100 and 200 mg/kg and compared with Furosemide (20 mg/kg,o.p) as the standard. The rats treated with SCM of leaves in a dose of 200 mg/kg shown near similar urine output and electrolytes excretion when compared to the respective control. The analgesic activity of SCM of leaves is estimated using tail flick in mice. Results demonstrated that SCM of leaves exhibited a potent dose-dependent analgesic activity in all tested models for analgesia. This report could be used for medicinal and pharmaceutical exploration in the future.

**Keywords:** Methanolic extract, snake wood tree, Streptozocin, glibenclamide, Furosemide, Lipschitz test, tail flick method.

## INTRODUCTION

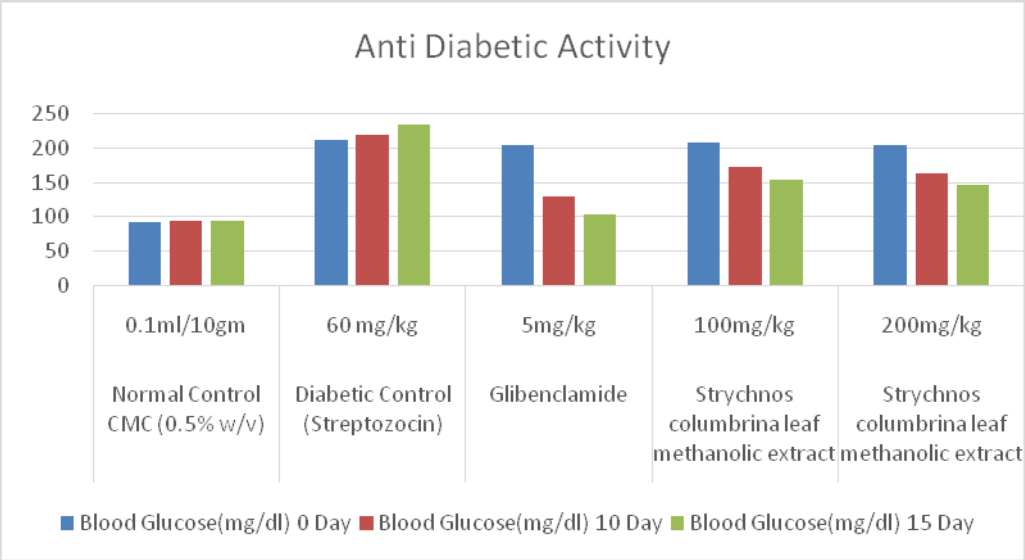
Plants form the basis of various traditional medicines throughout the world. Phyto medicines derived from green plants have been used by about 65% of the world's population. All though there are many ways to control diseases because of their secondary complications, phytomedicines are preferred due to minimum side effects and easy usage and preparation. The use of medicines and food supplements derived from plant has been increased in recent years. Botanists, microbiologists, Ethno pharmacologists, and chemists are searching the earth for phytochemicals and drugs which could be used for the treatment of many stubborn infectious diseases in a green and natural way. Today we have more concern with lifestyle disease like depression, cancer and heart troubles caused by stress and faulty nutrition. Because these diseases have emotional components, there is a growing concern that English medicine is largely unable to cure them all but it offers a temporary relief from pain and disease symptoms. So there is an urgent need for alternative therapy, to cover a good health for all. Herbal therapy will be one of the practices to overcome the illness (Gupta,and Chime, 2000).Many traditional and local plants are used for the treatment of diabetes mellitus throughout the world (Marles and Fransworth, 1995). Ayurvedic medicines are called the elixirs of life and they have an important role in improving health and disease treatment from ancient days to this modern time. Plant medicines provide good means for the treatment of many diseases that are either absent or incurable in other systems of medicine. Herbal plants, which form the backbone of alternative medicine, have in the last few decades been the subject for very intense pharmacological studies; this has been brought by the agreement of the value of medicinal plants as an important source of new compounds of therapeutic values in the drug development. Due to these facts over the past twenty years, a considerable revival of interest in the use of herbal medicine in the world has come up.

Diabetes mellitus is a metabolic disorder initially characterized by a loss of glucose homeostasis with disturbances of carbohydrate, fat and protein metabolism resulting from defects in insulin action, insulin secretion, or both (Barcelo and Rajpathak, 2001). If the glucose level in the blood remains high over a long period of time, this can result in long-term damage to organs, such as the kidneys, nerves, heart, liver, eyes and blood vessels. Complications in some of these organs can lead

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Table 1: Results of Antidiabetic activity.

| S.No | Treatment | Dose | Blood Glucose(mg/dl) | | |
|---|---|---|---|---|---|
| | | | 0 day | 10 day | 15 day |
| 1 | Normal Control CMC (0.5% w/v) | 0.1ml/10gm | 92.34 | 93.12 | 93.58 |
| 2 | Diabetic Control (Streptozocin) | 60 mg/kg | 213.04 | 220.72 | 235.34 |
| 3 | Streptozocin (60 mg/kg) + Standard drug-Glibenclamide (5mg/kg, p.o). | 5mg/kg | 205.78 | 130.3 | 104.24 |
| 4 | *Strychnos colubrina*leaf methanolic extract | Streptozocin(60 mg/kg) + Test 1 (100 mg/kg) | 208.14 | 173.8 | 153.94 |
| | | Streptozocin(60 mg/kg)+ Test 2 (200mg/kg) | 204.14 | 163.36 | 145.92 |



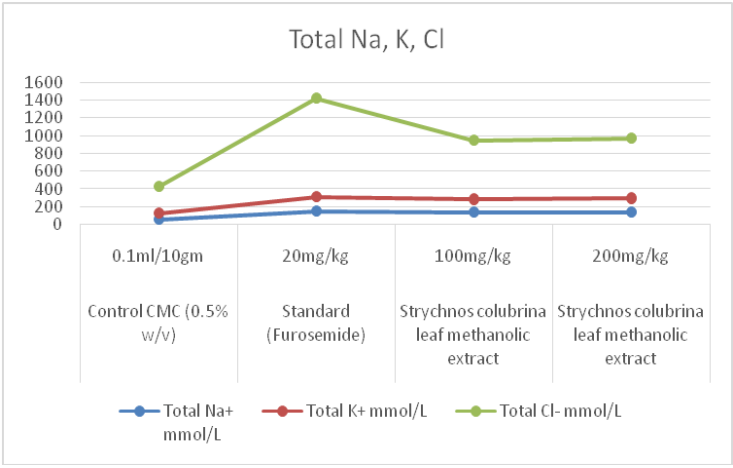

Graph: 1 showing antidiabetic activity.

Table 2: Results of Diuretic activity.

| S.No | Treatment groups | Dose (mg/kg) | Urine volume (ml/24hrs) | Total $Na^+$ mmol/L | Total $K^+$ mmol/L | Total $Cl^-$ mmol/L | $Na^+/K^+$ Ratio |
|---|---|---|---|---|---|---|---|
| 1 | Control CMC (0.5%w/v) | 0.1ml/10gm | 9.78 | 61.3 | 69.2 | 299.6 | 0.89 |
| 2 | Standard (Furosemide) | 20mg/kg | 34.5 | 150.4 | 158.2 | 1113.66 | 0.946 |
| 3 | *Strychnos colubrina* leaf methanolic extract | 100mg/kg | 28.06 | 139 | 145.2 | 661.6 | 0.952 |
| | | 200mg/kg | 30.76 | 142.06 | 150.84 | 681.96 | 0.936 |

to death (Pari and Saravanan, 2004). Diuretics, also called water pills, are drugs used to increase the quantity of water and salt excreted from the body as urine. There are three types of prescription diuretics. They are often prescribed to help treat high blood pressure, but they are used for other conditions as well. These medicines, when used for longer periods, may show side effects. An analgesic is a medicine that takes away the physical pain but these medicines, when used on a long-term basis, will give bad impact on vital organs like kidneys etc.

In this research work, I have examined the unexplored properties of medicinal plant *Strychnos colubrina* scientifically for its antidiabetic, diuretic and analgesic activities. In spite of its extensive use in folk, ayurvedic, herbal and tribal medicine the above properties of leaves of *Strychnos colubrina L.* were not properly reported. Hence the present study has been taken for this analysis.Various plant parts of *Strychnos colubrina L.*are being used in the Indian Ayurvedic system for the cure of various diseases.In Ayurveda, it is called Kupilu-lataa, Kuchilaalataa. Whereas in Maharashtra the folklore name




Graph: 2 showing amounts of Na, K, Cl, ions excreted for diuretic activity.

Table 3: Results of Analgesic activity.

| S.No | Treatment | Dose | Reaction time in seconds | | | |
|---|---|---|---|---|---|---|
| | | | Basal | 30 | 60 | 90 |
| 1 | Vehicle CMC (0.5%w/v) | 0.1ml/10gm | 4.14 | 4.16 | 4.17 | 4.15 |
| 2 | Standard (Pentazocin) | 30mg/kg | 4.21 | 9.05 | 11.05 | 12.42 |
| 3 | *Strychnos colubrina* leaf methanolic extract | 100mg/kg | 4.2 | 5.2 | 5.67 | 6.35 |
| | | 200mg/kg | 4.25 | 6.31 | 7.13 | 8.96 |

is Kaajar-vel. In Malayalam, its common name is Vallikanjiram and Modirakanjiram.

This taxon is found in Western Peninsular India covering parts of Karnataka and Kerala; it is so farrecorded at penchalakona of Nellore district in Eastern PeninsularIndia. Theexistence of the plant also recorded in Chittoor District particularly at Brahmadevudigundam (Mamandur), Kambakkam hills, Ambakkam, Sadhumalammakona, (Madhava Chetty, *et al.*, 2011). First Red list of Medicinal plants of Andhra Pradesh, India – Conservation Assessment and Management planning is reported it as an Endangered Species in Andhra Pradesh, India[1]. Woody climbers; very bitter, with tendrils[2]. *Strychnos colubrina L.*Wood is also used for malarial fever and cutaneous eruptions and Rheumatism. The tribal people used the root of this plant for the snake bite. Fruit is used to prevent Mania. Leaves and roots are boiled in oil and applied to rheumatic swellings. Root is purgative, febrifugal, anthelmintic. The roots, wood, bark, and seeds contain alkaloids (bark wood), consisting of brucine and strychnine. Beta-sitosterol has been reported in the plant[3]. The Order exhibits febrifuge and tetanic properties. Itis very rich in alkaloids- brucine, bakankosine, curine, curarine, gelsemidine, gelsemine, gelseminine. gelsemoidine, koumine, kouminicint, kouminidine, kouminine, protucurarine, protocuridine, rrotocurine, sempervine, sempervirine, spigeline, struxine, strychnicine. Strychnine, tubocurarine. The presence of a glucoside, aesculin, has been recorded[3].

## MATERIALS AND METHODS

*Plant collection and identification*

The plant material (leaves) of *Strychnos colubrina L.* of family Loganiaceae, were collected from Penchalakona forest of the Eastern Ghats, Nellore district, Andhra Pradesh in July 2017. The plant was identified with the help of' The flora of Nellore district' and 'Flora of Madras'[4,5]. The leaves of *Strychnos colubrina L.* plant material were shade dried, powdered and stored in desiccators until further use. All the specimens at different leaf stages were documented in the form of herbarium sheets which have been deposited in the Herbarium, Department of Botany, Vikramasimhapuri University, P.G Centre, and Kavali, Andhra Pradesh, India.

The powdered material was then extracted using solvents methanol in the ratio 1:10 using Soxhlet apparatus. (Khan *et al.*, 1988). The solvent was evaporated under reduced pressure in the rotatory evaporator to get methanol extract. The components were separated to the solvents based on their polarity. The extract was subjected to the rotary evaporator at $40^{0C}$ to remove the excess solvent from the extract. After extracting all colouring material, the solvent was removed by evaporating in a water bath, which gave rise to a solid isolate of extract used for determining antidiabetic, diuretic and analgesic activities.

*Determination of the Ant diabetic activity of Strychnos colubrina methanolic(SCM) leaf extracts*

Healthy Wistar rats (150 to 200 gm) of either sex were selected. Before and during the experiment, rats were fed with the standard diet. After randomization into various groups and before initiation of the experiment; the rats were acclimatized for a period of 7 days under standard environmental conditions of temperature, relative humidity, and dark/light cycle. Blood samples were collected through tail vein puncture method at weekly intervals over a period of 28 days. Animals described as fasting, which were deprived of food and water for 18 hours.

Table 4: Maximum possible effects of drugs in tail flick model of analgesia in rats.

| S.No | Drugs | Dose | % Maximum possible effect in seconds | | |
|---|---|---|---|---|---|
| | | | 30 | 60 | 90 |
| 1 | Vehicle CMC (0.5%w/v) | 0.1ml/10gm | ----- | ---- | --- |
| 2 | Standard (Pentazocin) | 30mg/kg | 44.85 | 63.39 | 76 |
| 3 | *Strychnos colubrina* leaf methanolic extract | 100mg/kg | 9.25 | 15.87 | 23.22 |
| | | 200mg/kg | 19.16 | 26.79 | 50.63 |

After fasting, DM was induced by IP injection of Streptozocin (STZ) at a dose of 60 mg/Kg. The animals were given to drink 5% glucose solution overnight to overcome the drug-induced hypoglycemia. After 72 hrs, STZ-treated animals were treated as diabetic when the fasting blood glucose levels observed above 200 mg/dL with glucosuria[6]. Fasting blood glucose was measured by glucose oxidase-peroxidase (GOD-POD) method (Trinder, 1969) in mg/dl using a digital glucometer (Braun Omnitest REZ, Germany).

5 rats in each group which were as follows:

Group I: Normal control (saline).

Group II: Streptozocin treated control (60 mg/kg.ip).

Group III: Streptozocin (60 mg/kg) + Standard drug-Glibenclamide (5mg/kg, p.o).

Group IV: Streptozocin (60 mg/kg) + Test 1(100 mg/kg)

Group V: Streptozocin (60 mg/kg) + Test 1(200 mg/kg)

The vehicle, Test samples, and Glibenclamide were administered once daily for 15 days from the day of induction. Blood was drawn from the tail tip of rat and the blood glucose level was estimated on 0, $10^{th}$ and $15^{th}$ day of experiment with the help of glucometer using strip method.

*Determination of the Diuretic activity of Strychnos colubrina(SCM) leaf extracts*

The diuretic activity in Wistar rats was studied by the Lipschitz Test[7] (1943). The test is based on water and sodium excretion in test animals and compared to rats treated with a high dose of Furosemide.

Four groups of Wistar rats were used to evaluate the diuretic activity of methanolic extract of leaves of *Strychnos colubrina*(SCM)by using metabolic cages. The group I served as normal control given vehicle (CMC 0.5% w/v in normal saline), group II with Furosemide (20 mg/Kg, p.o), Groups III and IV with 100 mg/kg, 200 mg/ doses ofSCM respectively.Immediately after the treatment with the standard and test all the rats were hydrated with saline (15 ml/kg) and placed in the metabolic cage, specially designed to separate urine and feces and kept at 21°C±0.5°C.

Estimation of Urinary Electrolytes

Urine electrolytes (sodium, potassium, and chloride) were determined by Ion Selective Electrode method as described by the user manual of the biochemical kits (NRI Technologies, Malleswaram, Bengaluru)

5 rats in each group which were as follows:

Group I: Normal control (CMC 0.5% w/v in normal saline).

Group II: Furosemide (20 mg/kg, p.o).

Group III: Test 1(100 mg/kg)

Group IV: Test 1(200 mg/kg)

The total volume of urine collected after 24 hrs was measured at the end. During this time no water and food were given to rats. Different parameters like total urine volume and amount of sodium, potassium, and chloride in the urine were measured and calculated respectively. The ratio of Sodium to Potassium ions is also estimated.

*Determination of the Analgesic activity of Strychnoscolubrinamethanolic (SCM)leaf extracts:*

Analgesia was measured using a modified method of D. Amour and Smith[8] called as tail flick method using an analgesiometer. The tail flick method was commonly used to measure the analgesic activity. The tail flick method was utilized to study the analgesic activity in rats. A radiant heat automatic tail flick analgesiometer was used to measure reaction latencies. (Using tail flick analgesiometer type 812, UGO BASILE®, Germany). Animals were divided into four groups of 5 ratseach. Group, I served as normal control and received the vehicle (CMC 0.5% w/v in normal saline), where group IIwas injected by Pentazocin 30 mg/kg, i.p to act as a positive control. Group III and IV received SCM at doses 100 mg/kg and 200 mg/kg respectively. All drugs were injected intraperitoneally (i.p)30 min prior to the experiment. The pain was induced by giving radiant heat on the tail of the mice 5 cm away from the tip of the tail. Mice were held loosely during the test.Percentage of analgesia was calculated using the following formula:

% Analgesia = MPE=TL-BL / ML-BL × 100

Where M.P.E. = Maximum possible effect, M.L. = Maximum latency or cut off time

T.L. = Test latency, B.L. = Basal latency or control latency

5 rats in each group which were as follows:

Group I: Normal control (CMC 0.5% w/v in normal saline)

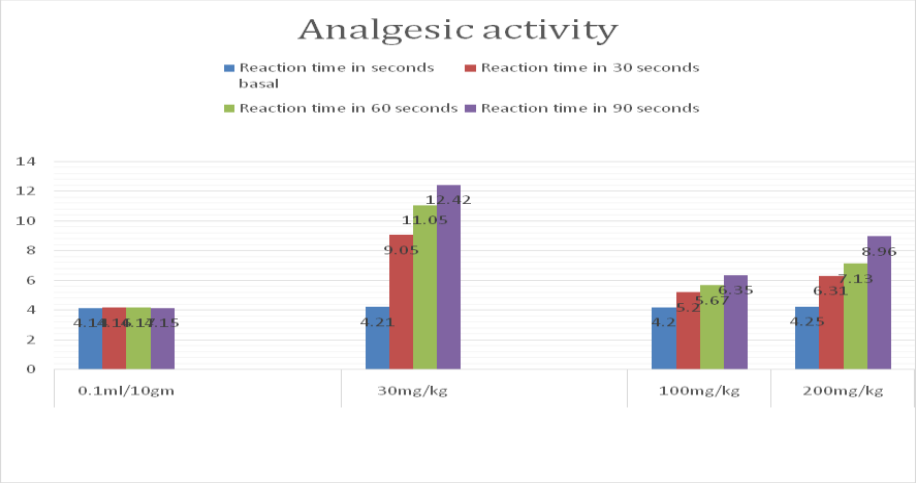
Group II: Pentazocin (30 mg/kg, i.p)

Group III: Test 1(100 mg/kg)

Group IV: Test 1(200 mg/kg)

Reaction time was recorded as the interval time of exposing the tail to the light beam and the withdrawal of the tail. The latency period for responses was noted at various time intervals. The basal reaction time of animals to radiant heat was recorded by locating the tipm(Last 1-2 cm) of the tail on the radiant heat source. The tail removal from the radiant warmth was taken as an endpoint. The cutoff time of 15 seconds was used to avoid tail injury by radiation[9]. The latent period of the tail-flick response was determined at 30, 60 and 90 minutes after the administration of standard and test.

**RESULTS**




Graph 3: Showing Analgesic Activity.

*The effect of Strychnos colubrina methanolic (SCM) leaf extracts on blood Glucoselevel*

Administration of streptozotocin produced 229.6% increase in fasting blood glucose levels of diabetic control rats compared to the normal control rats and the increased glucose levels in group I rats was maintained over a period of four weeks. Administration of *Strychnos colubrina* methanolic (SCM) leaf extracts to streptozotocin-induced diabetic rats for four weeks produced a significant blood glucose reduction (Table 1). Change orreduction in blood glucose level was observed from the first week by both SCM extract and glibenclamide. At the end of 4th week, 100 mg/kg b.w. of extract produced 27.2% blood glucose reduction in group IV rats. Similar to group IV rats, there was a lowering of 29.2% blood glucose in the rats treated with 200 mg/kg b.w. of the extract. Among the two doses of the extracts used, 200 mg/kg b.w. of the extract showed a greater reduction in blood glucose level which was comparable to glibenclamide.

*The diuretic effect of Strychnos colubrina methanolic (SCM) leaf extracts*

In this model when compared to control group the *Strychnos colubrina* methanolic (SCM) leaf extractstreated groups at different dose levels (100and 200 mg/kg) was noted with a great increase in the urine volume and also profoundly increased the excretion of ions like Sodium, Potassium and Chloride in urine.100 mg/kg b.w. of extract produced 81.4% of total urine output, 92.4% sodium ions, 91.2% potassium ions and 59.3% chloride ions excreted in group III rats. Similarly in group IV rats, there was 89.9% of urine output,94.4% sodium ions, 95.3% potassium ions and 61.23% chloride ions excreted in the rats treated with 200 mg/kg b.w. of the extract. Among the two doses of the extracts used, 200 mg/kg b.w. of the extract showed a greater diuretic effect by pumping out more urine and ions which was comparable toFurosemide (standard).

*Analgesic effect of Strychnos colubrina methanolic (SCM) leaf extracts*

In tail flick test, SCM in a concentration-dependent manner, exhibited significant analgesic activity by increasing the latency time of responses in rats in the two tested doses 100mg/kg and 200 mg/kg, as can be seen in Table 3. In comparison to standard drug (Pentazocin)100 mg /kg of SCM produced 30% and 200 mg/kg of SCM produced 66% analgesic activity in tail flick examination. Between two tested samples, 200 mg/kg has shown more analgesic activity than the former one.Maximum possible effects of drugs in tail flick model of analgesia in rats is shown in table 4.

## DISCUSSION

The effect of two different doses of *Strychnos colubrine* methanolic (SCM) leaf extracts on the fasting blood glucose levels of diabetic rats is given in Table 1 and graph 1. In the diabetic rats, the methanolic extract at a dose of 200 mg/kg b.w. produced a 29.2% fall in the blood glucose levels at the end of the experimental period. The glibenclamide treated diabetic rats showed a greater reduction in the blood glucose level than the extract treated rats. Even though there was a reduction in blood glucose levels with 200 mg/kg b.w. of the extract, the decrease was much lower when compared to group III (glibenclamide) animals.

Analgesics are drugs that act on the central or peripheral nervous system to relieve pain selectively without altering consciousness[10]. Basically analgesics act by increasing the threshold for pain and changing the physiological response to pain.The analgesic activity of SCM was studied by the tail flick tests, which is a standard pharmacological model for the analysis of pain by natural products[11]. Tail flick method is used generally for centrally acting analgesics[12]. Results have shown that a single dose administration of standard Furosemide and *Strychnos colubrina* methanolic (SCM) leaf extracts significantly increased the urine output along with an increase in the elimination of Sodium, Potassium, and Chloride ions. *Strychnos colubrina* methanolic (SCM) leaf extracts of 200 mg/Kg produced a comparable diuretic activity with standard Furosemide.

## CONCLUSION

The present study demonstrates that *Strychnos colubrina* methanolic (SCM) leaf extracts act as a potent antidiabetic, diuretic, and analgesic agent. The analgesic activity may be due to its ability to activate opioid receptors in the central nervous system. It may also inhibit endogenous pain substances, which are involved in the peripheral analgesia. The results obtained here with support the folkloric claims regarding the plant and its medicinal values. This paper helps in formulating natural principles to combat drug resistance of certain. It is, therefore, implied the isolation and proper characterization of the active constituents from the extracts of this plant species as possible antidiabetic, diuretic and analgesic agent.Quantitative analysis of the active compound in *Strychnos colubrina L.* leaf extracts should be further studied in the nearest future. Hencethis report provides insight into the medical potential of the phytomedicine and for further research on these drugs.

**CONFLICTS OF INTEREST**

The authors declare that they have no conflict of interests.

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# Proceedings of the National Symposium on plastic POLLUTION

Feb 15-16, 2019.



**Edited by Dr V. Sailaja**

*Dept of Zoology*

*Vikrama Simhapuri University P.G Centre,*

*Kavali, Nellore District, AP.*

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on

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15 – 16 February, 2019

*Organized by*

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**VIKRAMA SIMHAPURI UNIVERSITY PG CENTRE**
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# BIOPLASTICS AND THE DAWN OF NEW MATERIALS- A REVIEW

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"**Bioplastics are the workhorse material** of the modern economy"

## ABSTRACT

Plasticsthat have been universally used in our daily lives are now causing serious environmental problems. Petroleum derived plastics dominate the packaging industry even today. It accounts for the largest usage of plastics worldwide and is used in numerous applications.Millions of tons of these non- degradable plastics accumulate in the environment each year. Bioplastics are a suitable alternative to petroleumbased plastics. They are highly complex and sophisticated materials that can help make plastic products more sustainable and eco-friendly. Bioplastics today are a large family of materials with differing properties and applications. The review is an attempt to investigate the facts about different types of bioplastics, their current status, major advantages and other related issues.

Key words: Bio-plastics, Petro-plastics, Sustainability

## INTRODUCTION:

Plastics have become a vital part of our life.The environmental crisis arising from the use of petroleum based non-degradable plastics led the globe to find alternatives. Biomaterial based plastic is one such alternative.They comprise bio-based materials featuring identical properties compared to their fossil-based versions as well as new materials featuring additional properties. These add-on qualities like biodegradabilityand bio-based property can reduce the impact on environment significantly.Moreover, the emission of greenhouse gases during production and degradation of bioplastics is very low when compared to conventional plastics.

## BIOPLASTICS: THE NOVEL MATERIALS

Bioplasticsare novel materials of 21st century and would be of great importance to the material world (Mohanty etal.,2002).The keen interest in bioplastics started way back in early 20th century when Henry Ford usedcorn and soybean oils to manufacture his automotive parts (Stevens E.S.,2003). Bioplastics are made from a number of renewable resources such as plant oils, cellulose, starches, sugars, carbohydrates, bacteria and algae. Bioplastics are not single substances; they comprise of a whole family of materials with differing properties and applications. According to European Bioplastics,a plastic material is defined as a bioplastic, if it is either bio-based orbiodegradableor features both the properties(Eu.Bio.,2016). Bioplastics are eco-friendly alternative to traditional plastics and are extracted from renewable resources like corn, sugarcane, cellulose, potato or starch. These are 100% degradable, equally resistant and versatile, already used in agriculture, textile industry, medicine and forpackaging.

## CLASSIFICATIONOF BIOPLASTICS:

The world of bioplastics has exploded, and there is an amazing breadth of materials that can be classified as bioplastics. The term bioplastic refers to several groups of plastics namely bio-based plastics(from renewable resources) and bio-degradable including compostable plastics.

### Biobased plastics

Biobased plastics are those that are derived from plant-based polymers, such as corn starch, sugarcane or cellulose, potatoes, rice, soy, wheat and vegetable oil and are not derived from petroleum resources.The Business-NGO (non-government organization) Working

Group for Safer Chemicals and Sustainable Materials defines bio-based bioplastics as "plastics in which 100% of the carbon is derived from renewable agricultural and forestry resources such as corn starch, soybean protein and cellulose" (Alvarezetal.,2011)

**Biodegradable bioplastics**

Biodegradable bioplastics are fully degraded by microorganisms without leaving any visible toxic remainders. The term "biodegradable" refers to materials that can disintegrate naturally into biogas and biomass (mostly carbon dioxide and water) as a result of being exposed to a microbial environment and humidity (Alvarezetal.,2011)

**Compostable bioplastics**

Compostable bioplastics will biodegrade in a compost site. Microorganisms break it down into carbon dioxide, water, inorganic compounds and biomass leaving no toxic residues.The most commonly used raw material is corn starch, which is converted into a polymer with similar properties to traditional polyethylene plastic products. Other compostable plastics available are made from potato starch, soya bean protein, cellulose as well as from petroleum and its bye products. This shows that compostable plastics may be derived from both plantbased and petroleumderived polymers.

**TYPES OF BIOPLASTICS**:

Bioplastics are currently used in disposable items like packaging, containers, straws, bags and bottles, and in non-disposable carpets, plastic piping, phone casings, 3-D printing, car insulation and medical implants.

**A. Starch based plastics**

Starch is the key raw material for bioplastics which is found in seeds and in tubers or roots of the plants. Most of the starch produced worldwide is derived from corn (Asaf,2008). Today, thermoplastic starch, accounting for about 50% to 80% of the global bioplastics market, is the most significant and widely used bioplastic.Applications of thermoplastic starch are bags, yogurt tubs, cups, plant pots, cutlery, diaper foil, coated paper and cardboard.

**Polylacticacid (PLA)**: Polylactic acid is the polymer with the highest potential for a commercial production as bioplastic.PLA is a 100% bio-based plastic that is currently being used in packaging applications.Polylactic acid, the secondmost important bioplastic of the world in regard to consumption in volume(Garima etal). It is derived from renewable resources like corn starch or sugar cane. PLA is biodegradable and suitable for the manufacture of compostable packaging products.

**ii.PSM (Plastarch Material)**: PSM is a biodegradable, thermoplastic resin. It is composed of starch combined with several other biodegradable materials. PSM is currently used for a wide variety of applications in the plastic market, such as food packaging and utensils, personal care items, plastic bags, temporary construction tubing, industrial foam packaging, industrial and agricultural film, window insulations, construction stakes, and in horticulture (GGP,2009-10)

**iii. MATER-BI** : MATER-BI is biodegradable and compostable bioplastic synthesized mainly by starches, cellulose, vegetable oils and their combinations. BIO BIG is the world"s largest brand of certified compostable bags and films made from Mater-BI (NOVAMONT)

**B. Cellulose based Bioplastics**: Produced using cellulose esters and cellulose derivatives.

**i.Cellophane:** Cellophane is made from cellulose which is biodegradable.Cellophane films can be coloured and are well known as candy wrappings. The biodegradable films are available in a wide range of grades, and they can be used to pack products ranging from cheese to coffee and chocolates (O.J.P.C.,2018).

**ii.Cellulose acetate**: Cellulose acetate is thermoplasticwhich is rather expensive and rarely used in packaging applications.

**iii.Polybutylene succinate (PBS):** Biodegradable, particularly used in packaging industry.Other applications include disposable products such as tableware or medical articles.

In agriculture, PBS finds interest in the fabrication of mulching films or delayed release of materials for pesticides and fertilizers.

**C. Microbial synthesis**:

**I.Poly hydroxybutyrate (PHB)**: Poly hydroxybutyrate (PHB) is biodegradable; used in a wide variety of fields including packaging, ropes, bank notes and car parts. PHB has potential applications in a wide variety of fields such as industrial, biomedical, agricultural, domestic, and automobile.

**ii.Polyhydroxyalkanoate (PHA): PHAs** are polyesters produced in nature by numerous microorganisms through bacterial fermentation of sugar or lipids (Jingnanetal,2009). They are biodegradable and are used in the production of bioplastics. PHA is often used for medical applications such as sutures, slings, bone plates and skin substitutes; it is also used for single-use food packaging.

**D. Synthesis from oils**:

**Polyamides 11:** PA11 a biopolymer derived from natural oil known by the trade name Rilson B commercialized by Arkoma. It is prized for its thermal resistance that makes it valued for use in car fuel lines, pneumatic air brake tubing, electrical anti-termite cable sheathing and oil and gas flexible pipes and control fluid umbilicals(Nifisaetal.,2015).It is non biodegradable.

**E. Other Biopolymers :**

**Polyethylene(PE):** Polyethylene (PE) is a bio-based polymer generally extracted from sugar used in carry bags, films and bottles.

**Polyethylene terephthalate(PET):** Polyethylene terephthalate (PET) is one of the major polymers produced worldwide representing about 18 % of world polymer production and comes in third after Polyethylene and Polypropylene. It is known for its use in beverage bottles.Coca Cola introduced Plant Bottle Technology where the PET had been made from bio-based mono-ethylene glycol from sugarcane and terephthalic acid from petrochemicals.

**Polyglycolic acid** (PGA): This is used in medicine and specialized applications.

**Polyhydroxyvalerate** (PHBV): Used for films and paper coatings, with possible markets including biomedical applications and veterinary science.

**Polyvinyl alcohol** (PHV): Used in packaging designed to dissolve in water to release products such as laundry detergent, pesticides, and hospital washables.

**Polycaprolactone(PCL)**: Biodegradable polyester, with low melting temperature and easily biodegradable. Widely used for mulch, seeding containers andbiomedical applications.

**Poly butyrate adipate terephthalate (PBAT)**: PBAT is a biodegradable and compostable biopolymerandis known for its flexibility and toughness which makes it ideal for combination with other biodegradable polymers that are brittlewith high modulus and strength.Widely used in garbage bags, wrapping films, disposable plastic products.

**Polyethylene furanoate(PEF)** PEF, a new polymer that is expected to enter the market in 2020. PEF is made entirely from vegetable raw materials and is also recyclable. It is considered to be the packaging material of the future, particularly for food and beverages.PEF finds applications in the packaging industry for fruit juices, milk, soft drinks, fresh tea or water.

**Bioplasticspackaging:** Bioplastic packaging is being used extensively in a wide array of industries including textiles, consumer goods , automotive and transport sectors.In 2018, global production capacities of bioplastics amounted to about 2.11 million tons with almost 65 percent of the volume destined for the packaging market,the biggest market segment within the bioplastics industry(Euro.Bio).There is a high demand for packaging made from bioplastics to be used for wrapping organic foods as well as for premium and branded products with a particular requirement. All types of bioplastics used in packaging offer one

overcome the environmental impact.Bio-PET and PLA are the major types of bioplastics
for packaging around the world.

**Advantages of Bioplastics:** Bioplastic is a much younger industry than conventional c
oil plastics. Bio-based plastics often shows good performance and a better environme
footprint when compared to conventional plastics. They have a less carbon footprint
helps to save resources and reduce crude oil dependency. Bioplastics can help the pla
industry and plastics consuming brands grow more sustainably. Bioplastics and
bioeconomy overall have the potential to unite the agricultural, chemical and indus
sectors. Bioplastics and bio-economy also help to create new jobs elsewhere both within
industry as well as in the entire value chain.

**Disadvantages of Bioplastics**:Although bioplastics show promising potential as
alternative to conventional plastics, it is equally important to consider their drawbacks. M
people believe that bioplastics are biodegradable. This is only partially true, as so
bioplastics are biodegradable while others are not (Grabianowski,2018). Surprisingly, m
bioplastics won't degrade at all, if placed in landfill with other garbage. Although bioplas
don't result in fossil-fuel emissions, they do require large amounts of fertilizers and pestici
(Grabianowski,2018). More over Bioplastics are basically designed to be composted,
recycled. Another drawback of bioplastics is their indistinguishability. To overcome th
users must be educated about bioplastics and proper recycling techniques to discern wh
bioplastics are biodegradable and which are compostable (Creative Mechanisms Staff, 201
Further, most bioplastics require high temperatures to degrade, and most cities lack t
infrastructure for proper bioplastic composting. As a result, many bioplastics end up in t
trash, are deprived of oxygen, and release harmful methane into the environment (Ch
2017).Waste collection and resource management needs to be standardized along with t
packaging industry to create some synchronized systems for waste to resource managemer
Bioplastics are often produced from genetically modified food crops such as corn, potatoe
and soybeans, a practice that carries a high risk of contaminating our food supply. Also, co
and soybean producers typically apply large amounts of chemical pesticides and fertilize
that pollute our air and water.

**Innovations in the field of Bioplastics continues –**

- Researchers around the world continue to develop greener varieties of Bioplastics th
can be more effectively reduce plastic pollution and the carbon footprint.
- More durable bioplastics are being designed for automotive,electronics and consume
goods such as Electrolux's new refrigerator made from corn and sugarcane bioplasti
material.
- Newer bioplastics are being made in laboratories from straw, wood chips and foo
waste.
- Bioplastics can be genetically engineered from Pseudomonas by the mutation of som
of the genes involved in the β-oxidation pathway.

**Conclusion:** Even though the production of bioplastics is costly, their applicationsare o
interest owing to the drawbacks of conventional plastics.Industrial progress in packaging
technology in future appears to be moving towards newer breed of bio-materials. The trend i
to maximize the production of bioplastics by enhancing the properties of bioplastics
producing microorganisms, plants and algae. It is clear that bioplastics can reduce many o
the environmental problems posed by the conventional plastics.

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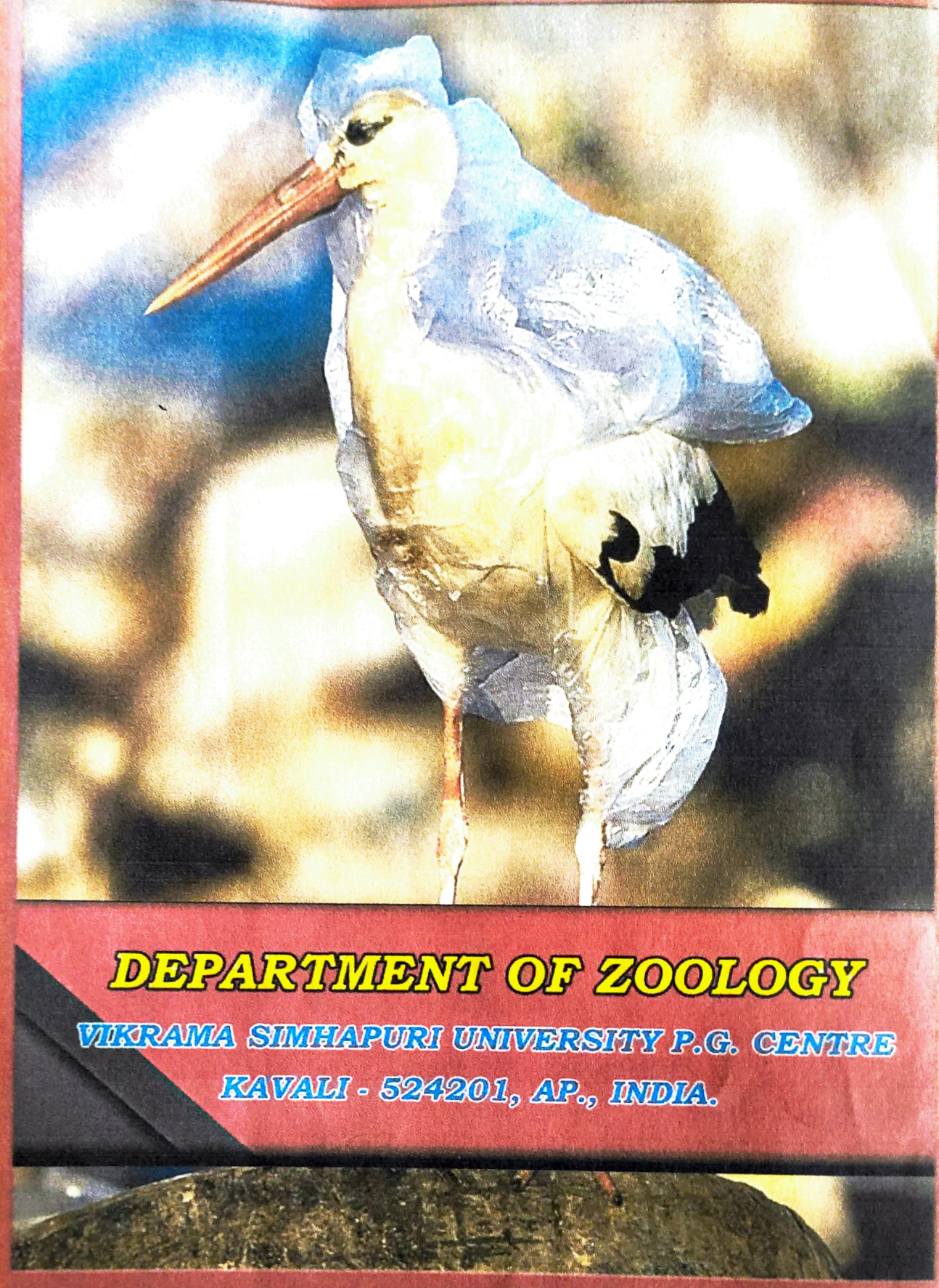
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## BIODEGRADABLE PLASTICS –AN OVERVIEW

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### ABSTRACT

Plastics are synthetic or semi-synthetic materials which are typically polymers of high molecular mass obtained from petroleum and natural gas. Bioplastic is the universal term for polymers made of renewable biomass sources. Bioplastics are an alternative to traditional plastics. As a consequence, bioplastic is biodegradable in about 180 days in opposition to traditional plastics, which remain in the environment for 500 to 1000 years. Bioplastics are made of different sources of biomass, such as corn or potato starch and cellulose. These substances are naturally produced by plants. Biodegradable plastics are the type of plastics that undergo decomposition over a period of time under composting conditions. The global biodegradable plastics market accounts for less than 1% of the overall plastics market, however, it is expected to grow at a fast pace over the next 5 years. Organic

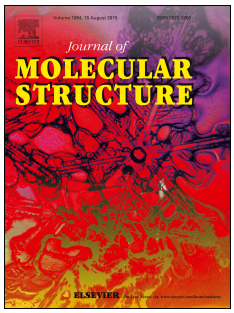


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# Accepted Manuscript




Synthesis, conformational, characterisation and reactivity study of 1,7-bis(4-bromophenyl)heptane-1,7-dione

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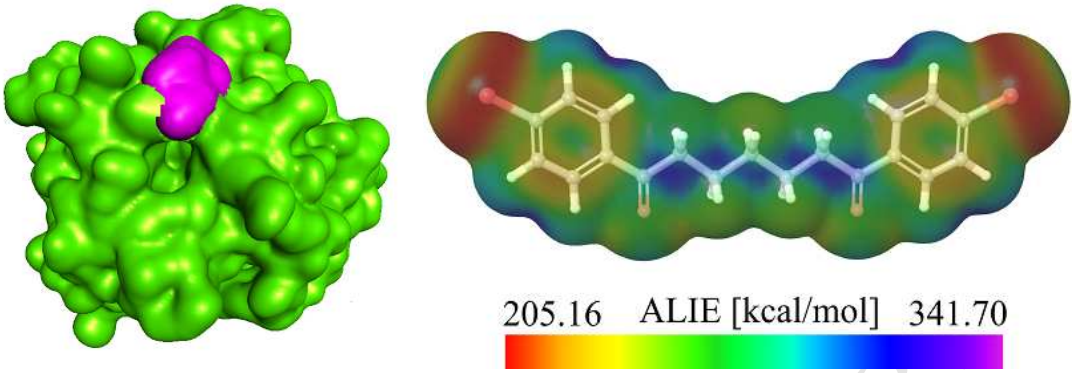
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# Synthesis, conformational, characterisation and reactivity study of 1,7-bis(4-bromophenyl)heptane-1,7-dione

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**Abstract**

In the present study, the title compound 1,7-bis(4-bromophenyl)heptane-1,7-dione (BBPHD) was synthesized according to the procedure described in literature, and its solid state crystal structure was characterised by the single crystal x-ray diffraction study. The complete crystallographic information has been reported in the present work. Physicochemical characterization by various spectral tools such as FT-IR, FT-Raman, $^{1}$H-NMR, $^{13}$C-NMR and UV-visible, have been performed as well and these results have been correlated with the theoretical data. The ground state geometrical optimization of the title compound has been performed using the DFT/B3LYP/6-311++G(d,p) level of theory in gas phase. Extracted molecular structure obtained by x-ray difractometry has been used as the starting molecular structure for geometrical optimizations. Computationally obtained structural and geometric parameters are in good

agreement with the experimentally obtained values. The experimental FT-IR and FT-Raman spectral data were compared with the theoretical spectral data and the complete assignment of vibrational wave numbers has been done on the basis of potential energy distribution (PED). In addition, reactive properties have been addressed on the basis of frontier molecular orbital analysis, global chemical reactivity descriptors, natural bond order (NBO) analysis, nonlinear optical (NLO) properties, molecular electrostatic potential (MEP) and average local ionization energy (ALIE) surfaces. Molecular dynamics (MD) simulations have been used in order to study the influence of water to the title compound. The docked ligand forms a stable complex with feruloyl esterase inhibitor and could be considered as a lead compound for the development of new antioxidant drug.

**Key words:** DFT; Hirshfeld surfaces; ALIE; RDF; Molecular docking.

## 1. Introduction

Owing to their abundance in natural products and pharmacologically active compounds, the significance of halogenated compounds is increasing [1-3]. This class of molecules has been successfully applied for the development of paints, dyes, adhesives, flame retardants, imaging agents in medical diagnosis, hydraulic and heat transfer fluids, refrigerants, solvents and in materials science [4-6]. Halogenated aromatic organic substrates are of great importance for the organic chemistry transformations, especially in the area of cross-coupling chemical reactions [7]. Although the halogenation is frequently followed by toxic chemicals, this procedure is highly developed and frequently used. There are number of advantages when it comes to the employment of halogens for the development of new molecules. For example, the introduction of carbon-halogen bond increases the thermal and oxidative stability, which leads to the lower sensitivity towards the oxidation by the liver P450 detoxification [6]. The same group of authors also indicates that carbon halogen bond increases the biological membrane permeability. Halogenated compounds are especially important in the area of agriculture and halogenation proved to be an important tool for development of efficient agricultural products. Jeschke [8] reports the information that since 2010, 96%of launched agricultural products, including herbicides, fungicides, insecticides/acaricides and nematicides, are containing halogen atoms. Positive effects of halogen atoms and halogen-containing groups are owed to steric and electronic effects [9], polarity of carbon-halogen bond [10] and pKa values effects [8]. One of the most important parameters in terms of pharmacokinetics, molecular lipophilicity, turned out to be adjustable by the substitution with halogen atoms [11]. Recently, Chen et al. [12] reported specific

nematic liquid crystal (LC) whose synthesis is based on the title compound (BBPHD). Taking into account the importance of their work, and importance of BBPHD for the synthesis of some other new specific nematic liquid crystals, we have decided to study BBPHD in details by spectroscopic and computational approaches. Density functional theory (DFT) represents irreplaceable tool for performing efficient and inexpensive computational studies in many areas [13-16]. DFT calculations with the hybrid exchange correlation functional B3LYP (Becke's three parameter (B3) exchange in conjunction with the Lee-Yang-Parr's (LYP) correlation functional) are of particular significance for studying systems comprising of extensive electron conjugation and/or electron lone pairs [17-20]. These structures have been the subject of many experimental and theoretical studies, especially when it comes to understandings of their structure, molecular properties and reaction mechanisms. Computational molecular modelling based on DFT calculations has become practically indispensable tool for evaluation and prediction of various properties of molecules and structures [21, 22], while in this work DFT calculations have been used in order to address global and local reactivity descriptors, including frontier molecular orbitals, MEP and ALIE surfaces and Fukui functions. DFT calculations were also used for confirmation of spectroscopic characterization and elucidation of vibrational specificities. Natural bond orbital (NBO) analysis has also been performed. Because newly synthetized molecules such as BBPHD might find place in the new pharmaceutical products, it is quite possible that they might end up in different water resources [23-27]. The introduction of halogen atoms also increases the persistency of compounds in environment, and in the same time hardening their degradation. This motivated us to also computationally study the degradation properties by calculation of bond dissociation energies for hydrogen abstraction (H-BDE) and stability in water by molecular dynamics (MD) simulations, another very important component of molecular modelling. Solid state crystal structure of BBPHD is elucidated by the single crystal X-ray diffraction studies, while contribution and quantification of various intermolecular interactions in crystal structure has been determined by the Hirshfeld surface analysis.

## 2. Material and methods

### 2.1. General remarks

The synthesis of BBPHD was carried according to the procedure reported in paper by Chen et al. [12]. Colourless prism like suitable crystals used for the structure determination was obtained by slow evaporation of ethanol at ambient temperature. FT-IR spectrum (Fig.S1-

supporting information) of title compound was recorded using the KBr pellets in the range of 4000-600 $cm^{-1}$ region, with the ATR module ALPHA-T Bruker FT-IR spectrophotometer. FT-Raman spectrum (Fig.S2-supporting information) of the title compound was recorded by Bruker RFS 100/s (Germany) using the Nd:YAG laser source, excitation wavelength of 1064 nm and spectral resolution of 2 $cm^{-1}$. $^{1}H$ and $^{13}C$-NMR spectra of the title compound was recorded (in ppm) on Bruker 400MHz spectrometer in $CDCl_3$ as solvent and TMS as internal standard.

**2.2. Data Collection and refinement details**

A suitable prism like crystal was selected and mounted on a Bruker APEX-II CCD diffractometer using the graphite monochromated MoKa ($\lambda$ = 0.71073 Å) radiation and detector (CCD). The crystal was kept at 296(2) K during data collection. The structure was solved using the Olex2 software [28] employing the olex2.solve [29] structure solution program and using the Charge Flipping. The structure was refined with the ShelXL [30] refinement package using the Least Squares minimization. All of the non-hydrogen atoms were revealed in the first difference Fourier map itself and were refined anisotropically. All of the hydrogen atoms were positioned geometrically, with C-H = 0.96 Å for methyl H, C-H = 0.93 Å for aromatic H, and refined using the riding model with $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl hydrogens and $U_{iso}(H) = 1.2U_{eq}(C)$ for aromatic hydrogens. The nitrogen bound hydrogen atom was located in a difference map and was refined isotropically with the bond length restraint of N-H = 0.86(2) Å. All of the geometrical calculations were carried out using the program PLATON [31] within the WinGXsuite [32]. The molecular and packing diagrams were generated using the MERCURY program [33].

**2.3. Computational details**

Molecular structure of BBPHD is extracted from the X-ray structure for computational studies. The molecular geometry optimization, vibrational analysis, frontier orbital analysis (HOMO-LUMO), MEP, surface analysis and Mullikan atomic charges were calculated at DFT/6-311G++(d,p)(5D, 7F) level using Gaussian 09 program package [34]. The assignment and PED analysis of wave number were performed by GaussView5.0 program [35] and GAR2PED software package [36]. For better agreement of calculated wavenumber numbers with experimental values, the wave numbers were scaled by the scaling factor of 0.9613 [37]. Schrödinger Materials Science Suite 2017-3 [38] was also used for computational study of global and local reactive properties of the newly synthetized BBPHD molecule. Particularly, Jaguar 9.7

program [39] has been used for DFT calculations, combined with Desmond program [40-43] for simulations based on molecular dynamics. Computational study based on DFT approach with SMSS has been also done with Becke-Lee, Parr i Yang (B3LYP) [44] exchange-correlation functional with 6-311++G(d,p), 6-31+G(d,p) and 6-311G(d,p) basis sets, in order to respectively obtain ALIE, Fukui functions and bond dissociation energies (BDE). Molecular dynamics simulation has been done with OPLS3 force field [40, 45-47], with simulation time of 10 ns, temperature of 300 K, pressure of 1.0325 bar and cut off radius of 12 Å. System was of isothermal–isobaric (NPT) ensemble class, while the simple point charge (SPC) solvent model [48] was chosen for the modelling of solvent properties. A single BBPHD molecule was placed into the cubic box with approximately 3000 water molecules. Analysis of electron density between atoms has been performed according to the works of Johnson et al. [49, 50], in order to identify formation of intra-molecular non-covalent interactions. Maestro GUI [51] was used for the preparation of input files and analysis of results when Schrödinger Materials Science Suite 2017-3 was employed.

### 2.4 Conformational Analysis

The solid structure of the title compound has been determined, by the X-ray diffraction spectroscopic technique, to be planar with $C_s$ symmetry, but it can be considered as near-$C_{2v}$ as well. Such configuration allows more efficient packing and facilitates the intermolecular interaction between the molecular layers. Very interestingly, the optimized strict $C_{2v}$ structure was verified to be a minimum with all computed frequencies being positive. The two carbonyl groups prefer to point away from the skeleton of the molecule to maintain up to a 6 kcal/mol more stable configuration than when one of them would eclipse any of the $CH_2$ units. Nevertheless, detailed conformational analysis revealed that other possible non-planar (*np*) forms can possibly exist, and their calculated energies are expected to be very comparable with the experimentally reported one. Understanding these conformations is of great importance, as the molecular structure in the crystalline packing could be sensitive to several parameters such as temperature and pressure. To explore the possible stable forms beside the one determined experimentally, detailed conformational analysis at the B3LYP/6-311++G(d,p) has been performed. The internal rotations about the C2-C3, C3-C4 and C5-C6 (Fig.S3-supporting information) were calculated and show three possible non-planar forms (*np*-1, *np*-2 and *np*-3, respectively) within a stability range of less than 1 kcal/mol compared to the $C_s$ form. The large-

amplitude rotation about these bonds exhibits a barrier in a range of 2-3 kcal/mol in the non-condensed phase, indicating the feasibility of the formation of other packing pattern when harsh conditions are applied.

### 2.5. Hirshfeld surfaces

We examined molecular surfaces, packing of molecules in their crystal structure, highlighting the contribution of significant inter molecular interactions between molecules that are responsible for the molecular arrangement in the crystalline state through Hirshfeld surface analysis. Hirshfeld surfaces [52-54] and the related 2D finger print plots (FP) [55-57] are unique for any crystal structure and provide a quantitative measure of the intermolecular interactions on the surface [52, 58]. The Hirshfeld surface analysis and finger print plots of BBPHD was generated by using Crystal Explorer 3.0 software [59] which accepts structure input file in the CIF format. The surfaces are mapped using a fixed colour scale red, white and blue, where red highlights contacts shorter than the sum of van der Waals (vdW) radii which is represented by negative sign values of $d_{norm}$, white for contacts around vdW separation with $d_{norm}$ values equal to zero, and blue for contacts longer than vdW sum with positive sign $d_{norm}$ values.

## 3. Result and discussions

### 3.1. Crystal structure analysis

The title compound crystallizes in orthorhombic space group *Abm2*, with the following unit cell parameters: $a$ = 7.1227(11) Å, $b$ = 42.536(4) Å, $c$ = 5.8126(6) Å and Z = 4. The molecule exhibits crystallographic inversion symmetry located at the C10 carbon atom and there is half-molecule in the asymmetric unit. The molecule is almost planar with root mean squared deviation of all atoms (excluding H-atoms) being 0.076Å. The crystal structure features C2-H2…$\pi_{aryl}$ and C5-H5…$\pi_{aryl}$ interactions, forming a three dimensional grid like architecture. The packing of molecules in the crystal lattice is shown in Fig.S4 (supporting information). The crystallographic data and refinement parameters are summarized in Table 1.

### 3.2. Hirshfeld surfaces

3D Hirshfeld surfaces and 2D finger print analysis illustrations of the title compound (BBPHD) are shown in Fig.5 (supporting information), where surfaces have been mapped over $d_{norm}$ and shape index -1.0-1.0 Å. A red spot close to the H2 hydrogen atom on the $d_{norm}$ surface and the centroid of the aromatic ring arises as a result of C2-H2…$\pi_{aryl}$ interactions present in the crystal. Similarly, a faint red spot close to H5 atom on the $d_{norm}$ surface is due to weak C5-

H5…$\pi_{aryl}$ interactions (Fig.S5a). The dark red spots close to the centroid of the two aromatic rings in the shape index is a result of the two C-H…$\pi_{aryl}$ interactions. The two C-H…$\pi_{aryl}$ interactions are mapped over the $d_{norm}$ surface to support the presence of these interactions (Fig. S5b). The relative contribution of different interactions to the Hirshfeld surface was calculated for BBPHD. It is evident from Fig.S5(c) that the H···H contacts account for about 34.7% of the total Hirshfeld surface area; the remaining contribution was mostly due to C···H (25.8%), O···H (12.4%), Br···H (15.0%), Br···Br (9.3%) interactions and only minor contribution from other interactions.

**3.3. Geometrical parameters**

In the present case the experimental C-C bond lengths are in the range of 1.4104-1.3785 Å and the calculated C-C bond lengths are in the range of 1.4057-1.3727 Å [60]. For the title compound, the C-Br bond length is 1.9237 Å (DFT) and 1.9055 Å (XRD), which is in agreement with the literature data [61]. The C=O bond length (1.1988) agrees with the reported literature values [60]. At C8 position, the bond angles (/DFTXRD) are C3-C8-C9 = 123.5/123.7°, C3-C8-Br1 =119.1/119.2° and C9-C8-Br1 = 117.3/117.1° and the asymmetry in angles is due to the electronegative bromine atom.

**3.4. IR and Raman spectra**

Table 2 contains the wavenumbers (calculated and observed) with vibrational assignments, while the atom labelling is provided in Fig.1. Phenyl rings at C5 and C27 are designated as PhI and PhII, respectively. The carbonyl stretching C=O vibrations [62-64] appear at 1668 $cm^{-1}$ (IR), 1680 $cm^{-1}$ (Raman) and theoretically at 1679 and 1678 $cm^{-1}$. The bands observed at 679, 662 $cm^{-1}$ (IR), 658, 551 $cm^{-1}$ (Raman) and at 678, 667, 553 $cm^{-1}$ (DFT) are assigned as C=O deformation modes [62]. The phenyl C-H stretching modes are assigned at 3081, 3062 $cm^{-1}$ (spectrum), 3079, 3059 $cm^{-1}$ (Raman) and in the range 3082-3064 $cm^{-1}$ based on DFT calculations [62, 65]. The ring stretching modes of the phenyl ring are assigned in the range 1558-1269 $cm^{-1}$ theoretically. The bands observed at 1570, 1530, 1450, 1374 $cm^{-1}$ (IR) and at 1565, 1279 $cm^{-1}$ (Raman) are assigned as the phenyl ring stretching modes. The band at 1042 $cm^{-1}$ (IR), 1042 $cm^{-1}$ (Raman) and 1040 $cm^{-1}$ (DFT) is assigned as the ring breathing mode of the para substituted phenyl ring [65], which is in agreement with the reported values at 1062 $cm^{-1}$ (IR) and 1061 $cm^{-1}$ (DFT) [66]. The in-plane and out-of-plane CH deformations are assigned theoretically in the range 1276-1087 $cm^{-1}$ and 965-788 $cm^{-1}$, respectively. Experimentally, these

modes are assigned at 1156, 1087 $cm^{-1}$ (IR), 1279, 1088 $cm^{-1}$ (Raman) and 963, 815, 801 $cm^{-1}$ (IR), 968, 818, 798 $cm^{-1}$ (Raman). The $CH_2$ stretching modes are assigned in the range 2965-2865 $cm^{-1}$ in IR spectrum, 2965-2877 $cm^{-1}$ in Raman spectrum and in the range of 2962-2873 $cm^{-1}$based on DFT calculations [62,67]. The $CH_2$ bending modes are observed in the ranges 1450-759 $cm^{-1}$ in the IR spectrum and 1440-738 $cm^{-1}$ in the Raman spectrum. According to the DFT calculations, these modes are in the range of 1453-706 $cm^{-1}$. The C-C stretching modes are assigned in the range 1173-780 $cm^{-1}$computationally. Bromine compounds [62] absorb strongly in the region of 635±85 $cm^{-1}$, due to the CBr stretching vibration and in the present case, bands at 615 $cm^{-1}$ (IR), 624 $cm^{-1}$ (Raman) and 616 $cm^{-1}$ (DFT) are assigned to this mode. Varghese et al. [68] reported the CBr stretching mode at 632 $cm^{-1}$ theoretically.

**3.5. NMR spectra analysis**

Chemical shift ($^{1}H$ and $^{13}C$) values of the investigated molecules have been computed with GIAO/B3LYP method [69] and compared with experimental values (Table S1-supporting information). The chemical shift values of $^{1}H$-NMR spectrum of title compound show two ranges; first one is consequence of the chemical shift of aliphatic C-H protons, which occurred in the range of 1.39-2.95/1.29-3.02 ppm (experimental/theoretical). The chemical shift of hydrogen atom attached to carbon near to the carbonyl group is higher than expected. H21, H22, H40 and H41 resonate at high frequency 2.95/3.02 (experimental/DFT), due to influence of carbonyl groups. Second one, around 7.60-7.81/7.69-8.06 (experimental/theoretical) ppm, occurred due to the aromatic protons. Chemical shift values of $^{13}C$-NMR for aromatic carbon atoms in general have values higher than 100 ppm [70,71]. Computational and experimental $^{13}C$ NMR values of carbon atoms of methylene groups of aliphatic chain are in good agreement as well: C17, C36 (24.02/27.40), C13 (28.97/32.69) and C20, C39 (38.37/42.69) ppm (experimental values/computational values). The chemical shift value at 199.26/205.26 ppm (experimental/computational) is assigned to the carbonyl carbon atoms C2 and C24. Signals observed in range of the 128.26-135.82/134.04-153.80 ppm (experimental/computational) correspond to carbon atoms of phenyl rings. From above result shows, the theoretical chemical shifts are good in agreement with experimental findings.

**3.6. Electronic properties and frontier molecular orbital analysis**

Chemical reactivity and kinetic stability of molecules depend upon the energy gap between HOMO and LUMO orbitals. These molecular orbitals are often known as frontier

molecular orbitals (FMOs). Based on the energy gap between frontier orbitals, molecules are frequently classified into soft and hard molecules. Energy gap between frontier orbitals is a critical parameter for prediction of the biological activity and transport properties. Frontier molecular orbitals have been visualized in Fig.S6 (supporting information). It can be seen that HOMO (MO109) is localized mainly at the carbonyl group and partially at the aliphatic chain, while LUMO (MO110) is localized mainly at the benzene ring and partially at the carbonyl group. Based on the HOMO to LUMO transitions, it can be concluded that the transfer of electron cloud occurs mainly from carbonyl group to benzene ring. In the present case, the calculated energy values of HOMO and LUMO are -7.20 eV and -2.16 eV, respectively and the energy gap between HOMO and LUMO is 5.04 eV. The higher the energy gap between HOMO-LUMO is, the harder the molecule is. In order to understand the chemical reactivity of title compound, global reactivity parameters were evaluated by DFT method. Single point calculation was carried out at DFT/6-311++G(d,p) level of theory. Vertical ionization potential (IP) and vertical electron affinity (EA) parameters have been calculated. These parameters were defined according to the following equations:

$$IP = E_{n-1(\text{cation})} - E_{N(\text{neutral})},$$

$$EA = E_{N(\text{neutrail})} - E_{N+1(\text{anion})},$$

where $E_{N+1(\text{anion})}$, $E_{N(\text{neutral})}$ and $E_{N-1(\text{cation})}$ are total energies of anion, neutral and cation forms of investigated molecule, respectively [72, 73]. These parameters were used in order to calculate the values of global reactivity descriptor, summarized in Table S2 of the Supplementary Materials. TD-DFT calculations have been performed at B3LYP/6-311++G(d,p) level of theory, while theoretical UV transitions have been characterized by vertical excitation energies, wavelength and oscillator strength. These results are summarized in Table S3 of the Supplementary Materials. The UV spectrum of the title compound (Fig.S7-supporting information) is characterized by electronic absorption band located at 268 nm, which is the consequence of the transitions: HOMO-1→LUMO and HOMO→LUMO+1(π-π transition).

### 3.7. Nonlinear optical properties

With regards to optoelectronic applications [74], the NLO active materials receive significant attention. Some of the properties that are important for optoelectronic applications can be obtained by DFT calculations and these include dipole moment, polarizability, first and

second hyperpolarizabilities. Respectively, these parameters have been calculated to be 4.102 Debye, $4.149\times10^{-23}$ esu, $6.227\times10^{-30}$ esu and $-71.736\times10^{-37}$ esu. It is interesting to notice that the first hyperpolarizability of the title compound is 31.98 times higher than in the case of urea, revealing possibility of the title compound to possess representative NLO properties, comparable with similar derivatives [75].

### 3.8. Molecular electrostatic potential

Analysis of charge distribution by mapping of MEP to the electron density surface is valuable approach in molecular modelling, when it comes to the biological recognition, hydrogen bonding interactions and visualization of reactive molecular sites [76, 77]. Optimized molecular structure was used for the generation of 3D MEP and 2D counter surfaces plots with rainbow colour scheme (electron reach regions are represented with red colour, while electron poor regions are represented with blue colour). For the title compound MEP took values from– 5.56a.u. (red) to 5.56a.u. (blue). MEP and surface analysis diagram of title compound, Fig.2, show that negative regions are mainly localized over oxygen atoms of the carbonyl groups, indicating the most sensitive sites towards the electrophilic attacks. On the other side, the maximal positive regions are localized over hydrogen atom of the aliphatic chain as well as phenyl rings, indicating sensitivity towards the nucleophilic attacks.

### 3.9. Natural Bond Orbital analysis

Natural bond orbital (NBO) calculations were performed using NBO 3.1 program [78] as incorporatedin the Gaussian09 package. In this case the DFT/SDD level of theory was used in order to understand various second-order interactions, principal interaction summarized in Tables S4 and S5 (supplementary materials). The strong intermolecular hyper conjugative interactions are: $C_2$-$C_5$ from $O_{16}$ of $n_2(O_{16}) \rightarrow \sigma^*(C_2\text{-}C_5)$ which increases the electron density 0.06345e that weakens the respective bond $C_2$-$C_5$ leading stabilization of 16.61 kJ/mol; $C_2$-$C_{20}$ from $O_{16}$ of $n_2(O_{16})\rightarrow\sigma^*(C_2\text{-}C_{20})$ which increases the electron density 0.05561e that weakens the respective bond $C_2$-$C_{20}$ leading stabilization of 17.56 kJ/mol; $C_{24}$-$C_{27}$ from $O_{35}$ of $n_2(O_{35})\rightarrow\sigma^*(C_{24}\text{-}C_{27})$ which increases the electron density 0.06345e that weakens the respective bond $C_{24}$-$C_{27}$ leading stabilization of 16.61 kJ/mol; and $C_{24}$-$C_{39}$ from $O_{35}$ of $n_2(O_{35})\rightarrow\sigma^*(C_{24}\text{-}C_{39})$ which increases the electron density 0.05561e that weakens the respective bond $C_{24}$-$C_{39}$ leading stabilization of 17.56 kJ/mol. The orbital with low occupation number are high energies are $n_2(O_{16})$, $n_2(O_{35})$ with energies -0.27360, -0.27360a.u. and considerable p-characters100,

99.99% and low occupation numbers 1.90859, 1.90859 while the orbital with high occupation numbers and low energies are: $n_1(O_{16})$, $n_1(O_{35})$ -0.68914, -0.68914a.u. and p-characters, 61.77, 61.77 and occupation numbers 1.97457, 1.97457. Thus, a very close to pure p-type lone pair orbital participates in the electron donation to the $\sigma^*(C_2\text{-}C_5)$ orbital for $n_2(O_{16}) \rightarrow \sigma^*(C_2\text{-}C_5)$, $\sigma^*(C_2\text{-}C_{20})$ orbital for $n_2(O_{16}) \rightarrow \sigma^*(C_2\text{-}C_{20})$, $\sigma^*(C_{24}\text{-}C_{27})$ orbital for $n_2(O_{35}) \rightarrow \sigma^*(C_{24}\text{-}C_{27})$, $\sigma^*(C_{24}\text{-}C_{39})$) orbital for $n_2(O_{35}) \rightarrow \sigma^*(C_{24}\text{-}C_{39})$ interactions in the title compound.

### 3.10. ALIE and MEP surface, Fukui functions and non-covalent interactions

Aside of the MEP surface, in this work ALIE values were mapped to the electron density surface in order to identify the molecule sites where electrons are least tightly bound. This enabled us to detect molecule sites that are the most sensitive towards the electrophilic attacks (Fig.3) [79-82]. The analysis of electron density between atoms revealed that the intra-molecular non-covalent interactions in the case of BBPHD molecule didn't form. The lowest ALIE values in the case of BBPHD molecule were calculated in the near vicinity of bromine atoms, with corresponding values of ~205 kcal/mol. On the other side, the highest ALIE values were calculated in the near vicinity of all hydrogen atoms with the corresponding values of ~342 kcal/mol. Additional insights into the local reactive properties of BBPHD molecule were obtained thanks to the calculation of Fukui functions, which are in the case of Jaguar program for DFT calculations obtained by the finite difference approach according to the following equations:

$$f^{+} = \frac{\left(\rho^{N+\delta}(r) - \rho^{N}(r)\right)}{\delta}, \qquad (1)$$

$$f^{-} = \frac{\left(\rho^{N-\delta}(r) - \rho^{N}(r)\right)}{\delta}, \qquad (2)$$

where $N$ represents the number of electrons in reference state of the molecule, while $\delta$ is fraction of electron which default value is set to be 0.01 [83]. After mapping of the values of the Fukui functions to the electron density surface the following corresponding surfaces have been obtained, Fig.4. In general Fukui functions track the changes in electron densities which are consequence of change in the overall charge of the observed molecule. The change in overall molecular charge influences the values of electron density at the molecular surface. By tracking of these changes in electron density, Fukui functions allow detection of molecule sites with electrophilic and nucleophilic properties. In this regard, purple colour for Fukui $f^{+}$ function in

Fig.4a is positive colour and indicates sites with increased electron density after the addition of charge. In Fig.4a it can be seen that blue-to-purple colour is located in the near vicinity of carbon atoms connected with oxygen atoms, which marks them as an electrophilic ones. On the other side, red colour for Fukui $f^-$ function is a negative colour and indicates sites with decreased electron density after the removal of charge. Inspection of Fig.4b indicates that the red colour is located in the central part of the molecule, marking this area as nucleophilic.

### 3.11. Sensitivity towards autoxidation and water

Taking into account the negative environmental impact of the pharmaceuticals, in this work we have also studied the sensitivity of BBPHD molecule towards the autoxidation mechanism [24, 84]. Oxidation mechanism represents one of the most important pathways for degradation of pharmaceuticals [85-88]. Thanks to the correlation between bond dissociation energies for hydrogen abstraction (H-BDE) and sensitivity towards the autoxidation mechanism, computational molecular modelling techniques can be used for determination of the molecule sites where degradation could start [89-95]. Fig.5 contains information about the H-BDE values. According to the results presented in Fig.5, for BBPHD molecule it can be concluded that it is highly stable towards the autoxidation mechanism, since there are no H-BDE values in the region between 70 and 90 kcal/mol [96, 97]. In the same time the lowest BDE value has been calculated for bromine atoms indicating that degradation could start by detaching of these atoms. Sensitivity towards water molecules was investigated by molecular dynamics simulation. The information on the obtained trajectories were used in order to calculate Radial Distribution Functions (RDF) for all atoms of the BBPHD molecule, with the goal to identify atoms with the most important interactions with water. RDFs were calculated with respect to the distance between the observed atom of the BBPHD molecule and oxygen atom of the water molecule. Representative RDFs have been presented in Fig.6. According to the results provided in Fig.6 it can be seen that BBPHD molecule has significant stability in water, as there are no hydrogen atoms with sharp g(r) curves located at distances below 2 Å. The highest g(r) value was calculated for bromine atoms, however their maximal g(r) values are located at distance of around 3.5 Å. On the other side, maximal g(r) values carbon atoms C16 and C35 are located at the distances lower than in case of the bromine atoms, but their maximal g(r) values are much lower. Maximal g(r) values of the carbon atoms C8 and C30 are somewhere between bromine

atoms at carbon atoms C16 and C35, however their peaks are located at high distances of over 4.5 Å.

### 3.12. Molecular docking

Based on the molecular structure, PASS (Prediction of Activity Spectra) [98] online tool for prediction of different types of activities has been applied. According to the results of PASS analysis, which have been summarized in Table 3, the title compound could serve as feruloyl esterase inhibitor, with probability to be active (Pa) value of 0.936. Antioxidants are necessary to control degenerative reactions produced by reactive oxygen and nitrogen species. These species are involved in several ailments including cancer and heart diseases. Several literatures suggest that heptane derivatives show promising antioxidant activities [99, 100]. Ferulic acid is the most abundant hydroxycinnamic acid in the plant world and is one of the most promising sources of antioxidants [101]. Feruloyl esterase is a class of enzymes used in biocatalysis for refinement of hydroxycinnamic acids. These compounds have shown to have antioxidant and antibacterial properties, FAEs and their hydrolytic or transesterification products are of great interest for various biotechnological applications, in particular as modified natural antioxidants or food flavour precursors [102].It prevents low-density lipoprotein from oxidation, exhibits inhibitory effects on tumour promotion [103] and protects against certain chronic diseases such as coronary heart disease and some cancers [104, 105]. Therefore the feruloyl esterase inhibitor is used as a target for docking study. High resolution crystal structure of feruloyl esterase inhibitor was downloaded from the RSCB protein data bank website with PDB ID: 1UWC. All molecular docking calculations were performed on Auto Dock-Vina software [106] and as reported in literature [74, 107]. The ligand binds at the active site of the substrate by weak non-covalent interactions and these interactions are depicted in Fig.S8 (supporting information). Amino acids forms strong hydrophobic interaction with the ligand. The docked ligand forms a stable complex with feruloyl esterase inhibitor (Fig.S9-supporting information) and got a binding affinity value of -5.7 kcal/mol (Table 4). Thus the title compound can be a lead compound for developing new antioxidant drug.

## 4. Conclusion

The title compound, 1,7-bis(4-bromophenyl)heptane-1,7-dione was characterized by single crystal XRD, FT-IR, FT-Raman as well as NMR spectroscopic studies. Within the framework of DFT, the vibrational wavenumbers are theoretically predicted and compared with

experimental wavenumbers. Conformation analysis shows that the two carbonyl groups prefer to point away from the skeleton of the molecule to maintain up to a 6 kcal/mol more stable configuration than when one of them would eclipse any of the $CH_2$ units. MEP plot showed that the negative regions are mainly localized over the oxygen atoms of the carbonyl groups while the maximal positive regions are localized over the hydrogen atom of the aliphatic chain as well as phenyl rings. The first hyperpolarizability of the title compound is 31.98 times that of urea. ALIE surfaces revealed that the near vicinity of bromine atoms could be the most sensitive parts of the BBPHD molecule in terms of electrophilic attacks. Additionally, Fukui functions revealed that the central part of BBPHD molecule could be considered as important reactive center when charge is added or removed. The values of H-BDE indicate that BBPHD molecule is highly stable towards the autoxidation mechanism, while the remaining BDE values indicate that degradation process might start with detaching of bromine atoms. Molecular dynamics study indicated that BBPHD molecule is highly stable in water as well, since there are no hydrogen atoms with significant interactions with water molecules. PASS analysis predicts feruloyl esterase inhibitor activity for the title compound and the docking studies suggest that the title compound can be a lead compound for developing new antioxidant drug.

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**Supplementary Material**

The cif file of the title compound have been assigned CCDC number1577497and can be obtained free of cost on application to CCDC 12 Union Road, Cambridge CB21 EZ, UK. (Fax: (+44) 1223 336-033: e-mail: data_request@ccdc.cam.ac.uk).

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**Figure captions**

Fig.1 Optimized geometry of 1,7-bis(4-bromophenyl)heptane-1,7-dione

Fig.2 MEP plot of 1,7-bis(4-bromophenyl)heptane-1,7-dione

Fig.3 ALIE surface of 1,7-bis(4-bromophenyl)heptane-1,7-dione molecule

Fig.4 Fukui functions of the 1,7-bis(4-bromophenyl)heptane-1,7-dione molecule a) $f^{+}$ and b) $f^{-}$

Fig.5 H-BDE values (blue colour) and BDE values of the remaining single acyclic bonds (red colour)

Fig.6 Significant RDFs of atoms of 1,7-bis(4-bromophenyl)heptane-1,7-dione molecule

ACCEPTED MANUSCRIPT

**Table 1: Crystal data and structure refinement for BBPHD**

| | | |
|---|---|---|
| CCDC Deposit | : | 1577497 |
| Empirical formula | : | $C_{19}H_{18}O_2Br_2$ |
| Formula weight | : | 434.13 |
| Temperature/K | : | 296.15 |
| Crystal system | : | Orthorhombic |
| Space group | : | Abm2 |
| a/Å | : | 7.1227(11) |
| b/Å | : | 42.536(4) |
| c/Å | : | 5.8126(6) |
| α/° | : | 90 |
| β/° | : | 90 |
| γ/° | : | 90 |
| Volume/$Å^3$ | : | 1761.1(4) |
| Z | : | 4 |
| $\rho_{calc}g/cm^3$ | : | 1.653 |
| $\mu/mm^{-1}$ | : | 4.610 |
| F(000) | : | 872.2 |
| Crystal size/$mm^3$ | : | 0.25×0.22×0.18 |
| Radiation | : | Mo Kα (λ = 0.71073) |
| 2Θ range for data collection/° | : | 3.84 to 57.74 |
| Index ranges | : | $-9 \leq h \leq 9$, $-56 \leq k \leq 57$, $-6 \leq l \leq 7$ |
| Reflections collected | : | 12635 |
| Independent reflections | : | 2095 [$R_{int}$ = 0.0808, $R_{sigma}$ = 0.0737] |
| Data/restraints/parameters | : | 2095/1/106 |
| Goodness-of-fit on $F^2$ | : | 1.101 |
| Final R indexes [I>=2σ (I)] | : | $R_1$ = 0.0630, $wR_2$ = 0.1306 |
| Final R indexes [all data] | : | $R_1$ = 0.1174, $wR_2$ = 0.1551 |
| Largest diff. peak/hole/ e $Å^{-3}$ | : | 1.14/-1.15 |
| Flack parameter | : | 0.11(3) |

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Table 2

Calculated scaled wavenumbers, observed IR, Raman bands with assignments

| B3LYP/6-311G++(d,p)(5D, 7F) | | | IR | Raman | Assignments[a] |
|---|---|---|---|---|---|
| υ($cm^{-1}$) | IRI | RA | υ($cm^{-1}$) | υ($cm^{-1}$) | - |
| 3082 | 0.89 | 432.59 | - | - | υCHII(51),υCHI(40) |
| 3082 | 1.48 | 33.26 | - | - | υCHI(51),υCHII(40) |
| 3081 | 2.11 | 8.85 | 3081 | 3079 | υCHII(55),υCHI(43) |
| 3081 | 4.68 | 5.75 | 3081 | 3079 | υCHI(55),υCHII(43) |
| 3069 | 0.41 | 52.50 | - | - | υCHI(66),υCHII(32) |
| 3069 | 0.99 | 34.13 | - | - | υCHII(66),υCHI(32) |
| 3064 | 0.53 | 74.49 | 3062 | 3059 | υCHII(50),υCHI(49) |
| 3064 | 7.37 | 24.17 | 3062 | 3059 | υCHI(50),υCHII(49) |
| 2962 | 66.90 | 25.95 | 2965 | 2965 | $\upsilon CH_2$(88) |
| 2954 | 0.01 | 0.22 | 2952 | - | $\upsilon CH_2$(92) |
| 2925 | 39.15 | 125.82 | - | 2928 | $\upsilon CH_2$(96) |
| 2920 | 2.24 | 0.72 | 2922 | - | $\upsilon CH_2$(98) |
| 2915 | 7.65 | 71.93 | - | - | $\upsilon CH_2$(94) |
| 2914 | 0.01 | 0.43 | - | - | $\upsilon CH_2$(92) |
| 2896 | 19.06 | 74.27 | - | 2897 | $\upsilon CH_2$(91) |
| 2890 | 22.32 | 288.27 | - | - | $\upsilon CH_2$(96) |
| 2890 | 31.55 | 0.65 | - | - | $\upsilon CH_2$(98) |
| 2873 | 16.97 | 81.11 | 2865 | 2877 | $\upsilon CH_2$(96) |
| 1679 | 338.34 | 190.30 | 1668 | 1680 | υC=O(80) |
| 1678 | 18.93 | 73.90 | 1668 | 1680 | υC=O(80) |
| 1558 | 69.35 | 343.39 | 1570 | 1565 | υPhII(26), υPhI(26) |
| 1558 | 176.92 | 213.32 | - | - | υPhI(27), υPhII(26) |
| 1539 | 8.18 | 16.46 | - | - | υPhII(36), υPhI(36) |
| 1539 | 40.30 | 17.65 | 1530 | - | υPhI(36), υPhII(36) |
| 1454 | 3.93 | 7.53 | - | - | υPhII(36), υPhI(36) |
| 1454 | 19.94 | 1.24 | 1450 | - | υPhII(36), υPhI(36) |
| 1453 | 12.69 | 0.75 | 1450 | - | $\delta CH_2$(86) |

| | | | | | |
|---|---|---|---|---|---|
| 1437 | 2.65 | 0.12 | - | 1440 | $\delta CH_2$(92) |
| 1430 | 0.04 | 27.52 | - | - | $\delta CH_2$(95) |
| 1404 | 14.77 | 7.51 | 1410 | - | $\delta CH_2$(88) |
| 1403 | 0.14 | 1.65 | - | - | $\delta CH_2$(88) |
| 1368 | 4.97 | 6.95 | 1374 | - | υPhI(32), υPhII(32), δCHII(11), δCHI(11) |
| 1368 | 73.82 | 3.16 | - | - | υPhI(31), υPhII(31), δCHII(11), δCHI(11) |
| 1351 | 3.25 | 0.59 | - | - | $\delta CH_2$(67), υCC(18) |
| 1345 | 0.01 | 0.64 | 1342 | 1340 | $\delta CH_2$(66) |
| 1320 | 141.41 | 0.85 | - | - | $\delta CH_2$(66), υCC(14) |
| 1284 | 0.06 | 0.16 | 1288 | - | $\delta CH_2$(94) |
| 1281 | 0.01 | 17.04 | 1281 | - | $\delta CH_2$(97) |
| 1280 | 9.05 | 12.74 | 1281 | 1279 | $\delta CH_2$(66) |
| 1276 | 1.64 | 0.01 | - | 1279 | υPhI(11), υPhII(10), δCHI(30), δCHII(30) |
| 1269 | 3.44 | 1.63 | - | - | δCHI(30), δCHII(30), υPhI(11), υPhII(10) |
| 1269 | 0.13 | 0.26 | - | - | υPhI(31), υPhII(31) |
| 1269 | 1.15 | 7.80 | - | - | υPhI(25),υPhII(25), $\delta CH_2$(26) |
| 1260 | 0.01 | 10.11 | 1258 | 1260 | $\delta CH_2$(86) |
| 1220 | 186.53 | 14.42 | 1219 | 1215 | $\delta CH_2$(60), υCC(16) |
| 1202 | 0.04 | 0.22 | - | - | $\delta CH_2$(96) |
| 1173 | 21.27 | 102.83 | 1172 | 1170 | υCC(32), $\delta CH_2$(16) |
| 1162 | 21.38 | 12.12 | 1156 | - | δCHII(44), δCHI(44) |
| 1153 | 13.45 | 88.30 | 1156 | - | δCHI(30), δCHII(31) |
| 1148 | 183.16 | 29.51 | - | 1149 | υCC(18),δCHI(15), δCHII(15) |
| 1095 | 0.01 | 2.44 | - | - | $\delta CH_2$(83) |
| 1087 | 3.80 | 5.47 | 1087 | 1088 | δCHI(25), δCHII(25), |

| | | | | | |
|---|---|---|---|---|---|
| | | | | | υPhI(16), υPhII(16) |
| 1087 | 7.87 | 2.87 | 1087 | 1088 | δCHI(25), δCHII(25), υPhI(15), υPhII(15) |
| 1061 | 0.55 | 58.77 | - | - | υCC(44), $\delta CH_2$(21) |
| 1058 | 0.01 | 0.60 | - | - | $\delta CH_2$(82) |
| 1040 | 78.39 | 8.97 | 1042 | 1042 | υPhI(27), υPhII(27) |
| 1040 | 17.01 | 100.46 | 1042 | 1042 | υPhI(27), υPhII(27) |
| 1028 | 20.51 | 3.71 | 1024 | 1030 | υCC(78) |
| 1008 | 16.55 | 0.09 | - | - | υCC(52) |
| 1000 | 0.17 | 22.49 | - | - | υCC(76) |
| 986 | 11.44 | 6.39 | - | - | δPhI(29),δPhII(29), υPhI(12), υPhII(12) |
| 985 | 92.40 | 0.36 | - | - | δPhI(33), δPhII(33) |
| 965 | 0.01 | 0.10 | - | 968 | γCHI(41), γCHII(41) |
| 964 | 0.81 | 0.06 | 963 | - | γCHII(42), γCHI(42) |
| 953 | 9.04 | 2.68 | - | - | υCC(32), δ(C=O)(14) |
| 937 | 0.00 | 0.29 | - | - | γCHI(32), γCHII(32) |
| 933 | 201.61 | 3.43 | - | - | υCC(46) |
| 932 | 0.03 | 0.19 | - | - | γCHI(38), γCHII(38) |
| 916 | 0.01 | 0.02 | 913 | - | $\delta CH_2$(59) |
| 837 | 14.44 | 0.34 | - | - | $\delta CH_2$(52),γCHI(10), γCHII(10), γ(C=O)(10) |
| 819 | 0.01 | 0.01 | - | 818 | γCHI(43),γCHII(43) |
| 813 | 8.39 | 0.01 | 815 | - | γCHI(44), γCHII(44) |
| 801 | 0.01 | 0.01 | 798 | 798 | γCHI(41), γCHII(41) |
| 788 | 74.69 | 0.03 | - | - | γCHI(33),γCHII(32), $\delta CH_2$(30) |
| 780 | 37.04 | 0.01 | - | - | υCC(32), $\delta CH_2$(12) |
| 759 | 7.71 | 35.99 | 759 | 758 | υCC(32), δPhII(14), δPhI(13) |
| 739 | 0.01 | 0.03 | 737 | 738 | $\delta CH_2$(66) |
| 706 | 12.10 | 0.01 | 706 | 699 | $\delta CH_2$(69) |

| | | | | | |
|---|---|---|---|---|---|
| 688 | 0.01 | 0.63 | - | - | τPhII(34), τPhI(34) |
| 688 | 0.03 | 0.14 | - | - | τPhII(33), τPhI(33) |
| 678 | 0.10 | 0.09 | 679 | - | δPhII(24), δPhI(23), δ(C=O)(38) |
| 668 | 2.62 | 9.28 | 662 | 658 | δ(C=O)(32), δPhII(20), δPhI(19) |
| 616 | 1.94 | 3.94 | 615 | 624 | δPhI(13), δPhII(12) υCBr(36) |
| 616 | 0.68 | 9.73 | 615 | 624 | δPhI(14), δPhII(12) υCBr(37) |
| 553 | 0.01 | 0.02 | - | 551 | γ(C=O)(36), δ$CH_2$(22) |
| 553 | 18.01 | 0.31 | - | 551 | γ(C=O)(37), δ$CH_2$(22), γCC(10) |
| 504 | 3.37 | 0.89 | - | 499 | δ(C=O)(34), δ$CH_2$(12), δCC(12) |
| 483 | 19.50 | 0.72 | - | 479 | δ(C=O)(34), δCC(14), υCBr(10) |
| 456 | 1.77 | 0.60 | - | 456 | δ$CH_2$(34), δ(C=O)(12) |
| 445 | 0.01 | 0.01 | - | - | γCBr(28), τPhI(24), τPhII(22), γCC(12) |
| 444 | 13.25 | 0.21 | - | - | γCBr(28), τPhI(24), τPhII(22), γCC(12) |
| 409 | 17.42 | 0.03 | - | 408 | δ(C=O)(38), δ$CH_2$(30), υCBr(14) |
| 399 | 0.01 | 0.01 | - | - | τPhII(42), τPhI(41) |
| 399 | 0.01 | 0.01 | - | - | τPhII(43), τPhI(39) |
| 372 | 1.92 | 1.14 | - | 369 | δ$CH_2$(28), υCBr(14) |
| 336 | 0.13 | 0.77 | - | 336 | δCC(30), δ$CH_2$(24), δCBr(12) |
| 283 | 11.14 | 0.54 | - | - | δCBr(40), δCC(22) |
| 264 | 0.15 | 2.61 | - | 262 | δCBr(32), δCC(10) |
| 240 | 1.14 | 0.01 | - | - | δCBr(38), δ$CH_2$(24), δ(C=O)(18) |

| | | | | | |
|---|---|---|---|---|---|
| 236 | 0.28 | 0.62 | - | - | γCC(36), γCBr(26), γ(C=O)(12) |
| 236 | 0.01 | 3.68 | - | 234 | γCC(38), γCBr(28), γ(C=O)(12) |
| 215 | 6.95 | 0.44 | - | - | δCBr(32), δPhII(15), δPhI(11) |
| 180 | 9.00 | 0.33 | - | 185 | δCBr(36), δ$CH_2$(32), δCC(18) |
| 144 | 1.72 | 0.01 | - | - | τ$CH_2$(82) |
| 141 | 0.01 | 0.03 | - | - | τ$CH_2$(77), τ(C=O)(13) |
| 134 | 0.01 | 0.97 | - | - | δCC(26), δCBr(24),δ$CH_2$(23) |
| 93 | 0.01 | 0.03 | - | 95 | τ$CH_2$(51), τ(C=O)(13) |
| 91 | 0.12 | 1.31 | - | - | δ(C=O)(22), δ$CH_2$(26) |
| 84 | 0.43 | 0.02 | - | - | τ$CH_2$(41) ,τ(C=O)(27) |
| 69 | 0.01 | 0.01 | - | - | τPhII(12), τCC(12) τ(C=O)(12),τPhI(14), γCC(14) |
| 66 | 3.13 | 0.01 | - | 66 | τPhII(16), τPhI(17), γCC(14) |
| 55 | 0.02 | 0.26 | - | - | δ$CH_2$(46), δ(C=O)(28), δCC(16) |
| 50 | 2.85 | 0.39 | - | - | τ(C=O)(30), τCC(30), τ$CH_2$(12) |
| 28 | 0.01 | 5.22 | - | - | τ(C=O)(34), τCC(29), τ$CH_2$(19) |
| 17 | 1.21 | 4.62 | - | - | τ$CH_2$(45),τ(C=O)(14), τCC(15) |
| 15 | 0.01 | 1.47 | - | - | δ$CH_2$(84), δ(C=O)(10) |
| 12 | 0.01 | 0.60 | - | - | τ$CH_2$(60),τ(C=O)(30) |

[a]υ-stretching; δ-in-plane deformation; γ-out-of-plane deformation; τ-torsion; $IR_I$-IR intensity(KM/Mole) ; $R_A$-Raman activity(Å$^4$/amu); the phenyl rings at C5 and C27 are designated as PhI and PhII.

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Table 3

PASS prediction for the activity spectrum of the1.7-bis(4-bromophenyl)heptane-1.7-dione (Pa represents probability to be active and Pi represents probability to be inactive)

| Pa | Pi | Activity |
|---|---|---|
| 0.936 | 0.003 | Feruloyl esterase inhibitor |
| 0.933 | 0.001 | Alkylglycerone-phosphate synthase inhibitor |
| 0.926 | 0.003 | Prolylaminopeptidase inhibitor |
| 0.918 | 0.005 | Aspulvinonedimethylallyltransferase inhibitor |
| 0.845 | 0.003 | L-glucuronate reductase inhibitor |
| 0.846 | 0.010 | Antineurotic |
| 0.840 | 0.005 | Arginine 2-monooxygenase inhibitor |
| 0.826 | 0.004 | Centromere associated protein inhibitor |
| 0.821 | 0.004 | Fatty-acyl-CoA synthase inhibitor |
| 0.823 | 0.013 | Mucomembranous protector |
| 0.812 | 0.009 | Nicotinic alpha6beta3beta4alpha5 receptor antagonist |
| 0.808 | 0.015 | Sugar-phosphatase inhibitor |
| 0.814 | 0.022 | Testosterone 17beta-dehydrogenase (NADP+) inhibitor |
| 0.782 | 0.007 | Bisphosphoglycerate phosphatase inhibitor |
| 0.776 | 0.005 | Phosphatidylserine decarboxylase inhibitor |
| 0.802 | 0.033 | Phobic disorders treatment |

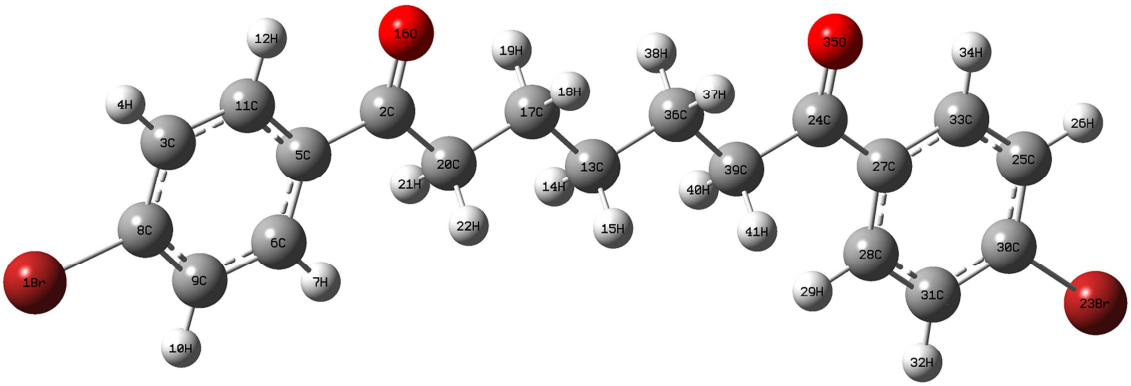
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Table 4

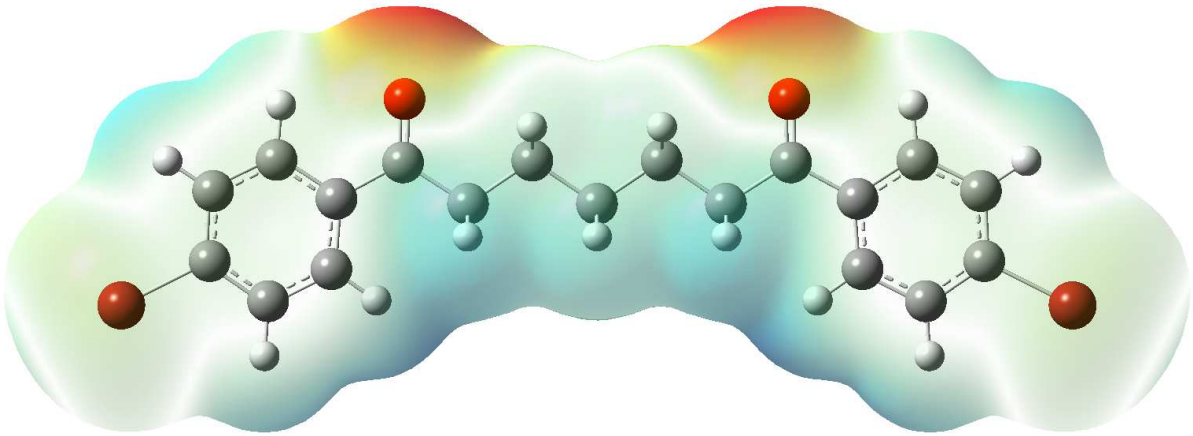
The binding affinity values of different poses of the 1,7-bis(4-bromophenyl)heptane-1,7-dionepredicted by Autodock Vina.

| Mode | Affinity (kcal/mol) | Distance from best mode (Å) | |
|---|---|---|---|
| - | - | RMSD l.b. | RMSD u.b. |
| 1 | -5.7 | 0.000 | 0.000 |
| 2 | -5.5 | 18.856 | 19.653 |
| 3 | -5.5 | 1.347 | 4.716 |
| 4 | -5.5 | 2.621 | 4.743 |
| 5 | -5.5 | 11.763 | 13.521 |
| 6 | -5.4 | 2.282 | 4.146 |
| 7 | -5.4 | 2.929 | 6.059 |
| 8 | -5.3 | 3.144 | 6.394 |
| 9 | -5.3 | 3.368 | 5.280 |

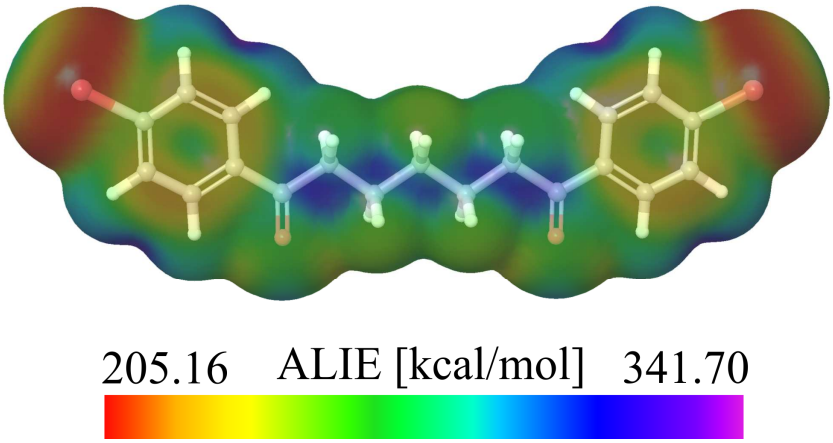
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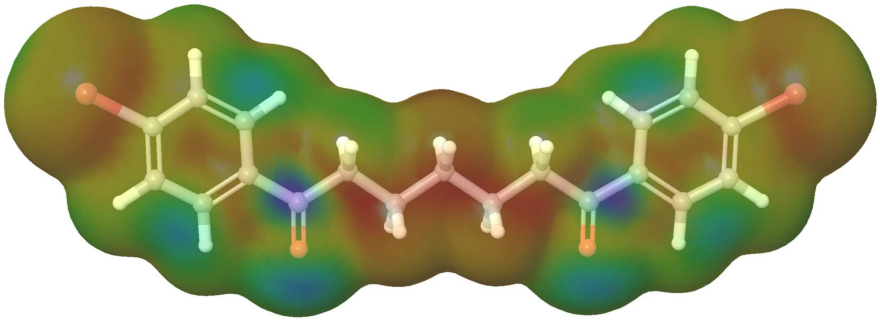


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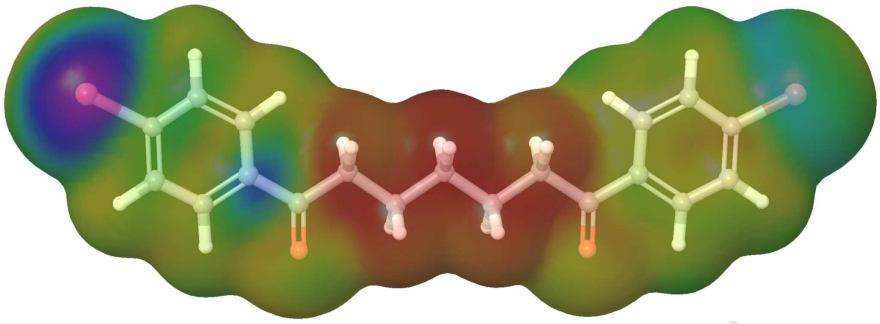



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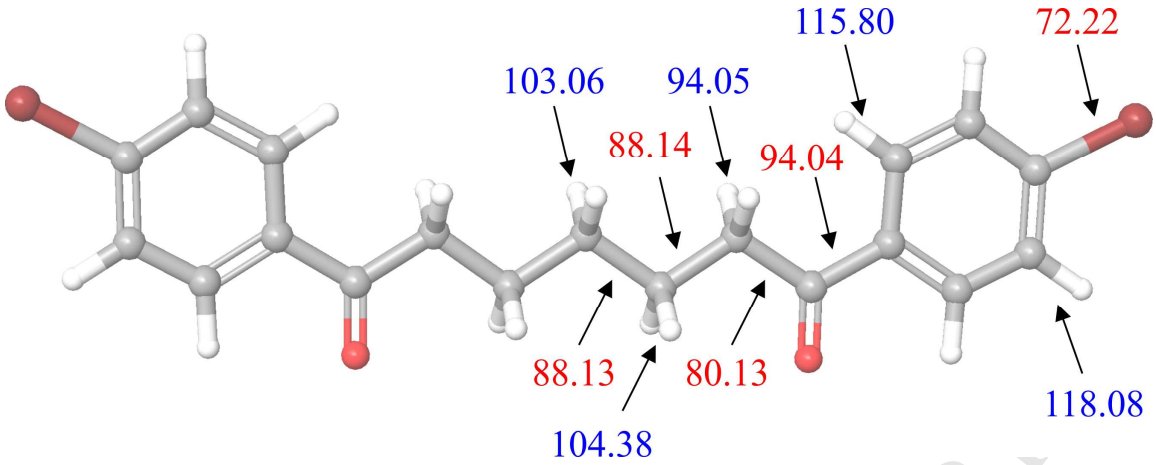
a)



b)

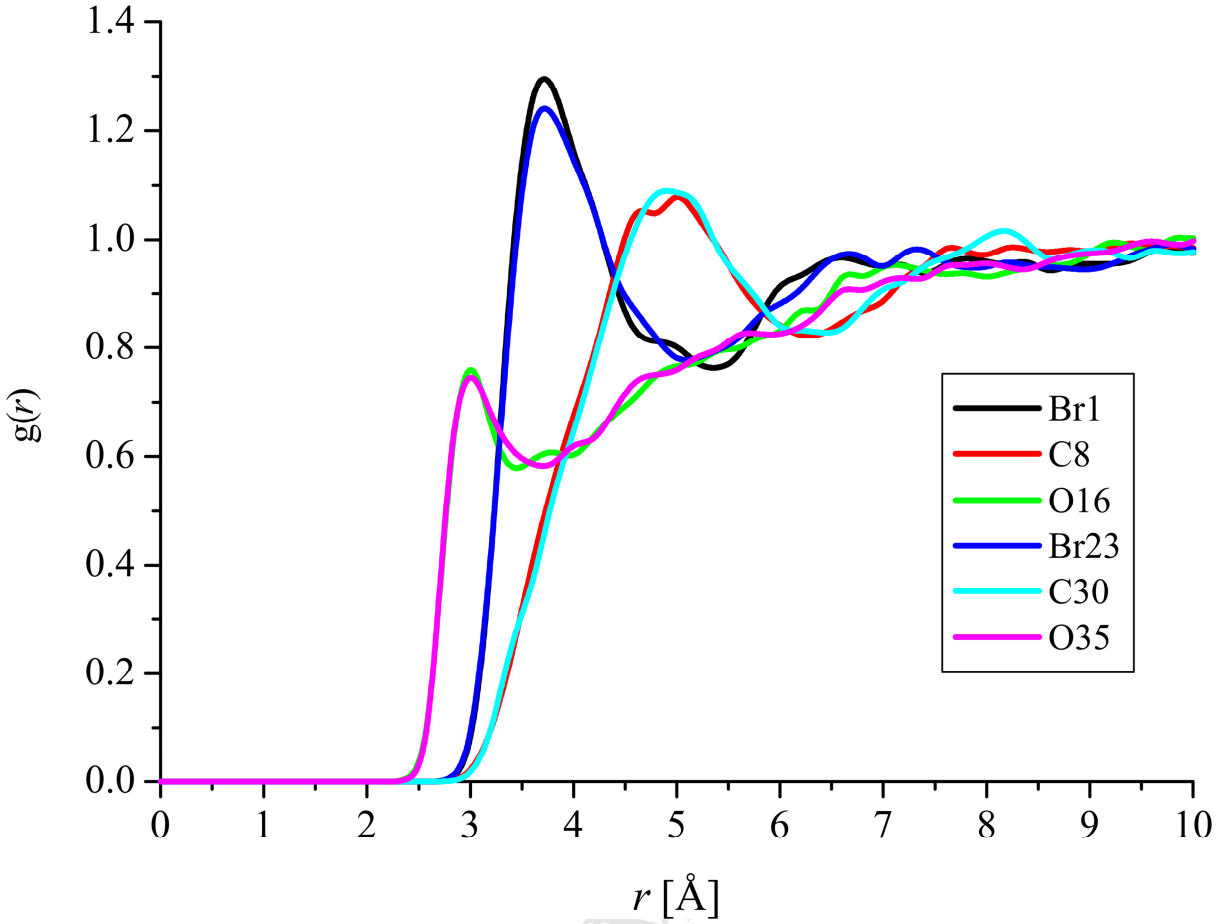


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- Single crystal XRD is reported
- Most reactive sites are identified
- Studied NLO properties, MEP and NBO
- Molecular docking studies have been discussed

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# ROLE OF MICROBES IN BIOLOGICAL DILAPIDATION OF PLASTICS

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## ABSTRACT

Plastics are economical, light, sturdy, corrosion resistant materials. Synthetic polymers are being utilized extensively in both food and commercial industries.The most commonly used non-degradable solid waste is polythene which is a linear hydrocarbon polymers consisting of long chains of the ethylene monomers. At present the Polythene is playing an important role in packaging of goods, food, medicine and garbage. The extensive use of these plastics leading to their accumulation in nature has several undesirable effects on the environment and human wellbeing. Burning of this plastic waste and burying of the plastics releases harmful toxic material which is a major pollutant in environment. At room temperatures,most of the plastic polymers are found to be non-toxic. When they are heated, they release toxic materials into food stuffs and thus they cause serious disorders in human and his domestic animals. Several microbes have a potentiality to decay the plastic waste to a larger extent. Present study deals with the types of plastics and their applications and decaying efficiency of microbes. Biodegradable plastics are environment friendly; they have an expanding range of potential applications in various fields of human endeavor.

**Key words**: Biodegradation; Biodegradable Plastics; Microorganisms; Hydrocarbons; Pollution

## INTRODUCTION:

Roughly 250 million tones of synthetic polymersare produced worldwide each year. These polymers areextremely stable, and do not readily enter into the degradationcycles of the biosphere. Environmental pollution bysynthetic polymers, such as waste plastics and water-solublesynthetic polymers in wastewater has been recognizedas a biggest environmental threat. In order to support unrelenting sustainabledevelopment throughout the world, this problemmust be addressed.

This accumulation of plastic waste has been produced serious hazard to biological sustainability. The environmental concerns include air, water and soil pollution. The dispersal of urban and industrial wastes contaminates the soil. The soil contaminations are mainly made by human activities. Environmental pollution is caused by synthetic polymers, such as wastes of plastic and water-soluble synthetic polymers in wastewater.Many animals die of waste plastics either by being caught in the waste plastic traps or by swallowing the waste plastic debris to exert ruinous effects on the ecosystem. Some of the plastic products cause human health problems because they mimic human hormone. Vinyl chloride is classified by the International Agency for the Research on Cancer (IARC) as carcinogenic to humans. It has also shown to be a mammary carcinogen in animals. PVC is used in numerous consumer products, including adhesives, detergents, lubricating oils, solvents, automotive plastics, plastic clothing, personal care products (such as soap, shampoo, deodorants, fragrances, hair spray, nail polish) as well as toys and building materials. Styrene is classified by IARC as possibly carcinogenic to humans and is shown to cause mammary gland tumors in animal



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studies. It also acts as an endocrine disrupter. BPA has been linked with premature birth, intrauterine growth retardation, preeclampsia and still birth. It has also been noted that prolonged exposure to BPA shows a significant effect on the sex hormones (progesterone) in females. Burning plastics usually produce some noxious gases like furans and dioxins which are dangerous greenhouse gases and play an important role in ozone layer depletion. In fact, dioxins cause serious problems in the human endocrine hormone activity, thus becoming a major concern for the human health. Dioxins also cause very serious soil pollution, causing a great concern for scientific community worldwide. Phthalates and Bisphenol A are closely related in thyroid causing dysfunction in humans.

Polyethylene terephthalate (PET) is used in making Drink bottles, peanut butter jars, plastic films, microwavable packaging etc. Polylactic acid (PLA) is a biodegradable thermoplastic that can be converted into a variety of aliphatic polyesters derived from lactic acid. Polyetherimide (PEI) A high-temperature, chemically stable polymer. Phenolics (PF) or (phenol) is a high-modulus, relatively heat-resistant and excellent fire resistant polymer used for insulating parts in electrical fixtures, paper laminated product and thermally insulation foams.

In view of this, the biodegradation of plastics has been studied extensively for the past three decades. Some types of plastic have been shown to be biodegradable, and their degradation mechanisms have progressively become clearer. This paper reviews the recent advances in this area.

**Microbes with biodegradable nature:**

Bacteria like Bacillus megatserium, Pseudomonas sp., Azotobacter sp., Ralstonia eutropha, Halomonas sp, Bacillus brevis, Acidovorax delafieldii, Paenibacillus amyloticus, Bacillus pumilus, Bordetella petrii, Pseudomonas aeruginosa, Shewanella sp. are some examples of bioplastic degrading bacteria. In past years polyethylene degrading bacteria has been reported such as, Acinetobacter baumannii, Arthrobacter spp, Viscosus spp, Pseudomonas spp, Arthrobacter viscosus, Bacillus amyloliquefaciens, B. thuringiensis, B. mycoides, B. cereus, Staphylococcus, Pseudomonas stutzeri, Xylosus spp, Pseudomonas fluorescens, Rahnella aquatills, Micrococcus luteus, Lylae, Paenibacillus macerans, Flavobacterium spp, Delftia acidovorans, Ralstonia spp Rhodococcus erythropolis, Pseudomonas aeruginosa and Bacillus brevies etcThe microbial species are associated with the degrading materials were identified as bacterial genus like (Pseudomonas, Streptococcus, Staphylococcus, Micrococcus, Moraxella) .

The growth of many fungi can also cause small-scale swelling and bursting, as the fungi penetrate the polymer solids. In recent years fungal strains have been reported for p;astic degradation such as Aspergillus versicolar, Aspergillus flavus, Chaetomium spp Mucor circinellodies species etc. The polythene bags were degraded by some fungal species identified such as, Aspergillus niger, A. ornatus,nidulans, A. cremeus, A. flavus, A. candidus and A. glaucus were the predominant species. The microbial species are associated with the degrading materials were identified fungi (Aspergillus niger, Aspergillus glaucus), . Sanchez et al., has reported that the PCL-degrading fungi, Aspergillus sp is effective in biodegradation as plastics studies.

Many studies on fungal degradation of the bioplastic have also been performed including Paecilomyces lilacinus, Fusarium moniliforme, Aspergillus flavus, Thermoascus aurantiacus, Tritirachium album, Paecilomyces verrucosum and Aspergillus. On the other hand, polylactic acid (PLA) is subjected to degradation by only two genera of fungi



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(Penicillium roqueforti and Tritirachium album) reported that Aspergillus niger van Tieghem had the ability to degrade PVC. PHB and polyesters are degraded by many fungal genera such as Acremonium, Cladosporium, Debaryomyces, Emericellopsis, Eupenicillium, Fusarium, Mucor, Paecilomyces, Penicillium, Pullularia, Rhodosporidium, and Verticillium. Similarly, PCL is degraded by Aspergillus, Aureobasidium, Chaetomium, Cryptococcus, Fusarium, Rhizopus, Penicillium, and Thermoascus. PEA is degraded by Aspergillus, Aureobasidium, Penicillium, Pullularia. Fungus like Alternaria solani, Spicaria sp., Aspergillus terreus, Aspergillus fumigates, Aspergillus flavus were isolated from soil where plastic have been dumped. These caused significant weight loss in the PS PUR blocks in the shaken cultures, reaching up to 100% in case of the isolate Fusarium solani .

Several actinomycetes including Amycolatopsis sp, Amycolatopsis sp, Saccharothrix, Kibdelosporangium aridum, Actinomadura keratinilytica T16-1, Amycolatopsis thailandensis, Streptomyces bangladeshensis, and Streptomyces thermoviolaceus subsp were reported as bioplastic degraders. Cryptococcus sp, and Pseudozyma Antarctica were reported to be bioplastic-degradings yeasts.

## MATERIALS AND METHODS:

### Sample collection:

Soil samples were collected from different areas were brought to the laboratory,preserved under laboratory conditions for further use.Polythene samples of different densities such as 10 micronand 40 micron were purchased from local market.

### Isolation of bacteria:

### Serial dilution method:

1.0 gram of soil sample was transferred into a conical flaskhaving 99ml of sterile distilled water. The mixture wasshaken and serially diluted (Cappuccino and Sherman.,1996).

### Petriplate method:

Further the Isolation of microorganism were carried out byspreading the dilution and the polythene strips of 3×3cmwere cut and placed on the nutrient agar plates. After theincubation the growth of microorganism were seen on thepolythene strips.Screening of polythene degrading microorganismThis was carried out by zone of clearance method where the0.5 concentrations of PEG were used in minimal mediacontaining salts of ammonium and potassium and the zone ofclearance around the colonies were observed by stainingwith Coomassiee blue this indicate its capacity to utilizepolythene as C-source and degrade polythene (Sowmya etal., 2014)

### Characterization and identification of microorganism:

After screening the isolates were characterized by variousmorphological and biochemical test, according to Bergey'smanual of determinative bacteriology (Holt et al., 1994).

### Pre-treatment of polythene:

The polyethylene bags were cut into the small strips andtransferred to a fresh solution having 70 ml Tween 80, 10 mlbleach, and 983 ml distilled water and stirring for 30 to 60minutes (El-Shafei et al., 1998). Then the strips weretransferred onto a beaker with distilled water and stirred for1 hour. Further, they were aseptically placed in the ethanolsolution 70% v/v for 30



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min. Finally, the polyethylene stripswere transferred to a Petri dish and used to disinfect thepolyethylene.

**Degradation of Pre Treated Polythene:**

Initially weighed strips of 3×3-cm size of 10 and 40 micronpolythene were aseptically transferred to the conical flaskcontaining 50 ml of nutrient broth medium and inoculatedwith bacteria (0.5ml). Control was maintained with plasticdiscs in the microbe-free medium. Different flasks will bekept in a shaker for 10, 20, 30 and 40 days respectively.After the respective duration of shaking, the polythene stripswere collected, washed thoroughly using distilled water,shade-dried and then weighed for final weight andpercentage weight loss were calculated using below formula.(Usha, et al. 2011)

Weight loss % = Initial weight - Final weight/ Initial weightx 100

**RESULTS:**

Various bacteria and fungi were recovered from different areas.Areas selected were petrol pump, hospital and local area.Maximum Degradation percentage was observed during 20days intervals in case of Staphylococcus species which shows no degradation in 10 micron whereas 10% for40 micron polythene and in case of Bacillus species,degradation percentage for 10 micron polythene was13.3% and 5% for 40 micron respectively and minimumdegradation was shown by Bacillus species and Pseudomonas species.During 10 day's time interval maximum degradation for 10and 40 micron polythene was shown by Bacillus species.

**DISCUSSION:**

Microorganisms play a vital role in biological decompositionof materials, including synthetic polymers in naturalenvironments. In the depolymerization process two categoriesof enzymes are actively involved in biological degradationof polymers: extracellular and intracellular depolymerases(Gu et al., 2000). During degradation, exo-enzymes frommicroorganisms break down complex polymers yieldingsmaller molecules of short chains, e.g., oligomers, dimers, andmonomers, and are smaller that can pass the semipermeableouter membranes of the microbes, and thenutilized as carbon and energy sources (Frazer, 1994;Hamilton et al., 1995).In the current study, two types of polythenes were used forthe observing the degradation percentage and those werehigh density and low density polythene of 40 micron and 10micron respectively. The degradation percentage increaseswith increase in size of the polythene that is the minimumdegradation is seen in the case of 10 micron polythenefollowed by maximum degradation by 70 micron polythenealong with moderate degradation by 40 micron polythene.As per the study concern the types of polythene used was 10and 40 micron, so in this case the maximum degradation wasshown by 40 micron polythene where as 10 micron showedthe minimum degradation.

**CONCLUSION:**

Several recent surveys have been described the harmful effect of plastic waste on the terrestrial and aquatic ecosystems, and thus, it has became one of themost important environmental threat. To the get rid of such a menace, people usually put them in landfills or burn it, but both these practices cause very serious problems to the environment and the ecosystem. Some plastics are designed to be biodegradable and can be broken down in a controlled environment such as landfill. Biodegradation of waste plastic is an innovative are of research solving many environmental problems. This review discusses on the literature of



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microbes used for biodegradation of plastic waste. Most of the plastic wastes are degrade by the microorganisms. Based on these literatures available one could conclude that in order to enhance biodegradation of plastics waste the following approaches could be adopted as the biodegradation studies of plastics in dumped soil.This knowledge is useful for the moleculardesign of biodegradable polymers and for the molecularevolution and breeding of degradation enzymes andmicrobes. Our increased understanding will contributetowards the development of biotechnology for polymerwaste treatment.Many different strains of bacteria mostly Bacillus sp. and fungi are involved in the degradation of plastic and its hydrocarbons. The degradative action of microbes on the polymeric material and their breakdown to the non living substrate plays a promising role in eco-friendly management of toxic wastes and chemical pollution in future.

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# USE PATTERN OF E-SODHSINDHU CONSORTIUM AMONG RESEARCH SCHOLARS AND STUDENTS OF SRI VENKATESWARA UNIVERSITY,TIRUPATI : A STUDY

(About Use of General E-Learning Resources)

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**Abstract:** This paper explains about terms and definitions of Digital libraries, e resources in E-sodh sindhu followed by aims and objectives of E- Resources , Internet, Internet Users. . It also explains how remarkable change had occurred with advent of E- sodh sindhu with reference to both print and online e-Journals. It also explains about subscription, usage and ease of publishing the Journal in terms of Money and Time.

**Kewords :** INFLIBNET, Consortia, E-SodhSindhu, Repository, Networking, Digital Library, Higher Education, Digital Library Consortium, NLIST, INDEST –AICET Consortium, Digital India., Internet.

## 1.0 Introduction:

Role of librarians as custodian, book keeper, changed according to information scientist, knowledge manager, information officer with the advent of technological changes with refers to e- resources like e-books-Journals, databases, repositories. E-Shodh Sindhu: UGC -Infonet Digital Library Consortium recently changed to E –Shodh Sindhu consortium for Higher Education E -resources in order to provide quality e –resources to support learning and research activities covering full text, bibliographical and factual databases. This has emerged as a super gateway for university academic community in India providing access to expensive scholarly resources since 2004 at free of cost. The consortium initiated providing access to current and archival 15,000 e- journals and databases extending the benefit to 139 – State universities, 40 central universities, 22 – deemed universities, 15 law universities, 6 of IUCs of UGC, 72 – AICIT E funded colleges, 4000colleges and IITs, IIMs, IISc etc. Available in the E -Shodh Sindhu Collection 135000 E – Books, 40 Resources, 16 databases and15000+ Electronic resources.

## 2.0 Developmen of Digital Libraries

A Digital library is a special Library with a focused collection of digital objects that can including text, visuals, me trails, audio material, video tapes, storage as electronic media formats organizing, storing and retrieval of information in the library collection. The digital library content can be access remotely via computer networks, the academic institutions using digital libraries for institutional repositories and electronic resources for scholarly communication. Digital Libraries are searchable repositories of scientific material and their efficiency depends on progress achieved in information systems, the bibliometric approach to digital libraries are predicts that information system that does not rely on the core properties of the language will not be optimal.

## 3.0 Objectives of study :

A) To evaluate level of understanding regarding e-Sodh Sindhu among student, teaching, and research peer groups.
B) To understand purpose of usage on e-Sodh Sindhu

**Table 6 : Why that Particular Browser ?**

| Speed | Comfortable | Availability | Useful adapt one | Smart extension |
|---|---|---|---|---|
| 09 | 20 | 20 | 05 | 05 |

**Table 7 : If Downloading, What Type of Storage Media You Are Using to Download the Data / Information ?**

| External disk | Hard disks | Cloud | Removal Pen drive | Other |
|---|---|---|---|---|
| 09 | 10 | - | 40 | - |

**Table 8 : Does Your Library Have Sufficient Number Of Internet Connected Systems ?**

| Yes | No |
|---|---|
| 50 | 09 |

**Table 9 : You Are Familiar With What Type Of Operating System ?**

| Windows | Linux | Macintosh | Solaris | Unix | Other |
|---|---|---|---|---|---|
| 40 | 05 | 05 | 05 | 14 | |

**Table 10 : Do The Library Staff Have Enough Expertise To Assist You In E-Sodh Sindhu In Terms of Its Usage?**

| Least usage | Average use | Good use | High usage |
|---|---|---|---|
| 1 | 2 | 3 | 4 |
| 04 | 10 | 30 | 15 |

**Table 11 : What are the Difficulties Faced by You in Accessing E-Sodh Sindhu ? How do You Solve Problem at Your Library**

| Library Staff | Colleagues | Self |
|---|---|---|
| 25 | 25 | 09 |

**Table 12 : How Frequently You Use E-Sodhu Sindhu / Electronic Journals for Your Research Work ?**

| Never | Occasional | Often | Very often |
|---|---|---|---|
| 1 | 2 | 3 | 4 |
| - | 09 | 25 | 25 |

**Table 13 : Whom Do You Convey the Insufficiency of Journal Database at Your Library if Any ?**

| Librarian | Publisher /Aggregator | HOD | E-Sodhu Sindhu |
|---|---|---|---|
| 10 | 05 | 05 | 39 |

**Table 14 : Awareness on E-Sodh Sindhu ?**

| Librarian/Friends/Staff | Internet Websites | Lecturers/Seminars/Orientation programme | University/Library Websites | Books/Journals | Faculty |
|---|---|---|---|---|---|
| 15 | 10 | 20 | 05 | 05 | 04 |

**Table 15 : Purpose of Seeking E-Sodhu Sindhu ?**

| Writing Papers | Seminars | Research/ Teaching | To abreast knowledge with latest developments | Under taken projects | Any other |
|---|---|---|---|---|---|
| 20 | 20 | 05 | 05 | 09 | - |

C) To detect problems, challenges in using e-Sodh Sindhu
D) To evaluate satisfactory level of users

## 4.0 Review of Literature :

Arora, Jagdish (2003) found the efforts made by Indian libraries and institutions towards the formation of consortia of libraries for buying access to electronic resources. Cooperation amongst institutions for sharing their library resources has been practiced for decades. Consortia- based subscriptions" to journals everywhere in the world. Shared subscriptions to electronic resources through consortia of libraries is a feasible strategy to meet the pressures such as diminishing budgets, increased user demands, and rising costs of journals. The libraries and information Centers, with their d diminishing (or at best static) financial allocations, have to consider new ways to consolidate global resources in order to maximize their limited financial resources. Yi and others (2004) discussed the advantages of consortium acquisition and the s et up of local mirror sites as well as efficiency of the consortium acquisition for electronic resources based on the review and discussion it further makes detailed analysis on the necessity of the consortium acquisition and role of consortium acquisition on the library electronic resources development.Ali, Naushad (2005) examines the use of electronic information services among the users of IIT Library, Delhi. The study found that Boolean logic and truncation are the most often used search facilities by IIT users, lack of trained staff infrastructural facilities such as printers, terminals would discourage users from accessing e- resources and majority users facing difficulty while browsing. Dillion, LF, and Hahn, K (2002) In spring of 2001, a large -scale online survey was administered to the whole faculty and sample of graduate students at the university of Maryland. Email messages were sent to all the participants i.e. 3500 inviting them to fill out online survey. The response rate was 39 for the faculty member s. About half of the faculty

## 5.0 Methodology :

Survey method is employed to collect data from the user community on usage of E-Sodh sindhu by using structured questionnaire which is distributed to Teachers , students, and Research scholars of both Sri Venkateswara University and Sri Padmavathi University. Total of 100 questionnaire were distributed and 60 respondents we received. The questionnaire was distributed personally by visiting departments, hostels, library. The collected data 60 filled questionnaire were analyzed. The analyzed data were presented in the form of tables and graphs. A simple statistical technique percentage method is used to analyze the questionnaire.

## 6.0 Data Analysis and Interpretations:

**Table 1: Gender Wise Distribution of Respondents**

| | Male | Female | Total |
|---|---|---|---|
| Frequency | 34 | 25 | 59 |
| Percentage | 57 | 42 | 59 |

The table 1 showing gender wise respondents Male 57 percentage Female 42 percentage from total respondents 59 and majority of respondents are from male.

**Table 2 : Familiar with Internet Access**

| | Internet Access |
|---|---|
| Frequency | 59 |
| Percentage | 100 |

**Table 3 : Frequency of Internet Use**

| | Daily | Weekly |
|---|---|---|
| Frequency | 59 | - |
| Percentage | 100 | - |

**Table 4 : Internet Use Per Day in Hours**

| | 0.30 to 1 | 2 to 3 | More than 3 |
|---|---|---|---|
| Frequency | 22 | 20 | 17 |
| Percentage | 37 | 33 | 28 |

**Table 5 : Which Browser Do You Prefer For Internet Access ?**

| Internet Explorer | Google Chrome | Mozilla | Other |
|---|---|---|---|
| 08 | 43 | 08 | |

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**Table 16 : Problems in Accessing E-Sodh Sindhu ?**

| | |
|---|---|
| Lack of speed of Internet | 20 |
| Lack of electricity | 05 |
| Lack of cooperation from library staff | 05 |
| Lack of Infrastructure Facilities | 15 |
| Lack of sufficient information | 05 |
| Difficulty in finding relevant Information | 04 |
| Unfamiliar with searching strategy | 05 |

**Table 17 : Impact of E-Sodhu Sindhu on your Learning /Research work ?**

| | |
|---|---|
| Improved Research Quality | 25 |
| Developed Technical Skills | 10 |
| Improved Searching Skills | 10 |
| Improved In academics | 09 |
| Improved Knowledge | 05 |

## 7.0 Findings:

- More than half of respondents satisfied with the E-Sodhu Sindhu for their Academics
- Half of respondents not satisfy with the Internet speed In the library to freely access E-Sodhu Sindhu.
- Half of respondents satisfy with the E- Sodhu Sindhu as it useful in paper writing/ seminars.
- All most all respondents satisfy E-Sodhu Sindhu as it is useful in their research.

## 8.0 Suggestions :

- Conducting orientation programme on E-Sodhu Sindhu
- Conducting Workshops
- Conducting Seminars
- Conducting awareness programmes
- Conducting Training Programmes

## 9.0 References:

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# A Novel approach for Privacy Protection in Web Collaboration for Software Engineering using Component based Multi Attribute Restriction Model

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## Abstract

In a collaborative environment, not all the user has access to the entire resource present in the system. Each user has their own access to certain resources which is restricted according to their nature of job and their responsibilities. The user profile is one which represents the list of users and their access permissions. To restrict the users from accessing illegal resources is not permitted for them. By adapting the user profile based approach, the users can be restricted from accessing the illegal resource or component. The web based collaborative development has many issues and restricting multiple users in various aspects is still a challenging issue. To solve the problems in collaborative software development the novel approaches namely "Component Based Multi Attribute Restriction Model" has been proposed. The method maintains the software objects as components and maintains several user profiles. For each user, a list of components with attributes has been maintained. Based on the profile with requesting attributes, the model validates the user access. Based on identified attributes claimed and attributes given access, the method estimates the Component Access Measure (CAM). The estimated CAM value has been used to validate the client access in the collaborative environment. The method produces efficient results on web based collaborative model and improves the software development performance.

**Keyword:** Collaborative environment, Software development, Component Based Multi Attribute Restriction Model, User profiles.

## 1. Introduction

The collaborative environment is one which contains large number of users as the actors and each actor can perform different actions in the same resource which is shared between the users of the environment. In particular, the development work of the software development process can be performed by two different units of employees, so that an update or modification performed on any part of the development process should reflect on the original resource. This helps the organization to coordinate any process with the employees of its own but located in different part of the country or the world. In modern development system, each part of the system is considered as a component. The software is the collection of statements which can be executed by the computing device. Such statements have various parts and each part has its own dedicated job to perform. Such tiny tasks can be poured into a container which performs a single job as dedicated. In this way, there are number of components that are present in the software development system. The component has its own job to

be performed and it accesses various properties or methods of the system. Internally the component can invoke number of operations or components and each of them would access various properties of the system. In a collaborative environment, each user has their own access to certain resources which is restricted according to their job and responsibilities. The profile of the user is the one which represents the list of customers and their granted permissions. To avoid the users from access to illegal resources which are not permitted for them, the user profile based approach can be used. For example, if a programmer exists, then he/she can access certain components which perform certain computations but they cannot access certain components which performs modification of another component designs or system design which is allowed only for the designer of the system. By adapting the user profile based approach, the users can be restricted from accessing the illegal resource or component. The capacity to make effective, the collaborative environments is more crucial for network systems. The resources and abilities of a set of individuals permit the complicated issues and project to be finished. The present state of software system and network technology permits the cooperative method to increase further than the traditional environment. Collaborative Environments (CEs) square measure platforms and distributed software system which allows each and every individual and the cluster shared among them to perform in several parts, together with analysis, business and learning. Inside the CE, entity is categorized into different classes and different projects to complete the given tasks. Collaborative background suffers from a major issue which has to be self-addressed by providing security, privacy and management for entities those who use the background. Enabling certain secrecy in CEs needs the utilization of privacy strategy which permits individuals to stipulate however they need their confidential data to be utilized by others members. Some additional approaches are needed for the privacy strategy to be processed throughout the method. Since, it is a dynamic environment, when a single collaborator will amendment a specific role, action or with whom collaborating is taken place throughout runtime. Any protection system for CEs should be ready to decide and conclude when the scenario changes and what data to be shared between them.

## 2. Literature Review

There are number of approaches which has been proposed earlier for the restriction of users in the collaborative environment. This section discuss about various methods relate to the problem of access restriction in collaborative environment.

In recent years, large number of organizations have begun to collaborate in order to glean new insights and reach new markets so that they can gain competitive advantages which help them to generate revenue, or reduce operational and also the cost used for development. Computers and communication networks have created unprecedented opportunities to develop new integrated and sophisticated environments that make it possible for information sharing and resource exchange across boundaries of organizations. Proliferation of the Internet and web-based technologies such as Grid and Cloud computing also enables the development of large scale distributed applications and systems. Collaboration has become a daily routine. On the other hand, many environments used for collaboration can be victims of both malicious attacks and inadvertent damage. The number of reported cyber-attacks increased six fold in three years according to[1]. There are more than one lakh known viruses and worms. Every week, there are on average 200 new ones reported [2]. Not only their numbers are on the rise, but these attacks are also becoming increasingly sophisticated and severe. The number of large-scale attacks has also grown exponentially. Finally, these environments are vulnerable to insider attacks.

Allyson (2015) has shown that one of the major threats for distributed environments is unauthorized accesses by insiders. The problem of security is prominent in collaborative environments that span over multiple organizations [3]. It is estimated that the cost of PC viruses in businesses is approximately $50 billion in damages in the year 2003. 20,000 phishing complaints were reported in May 2006, when compared to the previous year 34% increase taken place, according to the US Department of Justice report. In the year of 2009

alone, hackers attacked 75% of enterprises worldwide [4]. Even FBI partners were attacked. According to Fox News, in 2010 a data breach cost organizations an average of $8.2 million, up 7% from the year before. The total costs of breach have grown every year since 2006. The average cost of one compromised record in 2010 is $214, a 5% increase from 2009. There is also a reported 39% increase of cyber-attacks on federal government in 2010[5]. The pervasion of these intrusions and attacks brings up a great deal of concerns on security and privacy when designing and using these environments. Cooperating parties must strive to maintain a balance between sharing resources while keeping safety and privacy.

Collaborative business environment based enforcing the contexts sensitive policies contain the elements which are tied to changing the contractual relationships for enforcing the access control policies to obtain from the external sources [6]. Collaborative virtual environment based path restricted parallel Q-learning algorithm[7] proposed a path restriction by Q-learning algorithm is to improve the effect of collaborative navigation control by constructing the exact distance between virtual environment based mobile agent and its destination of reinforcement learning into a status function.

Context Aware Method is used for controlling strategies, enabling the client to make use of the context of data. An upgrade of RBAC model was proposed by [8] with the apprehension of environment condition with the goal of providing security mindful applications [9]. Assets are likewise bound with situation data under which execution takes place [10]. A CBAC model may likewise hold distinctive shifting ranges for allowing asset utilization [11].

The proximity-based approaches are about restricting the users of collaborative environment according to the proximity value computed for any user. Ardagna et. al., (2006) is an improvement of the most well-known Location-based Access Control (LBAC), which itself is a unique instance of CBAC, where the condition is area [12]. In PBAC, access direction depends on the reach ability of the end client to particular resources for deciding access controls. Hasan (2013) discussed setting mindful security arrangement implementations in which he conveyed context mindfulness into security systems to let the approval of security procedure capably adjusted by the movements of setting information in this way giving dynamical, advanced and steady security setting[13].In Rodriguez et.al.,(2004) a critical representation is exhibited where healthcare workers are currently concentrated; they are continually hinting at change zone during their consistent work, which fuses passing by patients, discovering assets, for instance, restorative records or counseling with different authorities[14]. Kolter, pernul and kernchen [15] describes the solutions to provide the privacy protection for utilizing the two main elements and also explores the idea of collaborative privacy management for users in World Wide Web. The first parts have been tasked with giving experiences, feedback and rating is known as privacy community about the private policies of web service providers. This privacy community acts as the privacy architecture of central element [15].

## 3. Research Methodology

### 3.1 Component Based Multi Attribute Restriction Model:

The component based multi attribute restriction model as shown in Figure receives the user request and identifies the list of components and their attributes required to process the request. Then the method performs the behavior analysis of the user on accessing the various components. Based on the result of behavior analysis, the method performs multi attribute access restriction. The method has number of stages and each will be discussed in detail in this section.

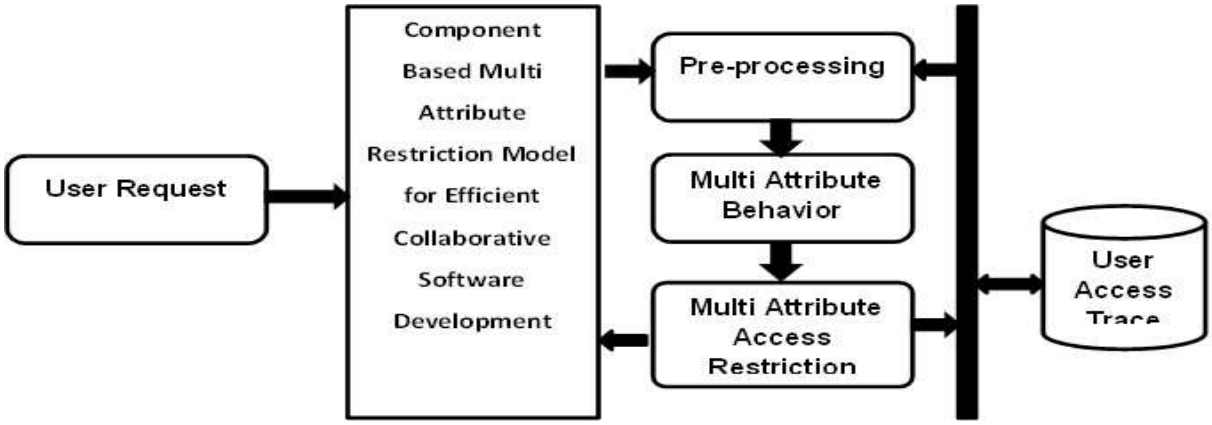



Figure.1 Architecture of Component based Multi- Attribute Restriction model

### 3.1.1 Pre-processing

The method maintains a large set of logs about the access performed by various users. Whenever a user access as the resource from the collaborative environment and a request is being processed at that time, the method monitors the list of properties or attributes that have been modified or accessed. Such information has been stored in the form of traces and at the preprocessing stage, with a request to access and collect, the method identifies the number of attributes the traces produced while accessing the same attributes. From the traces the method removes the incomplete one and using the rest the method splits each attribute access and their status.

**Algorithm**

Input: Access Trace At, User Request Ur

Output: Pre-processed Trace Pt

Step1: Start

Step2: Read user request Ur

Step 3: read access trace At.

Step 4: identify list of traces of user previous request Ur.

$$\text{Trace set Pt} = \sum_{i=1}^{size(At)} At(i).request == Ur$$

Step 5: for each trace Ti

If Ts(i) !t∈ $\sum Attributes(Ts)$ then

Remove the trace as incomplete.

Else

Leave the trace.

End

End

Step6: Stop.

### 3.1.2 Behaviors on collaborative environment

The users of the collaborative environment could perform various activities like read, write and delete. However not the entire user can perform such activities. They can be restricted in different levels according to various parameters. In this section we brief the list of actions the user can perform.

#### 3.1.2.1 Access Completeness

The user of the environment can access the resource according to his access control provided. Each user of the environment does not have access to all the resources. Each resource has different access permission towards different resources. However it cannot be sure that the legitimate user accesses the resource in genuine manner. For example, the user claims to read or modify the data present in the collaborative environment. In this behavior, the user completes the service access and finishes the service in success stage. This helps the service provider to maintain the public auditing. The user in the collaborative environment would perform any action on the service access and the service would navigate through number of actions and the user completes all the actions of the service access. This makes the service access as the complete one.
The Table 1 shows the details of service access with complete state and each access of the service has finished with complete states.

Table 1 Details of trace with complete state

| Service | State I | State II | State III | State IV | State V |
|---|---|---|---|---|---|
| S001 | C | C | C | C | C |
| S002 | C | C | C | C | C |
| S003 | C | C | C | C | C |

#### 3.1.2.2 Hanging Access

The hanging access is the problem of incomplete one and the user leaves the access in the middle. The service would have number of states in the access and the user starts the access and leaves in the middle itself. The user completes set of middle states and does not complete the remaining states. This makes the service access as incomplete one and questions the public auditing to be provided. The environment does not identify the state, which state the user has completed and in which it must be closed. The user would have crossed set of states and does not complete the remaining states of the service access.

The Table 2 shows the details of service access with hanging state and the service access S002, has finished with INC mode, which specifies the hanging state.

Table 2 Details of trace with hanging state

| Service | State I | State II | State III | State IV | State V |
|---|---|---|---|---|---|
| S001 | C | C | C | C | C |
| S002 | C | C | INC | - | - |
| S003 | C | C | C | C | C |

### 3.1.2.3 Incomplete Access

Even though there are number of states present in the service access the user completes the few states, but he may initialize another state and does not complete that one. This introduces the incomplete state in the service access. Such state is identified to produce the incomplete state trace.

The Table 3 shows the details of service access with incomplete state and the service access S002, has finished with IC mode, which specifies the incomplete state.

Table 3 Details of trace with incomplete state

| Service | State I | State II | State III | State IV | State V |
|---|---|---|---|---|---|
| S001 | C | C | C | C | C |
| S002 | C | C | IC | - | - |
| S003 | C | C | C | C | C |

### 3.1.3 Multi Attribute Behavioral Analysis

The problem of access control in a collaborative environment has been studied in various situations. A detailed study has been made of many methods. Still the methods suffer from poor performance in access control affecting the performance of the collaborative systems. The multi attribute behavior analysis model uses different attributes to compute the trustworthy of the user. The method receives the request from the user and identifies the set of all attributes being accessed to complete the process. Based on identified attributes, the method collects the traces produced by accessing the attributes. Using the traces available, the method performs behavioral analysis to computes the trustworthiness of accessing the same attributes and also others. Based on the trustworthy value, the access of the request is decided by this method. This technique improves the performance of the collaborative environment and that of the throughput also.

The multi attribute behavior analysis model maintains traces of the access of various uses of the collaborative environment. The method monitors the behavior of users of the environment and generates patterns of access at each time window. The method computes the trust weight for the user on that basis on the request the use of restricts the user and control over malicious access. Using the result of pre-processing, the method computes the trust factor for each attribute on the basis of the previous trace. The method computes the trust factor on each attribute on the basis of the user's behavior represented by the access trace and based on the completeness of the access and how genuine the user has accessed the attributes in earlier days. Based on multi attribute trust factor the method computes trustworthy measure called CAM to decide the access control for the user.

**Algorithm**

Input: Pre-processed Trace Ts

Output: CAM

Step1: start

Step2: read preprocessed trace Ts

Step 3: identify list of all attributes of the access

Attribute set As = $\sum_{i=1}^{size(Ts)} Ts(i).Attribute! \in As$

Step 4: for each attribute Ai

Compute number of access Na = $\sum_{i=1}^{size(Ts)} Ts(i).Attribute == Ai$

Compute number of successful access Nsa = $\sum_{i=1}^{size(Ts)} Ts(i).Attribute == Ai \&\& Status == Success$

Compute trust factor Tf = $\frac{Nsa}{Na} \times size(Ts)$

End

Step 5 : compute cumulative access measure CAM = $\frac{\sum Tf}{Numberofattributes}$

Step 6: stop

The above discussed algorithm computes the trust factor for each attribute and based on them the cumulative access measure is computed.

### 3.1.4 Multi Attribute Access restriction

At this stage, the method first performs preprocessing using the input user request and the user access trace. Then the method performs the multi attribute behavior analysis using the preprocessed trace. Based on computed trust factor and the cumulative access measure the method performs access restriction.

**Algorithm**

Input: User Request Ur

Output: Boolean

Step1: start

Step2: read user request Ur.

Step 3: perform preprocessing

Step 4: cumulative access measure CAM = perform multi attribute behavior analysis

Step 5: if CAM >TTh //trust threshold

Allow access

Else

Deny the request.

End

Step 6: stop.

The above discussed algorithm computes the access trust measure and cumulative access measure from behavior analysis. Based on the trust measure the method performs the access restriction.

## 4. Results and Discussion

The proposed work was implemented in two stages, viz, multi attribute behavior analysis approach and component based multi access restriction approach. The comparison is carried out with existing algorithms. The proposed multi attribute behavior analysis approach has been executed and assessed for proficiency. The technique produces proficient outcomes in every one of the elements of the nature of the administration in synergistic condition. The strategy has been tried and assessed utilizing different reproduction parameters. The component based multi-level access restriction approach has been executed and assessed for productivity. The technique produces effective outcomes in every one of the variables of nature of administration in community oriented condition.

### 4.1 Comparison of CBAR with RBAC and MABA using Security Efficiency

An evaluation of security efficiency generated by various methods and it depicts clearly that the stated approach has obtained higher efficiency related to other approaches is shown in figure.2.

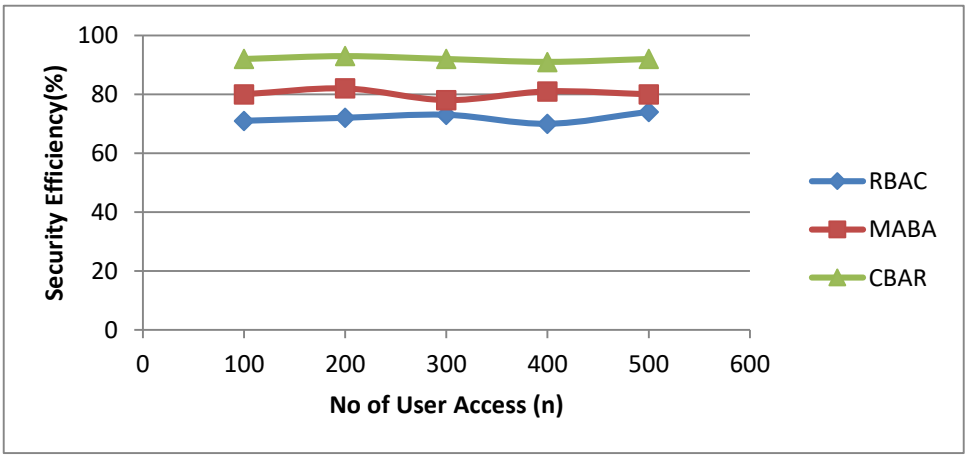



Figure.2 Comparison of security efficiency

### 4.2 Comparison of CBAR with MABA and RBAC using Fault classification Ratio

The evaluation results of false classification ratio generated by various methods and it depicts clearly that the stated approach has obtains a smaller false classification ratio related to other approaches is shown in figure.3.

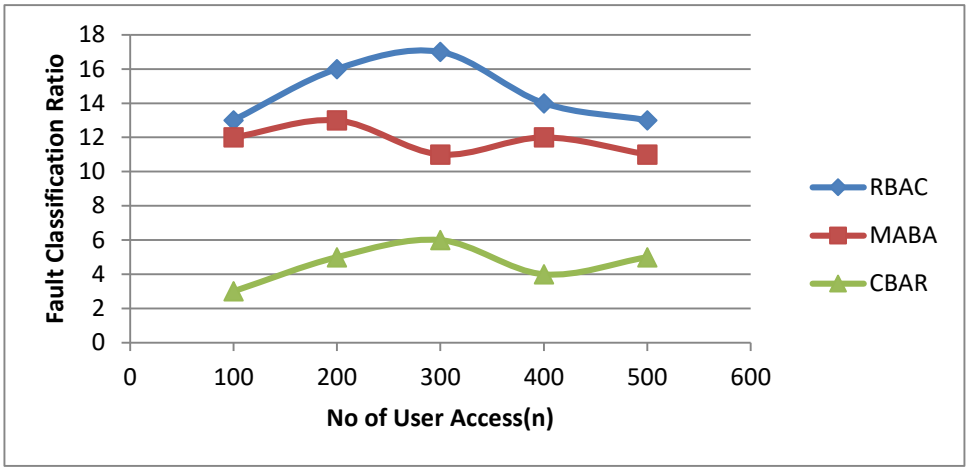



Figure 3 Comparison of false classification ratio

### 4.3 Comparison of CBAR with MABA and RBAC using Query Execution Time

The evaluation of time complexity generated by various methods and the stated approach has obtained less time compared to other approaches is shown in figure.4.

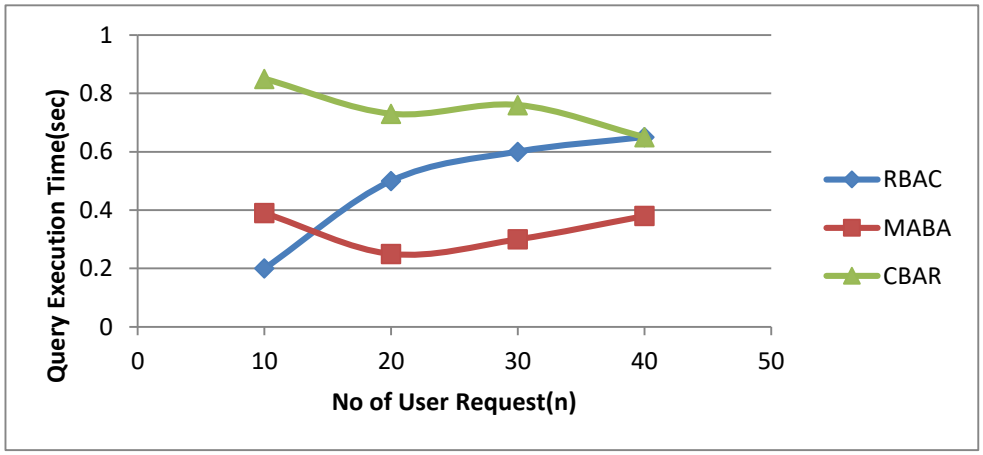



Figure.4 Comparison of Query Execution Time

### 4.4 Comparison of CBAR with MABA and RBAC using Client Hit Ratio

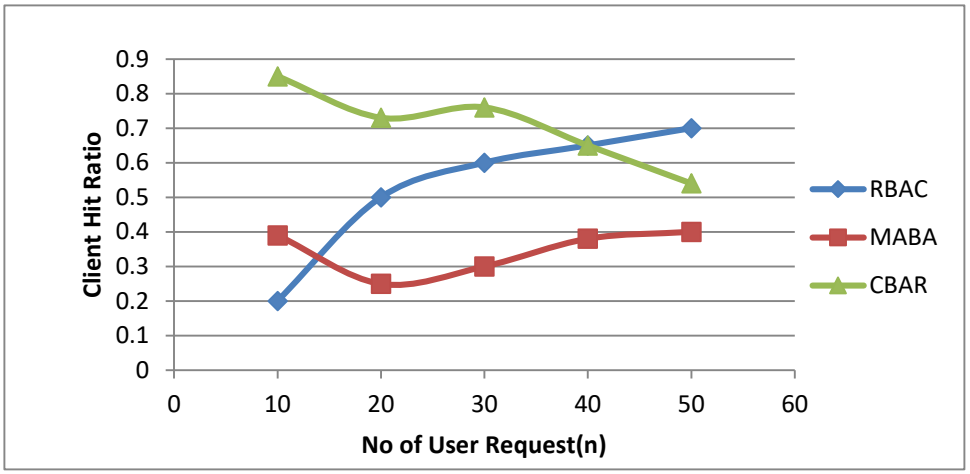



Figure 5 Comparison of Client Hit Ratio

The evaluation of hit ratio generated by various methods and the stated approach has obtained higher hit ratio compared to other approaches is shown in figure.5.

## 5. Conclusion

In this work, the researcher has proposed a novel Component based Multi- Attribute Restriction model for improvement of the security in a collaborative environment and the quality of service. The method preprocesses the previous traces to eliminate the noisy data traces. The method first receives the request from the user and identifies the component being claimed. Later the method detects the list of attributes being required. Then the method collects the traces being accessed on the attributes. Each trace has been validated for its completeness and noisy records have been removed from the trace. Then the method performs the multi attribute behavior analysis to compute the trust factor. On the basis of trust factor the method compute the cumulative access measure. The computed trust factor and the access measure have been used to restrict the user from accessing the component maliciously. The method has produces efficient results on access restriction and increases the throughput performance.

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ORIGINAL RESEARCH PAPER

Information Technology

# ACCESS RESTRICTION EFFICIENCY OF MULTI ATTRIBUTE BEHAVIOUR ANALYSIS BASED RESTRICTION IN COLLABORATIVE ENVIRONEMNT

**KEY WORDS:** Collaborative environment; Privacy Protection; Users; User restriction; multi Attribute Behaviour

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**ABSTRACT**

The collaborative environment (CE) is one which contains large number of users as actors and each actor can perform different actions in the same resource which is shared. All the users do not have access to the entire resource present in the collaborative system, to restrict data tampering, misuse and illicit use. It is a major problem to provide privacy protection and control for the individuals who use the environment. Ensuring privacy in CEs requires the use of privacy policies which allow individuals to outline how they wish their private information to be used by others. Number of approaches have been proposed earlier for the restriction of users in the collaborative environment. In this paper, we discuss the efficacy of Multi Attribute behavior Analysis Based Restriction as a privacy protection tool in collaborative environment.

## INTRODUCTION:

Collaborative environment has become the back bone for modern information technology sector which supports various activities of the IT sector to be performed in different locations without contradicting location dependency. In a software development system, a number of components are present, performing different tasks. Collaborative environment includes a number of users who have differential access to the resources being used for development of a particular software/program. To protect privacy and operate securely, users are often restricted by user profile based approach. Collaborative Environments (CEs) are distributed software applications and platforms that support both individual and group shared work in many areas, including research, business and learning (Q. Li, M. Abel, J. Barthčs, 2014). Privacy protection is a considerable problem in CEs, and any privacy protection system for CEs must be able to determine and infer how information should be shared as the situation changes.

## ATTEMPTS AT PRIVACY PROTECTION FOR CEs:

Management of personally identifaiable information (PII) and the challenges involved are studied well. An agent-based prototype is described to support automated enterprise management of PII (Korba et.al., 2007). Several data mining techniques are combined to achieve the life cycle of private data, including individual data discovery, social network analysis, knowledge visualization, and effective human-computer interaction. The developed prototype can automate the management of PII within an organization by collecting, analyzing and applying security policies on that PII. One drawback of this approach is that it has the potential to actively monitor and analyze all user activity and behaviours within a collaborative environment. This monitoring can cause concerns among the users of the prototype. The work by Korba et al., (2007) is concerned with the discovery of PII through data mining, the collection of the discovered PII and the management of the collected PII. This differs from the collaborative privacy architecture which does not collect and analyze personal information. As well, while the work by Korba et. al., (2007) discusses the use of privacy policies, it does not detail what these privacy policies should look like.

Kanovich, Rowe and Scedrov (2007) propose an abstract formal model of collaboration which addresses privacy concerns. A state transition system is used to model private data through the use of a syntactic convention on a predicate symbol. The goal of this model is to describe how to generate a collaborative plan by providing some privacy guarantees to the participants. The created concerted plan is a sequence of transitions which will transform the environment from an initial state into a specific goal state. The work by Kanovich, Rowe and Scedrov (2007) has a different definition of privacy. The authors equate privacy with secrecy and are focused on developing a proper balance between the protection and release of information and resources (2007). This differs from the approach to privacy, as privacy is not considered to be just the isolation of private information. Instead, privacy includes the ability to understand how information is being used, why it is being used, and to have some influence over these decisions.

Burnap et. al., (2012) describe a method of using "sticky policies" to retain access control even after information has been moved to an autonomous computer system outside the control of the information owner. This ability is achieved by attaching a privacy policy alongside the private information, while at the same time distributing the access control elements. By attaching the policy with the information, the information gatherer will always have access to the access control document they must check against. Similarly, distributing the access control elements allows both the information collector and the information owner to access the policy decision maker even from different environments. This access will let for the information collector to check their access rights and will allow the information owner to change the access rights (Burnap et. al., 2012). The idea of being able to retain a measure of control over information that has been released into a collaborative environment is an important one.

This approach by Burnap et. al., (2012). shows one technical method to how this could be accomplished. This work differs from the architecture as the access control available through sticky policies only permit access based on roles, and does not take into consideration how an individual may be using the information.

Malik and Dustdar (2011) describe a method for sharing private information in a collaborative working scenario through an expansion to the RBAC NIST standard (2014) The scenarios considered by the authors of this work are similar to the situation, where overlapping teams work to complete shared tasks. In the approach taken by Malik and Dustdar, five main data elements are identified: enterprise, team, task, role and user (Malik and Dustdar, 2011). The use of a task element differs from the approach, which instead considers projects. Malik and Dustdar do not formally describe their privacy policy. However, Malik and Dustdar do identify some privacy requirements that are similar to the privacy rules introduced. The work by Malik and Dustdar is complementary, as they describe issues related to access control, considers information usage and provides extended features through the CPM.

Flight planning in the future collaborative environment (Stéphane Mondoloni, 2015) focused on obtaining using feedback, data sharing and simulation. Enforcing Context-Sensitive Policies in Collaborative Business Environments (Alberto Sardinha, Jinghai Rao, & Norman Sadeh 2007) includes enforcing access control policies whose elements are tied to changing contractual relationships or to information obtained from external sources (e.g. ratings, credit worthiness, export restrictions, etc.). Path-Restricted Parallel Q-Learning Algorithm in Collaborative Virtual

Environment (Zhigang Wang and Li Xiao, 2007) proposed to improve the application effect of the collaborative navigation control, a Q-learning algorithm based on the path restriction is proposed by constructing the absolute distance between a mobile agent of the virtual environment and its destination into a status function of reinforcement learning. Poster's Collaborative data exploration using two navigation strategies (Omar Gomez et. al., 2009) shows how two different modes of collaboration can affect user performance in a specific exploration task. Fair Trade Metaphor as a Control Privacy Method for Pervasive Environments: Concepts and Evaluation (Abraham Esquivel et.al., 2015), presents a proof of concept from which the metaphor of "fair trade" is validated as an alternative to manage the private information of users. This privacy solution deals with user's privacy as a tradable good for obtaining environmental services. Supporting Fine-Grained Concurrent Tasks and Personal Workspaces for a Hybrid Concurrency Control Mechanism in a Networked Virtual Environment (Jun lee et. al., 2012) propose a hybrid concurrency control mechanism that reduces restrictions of non-owners' behaviour and task-surprises in a networked virtual environment. Regulation was proposed as an Enabler for Collaborative Software Development (Allyson F Hardwin, 2015). Widespread availability and adoption of social channels has led to a culture where today's developers participate and collaborate more frequently with one another. TAMRI presents TAMRI, a planning tool for identifying task assignments based on multiple criteria and weighted project goals. Its implementation combines a distributed systems approach with Bayesian networks. The tool can be adapted to specific organizational environments by exchanging the underlying Bayesian network. A Tool for Supporting Task Distribution in Global Software Development (Lamersdorf, A. & Munch, J. 2009) presents an overview of task distribution approaches, gives three application scenarios for the tool, and shows the implementation of the tool as well as its application in the scenarios.

### Multi Attribute Behavioural Analysis

Using the result of pre-processing, the method computes the trust factor for each attribute on the basis of the previous trace. The method computes the trust factor on each attribute on the basis of the users' behaviour represented by the access trace and based on the completeness of the access and how genuine the user has accessed the attributes in earlier days. Based on multi attribute trust factor the method computes trustworthy measure called CAM to decide the access control for the user.

**Algorithm:**

Input: Pre-processed Trace Ts
Output: CAM
Step1: start
Step2: read preprocessed trace Ts
Step 3: identify list of all attributes of the access

Attribute set As = $\sum_{i=1}^{size(Ts)} Ts(i).Attribute! \in As$

Step 4: for each attribute Ai
Compute number of access Na = $\sum_{i=1}^{size(Ts)} Ts(i).Attribute == Ai$

Compute number of successful access Nsa = $\sum_{i=1}^{size(Ts)} Ts(i).Attribute == Ai \&\& Status == Success$

Compute trust factor Tf = $\frac{Nsa}{Na} \times size(Ts)$
End

Step 5 : compute cumulative access measure $CAM = \frac{\sum Tf}{Numberofattributes}$

Step 6: stop
The algorithm discussed above computes the trust factor for each attribute and based on them the cumulative access measure is computed.

### Multi Attribute Access Restriction

At this stage, the method first performs pre-processing using the input user request and the user access trace. Then the method performs the multi attribute behaviour analysis using the pre-processed trace. Based on computed trust factor and the cumulative access measure the method performs access restriction.

Algorithm:
Input: User Request Ur
Output: Boolean
Step1: start
Step2: read user request Ur.
Step 3: perform preprocessing
Step 4: cumulative access measure CAM = perform multi attribute behaviour analysis
Step 5: if CAM >TTh //trust threshold
Allow access
Else
Deny the request.
End
Step 6: stop.
The above discussed algorithm computes the access trust measure and cumulative access measure from behaviour analysis. Based on the trust measure the method performs the access restriction.

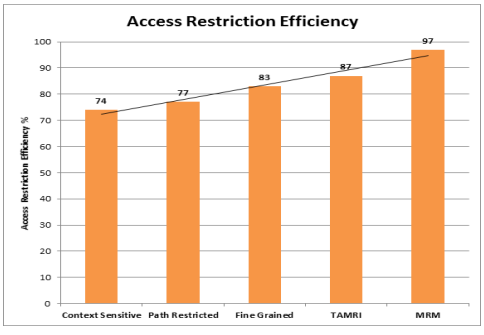
### RESULTS AND DISCUSSION:

The proposed multi attribute behaviour analysis based restriction model has been implemented and evaluated for its efficiency. The method has been evaluated for its performance by simulating in different conditions. The method has produced the following results and the details of the simulation are presented below.

| Sl.No | Parameter | Value |
|---|---|---|
| 1 | Number of Services | 20 |
| 2 | Number of Users | 100 |
| 3 | Size of Trace | 500 |
| 4 | Tool Used | Advanced Java |

**Table 1: Details Of Simulation**

Table 1, shows the details of simulation and the number of services and users being considered for the evaluation purpose.




**Graph 1: Comparison On Access Restriction Efficiency**

Graph 1 shows the comparison on access restriction efficiency produced by different methods. The access restriction efficiency achieved by the proposed system MRM is 96%. The results show that the proposed approach has produced higher efficiency than other methods. This study claims that the proposed mechanism is best to compare than other existing systems regarding access restriction.

When we compared the throughput performance produced by various methods, The throughput value of our proposed system is 98 %. The proposed method shows better results when compared to the other existing systems. So the deduction of access restriction is accurate by this MRM model when compared to other systems.

### CONCLUSION:

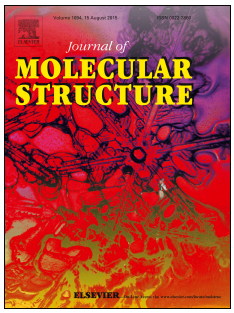
In this paper, an efficient Multi Attribute Restriction Model (MRM) has been proposed to improve the access restriction in collaborative environment. The method first receives the user request and identifies the component being claimed. Then the method identifies the list of attributes being required. Then the method collects the traces being accessed on the attributes. Each trace has been validated for its complete and noisy records have

been removed from the trace. Then the method performs the multi attribute behaviour analysis to compute the trust factor. Based on the trust factor, the method computes the cumulative access measure. The computed trust factor and the access measure have been used to restrict the user from accessing the component maliciously. The method has produced efficient results on access restriction and increases the throughput performance.

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# Accepted Manuscript




Synthesis, conformational, characterisation and reactivity study of 1,7-bis(4-bromophenyl)heptane-1,7-dione

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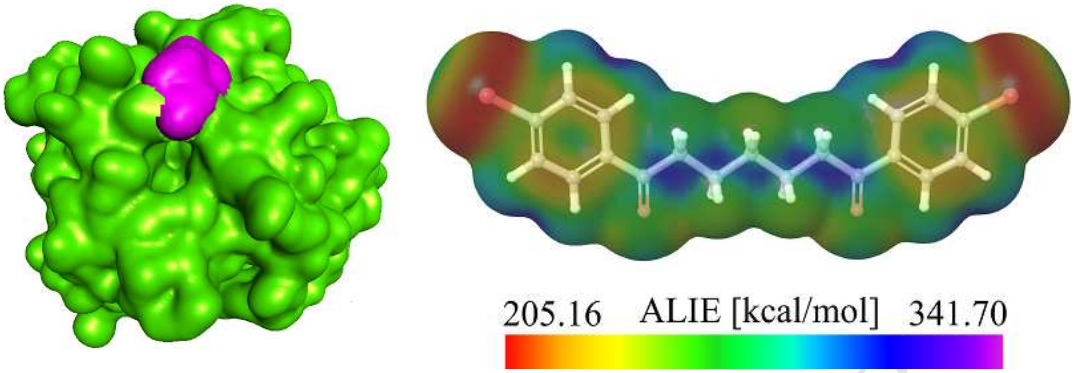
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# Synthesis, conformational, characterisation and reactivity study of 1,7-bis(4-bromophenyl)heptane-1,7-dione

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**Abstract**

In the present study, the title compound 1,7-bis(4-bromophenyl)heptane-1,7-dione (BBPHD) was synthesized according to the procedure described in literature, and its solid state crystal structure was characterised by the single crystal x-ray diffraction study. The complete crystallographic information has been reported in the present work. Physicochemical characterization by various spectral tools such as FT-IR, FT-Raman, $^{1}$H-NMR, $^{13}$C-NMR and UV-visible, have been performed as well and these results have been correlated with the theoretical data. The ground state geometrical optimization of the title compound has been performed using the DFT/B3LYP/6-311++G(d,p) level of theory in gas phase. Extracted molecular structure obtained by x-ray difractometry has been used as the starting molecular structure for geometrical optimizations. Computationally obtained structural and geometric parameters are in good

agreement with the experimentally obtained values. The experimental FT-IR and FT-Raman spectral data were compared with the theoretical spectral data and the complete assignment of vibrational wave numbers has been done on the basis of potential energy distribution (PED). In addition, reactive properties have been addressed on the basis of frontier molecular orbital analysis, global chemical reactivity descriptors, natural bond order (NBO) analysis, nonlinear optical (NLO) properties, molecular electrostatic potential (MEP) and average local ionization energy (ALIE) surfaces. Molecular dynamics (MD) simulations have been used in order to study the influence of water to the title compound. The docked ligand forms a stable complex with feruloyl esterase inhibitor and could be considered as a lead compound for the development of new antioxidant drug.

**Key words:** DFT; Hirshfeld surfaces; ALIE; RDF; Molecular docking.

## 1. Introduction

Owing to their abundance in natural products and pharmacologically active compounds, the significance of halogenated compounds is increasing [1-3]. This class of molecules has been successfully applied for the development of paints, dyes, adhesives, flame retardants, imaging agents in medical diagnosis, hydraulic and heat transfer fluids, refrigerants, solvents and in materials science [4-6]. Halogenated aromatic organic substrates are of great importance for the organic chemistry transformations, especially in the area of cross-coupling chemical reactions [7]. Although the halogenation is frequently followed by toxic chemicals, this procedure is highly developed and frequently used. There are number of advantages when it comes to the employment of halogens for the development of new molecules. For example, the introduction of carbon-halogen bond increases the thermal and oxidative stability, which leads to the lower sensitivity towards the oxidation by the liver P450 detoxification [6]. The same group of authors also indicates that carbon halogen bond increases the biological membrane permeability. Halogenated compounds are especially important in the area of agriculture and halogenation proved to be an important tool for development of efficient agricultural products. Jeschke [8] reports the information that since 2010, 96%of launched agricultural products, including herbicides, fungicides, insecticides/acaricides and nematicides, are containing halogen atoms. Positive effects of halogen atoms and halogen-containing groups are owed to steric and electronic effects [9], polarity of carbon-halogen bond [10] and pKa values effects [8]. One of the most important parameters in terms of pharmacokinetics, molecular lipophilicity, turned out to be adjustable by the substitution with halogen atoms [11]. Recently, Chen et al. [12] reported specific

nematic liquid crystal (LC) whose synthesis is based on the title compound (BBPHD). Taking into account the importance of their work, and importance of BBPHD for the synthesis of some other new specific nematic liquid crystals, we have decided to study BBPHD in details by spectroscopic and computational approaches. Density functional theory (DFT) represents irreplaceable tool for performing efficient and inexpensive computational studies in many areas [13-16]. DFT calculations with the hybrid exchange correlation functional B3LYP (Becke's three parameter (B3) exchange in conjunction with the Lee-Yang-Parr's (LYP) correlation functional) are of particular significance for studying systems comprising of extensive electron conjugation and/or electron lone pairs [17-20]. These structures have been the subject of many experimental and theoretical studies, especially when it comes to understandings of their structure, molecular properties and reaction mechanisms. Computational molecular modelling based on DFT calculations has become practically indispensable tool for evaluation and prediction of various properties of molecules and structures [21, 22], while in this work DFT calculations have been used in order to address global and local reactivity descriptors, including frontier molecular orbitals, MEP and ALIE surfaces and Fukui functions. DFT calculations were also used for confirmation of spectroscopic characterization and elucidation of vibrational specificities. Natural bond orbital (NBO) analysis has also been performed. Because newly synthetized molecules such as BBPHD might find place in the new pharmaceutical products, it is quite possible that they might end up in different water resources [23-27]. The introduction of halogen atoms also increases the persistency of compounds in environment, and in the same time hardening their degradation. This motivated us to also computationally study the degradation properties by calculation of bond dissociation energies for hydrogen abstraction (H-BDE) and stability in water by molecular dynamics (MD) simulations, another very important component of molecular modelling. Solid state crystal structure of BBPHD is elucidated by the single crystal X-ray diffraction studies, while contribution and quantification of various intermolecular interactions in crystal structure has been determined by the Hirshfeld surface analysis.

## 2. Material and methods

### 2.1. General remarks

The synthesis of BBPHD was carried according to the procedure reported in paper by Chen et al. [12]. Colourless prism like suitable crystals used for the structure determination was obtained by slow evaporation of ethanol at ambient temperature. FT-IR spectrum (Fig.S1-

supporting information) of title compound was recorded using the KBr pellets in the range of 4000-600 $cm^{-1}$ region, with the ATR module ALPHA-T Bruker FT-IR spectrophotometer. FT-Raman spectrum (Fig.S2-supporting information) of the title compound was recorded by Bruker RFS 100/s (Germany) using the Nd:YAG laser source, excitation wavelength of 1064 nm and spectral resolution of 2 $cm^{-1}$. $^{1}H$ and $^{13}C$-NMR spectra of the title compound was recorded (in ppm) on Bruker 400MHz spectrometer in $CDCl_3$ as solvent and TMS as internal standard.

**2.2. Data Collection and refinement details**

A suitable prism like crystal was selected and mounted on a Bruker APEX-II CCD diffractometer using the graphite monochromated MoKa ($\lambda$ = 0.71073 Å) radiation and detector (CCD). The crystal was kept at 296(2) K during data collection. The structure was solved using the Olex2 software [28] employing the olex2.solve [29] structure solution program and using the Charge Flipping. The structure was refined with the ShelXL [30] refinement package using the Least Squares minimization. All of the non-hydrogen atoms were revealed in the first difference Fourier map itself and were refined anisotropically. All of the hydrogen atoms were positioned geometrically, with C-H = 0.96 Å for methyl H, C-H = 0.93 Å for aromatic H, and refined using the riding model with $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl hydrogens and $U_{iso}(H) = 1.2U_{eq}(C)$ for aromatic hydrogens. The nitrogen bound hydrogen atom was located in a difference map and was refined isotropically with the bond length restraint of N-H = 0.86(2) Å. All of the geometrical calculations were carried out using the program PLATON [31] within the WinGXsuite [32]. The molecular and packing diagrams were generated using the MERCURY program [33].

**2.3. Computational details**

Molecular structure of BBPHD is extracted from the X-ray structure for computational studies. The molecular geometry optimization, vibrational analysis, frontier orbital analysis (HOMO-LUMO), MEP, surface analysis and Mullikan atomic charges were calculated at DFT/6-311G++(d,p)(5D, 7F) level using Gaussian 09 program package [34]. The assignment and PED analysis of wave number were performed by GaussView5.0 program [35] and GAR2PED software package [36]. For better agreement of calculated wavenumber numbers with experimental values, the wave numbers were scaled by the scaling factor of 0.9613 [37]. Schrödinger Materials Science Suite 2017-3 [38] was also used for computational study of global and local reactive properties of the newly synthetized BBPHD molecule. Particularly, Jaguar 9.7

program [39] has been used for DFT calculations, combined with Desmond program [40-43] for simulations based on molecular dynamics. Computational study based on DFT approach with SMSS has been also done with Becke-Lee, Parr i Yang (B3LYP) [44] exchange-correlation functional with 6-311++G(d,p), 6-31+G(d,p) and 6-311G(d,p) basis sets, in order to respectively obtain ALIE, Fukui functions and bond dissociation energies (BDE). Molecular dynamics simulation has been done with OPLS3 force field [40, 45-47], with simulation time of 10 ns, temperature of 300 K, pressure of 1.0325 bar and cut off radius of 12 Å. System was of isothermal–isobaric (NPT) ensemble class, while the simple point charge (SPC) solvent model [48] was chosen for the modelling of solvent properties. A single BBPHD molecule was placed into the cubic box with approximately 3000 water molecules. Analysis of electron density between atoms has been performed according to the works of Johnson et al. [49, 50], in order to identify formation of intra-molecular non-covalent interactions. Maestro GUI [51] was used for the preparation of input files and analysis of results when Schrödinger Materials Science Suite 2017-3 was employed.

### 2.4 Conformational Analysis

The solid structure of the title compound has been determined, by the X-ray diffraction spectroscopic technique, to be planar with $C_s$ symmetry, but it can be considered as near-$C_{2v}$ as well. Such configuration allows more efficient packing and facilitates the intermolecular interaction between the molecular layers. Very interestingly, the optimized strict $C_{2v}$ structure was verified to be a minimum with all computed frequencies being positive. The two carbonyl groups prefer to point away from the skeleton of the molecule to maintain up to a 6 kcal/mol more stable configuration than when one of them would eclipse any of the $CH_2$ units. Nevertheless, detailed conformational analysis revealed that other possible non-planar (*np*) forms can possibly exist, and their calculated energies are expected to be very comparable with the experimentally reported one. Understanding these conformations is of great importance, as the molecular structure in the crystalline packing could be sensitive to several parameters such as temperature and pressure. To explore the possible stable forms beside the one determined experimentally, detailed conformational analysis at the B3LYP/6-311++G(d,p) has been performed. The internal rotations about the C2-C3, C3-C4 and C5-C6 (Fig.S3-supporting information) were calculated and show three possible non-planar forms (*np*-1, *np*-2 and *np*-3, respectively) within a stability range of less than 1 kcal/mol compared to the $C_s$ form. The large-

amplitude rotation about these bonds exhibits a barrier in a range of 2-3 kcal/mol in the non-condensed phase, indicating the feasibility of the formation of other packing pattern when harsh conditions are applied.

### 2.5. Hirshfeld surfaces

We examined molecular surfaces, packing of molecules in their crystal structure, highlighting the contribution of significant inter molecular interactions between molecules that are responsible for the molecular arrangement in the crystalline state through Hirshfeld surface analysis. Hirshfeld surfaces [52-54] and the related 2D finger print plots (FP) [55-57] are unique for any crystal structure and provide a quantitative measure of the intermolecular interactions on the surface [52, 58]. The Hirshfeld surface analysis and finger print plots of BBPHD was generated by using Crystal Explorer 3.0 software [59] which accepts structure input file in the CIF format. The surfaces are mapped using a fixed colour scale red, white and blue, where red highlights contacts shorter than the sum of van der Waals (vdW) radii which is represented by negative sign values of $d_{norm}$, white for contacts around vdW separation with $d_{norm}$ values equal to zero, and blue for contacts longer than vdW sum with positive sign $d_{norm}$ values.

## 3. Result and discussions

### 3.1. Crystal structure analysis

The title compound crystallizes in orthorhombic space group *Abm2*, with the following unit cell parameters: $a$ = 7.1227(11) Å, $b$ = 42.536(4) Å, $c$ = 5.8126(6) Å and Z = 4. The molecule exhibits crystallographic inversion symmetry located at the C10 carbon atom and there is half-molecule in the asymmetric unit. The molecule is almost planar with root mean squared deviation of all atoms (excluding H-atoms) being 0.076Å. The crystal structure features C2-H2…$\pi_{aryl}$ and C5-H5…$\pi_{aryl}$ interactions, forming a three dimensional grid like architecture. The packing of molecules in the crystal lattice is shown in Fig.S4 (supporting information). The crystallographic data and refinement parameters are summarized in Table 1.

### 3.2. Hirshfeld surfaces

3D Hirshfeld surfaces and 2D finger print analysis illustrations of the title compound (BBPHD) are shown in Fig.5 (supporting information), where surfaces have been mapped over $d_{norm}$ and shape index -1.0-1.0 Å. A red spot close to the H2 hydrogen atom on the $d_{norm}$ surface and the centroid of the aromatic ring arises as a result of C2-H2…$\pi_{aryl}$ interactions present in the crystal. Similarly, a faint red spot close to H5 atom on the $d_{norm}$ surface is due to weak C5-

H5…$\pi_{aryl}$ interactions (Fig.S5a). The dark red spots close to the centroid of the two aromatic rings in the shape index is a result of the two C-H…$\pi_{aryl}$ interactions. The two C-H…$\pi_{aryl}$ interactions are mapped over the $d_{norm}$ surface to support the presence of these interactions (Fig. S5b). The relative contribution of different interactions to the Hirshfeld surface was calculated for BBPHD. It is evident from Fig.S5(c) that the H···H contacts account for about 34.7% of the total Hirshfeld surface area; the remaining contribution was mostly due to C···H (25.8%), O···H (12.4%), Br···H (15.0%), Br···Br (9.3%) interactions and only minor contribution from other interactions.

**3.3. Geometrical parameters**

In the present case the experimental C-C bond lengths are in the range of 1.4104-1.3785 Å and the calculated C-C bond lengths are in the range of 1.4057-1.3727 Å [60]. For the title compound, the C-Br bond length is 1.9237 Å (DFT) and 1.9055 Å (XRD), which is in agreement with the literature data [61]. The C=O bond length (1.1988) agrees with the reported literature values [60]. At C8 position, the bond angles (/DFTXRD) are C3-C8-C9 = 123.5/123.7°, C3-C8-Br1 =119.1/119.2° and C9-C8-Br1 = 117.3/117.1° and the asymmetry in angles is due to the electronegative bromine atom.

**3.4. IR and Raman spectra**

Table 2 contains the wavenumbers (calculated and observed) with vibrational assignments, while the atom labelling is provided in Fig.1. Phenyl rings at C5 and C27 are designated as PhI and PhII, respectively. The carbonyl stretching C=O vibrations [62-64] appear at 1668 $cm^{-1}$ (IR), 1680 $cm^{-1}$ (Raman) and theoretically at 1679 and 1678 $cm^{-1}$. The bands observed at 679, 662 $cm^{-1}$ (IR), 658, 551 $cm^{-1}$ (Raman) and at 678, 667, 553 $cm^{-1}$ (DFT) are assigned as C=O deformation modes [62]. The phenyl C-H stretching modes are assigned at 3081, 3062 $cm^{-1}$ (spectrum), 3079, 3059 $cm^{-1}$ (Raman) and in the range 3082-3064 $cm^{-1}$ based on DFT calculations [62, 65]. The ring stretching modes of the phenyl ring are assigned in the range 1558-1269 $cm^{-1}$ theoretically. The bands observed at 1570, 1530, 1450, 1374 $cm^{-1}$ (IR) and at 1565, 1279 $cm^{-1}$ (Raman) are assigned as the phenyl ring stretching modes. The band at 1042 $cm^{-1}$ (IR), 1042 $cm^{-1}$ (Raman) and 1040 $cm^{-1}$ (DFT) is assigned as the ring breathing mode of the para substituted phenyl ring [65], which is in agreement with the reported values at 1062 $cm^{-1}$ (IR) and 1061 $cm^{-1}$ (DFT) [66]. The in-plane and out-of-plane CH deformations are assigned theoretically in the range 1276-1087 $cm^{-1}$ and 965-788 $cm^{-1}$, respectively. Experimentally, these

modes are assigned at 1156, 1087 $cm^{-1}$ (IR), 1279, 1088 $cm^{-1}$ (Raman) and 963, 815, 801 $cm^{-1}$ (IR), 968, 818, 798 $cm^{-1}$ (Raman). The $CH_2$ stretching modes are assigned in the range 2965-2865 $cm^{-1}$ in IR spectrum, 2965-2877 $cm^{-1}$ in Raman spectrum and in the range of 2962-2873 $cm^{-1}$based on DFT calculations [62,67]. The $CH_2$ bending modes are observed in the ranges 1450-759 $cm^{-1}$ in the IR spectrum and 1440-738 $cm^{-1}$ in the Raman spectrum. According to the DFT calculations, these modes are in the range of 1453-706 $cm^{-1}$. The C-C stretching modes are assigned in the range 1173-780 $cm^{-1}$computationally. Bromine compounds [62] absorb strongly in the region of 635±85 $cm^{-1}$, due to the CBr stretching vibration and in the present case, bands at 615 $cm^{-1}$ (IR), 624 $cm^{-1}$ (Raman) and 616 $cm^{-1}$ (DFT) are assigned to this mode. Varghese et al. [68] reported the CBr stretching mode at 632 $cm^{-1}$ theoretically.

**3.5. NMR spectra analysis**

Chemical shift ($^{1}H$ and $^{13}C$) values of the investigated molecules have been computed with GIAO/B3LYP method [69] and compared with experimental values (Table S1-supporting information). The chemical shift values of $^{1}H$-NMR spectrum of title compound show two ranges; first one is consequence of the chemical shift of aliphatic C-H protons, which occurred in the range of 1.39-2.95/1.29-3.02 ppm (experimental/theoretical). The chemical shift of hydrogen atom attached to carbon near to the carbonyl group is higher than expected. H21, H22, H40 and H41 resonate at high frequency 2.95/3.02 (experimental/DFT), due to influence of carbonyl groups. Second one, around 7.60-7.81/7.69-8.06 (experimental/theoretical) ppm, occurred due to the aromatic protons. Chemical shift values of $^{13}C$-NMR for aromatic carbon atoms in general have values higher than 100 ppm [70,71]. Computational and experimental $^{13}C$ NMR values of carbon atoms of methylene groups of aliphatic chain are in good agreement as well: C17, C36 (24.02/27.40), C13 (28.97/32.69) and C20, C39 (38.37/42.69) ppm (experimental values/computational values). The chemical shift value at 199.26/205.26 ppm (experimental/computational) is assigned to the carbonyl carbon atoms C2 and C24. Signals observed in range of the 128.26-135.82/134.04-153.80 ppm (experimental/computational) correspond to carbon atoms of phenyl rings. From above result shows, the theoretical chemical shifts are good in agreement with experimental findings.

**3.6. Electronic properties and frontier molecular orbital analysis**

Chemical reactivity and kinetic stability of molecules depend upon the energy gap between HOMO and LUMO orbitals. These molecular orbitals are often known as frontier

molecular orbitals (FMOs). Based on the energy gap between frontier orbitals, molecules are frequently classified into soft and hard molecules. Energy gap between frontier orbitals is a critical parameter for prediction of the biological activity and transport properties. Frontier molecular orbitals have been visualized in Fig.S6 (supporting information). It can be seen that HOMO (MO109) is localized mainly at the carbonyl group and partially at the aliphatic chain, while LUMO (MO110) is localized mainly at the benzene ring and partially at the carbonyl group. Based on the HOMO to LUMO transitions, it can be concluded that the transfer of electron cloud occurs mainly from carbonyl group to benzene ring. In the present case, the calculated energy values of HOMO and LUMO are -7.20 eV and -2.16 eV, respectively and the energy gap between HOMO and LUMO is 5.04 eV. The higher the energy gap between HOMO-LUMO is, the harder the molecule is. In order to understand the chemical reactivity of title compound, global reactivity parameters were evaluated by DFT method. Single point calculation was carried out at DFT/6-311++G(d,p) level of theory. Vertical ionization potential (IP) and vertical electron affinity (EA) parameters have been calculated. These parameters were defined according to the following equations:

$$IP = E_{n-1(\text{cation})} - E_{N(\text{neutral})},$$

$$EA = E_{N(\text{neutrail})} - E_{N+1(\text{anion})},$$

where $E_{N+1(\text{anion})}$, $E_{N(\text{neutral})}$ and $E_{N-1(\text{cation})}$ are total energies of anion, neutral and cation forms of investigated molecule, respectively [72, 73]. These parameters were used in order to calculate the values of global reactivity descriptor, summarized in Table S2 of the Supplementary Materials. TD-DFT calculations have been performed at B3LYP/6-311++G(d,p) level of theory, while theoretical UV transitions have been characterized by vertical excitation energies, wavelength and oscillator strength. These results are summarized in Table S3 of the Supplementary Materials. The UV spectrum of the title compound (Fig.S7-supporting information) is characterized by electronic absorption band located at 268 nm, which is the consequence of the transitions: HOMO-1→LUMO and HOMO→LUMO+1(π-π transition).

### 3.7. Nonlinear optical properties

With regards to optoelectronic applications [74], the NLO active materials receive significant attention. Some of the properties that are important for optoelectronic applications can be obtained by DFT calculations and these include dipole moment, polarizability, first and

second hyperpolarizabilities. Respectively, these parameters have been calculated to be 4.102 Debye, $4.149\times10^{-23}$ esu, $6.227\times10^{-30}$ esu and $-71.736\times10^{-37}$ esu. It is interesting to notice that the first hyperpolarizability of the title compound is 31.98 times higher than in the case of urea, revealing possibility of the title compound to possess representative NLO properties, comparable with similar derivatives [75].

### 3.8. Molecular electrostatic potential

Analysis of charge distribution by mapping of MEP to the electron density surface is valuable approach in molecular modelling, when it comes to the biological recognition, hydrogen bonding interactions and visualization of reactive molecular sites [76, 77]. Optimized molecular structure was used for the generation of 3D MEP and 2D counter surfaces plots with rainbow colour scheme (electron reach regions are represented with red colour, while electron poor regions are represented with blue colour). For the title compound MEP took values from– 5.56a.u. (red) to 5.56a.u. (blue). MEP and surface analysis diagram of title compound, Fig.2, show that negative regions are mainly localized over oxygen atoms of the carbonyl groups, indicating the most sensitive sites towards the electrophilic attacks. On the other side, the maximal positive regions are localized over hydrogen atom of the aliphatic chain as well as phenyl rings, indicating sensitivity towards the nucleophilic attacks.

### 3.9. Natural Bond Orbital analysis

Natural bond orbital (NBO) calculations were performed using NBO 3.1 program [78] as incorporatedin the Gaussian09 package. In this case the DFT/SDD level of theory was used in order to understand various second-order interactions, principal interaction summarized in Tables S4 and S5 (supplementary materials). The strong intermolecular hyper conjugative interactions are: $C_2$-$C_5$ from $O_{16}$ of $n_2(O_{16}) \rightarrow \sigma^*(C_2\text{-}C_5)$ which increases the electron density 0.06345e that weakens the respective bond $C_2$-$C_5$ leading stabilization of 16.61 kJ/mol; $C_2$-$C_{20}$ from $O_{16}$ of $n_2(O_{16})\rightarrow\sigma^*(C_2\text{-}C_{20})$ which increases the electron density 0.05561e that weakens the respective bond $C_2$-$C_{20}$ leading stabilization of 17.56 kJ/mol; $C_{24}$-$C_{27}$ from $O_{35}$ of $n_2(O_{35})\rightarrow\sigma^*(C_{24}\text{-}C_{27})$ which increases the electron density 0.06345e that weakens the respective bond $C_{24}$-$C_{27}$ leading stabilization of 16.61 kJ/mol; and $C_{24}$-$C_{39}$ from $O_{35}$ of $n_2(O_{35})\rightarrow\sigma^*(C_{24}\text{-}C_{39})$ which increases the electron density 0.05561e that weakens the respective bond $C_{24}$-$C_{39}$ leading stabilization of 17.56 kJ/mol. The orbital with low occupation number are high energies are $n_2(O_{16})$, $n_2(O_{35})$ with energies -0.27360, -0.27360a.u. and considerable p-characters100,

99.99% and low occupation numbers 1.90859, 1.90859 while the orbital with high occupation numbers and low energies are: $n_1(O_{16})$, $n_1(O_{35})$ -0.68914, -0.68914a.u. and p-characters, 61.77, 61.77 and occupation numbers 1.97457, 1.97457. Thus, a very close to pure p-type lone pair orbital participates in the electron donation to the $\sigma^*(C_2\text{-}C_5)$ orbital for $n_2(O_{16}) \rightarrow \sigma^*(C_2\text{-}C_5)$, $\sigma^*(C_2\text{-}C_{20})$ orbital for $n_2(O_{16}) \rightarrow \sigma^*(C_2\text{-}C_{20})$, $\sigma^*(C_{24}\text{-}C_{27})$ orbital for $n_2(O_{35}) \rightarrow \sigma^*(C_{24}\text{-}C_{27})$, $\sigma^*(C_{24}\text{-}C_{39})$) orbital for $n_2(O_{35}) \rightarrow \sigma^*(C_{24}\text{-}C_{39})$ interactions in the title compound.

### 3.10. ALIE and MEP surface, Fukui functions and non-covalent interactions

Aside of the MEP surface, in this work ALIE values were mapped to the electron density surface in order to identify the molecule sites where electrons are least tightly bound. This enabled us to detect molecule sites that are the most sensitive towards the electrophilic attacks (Fig.3) [79-82]. The analysis of electron density between atoms revealed that the intra-molecular non-covalent interactions in the case of BBPHD molecule didn't form. The lowest ALIE values in the case of BBPHD molecule were calculated in the near vicinity of bromine atoms, with corresponding values of ~205 kcal/mol. On the other side, the highest ALIE values were calculated in the near vicinity of all hydrogen atoms with the corresponding values of ~342 kcal/mol. Additional insights into the local reactive properties of BBPHD molecule were obtained thanks to the calculation of Fukui functions, which are in the case of Jaguar program for DFT calculations obtained by the finite difference approach according to the following equations:

$$f^{+} = \frac{\left(\rho^{N+\delta}(r) - \rho^{N}(r)\right)}{\delta}, \qquad (1)$$

$$f^{-} = \frac{\left(\rho^{N-\delta}(r) - \rho^{N}(r)\right)}{\delta}, \qquad (2)$$

where $N$ represents the number of electrons in reference state of the molecule, while $\delta$ is fraction of electron which default value is set to be 0.01 [83]. After mapping of the values of the Fukui functions to the electron density surface the following corresponding surfaces have been obtained, Fig.4. In general Fukui functions track the changes in electron densities which are consequence of change in the overall charge of the observed molecule. The change in overall molecular charge influences the values of electron density at the molecular surface. By tracking of these changes in electron density, Fukui functions allow detection of molecule sites with electrophilic and nucleophilic properties. In this regard, purple colour for Fukui $f^{+}$ function in

Fig.4a is positive colour and indicates sites with increased electron density after the addition of charge. In Fig.4a it can be seen that blue-to-purple colour is located in the near vicinity of carbon atoms connected with oxygen atoms, which marks them as an electrophilic ones. On the other side, red colour for Fukui $f^-$ function is a negative colour and indicates sites with decreased electron density after the removal of charge. Inspection of Fig.4b indicates that the red colour is located in the central part of the molecule, marking this area as nucleophilic.

### 3.11. Sensitivity towards autoxidation and water

Taking into account the negative environmental impact of the pharmaceuticals, in this work we have also studied the sensitivity of BBPHD molecule towards the autoxidation mechanism [24, 84]. Oxidation mechanism represents one of the most important pathways for degradation of pharmaceuticals [85-88]. Thanks to the correlation between bond dissociation energies for hydrogen abstraction (H-BDE) and sensitivity towards the autoxidation mechanism, computational molecular modelling techniques can be used for determination of the molecule sites where degradation could start [89-95]. Fig.5 contains information about the H-BDE values. According to the results presented in Fig.5, for BBPHD molecule it can be concluded that it is highly stable towards the autoxidation mechanism, since there are no H-BDE values in the region between 70 and 90 kcal/mol [96, 97]. In the same time the lowest BDE value has been calculated for bromine atoms indicating that degradation could start by detaching of these atoms. Sensitivity towards water molecules was investigated by molecular dynamics simulation. The information on the obtained trajectories were used in order to calculate Radial Distribution Functions (RDF) for all atoms of the BBPHD molecule, with the goal to identify atoms with the most important interactions with water. RDFs were calculated with respect to the distance between the observed atom of the BBPHD molecule and oxygen atom of the water molecule. Representative RDFs have been presented in Fig.6. According to the results provided in Fig.6 it can be seen that BBPHD molecule has significant stability in water, as there are no hydrogen atoms with sharp g(r) curves located at distances below 2 Å. The highest g(r) value was calculated for bromine atoms, however their maximal g(r) values are located at distance of around 3.5 Å. On the other side, maximal g(r) values carbon atoms C16 and C35 are located at the distances lower than in case of the bromine atoms, but their maximal g(r) values are much lower. Maximal g(r) values of the carbon atoms C8 and C30 are somewhere between bromine

atoms at carbon atoms C16 and C35, however their peaks are located at high distances of over 4.5 Å.

### 3.12. Molecular docking

Based on the molecular structure, PASS (Prediction of Activity Spectra) [98] online tool for prediction of different types of activities has been applied. According to the results of PASS analysis, which have been summarized in Table 3, the title compound could serve as feruloyl esterase inhibitor, with probability to be active (Pa) value of 0.936. Antioxidants are necessary to control degenerative reactions produced by reactive oxygen and nitrogen species. These species are involved in several ailments including cancer and heart diseases. Several literatures suggest that heptane derivatives show promising antioxidant activities [99, 100]. Ferulic acid is the most abundant hydroxycinnamic acid in the plant world and is one of the most promising sources of antioxidants [101]. Feruloyl esterase is a class of enzymes used in biocatalysis for refinement of hydroxycinnamic acids. These compounds have shown to have antioxidant and antibacterial properties, FAEs and their hydrolytic or transesterification products are of great interest for various biotechnological applications, in particular as modified natural antioxidants or food flavour precursors [102].It prevents low-density lipoprotein from oxidation, exhibits inhibitory effects on tumour promotion [103] and protects against certain chronic diseases such as coronary heart disease and some cancers [104, 105]. Therefore the feruloyl esterase inhibitor is used as a target for docking study. High resolution crystal structure of feruloyl esterase inhibitor was downloaded from the RSCB protein data bank website with PDB ID: 1UWC. All molecular docking calculations were performed on Auto Dock-Vina software [106] and as reported in literature [74, 107]. The ligand binds at the active site of the substrate by weak non-covalent interactions and these interactions are depicted in Fig.S8 (supporting information). Amino acids forms strong hydrophobic interaction with the ligand. The docked ligand forms a stable complex with feruloyl esterase inhibitor (Fig.S9-supporting information) and got a binding affinity value of -5.7 kcal/mol (Table 4). Thus the title compound can be a lead compound for developing new antioxidant drug.

## 4. Conclusion

The title compound, 1,7-bis(4-bromophenyl)heptane-1,7-dione was characterized by single crystal XRD, FT-IR, FT-Raman as well as NMR spectroscopic studies. Within the framework of DFT, the vibrational wavenumbers are theoretically predicted and compared with

experimental wavenumbers. Conformation analysis shows that the two carbonyl groups prefer to point away from the skeleton of the molecule to maintain up to a 6 kcal/mol more stable configuration than when one of them would eclipse any of the $CH_2$ units. MEP plot showed that the negative regions are mainly localized over the oxygen atoms of the carbonyl groups while the maximal positive regions are localized over the hydrogen atom of the aliphatic chain as well as phenyl rings. The first hyperpolarizability of the title compound is 31.98 times that of urea. ALIE surfaces revealed that the near vicinity of bromine atoms could be the most sensitive parts of the BBPHD molecule in terms of electrophilic attacks. Additionally, Fukui functions revealed that the central part of BBPHD molecule could be considered as important reactive center when charge is added or removed. The values of H-BDE indicate that BBPHD molecule is highly stable towards the autoxidation mechanism, while the remaining BDE values indicate that degradation process might start with detaching of bromine atoms. Molecular dynamics study indicated that BBPHD molecule is highly stable in water as well, since there are no hydrogen atoms with significant interactions with water molecules. PASS analysis predicts feruloyl esterase inhibitor activity for the title compound and the docking studies suggest that the title compound can be a lead compound for developing new antioxidant drug.

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**Supplementary Material**

The cif file of the title compound have been assigned CCDC number1577497and can be obtained free of cost on application to CCDC 12 Union Road, Cambridge CB21 EZ, UK. (Fax: (+44) 1223 336-033: e-mail: data_request@ccdc.cam.ac.uk).

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**Figure captions**

Fig.1 Optimized geometry of 1,7-bis(4-bromophenyl)heptane-1,7-dione

Fig.2 MEP plot of 1,7-bis(4-bromophenyl)heptane-1,7-dione

Fig.3 ALIE surface of 1,7-bis(4-bromophenyl)heptane-1,7-dione molecule

Fig.4 Fukui functions of the 1,7-bis(4-bromophenyl)heptane-1,7-dione molecule a) $f^{+}$ and b) $f^{-}$

Fig.5 H-BDE values (blue colour) and BDE values of the remaining single acyclic bonds (red colour)

Fig.6 Significant RDFs of atoms of 1,7-bis(4-bromophenyl)heptane-1,7-dione molecule

ACCEPTED MANUSCRIPT

**Table 1: Crystal data and structure refinement for BBPHD**

| | | |
|---|---|---|
| CCDC Deposit | : | 1577497 |
| Empirical formula | : | $C_{19}H_{18}O_2Br_2$ |
| Formula weight | : | 434.13 |
| Temperature/K | : | 296.15 |
| Crystal system | : | Orthorhombic |
| Space group | : | Abm2 |
| a/Å | : | 7.1227(11) |
| b/Å | : | 42.536(4) |
| c/Å | : | 5.8126(6) |
| α/° | : | 90 |
| β/° | : | 90 |
| γ/° | : | 90 |
| Volume/$Å^3$ | : | 1761.1(4) |
| Z | : | 4 |
| $\rho_{calc}g/cm^3$ | : | 1.653 |
| $\mu/mm^{-1}$ | : | 4.610 |
| F(000) | : | 872.2 |
| Crystal size/$mm^3$ | : | 0.25×0.22×0.18 |
| Radiation | : | Mo Kα (λ = 0.71073) |
| 2Θ range for data collection/° | : | 3.84 to 57.74 |
| Index ranges | : | $-9 \leq h \leq 9$, $-56 \leq k \leq 57$, $-6 \leq l \leq 7$ |
| Reflections collected | : | 12635 |
| Independent reflections | : | 2095 [$R_{int}$ = 0.0808, $R_{sigma}$ = 0.0737] |
| Data/restraints/parameters | : | 2095/1/106 |
| Goodness-of-fit on $F^2$ | : | 1.101 |
| Final R indexes [I>=2σ (I)] | : | $R_1$ = 0.0630, $wR_2$ = 0.1306 |
| Final R indexes [all data] | : | $R_1$ = 0.1174, $wR_2$ = 0.1551 |
| Largest diff. peak/hole/ e $Å^{-3}$ | : | 1.14/-1.15 |
| Flack parameter | : | 0.11(3) |

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Table 2

Calculated scaled wavenumbers, observed IR, Raman bands with assignments

| B3LYP/6-311G++(d,p)(5D, 7F) | | | IR | Raman | Assignments[a] |
|---|---|---|---|---|---|
| υ($cm^{-1}$) | IRI | RA | υ($cm^{-1}$) | υ($cm^{-1}$) | - |
| 3082 | 0.89 | 432.59 | - | - | υCHII(51),υCHI(40) |
| 3082 | 1.48 | 33.26 | - | - | υCHI(51),υCHII(40) |
| 3081 | 2.11 | 8.85 | 3081 | 3079 | υCHII(55),υCHI(43) |
| 3081 | 4.68 | 5.75 | 3081 | 3079 | υCHI(55),υCHII(43) |
| 3069 | 0.41 | 52.50 | - | - | υCHI(66),υCHII(32) |
| 3069 | 0.99 | 34.13 | - | - | υCHII(66),υCHI(32) |
| 3064 | 0.53 | 74.49 | 3062 | 3059 | υCHII(50),υCHI(49) |
| 3064 | 7.37 | 24.17 | 3062 | 3059 | υCHI(50),υCHII(49) |
| 2962 | 66.90 | 25.95 | 2965 | 2965 | $\upsilon CH_2$(88) |
| 2954 | 0.01 | 0.22 | 2952 | - | $\upsilon CH_2$(92) |
| 2925 | 39.15 | 125.82 | - | 2928 | $\upsilon CH_2$(96) |
| 2920 | 2.24 | 0.72 | 2922 | - | $\upsilon CH_2$(98) |
| 2915 | 7.65 | 71.93 | - | - | $\upsilon CH_2$(94) |
| 2914 | 0.01 | 0.43 | - | - | $\upsilon CH_2$(92) |
| 2896 | 19.06 | 74.27 | - | 2897 | $\upsilon CH_2$(91) |
| 2890 | 22.32 | 288.27 | - | - | $\upsilon CH_2$(96) |
| 2890 | 31.55 | 0.65 | - | - | $\upsilon CH_2$(98) |
| 2873 | 16.97 | 81.11 | 2865 | 2877 | $\upsilon CH_2$(96) |
| 1679 | 338.34 | 190.30 | 1668 | 1680 | υC=O(80) |
| 1678 | 18.93 | 73.90 | 1668 | 1680 | υC=O(80) |
| 1558 | 69.35 | 343.39 | 1570 | 1565 | υPhII(26), υPhI(26) |
| 1558 | 176.92 | 213.32 | - | - | υPhI(27), υPhII(26) |
| 1539 | 8.18 | 16.46 | - | - | υPhII(36), υPhI(36) |
| 1539 | 40.30 | 17.65 | 1530 | - | υPhI(36), υPhII(36) |
| 1454 | 3.93 | 7.53 | - | - | υPhII(36), υPhI(36) |
| 1454 | 19.94 | 1.24 | 1450 | - | υPhII(36), υPhI(36) |
| 1453 | 12.69 | 0.75 | 1450 | - | $\delta CH_2$(86) |

| | | | | | |
|---|---|---|---|---|---|
| 1437 | 2.65 | 0.12 | - | 1440 | $\delta CH_2$(92) |
| 1430 | 0.04 | 27.52 | - | - | $\delta CH_2$(95) |
| 1404 | 14.77 | 7.51 | 1410 | - | $\delta CH_2$(88) |
| 1403 | 0.14 | 1.65 | - | - | $\delta CH_2$(88) |
| 1368 | 4.97 | 6.95 | 1374 | - | υPhI(32), υPhII(32), δCHII(11), δCHI(11) |
| 1368 | 73.82 | 3.16 | - | - | υPhI(31), υPhII(31), δCHII(11), δCHI(11) |
| 1351 | 3.25 | 0.59 | - | - | $\delta CH_2$(67), υCC(18) |
| 1345 | 0.01 | 0.64 | 1342 | 1340 | $\delta CH_2$(66) |
| 1320 | 141.41 | 0.85 | - | - | $\delta CH_2$(66), υCC(14) |
| 1284 | 0.06 | 0.16 | 1288 | - | $\delta CH_2$(94) |
| 1281 | 0.01 | 17.04 | 1281 | - | $\delta CH_2$(97) |
| 1280 | 9.05 | 12.74 | 1281 | 1279 | $\delta CH_2$(66) |
| 1276 | 1.64 | 0.01 | - | 1279 | υPhI(11), υPhII(10), δCHI(30), δCHII(30) |
| 1269 | 3.44 | 1.63 | - | - | δCHI(30), δCHII(30), υPhI(11), υPhII(10) |
| 1269 | 0.13 | 0.26 | - | - | υPhI(31), υPhII(31) |
| 1269 | 1.15 | 7.80 | - | - | υPhI(25),υPhII(25), $\delta CH_2$(26) |
| 1260 | 0.01 | 10.11 | 1258 | 1260 | $\delta CH_2$(86) |
| 1220 | 186.53 | 14.42 | 1219 | 1215 | $\delta CH_2$(60), υCC(16) |
| 1202 | 0.04 | 0.22 | - | - | $\delta CH_2$(96) |
| 1173 | 21.27 | 102.83 | 1172 | 1170 | υCC(32), $\delta CH_2$(16) |
| 1162 | 21.38 | 12.12 | 1156 | - | δCHII(44), δCHI(44) |
| 1153 | 13.45 | 88.30 | 1156 | - | δCHI(30), δCHII(31) |
| 1148 | 183.16 | 29.51 | - | 1149 | υCC(18),δCHI(15), δCHII(15) |
| 1095 | 0.01 | 2.44 | - | - | $\delta CH_2$(83) |
| 1087 | 3.80 | 5.47 | 1087 | 1088 | δCHI(25), δCHII(25), |

| | | | | | |
|---|---|---|---|---|---|
| | | | | | υPhI(16), υPhII(16) |
| 1087 | 7.87 | 2.87 | 1087 | 1088 | δCHI(25), δCHII(25), υPhI(15), υPhII(15) |
| 1061 | 0.55 | 58.77 | - | - | υCC(44), $\delta CH_2$(21) |
| 1058 | 0.01 | 0.60 | - | - | $\delta CH_2$(82) |
| 1040 | 78.39 | 8.97 | 1042 | 1042 | υPhI(27), υPhII(27) |
| 1040 | 17.01 | 100.46 | 1042 | 1042 | υPhI(27), υPhII(27) |
| 1028 | 20.51 | 3.71 | 1024 | 1030 | υCC(78) |
| 1008 | 16.55 | 0.09 | - | - | υCC(52) |
| 1000 | 0.17 | 22.49 | - | - | υCC(76) |
| 986 | 11.44 | 6.39 | - | - | δPhI(29),δPhII(29), υPhI(12), υPhII(12) |
| 985 | 92.40 | 0.36 | - | - | δPhI(33), δPhII(33) |
| 965 | 0.01 | 0.10 | - | 968 | γCHI(41), γCHII(41) |
| 964 | 0.81 | 0.06 | 963 | - | γCHII(42), γCHI(42) |
| 953 | 9.04 | 2.68 | - | - | υCC(32), δ(C=O)(14) |
| 937 | 0.00 | 0.29 | - | - | γCHI(32), γCHII(32) |
| 933 | 201.61 | 3.43 | - | - | υCC(46) |
| 932 | 0.03 | 0.19 | - | - | γCHI(38), γCHII(38) |
| 916 | 0.01 | 0.02 | 913 | - | $\delta CH_2$(59) |
| 837 | 14.44 | 0.34 | - | - | $\delta CH_2$(52),γCHI(10), γCHII(10), γ(C=O)(10) |
| 819 | 0.01 | 0.01 | - | 818 | γCHI(43),γCHII(43) |
| 813 | 8.39 | 0.01 | 815 | - | γCHI(44), γCHII(44) |
| 801 | 0.01 | 0.01 | 798 | 798 | γCHI(41), γCHII(41) |
| 788 | 74.69 | 0.03 | - | - | γCHI(33),γCHII(32), $\delta CH_2$(30) |
| 780 | 37.04 | 0.01 | - | - | υCC(32), $\delta CH_2$(12) |
| 759 | 7.71 | 35.99 | 759 | 758 | υCC(32), δPhII(14), δPhI(13) |
| 739 | 0.01 | 0.03 | 737 | 738 | $\delta CH_2$(66) |
| 706 | 12.10 | 0.01 | 706 | 699 | $\delta CH_2$(69) |

| | | | | | |
|---|---|---|---|---|---|
| 688 | 0.01 | 0.63 | - | - | τPhII(34), τPhI(34) |
| 688 | 0.03 | 0.14 | - | - | τPhII(33), τPhI(33) |
| 678 | 0.10 | 0.09 | 679 | - | δPhII(24), δPhI(23), δ(C=O)(38) |
| 668 | 2.62 | 9.28 | 662 | 658 | δ(C=O)(32), δPhII(20), δPhI(19) |
| 616 | 1.94 | 3.94 | 615 | 624 | δPhI(13), δPhII(12) υCBr(36) |
| 616 | 0.68 | 9.73 | 615 | 624 | δPhI(14), δPhII(12) υCBr(37) |
| 553 | 0.01 | 0.02 | - | 551 | γ(C=O)(36), δ$CH_2$(22) |
| 553 | 18.01 | 0.31 | - | 551 | γ(C=O)(37), δ$CH_2$(22), γCC(10) |
| 504 | 3.37 | 0.89 | - | 499 | δ(C=O)(34), δ$CH_2$(12), δCC(12) |
| 483 | 19.50 | 0.72 | - | 479 | δ(C=O)(34), δCC(14), υCBr(10) |
| 456 | 1.77 | 0.60 | - | 456 | δ$CH_2$(34), δ(C=O)(12) |
| 445 | 0.01 | 0.01 | - | - | γCBr(28), τPhI(24), τPhII(22), γCC(12) |
| 444 | 13.25 | 0.21 | - | - | γCBr(28), τPhI(24), τPhII(22), γCC(12) |
| 409 | 17.42 | 0.03 | - | 408 | δ(C=O)(38), δ$CH_2$(30), υCBr(14) |
| 399 | 0.01 | 0.01 | - | - | τPhII(42), τPhI(41) |
| 399 | 0.01 | 0.01 | - | - | τPhII(43), τPhI(39) |
| 372 | 1.92 | 1.14 | - | 369 | δ$CH_2$(28), υCBr(14) |
| 336 | 0.13 | 0.77 | - | 336 | δCC(30), δ$CH_2$(24), δCBr(12) |
| 283 | 11.14 | 0.54 | - | - | δCBr(40), δCC(22) |
| 264 | 0.15 | 2.61 | - | 262 | δCBr(32), δCC(10) |
| 240 | 1.14 | 0.01 | - | - | δCBr(38), δ$CH_2$(24), δ(C=O)(18) |

| | | | | | |
|---|---|---|---|---|---|
| 236 | 0.28 | 0.62 | - | - | γCC(36), γCBr(26), γ(C=O)(12) |
| 236 | 0.01 | 3.68 | - | 234 | γCC(38), γCBr(28), γ(C=O)(12) |
| 215 | 6.95 | 0.44 | - | - | δCBr(32), δPhII(15), δPhI(11) |
| 180 | 9.00 | 0.33 | - | 185 | δCBr(36), δ$CH_2$(32), δCC(18) |
| 144 | 1.72 | 0.01 | - | - | τ$CH_2$(82) |
| 141 | 0.01 | 0.03 | - | - | τ$CH_2$(77), τ(C=O)(13) |
| 134 | 0.01 | 0.97 | - | - | δCC(26), δCBr(24),δ$CH_2$(23) |
| 93 | 0.01 | 0.03 | - | 95 | τ$CH_2$(51), τ(C=O)(13) |
| 91 | 0.12 | 1.31 | - | - | δ(C=O)(22), δ$CH_2$(26) |
| 84 | 0.43 | 0.02 | - | - | τ$CH_2$(41) ,τ(C=O)(27) |
| 69 | 0.01 | 0.01 | - | - | τPhII(12), τCC(12) τ(C=O)(12),τPhI(14), γCC(14) |
| 66 | 3.13 | 0.01 | - | 66 | τPhII(16), τPhI(17), γCC(14) |
| 55 | 0.02 | 0.26 | - | - | δ$CH_2$(46), δ(C=O)(28), δCC(16) |
| 50 | 2.85 | 0.39 | - | - | τ(C=O)(30), τCC(30), τ$CH_2$(12) |
| 28 | 0.01 | 5.22 | - | - | τ(C=O)(34), τCC(29), τ$CH_2$(19) |
| 17 | 1.21 | 4.62 | - | - | τ$CH_2$(45),τ(C=O)(14), τCC(15) |
| 15 | 0.01 | 1.47 | - | - | δ$CH_2$(84), δ(C=O)(10) |
| 12 | 0.01 | 0.60 | - | - | τ$CH_2$(60),τ(C=O)(30) |

[a]υ-stretching; δ-in-plane deformation; γ-out-of-plane deformation; τ-torsion; $IR_I$-IR intensity(KM/Mole) ; $R_A$-Raman activity(Å$^4$/amu); the phenyl rings at C5 and C27 are designated as PhI and PhII.

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Table 3

PASS prediction for the activity spectrum of the1.7-bis(4-bromophenyl)heptane-1.7-dione (Pa represents probability to be active and Pi represents probability to be inactive)

| Pa | Pi | Activity |
|---|---|---|
| 0.936 | 0.003 | Feruloyl esterase inhibitor |
| 0.933 | 0.001 | Alkylglycerone-phosphate synthase inhibitor |
| 0.926 | 0.003 | Prolylaminopeptidase inhibitor |
| 0.918 | 0.005 | Aspulvinonedimethylallyltransferase inhibitor |
| 0.845 | 0.003 | L-glucuronate reductase inhibitor |
| 0.846 | 0.010 | Antineurotic |
| 0.840 | 0.005 | Arginine 2-monooxygenase inhibitor |
| 0.826 | 0.004 | Centromere associated protein inhibitor |
| 0.821 | 0.004 | Fatty-acyl-CoA synthase inhibitor |
| 0.823 | 0.013 | Mucomembranous protector |
| 0.812 | 0.009 | Nicotinic alpha6beta3beta4alpha5 receptor antagonist |
| 0.808 | 0.015 | Sugar-phosphatase inhibitor |
| 0.814 | 0.022 | Testosterone 17beta-dehydrogenase (NADP+) inhibitor |
| 0.782 | 0.007 | Bisphosphoglycerate phosphatase inhibitor |
| 0.776 | 0.005 | Phosphatidylserine decarboxylase inhibitor |
| 0.802 | 0.033 | Phobic disorders treatment |

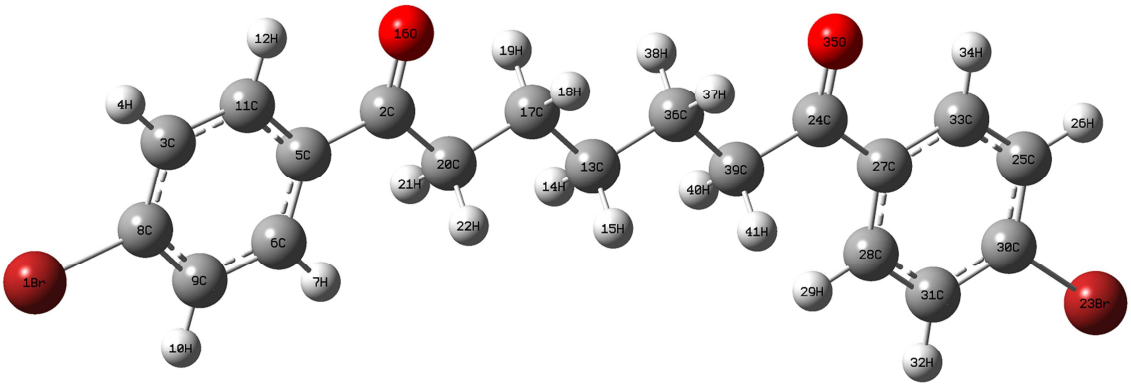
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Table 4

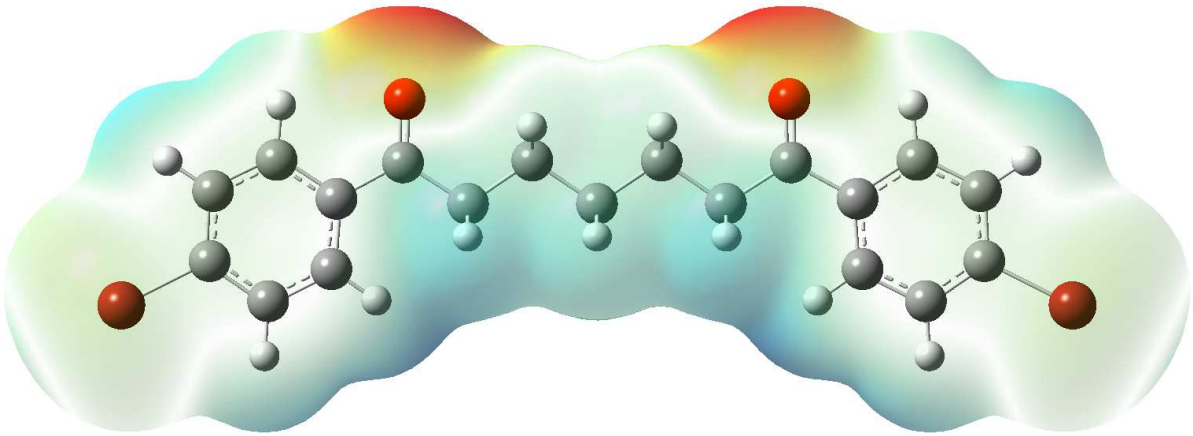
The binding affinity values of different poses of the 1,7-bis(4-bromophenyl)heptane-1,7-dionepredicted by Autodock Vina.

| Mode | Affinity (kcal/mol) | Distance from best mode (Å) | |
|---|---|---|---|
| - | - | RMSD l.b. | RMSD u.b. |
| 1 | -5.7 | 0.000 | 0.000 |
| 2 | -5.5 | 18.856 | 19.653 |
| 3 | -5.5 | 1.347 | 4.716 |
| 4 | -5.5 | 2.621 | 4.743 |
| 5 | -5.5 | 11.763 | 13.521 |
| 6 | -5.4 | 2.282 | 4.146 |
| 7 | -5.4 | 2.929 | 6.059 |
| 8 | -5.3 | 3.144 | 6.394 |
| 9 | -5.3 | 3.368 | 5.280 |

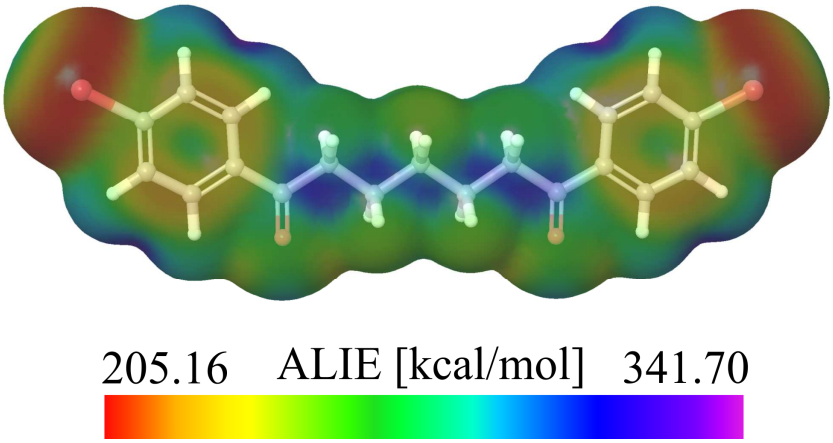
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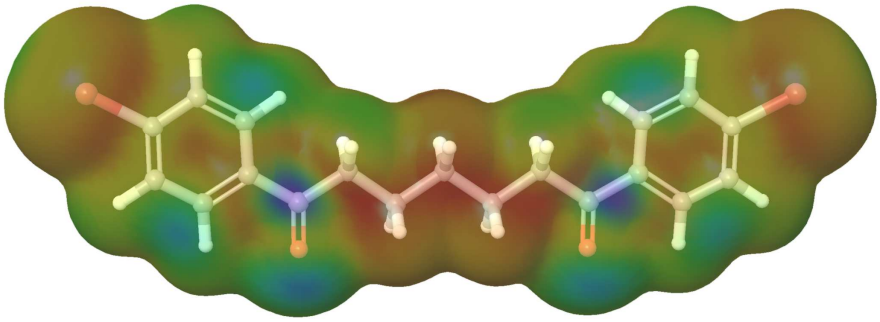


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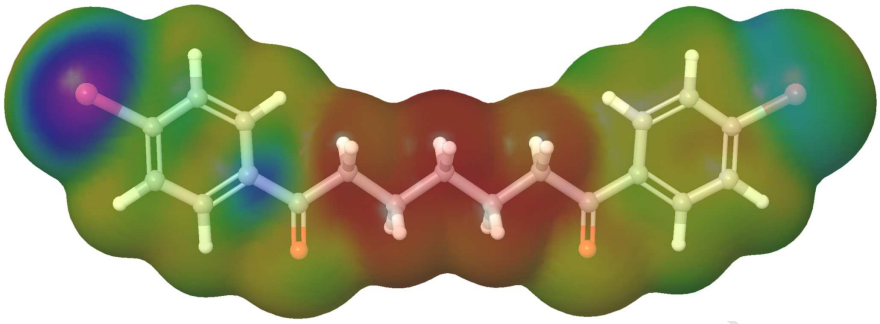



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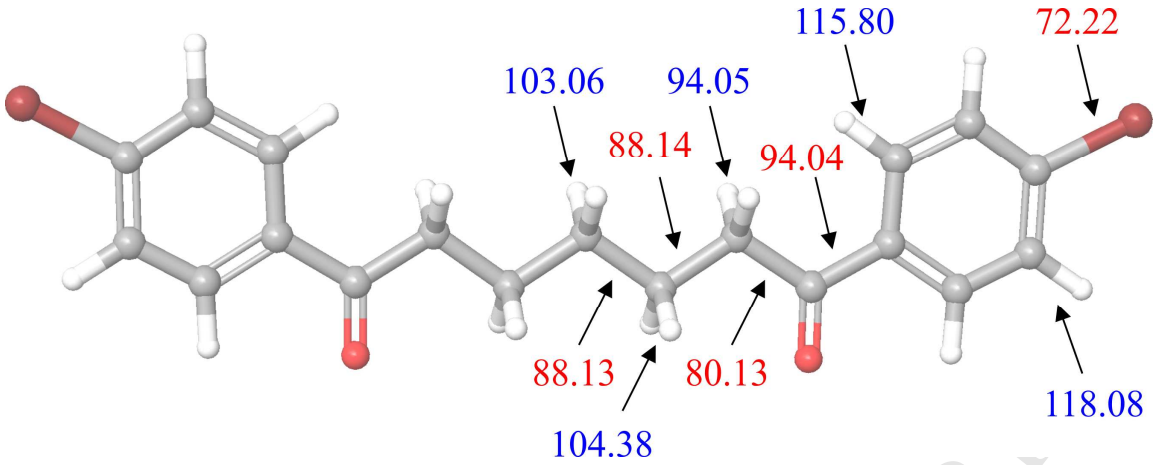
a)



b)

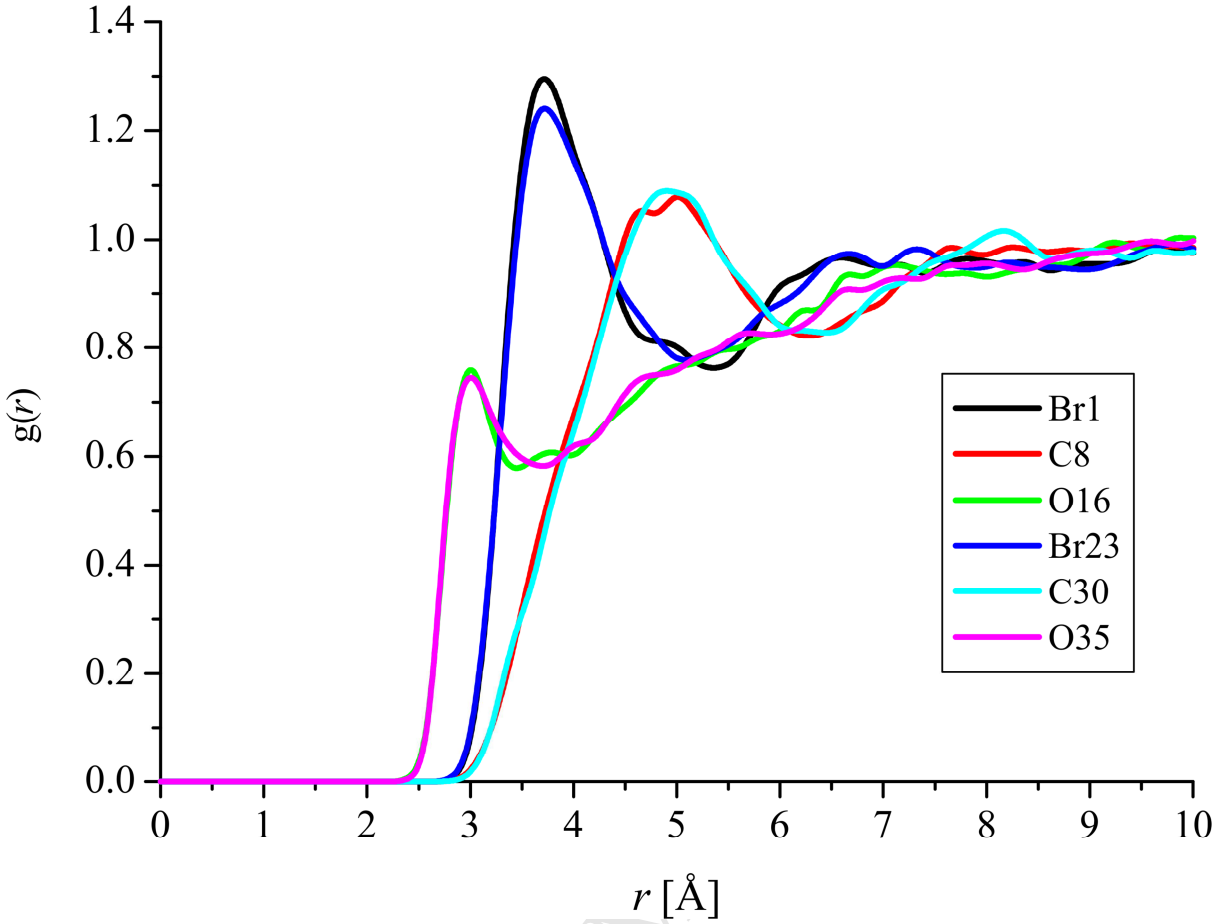


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- Single crystal XRD is reported
- Most reactive sites are identified
- Studied NLO properties, MEP and NBO
- Molecular docking studies have been discussed

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# Formulations and Analytical Method Developments for Poor Soluble Drugs: A Review on Applications of Nano Chemistry

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**Abstract-** In this review, various approaches for nano-formulations for poor soluble and low permeable drugs are focused, advantages and future scope for the nono formulations in pharmaceutical industries are elaborated. For the manufacture of new medicines new manufacturing technology is needed. In the pharmaceutical formulations pellets dosage forms gives the improved results compare to tablet dosage forms. According to ICH BCS (BIOPHARMACEUTICS CLASSIFICATION SYSTEM) drugs class four, Low solubility, Low permeability drugs. Improved use of Low solubility, Low permeability drugs pelletized formulation at Nano level is proposed. Nano level pelletized drug formulations gives the better results compared to normal, micro level pelletized drug formulations.

**Key words-** Analytical method development, Nano-formulation, and Nano-chemistry

## 1. INTRODUCTION

Our daily life is depends on quality of the food we eat, the medicine we use the water we drink, and the air we breathe. The compound which is interacts with a biological organism to produce a biological response that may be favorable or harmful. Favorable is known as medicine, harmful is known as poison. Due to expressed development in the field of science and technology new medications are rapidly coming in to the market for new syndrome. For the manufacture of new medicines new manufacturing technology is needed. In the pharmaceutical formulations pellets dosage forms gives the improved results compare to tablet dosage forms. These dosage forms summarized in terms of safety, purity, efficacy and stability. Final pharmaceutical pellets dosage forms comprises an active pharmaceutical ingredient (API) combined with a varying number of excipients. Some of the Active pharmaceutical ingredients are Low solubility, Low permeability nature (BCS class four). To overcome the low solubility, low permeability problem we are proposing nano level formulations methodology. Very few researchers are worked on the Nano technology applications for drug molecules, even though not related to Nano pelletized formulations. Nano pelletized formulations gives the improved results in controlling of various types of diseases compare to normal, micro level formulations. Due to this reason we are concentrating on nano level pelletized formulations, and its analytical method development. Our ultimate aim is "Best medication for Healthier world" with lesser price.

## 2. OBJECTIVES

- Our daily life is mainly depends on quality of the air, water, food medicine, without these we are unable to assume our life.
- The compound which is interacts with a biological system to produce a biological response that may be Beneficial is known as medicine, harmful is known as poison.
- Manufacturing of medicines are regulated by Food and Drug administration (FDA): International conference on harmonization (ICH): Current good manufacturing practices (cGMP): Pre-approval Inspections (PAIS): World health organization (WHO), ultimate aim is quality of medicines for healthier world.
- The pharmacopeias (USP, B.P, IP, and E.P) necessities for a pharmaceutical dosage form may be summarizing in terms of safety, purity, efficacy and stability.
- Final pharmaceutical formulations comprises an active pharmaceutical ingredient (API) combined with a varying number of excipients.
- The word "Pellet" describes a variety of systematically produced, geometrically defined agglomerates obtained from various starting materials utilizing different processing conditions.

- Pellets have various therapeutic advantages over traditional single units, such as tablets and powder-filled capsules.
- According to ICH BCS (BIOPHARMACEUTICS CLASSIFICATION SYSTEM) drugs class four, Low solubility, Low permeability drugs.
- Improved use of Low solubility, Low permeability drugs pelletized formulation at Nano level is proposed.
- Nano level pelletized drug formulations gives the better results compared to normal, micro level pelletized drug formulations.
- In house Analytical methods have to be developed and validated for the Analysis of nano level drug formulations.
- Our ultimate aim is to produce the best medicines for healthier world with lesser cost.

## 3. IMPORTANCE OF THE PROPOSED AREA IN THE PRESENT CONTEXT

With the aim of producing "Quality medicines in low prices for healthier world", we are reviewing of Nano level pelletized formulations for low solubility, Low permeability drug materials. According ICH these are BCS (BIOPHARMACEUTICS CLASSIFICATION SYSTEM) drugs class four. Very lesser number of researchers doing the research work related to Nano technology applications to drugs formulations, but not doing pelletized formulations in Nano level. These formulations gives the effective medicines with lesser side effects compare to normal, micro level formulations. Nano level pelletized formulations advantages as follows.

- Solubility of the drugs can be increases.
- Permeability of the drug in biological matter can be increases.
- Lesser amount of drug dosage is required to control the disease.
- Side effects are less compare to normal and micro level drug dosage formulations.
- Consumption of drugs dosage frequency is less.

Due to above advantages proposed Review i.e Nano level Pelletized formulations place important role in invention of Medicines.

The compound which is interacts with a biological organism to produce a biological response that may be favorable or harmful. favorable is known as medicine, harmful is known as poison. for example, penicillin reacts with bacterial cause to kill them.

Penicillin

Penicillin is a medicine for Humans due to it interacts with bacteria and kills them. In case of bacteria it is a (biological system) poison.

The articulated development in the field of science and technology utilized as on date merged with relatively stringent new regulations, namely federal drug authority, latestly called as food and drug administration (FDA):International conference on harmonization (ICH): Current good manufacturing practices(cGMP): Pre-approval Inspections(PAIS):World health organization(WHO), like organizations are now serving as a legal binding specifically for the pharmaceutical formulations and drug analysis.

## 4. ROLE OF API'S IN DRUG FORMULATIONS

APIs are core active substances mixed with a carrier in any medication. When any of the active substance is not easily absorbed by the human body; the substance is dissolved into or mixed with an excipient so that the human body easily receives it. Further these actives are used as medications.

4.1. According to ICH BCS (BIOPHARMACEUTICS CLASSIFICATION SYSTEM) drugs class four, Low solubility, Low permeability drugs. Consider example for API(Active pharmaceutical Ingredient)

- ACECLOFENAC ($C_{16}H_{13}Cl_2NO_4$), chemically [(2-{2, 6-dichlorophenyl) amino} phenylacetooxyacetic acid],
- Acyclovir (ACV): It also known as acyclovir is an antiviral medication. It is primarily used for the treatment of virus infections, chickenpox, and shingles.

*4.2. Pellets*

The word "Pellet" has been used to exemplify a variety of systematically produced, geometrically defined agglomerates obtained from various starting materials utilizing different processing conditions. Pellets range in size, typically, between 0.5 – 2.0 mm, though other sizes could be prepared.

4.3. Low solubility, Low permeability drugs pelletized formulations in Nano level, are useful as better medications for various types of diseases. Very few researchers did the work on Nano technology applications for drug molecules, even though not related to Nano pelletized formulations. So we are concentrating on the Nano level pelletized formulations for BCS drugs class four. These

formulations are use full for the society to control the various types' diseases with lesser side effects. Our ultimate aim is "Best medication for Healthier world" with lesser price.

*4.4. Analytical Method Development:* In house Analytical method is useful for the Analysis of Nano level formulated drugs to check the dissolution profile, Assay, stability of the various dosage forms; the method must be validated according to ICH guidelines, Parameters for approval

## 5. RESEARCH AND DEVELOPMENT IN THE SUBJECT

Review subject, Nano level pelletized formulations, literature reveals that

- Nano suspension drug delivery system (DDS) was firstly developed in 1994 for the poorly soluble drugs.
- Pharmaceutical medicinal products "curcumin nano crystal" have a significant role in treatment of various types diseases such as cancers of pancreas or colon or even multiple myeloma, psoriasis or myelodys plastic syndromes (Goel et al., 2008., Liu et al., 2013).
- In recent times all drugs with low solubility like curcumin can be approached by Nano crystal methods,
- One more important study in the field of Nano-formulated curcumin was done by Agarwal et al in 2007 (Garodia et al., 2007). In a study, curcumin was encapsulated with more than 97.5% potency in PLGA and PEG. It has been proved that nano-formulated curcumin represents more efficacy and faster cellular uptake than free curcumin in vitro.

Literature survey reveals that very lesser number of researchers did the work on Nano level pelletized formulations, but it reveals that excellent scope is present on this work because advantages are more on Nano level pelletized formulations

## 6. CONCLUSION

In order to be classified as a "nano pharmaceutical", we suggest the drug product has to meet two major criteria. First, nano engineering has to play a major role in the manufacturing process. Second, the nano material used has to be either essential for the therapeutic activity or has to confer additional and unique properties to the active drug entity. Above literature reviles that Worldwide very less research work is going on Nano level pelletized formulations.

Nano level pelletized drug formulations gives the better results compared to normal, micro level pelletized drug formulations.

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# HPLC METHOD FOR DTERMINATION OF IMPURITY PROFILE IN IBUPROFEN 200MG AND METHOCARBAMOL 500MG CAPLETS

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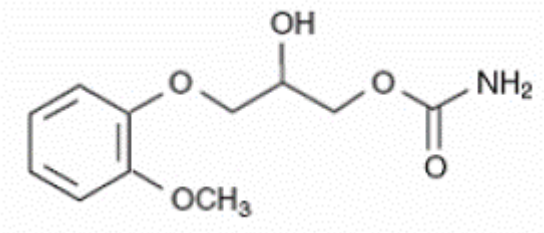
1. Associate professor, Department of H&S, K.G Reddy engineering college.2. Professor, Department of chemistry Bapatla college of Arts and Science, 3.Assistant professor, Department of H&S.

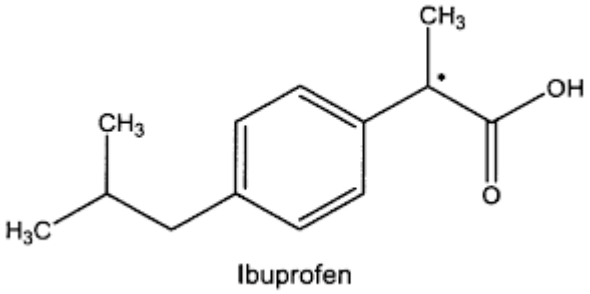
ABSTRACT: Methocarbamol and Ibuprofen caplet is combination product of two medications. It is used for to relieve pain associated with muscle spasm such as strains and sprains, back pain, and tense neck muscles. Methocarbamol belongs to a class of medications called muscle relaxants and they reduce muscle spasms. Ibuprofen belongs to a class of medications called nonsteroidal anti-inflammatory drugs (NSAIDs) that reduce pain and inflammation. This medication may be available under multiple brand names and/or in several different forms. This medication consists of related substances (impurities) β-Isomer, Guaifenesin, Dioxylonone, 2-(4-Isobutyryl phenyl) propionic acid. HPLC gradient method is developed for the determination of related substances (individual impurities and Total impurities). Detector wavelength is 220nm.we can obtained good results.

**Important words:** Methocarbamol, Ibuprofen, Muscle spasm, Non-steroidal anti-inflammatory, HPLC, Gradient method, wavelength.

**INTRODUCTION:** Methocarbamol and Ibuprofen caplet is combination product of two medications is used for to relive pain associated with muscle spasm such as strains and sprains, back pain, and tense neck muscles. This combination product contains various related substance (impurities), these are β-Isomer, Guaifenesin, Dioxylonone, 2-(4-Isobutyryl phenyl)prop ionic acid. To determine these related substances (impurities) high performance liquid chromatography, gradient method is developed. It is as follows

**Structures of Methocarbamol and Ibuprofen**




Ibuprofen

**Methodology:** High performance liquid chromatography, gradient method for related substance is developed. For this used

### Reagents:

Acetonitrile HPLC grade, Potassium dihydrogenate phosphate-AR grade, Orthophosphoric acid-AR grade

**Chromato graphic system:**

**Column:** C18, 150×4.6mm, 5µm(Devolosil ODS or equivalent)

**Detector wave length:** 220 nm

**Injection volume:** 10µl

**Runtime:** 50 minutes

**Flow rate:** 1.0ml/min

| Time(minutes) | Solution A | Solution B |
|---|---|---|
| 0.01 | 90 | 10 |
| 10 | 75 | 25 |
| 15 | 40 | 60 |
| 20 | 40 | 60 |
| 25 | 90 | 10 |
| 50 | 90 | 10 |

### Preparation of solutions:

**0.1M Potassium dihydrogen ortho phosphate preparation:** Transfer 13.6 g of potassium dihydrogen orthophosphate in 1000 mi of water.

**0.1M orthophosphoric acid preparation:** Transfer 6.5 ml of orthophosphoric acid in 1000 ml of water

### Mobile phase preparation:

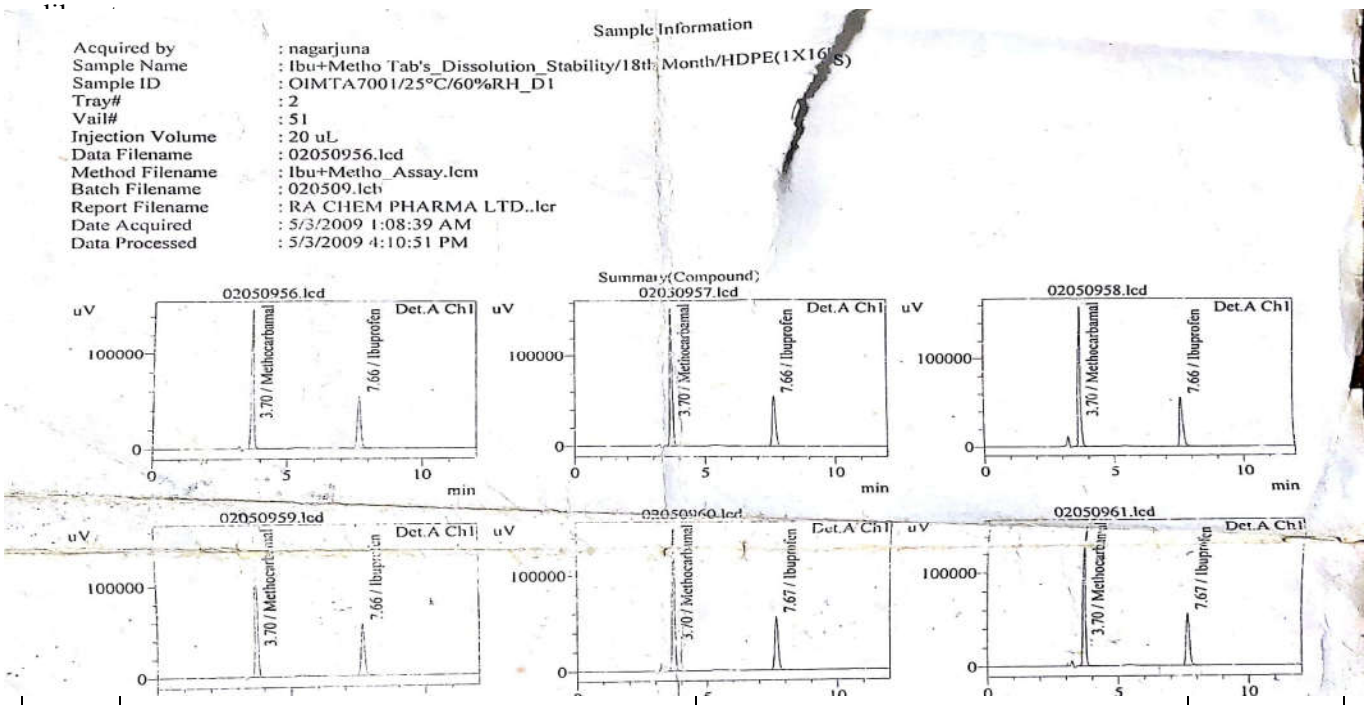
**Solution A:** To 800 ml of 0.1M potassium dihydrogen orthophosphate add 100 ml of 0.1M orthophosphoric acid,100 ml acetonitrile and mix well. Adjust the pH of the solution to 3.2 with diluted orthophosphoric or triethyl amine .Filter and degas the solution with 0.45µ filter paper.

**Solution B:** Acetonitrile

**Diluents'**: Mix 500 ml of solution A and 500 ml of Solution B

**Standard solution preparation :** Transfer 50 mg of Methocarbamol WS and 20 mg of Ibuprofen WS into a 10 ml volumetric flask add 2 ml of methanol solution and dissolve and make up to volume with

methanol. Transfer of this solution in to 100 ml volumetric flask and make up to the volume with diluents and transfer 5 ml of the resulting solution in to a 50 ml volumetric flask and make up to the volume with




| | | | |
|---|---|---|---|
| 1 | B-Isomer | 0.74 | 0.82 |
| 2 | Guaifenesin | 0.85 | 0.78 |
| 3 | Dioxylonone | 1.84 | 1.00 |
| 4 | 2-(4-Isobutyryl phenyl)propionic acid | 2.01 | 3.23 |
| 5 | methocarbamol | 1.00 | - |
| 6 | Ibuprofen | 2.45 | |

## Calculation:

For β –Isomer:

$$\frac{Area\ of\ \beta\ Isomer\ in\ sample\ solution}{Area\ of\ methocarbamol\ in\ stand\ solution} \times 0.1 \times 0.82$$

For Guaifenesin:

$$\frac{Area\ of\ Guaifenesin\ in\ sample\ solution}{Area\ of\ methocarbamol\ in\ stand\ solution} \times 0.1 \times 0.78$$

For Dioxylonone:

$$\frac{Area\ of\ Dioxylononein\ sample solution}{Area\ of\ methocarbamol\ in\ stand\ solution} \times 0.1 \times 1.00$$

For 2-(4-Isobutyryl phenyl )propionic acid

$$\frac{Area\ of\ 2-(4-Isobutyryl\ phenyl)propionic\ acid\ in\ sample\ solution}{Area\ of\ Ibuprofen\ in\ stand solution} \times 0.1 \times 3.23$$

For single maximum unknown impurity

$$\frac{Area\ of\ single\ maximum\ un\ known\ impurity\ tn\ sample\ solution}{Area\ of\ methocarbamol\ in\ standard\ solution} \times 0.1 \times 1.00$$

For Total unknown impurities

$$\frac{Area\ of\ Total\ un\ known\ impurities\ in\ sample\ solution}{Area\ of\ methocarbamol\ in\ standard\ solution} \times 0.1 \times 1.00$$

## Total impurities:

Sum of impurity content of β- isomer +Dioxylonone +Guaifenesin +2-(4-Isobutyryl phenyl) Propionic acid +Total un known impurities

**Conclusion:** The proposed method has been found to be better results than previously reported methods, because of its readily available mobile phase, low retention time (tR) and no internal standard. All these factors make this method suitable for quantification of impurities in Methocarbamol and Ibuprofen in pharmaceutical dosage forms without interference and can be successfully used for routine analysis. It can therefore be concluded that it can be used in small laboratories with very high accuracy.

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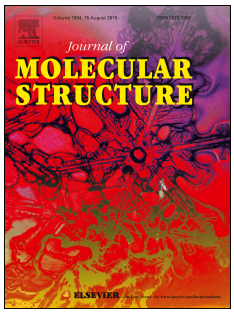
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# Accepted Manuscript




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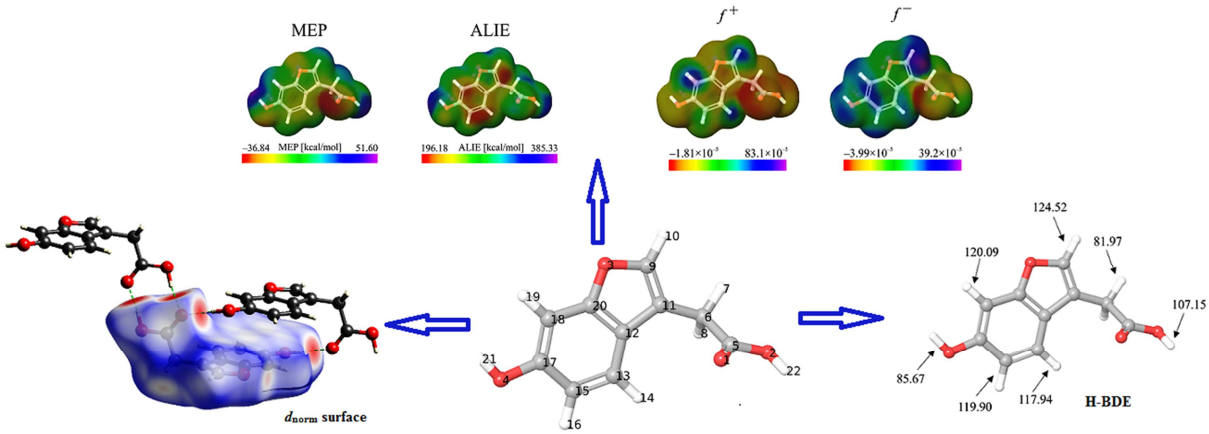
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ACCEPTED MANUSCRIPT

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# Structural and spectroscopic characterization, reactivity study and charge transfer analysis of the newly synthetized 2-(6-hydroxy-1-benzofuran-3-yl) acetic acid

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**Abstract**

The title compound 2-(6-hydroxy-1-benzofuran-3-yl) acetic acid (abbreviated as HBFAA) has been synthetized and characterized by FT-IR, FT-Raman and NMR spectroscopic techniques. Solid state crystal structure of HBFAA has been determined by single crystal X-ray diffraction technique. The crystal structure features O-H···O and C-H···O intermolecular interactions resulting in a two dimensional supramolecular architecture. The presence of various intermolecular interactions is well supported by the Hirshfeld surface analysis. The molecular properties of HBFAA were performed by Density functional theory (DFT) using B3LYP/6-311G++(d,p) method at ground state in gas phase, compile these results with experimental values and shows mutual agreement. The vibrational spectral analysis were carried out using FT-IR and FT-Raman spectroscopic techniques and assignment of each vibrational wavenumber made on the basis of potential energy distribution (PED). And also frontier orbital analysis (FMOs), global reactivity descriptors, non-linear optical properties (NLO) and natural bond orbital analysis (NBO) of HBFAA were computed with same method. Efforts were made in order to understand global and local reactivity properties of title compound by calculations of MEP, ALIE, BDE and Fukui function surfaces in gas phase, together with thermodynamic properties. Molecular dynamics simulation and radial distribution functions were also used in order to understand the influence of water to the stability of title compound. Charge transfer between molecules of HBFAA has been investigated thanks to the combination of MD simulations and DFT calculations.

**Key words**: Benzofuran; SCXRD; RDF; BDE; ALIE; Charge transfer analysis.

## 1. Introduction

2-(6-hydroxy-1-benzofuran-3-yl) acetic acid is a derivative of the privileged benzofuran core [1], is one of the key structural units because of its diverse biological profile [2]. The motif is

ubiquitous in natural products, bioactive active compounds and other pharmaceutical interest molecules [3-5]. For the past years, the privileged benzofuran core and its derivatives have attracted the interest of researchers from medicinal and synthetic chemistry due to their assorted biological applications including anticancer [6], antiviral [7], anti-Alzheimer's [8], immunomodulatory, anti-inflammatory [9], antitubercular [10], antidiabetic [11], antidepressant [12] andanalgesic activities [13]. Apart from pharmaceutical applications, the benzofuran derivatives also have important application in the field of dyes [14], polymer chemistry [15] and silver photography [16].

Benzofuran derivatives have been studied extensively; previous studies report the crystal structure, experimental and theoretical aspects. Recently, Gowda et al., reported the crystal structure of 2-(5-methoxy-1-benzofuran-3-yl) acetic acid [17]. Lee et al., reported the crystal structure of 2-(5-ethyl-3-methylsulfanyl-1-benzofuran-3-yl) acetic acid [18]. Yamato et al., reported synthesis, structural properties, electrophilic substitution reactions and DFT computational studies of calix[3]benzofurans using B3LYP/6-31G(d) method [19]. Aruna Kumar et al., carried out synthesis, crystal structural analysis along with detailed vibrational analysis of 1-benzofuran-2-carboxylic acid with in density functional theory [20].

The importance and applications of benzofuran scaffolds taking into account we endeavour synthesis, Hirshfeld surface analysis, and detailed experimental spectroscopic characterization of the 2-(6-hydroxy-1-benzofuran-3-yl) acetic acid (HBFAA) molecule, along with computational study by DFT. According to the best of our knowledge, an assignment of the vibrational spectrum of HBFAA with help of accurate DFT/B3LYP quantum calculation has not been reported. Along with frontier orbital analysis, NBO analysis, NLO calculations and Mulliken atomic charge analysis of the investigated compound calculated by using B3LYP/6-311++G(d,p) basic set in the ground state. And also efforts were made in order to understand global and local reactivity properties of investigated molecule by calculations of MEP, ALIE, BDE and Fukui function surfaces in gas phase. As well as analysis of charge transfer rates between title molecules investigated by Marcus semi-empiric approach. Taking into account that biological important molecules such as HBFAA represent great threat to water resources [21-26], we have also studied sensitivity of HBFAA towards autoxidation and hydrolysis, in order to gain vision into its possible degradation properties.

## 2. Experimental

### 2.1. General remarks

Infra-red spectrum was recorded using KBr pellets on JASCO FT-IR 4100 spectrometer in the range of 4000 – 400 $cm^{-1}$ at resolution of ± 2 $cm^{-1}$. The FT-Raman spectrum was recorded on LabRam HR800 Raman Spectrometer with spectral resolution 0.3 $cm^{-1}$ with a 10mW internal excitation source of laser wavelength 532 nm. $^{1}$H-NMR spectrum was recorded on a JEOL-400 MHz NMR instrument using DMSO-$d_6$ as solvent with chemical shifts being reported as δ units relative to TMS.

### 2.2. Synthesis

**Step-1:** Add resorcinol (5.0 g, 0.045 mmol) to conc. $H_2SO_4$ (25 mL) at 0$^{o}$C. After complete solubility of resorcinol, chloroethylacetoacetate (8.22 g, 0.049 mmol) was added drop by drop and then the reaction mixture was stirred for 24 hours at room temperature. After completion of reaction, the reaction mixture was poured into crushed ice, solid was filter and

washed with water followed by dried in vacuum. The product was recrystallized from ethyl acetate (3.5 g, yield: 70%, purity: 90%).

**Step-2:** Take 4-(chloromethyl)-7-hydroxy-2*H*-chromen-2-one (0.5 g, 2.38mmol) in round bottomed flask, to this add 10% NaOH solution (10 mL) and then the reaction mixture was refluxed for 4 hours. After completion of the reaction, the reaction mixture was poured into ice cold 10% HCl solution. The solid was filter and dried in vacuum to get 2-(6-hydroxy-1-benzofuran-3-yl) acetic acid as off white solid (0.45g, yield: 90%, purity: 96%)(Scheme1)[27].

Suitable crystals for X-ray diffraction studies were obtained by slow evaporation crystal growth technique at room temperature using ethyl acetate as solvent.

**2.3. X-ray Crystallography**

The unit cell parameters and the intensity data at 298K for the title compound was obtained on an Oxford Diffraction Xcalibur Gemini single crystal X-ray diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The CrysAlisPro software [28] was used for data collection, reduction and absorption correction.

The structure of the title compound was solved by direct methods and refined on $F^2$ by full-matrix least-squares procedures. The non-hydrogen atoms were refined using anisotropic thermal parameters. The hydrogen atoms were included in the structure factor calculations at idealized positions using a riding model. Structure solution and refinement were performed using SHELX-97 [29] programs available in the WinG-X package [30]. The Ortex6a [31] and Mercury [32] packages were used for molecular graphics. Crystallographic data and structure refinement are given in the Table1.

**2.4. Hirshfeld surface Analysis**

We examined molecular surfaces, packing of molecules in their crystal structure, highlighting the contribution of significant inter molecular interactions between molecules that are responsible for the molecular arrangement in the crystalline state through Hirshfeld surface analysis. Hirshfeld surfaces [33-35] and the related 2D fingerprint plots (FP) [36-38] are unique for any crystal structure and provide a quantitative measure of the intermolecular interactions on the surface [33, 39]. The Hirshfeld surface analysis and finger print plots of HBFAA was generated by using Crystal Explorer 3.0 software [40] which accepts structure input file in the CIF format. When the cif files were uploaded into the CrystalExplorer software, all bond lengths to hydrogen were automatically modified to typical standard neutron values i.e., C–H = 1.083 Å and N–H = 1.009 Å. The surfaces are mapped using a fixed color scale - red, white and blue, where red highlights contacts shorter than the sum of van der Waals (vdW) radii which is represented by negative sign values of $d_{norm}$, white for contacts around vdW separation with $d_{norm}$ values equal to zero, and blue for contacts longer than vdW sum with positive sign $d_{norm}$ values.

**2.5. Computational details**

All DFT calculations were performed with B3LYP hybrid exchange-correlation functional (three-parameter exchange functional of Becke B3 [41], combined with the Lee-Yang-Parr correlation functional LYP [42]) and with several different basis sets. DFT calculations were performed with Gaussian09 [43] and Jaguar 9.6 [44] programs. Geometrical optimization of the structure extracted from crystallographic information file was geometrically optimized with Gaussian09 program in the gas phase at B3LYP/6-311++G(d,p) level of theory. With

the same software and at the same level of theory, a vibrational analysis has been performed in order to assure that true ground state (characterized only by positive frequencies) has been obtained. The calculated wave numbers were scaled by a scaling factor of 0.9613 to obtain a better agreement with the experimental results [45]. The calculated frequencies were assigned by means of the potential energy distribution (PED) using VEDA4 program [46]. Gaussian09 program was also used for calculations of $^{1}$H-NMR chemical shifts, by using the GIAO approach, while the chemical shifts were calculated with reference to TMS. Further DFT single point energy calculations yielding MEP, ALIE, Fukui functions surfaces and BDE were performed with Jaguar program, with 6-311++G(d,p) basis sets for MEP and ALIE surfaces, 6-311+G(d,p) basis set for Fukui functions and 6-311G(d,p) basis set for BDE.

GaussView 5.0.8 [47] program was employed for preparation and manipulation of input/output files for calculations with Gaussian09 [43] program, while Maestro [48] GUI was employed for preparation and manipulation of input/output files for calculations with Jaguar 9.6 program.

MD simulation was performed with Desmond program [49-52] and with OPLS3 force field [49, 53-55]. The simulation time was 10 ns, while the cut-off radius was taken to be 10 Å. The system was of NPT ensemble class, modelled by placing of one HBFAA molecule into the cubic box with ~2500 water molecules. Simple point charge (SPC) model [56] was used for the modelling of solvent.

In order to investigate charge transfer between molecules of HBFAA, a combination of MD simulations and DFT calculations has been used. Charge transfer rates have been calculated for pairs of HBFAA from both crystal and amorphous phase. Pairs from crystal phase have been extracted from the corresponding crystallographic information file, while MD simulation has been used in order to simulate amorphous phase consisting of 64 molecules of HBFAA. The final snapshot of the MD simulation has been used in order to extract all possible pairs of HBFAA, considering pairs within the radius of 4 Å. For the obtained pairs, charge transfer rates have been calculated according to the Marcus semi-empiric approach [57, 58] which has been widely used for evaluation of optoelectronic properties of prospective molecular structures [59].

## 3. Result and discussion

### 3.1. Structure description

The title compound crystallizes in monoclinic, space group $P2_1/c$ with unit cell dimensions $a$ = 9.2532(14) Å, $b$ = 6.574(10) Å, $c$ = 14.033(2) Å, β= 91.115(15)˚ and Z = 4. *ORTEP* diagram of the title compound is shown in Figure S2. In the initial stage of packing, the molecules are connected into $R^2_2(8)$ dimers via a pair of $O_2$–$H_{22}\cdots O_1$ hydrogen bonds. The adjacent $R^2_2(8)$ synthons are connected via another dimeric $R^2_2(20)$ motifs via $O_4$–$H_{21}\cdots O_1$ hydrogen bonds, and thus, the two hydrogen bonds are bifurcated at the common acceptor $O_1$ atoms. The combined effect is to produce $C^2_2(14)$ chain that propagates parallel to the diagonal of the ab plane (Figure S3a). Further, in the crystal structure, C(5) chains of $C_{13}$-$H_{14}$…$O_3$ intermolecular interactions translate the molecule along the b axis (Figure S3b). The molecules related by 2-fold rotation are interlinked via $C_6$-$H_7\cdots O_2$ intermolecular interactions that link the molecules into C(4) chains along b axis (Figure S3c). The C(4) and C(5) chains together comprise a ribbon architecture running parallel to b axis (Figure S3d).

Thus, the structure overall displays two dimensional architecture. The geometric parameters for hydrogen bonds and other intermolecular contacts are listed in Table2.

**3.2. Optimized geometry**

The optimized geometrical parameters are compared with the XRD data are given in Table 3 and atom labelling is given in Fig. 1. The comparison of results indicate that most of the computational geometrical parameters are slightly more than that of experimental values, attributed to the fact that computational calculations are carried at for an isolated molecule in gas phase while the experimental results are of the molecules in solid state. The geometry of the solid state structure is subjected to intermolecular forces (Van der Waals interactions and crystal packing forces).

The C=O bond C5-O1 in the carboxylic group of the title compound has length of 1.201/1.208Å (DFT/XRD) while, the corresponding bond in the structure of similar reported derivatives has length C11-O2 = 1.217Å [60], C10-O2 = 1.216Å [61], C1-O1 = 1.223Å [62]. Similarly, the C-O bond length (C5-O2) of 1.359/1.304Å is in agreement with the reported values [60-62]. At C5 position the bond angles (DFT/XRD) are O2-C5-O1 = 122.7/123.1º, O2-C5-C6 = 110.3/112.1º and C6-C5-O1 126.9/124.8º. The asymmetry in the angles reveals the interaction between carbonyl and OH groups thereby supporting the existence of the intermolecular hydrogen bonding O2-H22...O1, O4-H21...O1 and C6-H7...O2. The interaction between O1 and H21 atoms and formation of intermolecular hydrogen bond O4-H21---O1 is evident from bond angles (DFT/XRD) O4-C17-C18 = 122.2/121.9º, C18-C17-C15 = 121.4/121.4º, C15-C17-O4 = 116.3/116.7º. The dihedral angle between the benzene ring and furan ring C18-C20-C12-C11 = 179.7º, C11-C12-C13-C15 = -179.6º, O3-C20-C12-C13 = -179.8º and C9-O3-C20-C18 = -179.7º shows good agreement with experimental values of -179.7, 179.1, 179.1 and – 179.8 respectively, and these values indicate that the two rings are planar. In the present case C-C bond lengths of benzene ring are in the range of 1.359-1.386Å and the calculated C-C bond lengths are in the range of 1.386-1.407Å and the values for similar derivatives are 1.371-1.394Å [60], 1.375-1.397Å [61] and 1.376-1.409Å [62]. For the furan ring of the title compound, the bond lengths (DFT/XRD) C9-O3 = 1.376/1.362Å, O3-C20 = 1.365/1.365Å are less than normal single C-O bond length of about 1.43 and the corresponding reported values of C-O bond length of similar derivatives are, 1.374, 1.375Å[60], 1.377, 1.377Å[61], 1.371, 1.377Å [62].

**3.3. Hirshfield surface analysis**

The 3D-Hirshfield surface analysis and 2D- finger print plots of HBFAA illustrated in Figure S4, shows surfaces that have been mapped over $d_{norm}$ (a), shape index (b) and curvedness (c) range of −0.750 - 1.083 Å, -1.0 - 1.0 and -4.0 - 0.4 Å. The investigated compound have dominant interaction between carboxylic acid O-H and oxygen atom (C=O) of carboxylic acid group leads to formation of $R^2_2(8)$ synthon, which can be visualized on Hirshfeld surface as the bright red areas marked with a and b, another dominant interaction between phenolic O-H and oxygen atom (C=O) of carboxylic acid group leads to formation of $R^2_2(20)$ synthon, which can be visualized on Hirshfeld surface as the bright red areas marked with c and d in Figure S4(A) and S4(B). The light red spot labelled as e represent weak C−H···O intermolecular interaction (Figure S4(A)). The $R^2_2(8)$ synthon and $R^2_2(20)$ synthon are formed by O-H···O hydrogen bonds, which are mapped on the $d_{norm}$ surface for visualizing the intermolecular contacts; the dotted lines represent the hydrogen bonds (Figure S4(B)).

In 2D fingerprint plots (Figure S4(C)), the O-H···Ointermolecular interactions appear as two distinct spikes (labeled as a and b) with almost equal length(Figure S4(C) are characteristics of nearly equal O(donor)···O(acceptor) distances leads to the formation of cyclic hydrogen-bonded $R^n_m(X)$ synthon. The upper spike marked as a in Figure S4(C) corresponds to the donor spike (H-atom of carboxylic acid group and phenolic group interacting with oxygen atom (C=O) of the COOH group), with the lower spike marked as b being an acceptor spike (oxygen atom (C=O) of carboxylic acid group interacting with the H-atom of carboxylic acid group as well as phenolic group).The wings encircled with red and black colour represents the C···H and H···H contacts (Figure S4(C)). It is evident that the H···H, O···H and C···H contacts can account for about 32.8%, 38.2% and 14.5% of the total Hirshfeld surface area. The other interactions are C···O, C···C, and O···O have only minor contribution.

**3.4. Vibrational assignments**

The calculated IR spectrum and Raman spectrum are shown (FigureS5 and S6) and assignments for each vibrational mode are given in Table4. In the following discussion, experimental values are compared with B3LYP/6-311G++(d,p) values, are good in agreement.

The carboxylic acid group is characterized by the -OH stretch, C=O stretch, OH out-of-plane deformation, C-O stretch and -OH in-plane deformation. The C=O stretching vibration mode observed as strong band in the region 1850-1550 $cm^{-1}$ [63]. In the present case C=O stretching vibration mode observed at 1750 $cm^{-1}$ in the IR spectrum, 1754 $cm^{-1}$ in the Raman spectrum and calculated value at 1753 $cm^{-1}$ high IR intensity and low Raman activity and with a PED 86%. The C(=O)O stretching mode coupled to OH in plane bending exhibits a band in the region 1250 ± 80 $cm^{-1}$, the B3LYP calculation give C-O stretching mode at 1280 $cm^{-1}$ and experimentally observed at 1282 $cm^{-1}$ (IR spectrum) and 1281 $cm^{-1}$ (Raman spectrum). The -OH in-plane deformation, coupled to the C-O stretching mode is expected in the region 1390±55 $cm^{-1}$ [63]and the band observed at 1312 $cm^{-1}$ in IR spectrum, 1317 $cm^{-1}$ in Raman spectrum and 1314 $cm^{-1}$ theoretically is assigned as the in-plane bending of -OH group which is not pure but contains contribution from other modes also. The deformation modes out-of-plane -OH, in-plane C=O and out of plane C=O are expected in the region 905 ± 65, 725 ± 95 and 595 ± 85 $cm^{-1}$, respectively [63, 64]. These bands are assigned at 909 $cm^{-1}$ (IR), 912 (Raman), 912 (B3LYP) and 617 (IR), 619 (Raman), 619(B3LYP) and 569 (Raman) and 571 (B3LYP), respectively. Ulahannan et al.,[65] reported the γ-OH mode at 926 $cm^{-1}$.

For the hydroxyl (-OH) group provides three normal vibrations; the stretching vibration, in-plane and out-of-plane deformations. The in-plane -OH deformation is expected in the region 1440 ± 40 $cm^{-1}$ [63]. The in-plane -OH deformation reported at 1429 $cm^{-1}$ in IR spectrum, 1428 $cm^{-1}$ in Raman spectrum, and at 1425 $cm^{-1}$ theoretically. For hydroxyl group -OH stretching vibration expected at 3380 ±200 $cm^{-1}$[63]. For title compound DFT calculations give OH stretching band at 3689 $cm^{-1}$ show PED 100% and a strong band observed at 3451 $cm^{-1}$ in the IR spectrum. The stretching of hydroxyl group aromatic moiety ν(C–O) appears at 1194 $cm^{-1}$ in the IR spectrum, 1196 $cm^{-1}$ in the Raman spectrum and the theoretical value is 1194 $cm^{-1}$ (B3LYP) this band is not pure, but contains significant contributions from other modes also and which is expected in the region 1220 ± 40 $cm^{-1}$ [66-68]. The out-of plane -OH deformation is observed at 617 $cm^{-1}$ in the IR spectrum, at 619 $cm^{-1}$ in the Raman spectrum and at 619 $cm^{-1}$ (B3LYP) theoretically, which is expected in the region 650 ± 80

$cm^{-1}$. Varghese et al., reported υ-OH at 3710 $cm^{-1}$ and δ-OH at 1332 $cm^{-1}$ theoretically and C–O stretching at 1245 $cm^{-1}$ in both IR and Raman spectra and 1242 $cm^{-1}$ theoretically [69]. For paracetamol, the C–O stretching mode and out-of-plane -OH are reported at 1240 and 620 $cm^{-1}$, respectively [70].

Compounds have one or more aromatic rings commonly exhibit multiple bands with weak to moderate in nature occur at above 3000 $cm^{-1}$ assigned as aromatic CH stretching vibrations [63, 64]. However, these bands are rarely useful because they overlap with one another bands resulting in stronger absorption in this region. The stretching vibrations bands observed at 3138, 3075, 3057, 3055 $cm^{-1}$ (B3LYP), 3073, 3065, 3054 $cm^{-1}$ (IR spectrum) and 3074, 3053 $cm^{-1}$(Raman spectrum)assigned as the νCH stretching modes for benzofuran ring. For aromatic CH in-plane and out-of-plane deformations are expected above and below 1000 $cm^{-1}$ [63, 64] and for in the present case, the bands assigned at 1250, 1242, 1194 $cm^{-1}$ (DFT), 1245, 1193 $cm^{-1}$ (IR spectrum), 1246, 1196, 1150 $cm^{-1}$ (Raman spectrum) (in-plane deformations) and at 912 $cm^{-1}$ (DFT), 909 $cm^{-1}$ (IR spectrum), 912 $cm^{-1}$ (Raman spectrum) (out-of-plane deformations).

For investigated compound, the phenyl ring C-C stretching modes are assigned at 1589, 1488, 1455, 1429, 1399, 1341 $cm^{-1}$ in the IR spectrum, 1581, 1508, 1487, 1444, 1427, 1392 $cm^{-1}$ in the Raman spectrum and at 1602, 1573, 1459, 1425, 1341 $cm^{-1}$ theoretically. The PED analysis gives ring breathing mode of PhI at 1041 $cm^{-1}$(DFT), 1040 $cm^{-1}$ (Raman spectrum) as expected [71] with a PED of 20% and low IR and Raman activity. According to literature [72, 73], the ring breathing mode of a polysubstituted phenyl ring is assigned at 1032, 1052 $cm^{-1}$ (DFT), 1025 $cm^{-1}$ (IR), 1027 $cm^{-1}$ (Raman) [72].

The vibrations of the $CH_2$ group, the asymmetric stretching ($\upsilon_{as}CH_2$), symmetric stretching ($\upsilon_sCH_2$), scissoring vibration, wagging, twisting and rocking appear in the region 3000 ± 50 $cm^{-1}$, 2885 ± 45 $cm^{-1}$ and 1445 ± 35 $cm^{-1}$, 1200-1100 $cm^{-1}$ and 1100-800 $cm^{-1}$ respectively [63, 66, 74]. The $CH_2$ vibrational modes of title compound are assigned at 2952 $cm^{-1}$ (DFT), 2950 $cm^{-1}$ (IR) , 2951 $cm^{-1}$ (Raman) (asymmetric stretching) and 2919 $cm^{-1}$ (DFT), 2917 $cm^{-1}$ (IR), 2917 $cm^{-1}$ (Raman) (symmetric stretching). In the present case, the scissoring mode of $CH_2$ observed at 1402 $cm^{-1}$ (IR), 1399 $cm^{-1}$ (Raman spectrum) and 1398 $cm^{-1}$ (DFT). The $CH_2$ wagging and twisting modes are assigned at 1341, 1167 $cm^{-1}$ (B3LYP), 1341, 1141 $cm^{-1}$ (IR), 1343, 1163 $cm^{-1}$ (Raman) respectively. The bands calculated at 912 $cm^{-1}$ are assigned as the rocking modes of $CH_2$.

### 3.5. $^1$H NMR spectrum

Precise prediction of molecular geometry measurement is necessary for reliable calculation of nuclear magnetic properties. Hence, after performing the full geometry optimization of title compound by DFT using B3LYP/6-311+G(d,p) basic set, chemical shift values computed by adopting Gauge-Independent Atomic Orbital (GIAO) approach [75, 76]. $^1$H-NMR spectrum provides information about the number of different types of protons and also the nature immediate environment to each of them. The experimental $^1$H-NMR spectrum of investigated compound recorded in DMSO-$d_6$ solvent with TMS as internal standard (Figure S7). The simulated nuclear magnetic spectra is computed by same method and calculated chemical shift values compile with experimental values, shows good in agreement (Table5). $^1$H NMR shows that aliphatic proton (7H and 8H) appeared in the upfield region at δ 3.591 ppm /3.47-3.58 ppm (experimental/ calculated). The signals of the aromatic proton were observed at in

range of δ 6.72-7.66 ppm, which are good in agreement with theoretical value of δ 6.68-7.34 ppm. The chemical shift values 14H in benzofuaran ring is calculated at δ 7.31 ppm which is good in agreement with the experimental value observed at δ 7.33 ppm and shows that the correlation between theoretical and experimental chemical shift values for title compound is good.

**3.6. Frontier Molecular Orbitals Analysis**

Electronic distribution and energy gap between highest occupied molecular orbitals (HOMO) and lowest molecular orbitals (LUMO), combination of these orbitals called as frontier molecular orbitals (FMOs) computed by DFT/B3LYP/6-311++G(d,p) method. The energy gap of HOMO and LUMO orbital reflect the biological activity, kinetic stability, chemical reactivity, Polarisability and hardness-softness of a molecule. The pictorial representation of HOMO-LUMO of the title compound shows (in Figure S8), it has continuous conjugation in it. The HOMO orbitals (electron donor) localized on $C_9$, $C_{11}$, $C_{15}$, $C_{17}$, $C_{18}$ aromatic carbon atoms, partially on phenolic –OH and aliphatic $–CH_2$ group, LUMO orbitals (electron acceptor) localized on $C_{11}$, $C_{12}$, $C_{15}$, $C_{15}$, $C_{17}$ aromatic carbon atoms and partially on phenolic –OH and aliphatic $–H_2C$-C=O group. The calculated energy value of HOMO (MO: 50) is -5.97 eV and LUMO (MO: 51) is -0.93 eV and the energy gap is 5.04 eV, it reflects that the stability whole molecule is appreciably high and less reactive. In order to understand the chemical reactivity of title compound, global reactivity parameters were calculated DFT method. Single point calculation was performed at DFT at 6-311++G(d,p) method. The difference in energies gave the vertical ionization potential (I) and vertical electron affinity (A) defined by equations, $I = E_{N-1} – E_N$, $A = E_N$-$E_{N+1}$, where $E_{N+1}$, $E_N$ and $E_{N-1}$ are the energies of the N+1, N and N-1 electron systems respectively [77, 78].The global chemical reactivity descriptors associated with title molecule are: ionization potential I = 7.7877 eV, electron affinity A = -0.3592 eV, electronegativity $\chi = (I+A)/2$ = 3.7142 eV, global hardness $\eta = (I-A)/2$ = 4.0734 eV, chemical potential $\mu = -(I+A)/2$ = -3.7142 eV and electrophilicity index $\omega = \mu^2/2\eta$ = 0.1227eV[79, 80].Electronic spectra of title compound calculated at TD-DFT/B3LYP/6-311++G(d,p) method and shown in Figure S9. In view of calculated absorption spectra, two absorption bands observed at 219 nm and 269 nm corresponding electron transitions from HOMO-1 to LUMO+1 and HOMO to LUMO, respectively. The transitions, wavelength, oscillator strength, CI coefficients can be seen in Table6.

**3.7. Local reactivity properties (MEP, ALIE and Fukui functions surfaces)**

Molecular electrostatic potential map (MEP) has been used to predict the reactive sites for electrophilic and nucleophilic attack, especially in studies of biological recognition and hydrogen bonding interactions [81, 82].The electrostatic interactions between receptor active sites and a molecule play an important role in determining its bio-reactivity. The molecular electrostatic potential V(r), at a given point r(x, y, z) in the vicinity of a molecule, is defined in terms of the interaction energy between the electrical charge generated from the molecule electrons and nuclei and a positive test charge (a proton) located at r.

Aside of the MEP, another frequently used quantum-molecular descriptor, very useful for the identification of molecule sites prone to electrophilic attacks, is average local ionization energy (ALIE). This descriptor is even better choice when it comes to the identification of molecule sites prone to electrophilic attacks and it is defined in the several papers by the group gathered around Peter Politzer[83-86].Both MEP and ALIE descriptors can be

visualized very intuitively, by mapping of their values to the electron density surface, Figure 2.

In Figure 2, red color marks the lowest values, while the purple color marks the highest values of MEP and ALIE. The electronegative (red) region is localized on the unprotonated atoms of $O_1$. However, the most electropositive region (blue-to-purple region) is located over the electron donating OH ($O_2$ and $O_4$) groups. Therefore, Figure 2 confirms the existence of an intermolecular $O_2$-$H_{22}$--$O_1$ and $O_4$-$H_{21}$--$O_1$ interactions. The value of the electrostatic potential is largely responsible for the binding of a substrate to its receptor binding sites since the receptor and the corresponding ligands recognize each other at their molecular surface [87].On the other side, the lowest ALIE values are located in the near vicinity of six-member and five-member rings, with the corresponding values of 196.18 kcal/mol. It can be seen, however, that ALIE surface doesn't recognize the unprotonated oxygen atom to be sensitive towards the electrophilic attacks. By comparison of MEP and ALIE surfaces in case of the HBFAA, it can be state that unprotonated oxygen atom of HBFAA is rich in electron density, however electron are tightly bound. Hydrogen atoms belonging to OH groups have been characterized by the highest MEP and ALIE values, and it can be expected that these atoms could have significant interactions with water, which will be investigated later.

Fukui functions have also been calculated, according to the finite difference approximation employed in the Jaguar program, and their values have been mapped to the electron density surface, similarly as in the case of MEP and ALIE values, Figure 3. Equations according to which Fukui functions have been calculated are as follows:

$$f^{+} = \frac{\left(\rho^{N+\delta}(r) - \rho^{N}(r)\right)}{\delta}, \tag{1}$$

$$f^{-} = \frac{\left(\rho^{N-\delta}(r) - \rho^{N}(r)\right)}{\delta}, \tag{2}$$

According to equations provided for Fukui functions it can be seen that Fukui $f^{+}$ function reflects the changes in electron density after the addition of the overall charge to the molecule. Oppositely, Fukui $f^{-}$ function reflects the changes in electron density after the removal of overall charge from the molecule.

The location of purple color in case of Fukui $f^{+}$ function indicates the locations where electron density increased after the addition of charge to the molecule HBFAA. It can be seen in Figure 3that such areas are located in near vicinities of hydrogen atoms attached to six-member and five-member ring. On the other side, negative color in the case of Fukui $f^{-}$ function indicates that electron density decreased in the near vicinity of unprotonated oxygen atom, marking it as a potentially important reactive site, same as in the case of MEP surface.

**3.8. NLO properties**

The NLO active materials receive much attention due to their various optoelectronic applications in the field telecommunication, optical mixing, optical phase conjugation and optical interconnection. For the title compound, the dipole moment, polarizability and first hyperpolarizability were calculated at DFT/B3LYP/6-311G++(d,p) (5D, 7F) basic set (listed in Table7) using Gaussian09W package and values are 0.6882 Debye, $10.7107 \times 10^{-24}$ esu and $4.49 \times 10^{-30}$ esu, respectively. The first hyperpolarizability of the title compound is 34.53 times

greater than that of standard NLO material urea [88].Therefore, the title compound is good candidates for future studies on NLO properties.

**3.9. NBO analysis**

The natural bond orbital (NBO) calculations were performed with NBO 3.1 program [89]which is implemented in the Gaussian09 package using B3LYP/ 6 -311++G(d,p) (5D, 7F) method which provides a convenient basis for investigation charge transfer or conjugative interactions in molecular system [90].

The second-order Fock-matrix was carried out to evaluate the donor–acceptor interactions. The interactions result in a loss of occupancy from the localized NBO of the idealized Lewis orbital into an empty non-Lewis orbital. For each donor (i) and acceptor (j) the stabilization energy (E2) associated with the delocalization i → j is determined as

$$E(2) = \Delta E_{ij} = q_i \frac{(F_{i,j})^2}{(E_j - E_i)} \quad (3)$$

$q_i$ → donor orbital occupancy;

$E_i$, $E_j$ → diagonal elements;

$F_{ij}$ → the off diagonal NBO Fock matrix element.

In NBO analysis largerE(2) value shows the intensive interaction between electron-donors and electron-acceptors, and greater the extent of conjugation of the whole system, the possible intensive interaction are given in Table 8 and 9. The second-order perturbation theory analysis of Fock-matrix in NBO basis shows strong intermolecular hyper conjugative interactions are formed by orbital overlap between n(O), and σ*(C-C), π*(C-C), σ*(O-C), π*(O-C), bond orbitals which result in ICT causing stabilization of the system. These interactions are observed as an increase in electron density (ED) in O-C and C-C anti bonding orbital that weakens the respective bonds. There occurs a strong inter molecular hyper conjugative interaction of $O_2$-$C_5$ from $O_1$ of $n_2(O_1)\rightarrow\sigma^*(O_2\text{-}C_5)$ which increases ED (0.10157e) that weakens the respective bonds $O_2$-$C_5$ leading to stabilization of 34.27 kJ/mol and also the hyper conjugative interaction of $C_5$-$C_6$ from $n_2(O_1)$ of $n_2(O_1)\rightarrow\sigma^*(C_5\text{-}C_6)$ which increases ED (0.07320e) that weakens the respective bonds $C_5$-$C_6$ leading to stabilization of 19.45 kJ/mol. There occurs a strong inter molecular hyper conjugative interaction of $O_1$-$C_5$ from $O_2$ of $n_2(O_2)\rightarrow\pi^*(O_1\text{-}C_5)$ which increases ED (0.20006e) that weakens the respective bonds $O_1$-$C_5$ leading to stabilization of 42.74 KJ/mol. There occurs a hyper conjugative interaction of $C_9$-$C_{11}$ from $O_3$ of $n_2(O_3)\rightarrow\pi^*(C_9\text{-}C_{11})$ which increases ED (0.23670e) that weakens the respective bonds $C_9$-$C_{11}$ leading to stabilization of 24.77 KJ/mol and also the hyper conjugative interaction of $C_{12}$-$C_{20}$ from $O_3$ of $n_2(O_3)\rightarrow\pi^*(C_{12}\text{-}C_{20})$ which increases ED (0.45633e) that weakens the respective bonds $C_{12}$-$C_{20}$ leading to stabilization of 25.90 kJ/mol. Again a hyper conjugative interaction of $C_{17}$-$C_{18}$ from $O_4$ of $n_2(O_4)\rightarrow\pi^*(C_{17}\text{-}C_{18})$ which increases ED (0.38606e) that weakens the respective bonds $C_{17}$-$C_{18}$ leading to stabilization of 27.63 kJ/mol. These interactions are observed as an increase in electron density (ED) in C-C and O-C anti bonding orbitals that weakens the respective bonds.

The electron density (ED) is transferred from the n(O) to the anti-bonding π* orbital of the C-C and O-C bonds. The hyper conjugative interaction energy was deduced from the second-order perturbation approach. Delocalization of electron density between occupied Lewis-type (bond or lone pair) NBO orbitals and formally unoccupied (anti bond or Rydberg) non-Lewis

NBO orbitals corresponds to a stabilizing donor-acceptor interaction. Hence the structure 2-(6-hydroxybenzofuran-3-yl)acetic acid is stabilized by these orbital interactions.

The NBO analysis also describes the bonding in terms of the natural hybrid orbital $n_2(O_1)$, which occupy a higher energy orbital (-0.28215 a.u) with considerable p-character (99.88%) and low occupation number (1.84362) and the other $n_1(O_1)$ occupy a lower energy orbital (-0.71498 a.u.) with p-character (41.21%) and high occupation number (1.97774). The NBO analysis also describes the bonding in terms of the natural hybrid orbital $n_2(O_2)$, which occupy a higher energy orbital (-0.35430 a.u) with considerable p-character (99.94%) and low occupation number (1.83167) and the other $n_1(O_2)$ occupy a lower energy orbital (-0.64576 a.u) with p-character (54.48%) and high occupation number (1.97781). The NBO analysis also describes the bonding in terms of the natural hybrid orbital $n_2(O_3)$, which occupy a higher energy orbital (-0.33746 a.u) with considerable p-character (99.94%) and low occupation number (1.74432) and the other $n_1(O_3)$ occupy a lower energy orbital (-0.58492 a.u) with p-character (62.47%) and high occupation number (1.97357). The NBO analysis also describes the bonding in terms of the natural hybrid orbital $n_2(O_4)$, which occupy a higher energy orbital (-0.33072 a.u) with considerable p-character (99.94%) and low occupation number (1.88100) and the other $n_1(O_4)$ occupy a lower energy orbital(-0.61369 a.u) with p-character (55.15%) and high occupation number (1.97904). Thus, a very close to pure (almost 100%) p-type lone pair orbital participates in the electron donation to the $\pi^*(C_{17}\text{-}C_{18})$ orbital for $n_2(O_4)\rightarrow\pi^*(C_{17}\text{-}C_{18})$, $\pi^*(C_{12}\text{-}C_{20})$ orbital for $n_2(O_3)\rightarrow\pi^*(C_{12}\text{-}C_{20})$ and $\pi^*(O_1\text{-}C_5)$ orbital for $n_2(O_2)\rightarrow\pi^*(O_1\text{-}C_5)$ interactions in the compound.

**3.10. Mulliken atomic charge analysis**

The Mulliken atomic charge values have been obtained by the Mulliken population analysis. The charge distribution on the molecule has an important role in the application of quantum chemical calculations, it helpful to describe the processes of electronegativity equalization and charge transfer in chemical reactions [91, 92],also to model of the electrostatic potential outside molecular surfaces [93-95].

The Mulliken population analysis in HBFAA molecule was computed using B3LYP/6-311++G(d,p) basic set and are listed in Table S10. Hydrogen atoms $H_{22}$, $H_{21}$ have maximum positive charge value -0.277 e and -0.262 e, respectively and other hydrogen atoms exhibit net positive charge its magnitudes between 0.143 e and 0.212 e. So, $H_{22}$, $H_{21}$hydrogen atoms have acidic in nature. The presence of more negative charge on oxygen atom ($O_1$, -0.247 e) and a net positive charge on hydrogen atom ($H_{22}$ (0.277 e), $H_{21}$ (0.262 e)) may also support the formation of$O_2$–$H_{22}\cdots O_1$ and $O_4$–$H_{21}\cdots O_1$ intermolecular hydrogen bonding in title compound.

**3.11. Temperature dependence of thermodynamic properties**

Thermodynamic parameters are very important for to obtain reliable relations among structural, energetic, and reactivity characteristics of the molecules. Density Functional Theory is a very well established and efficient tool to predict various statistical thermodynamic properties of the molecules.

The thermodynamic parameters dipole moment, thermal energy and zero point vibrational energies of HBFAA were calculated by using B3LYP/6-311++G (d,p) at 298.15 K and 1 atm pressure are listed in Table S11. Scale factors have been recommended [96] for a removal of anharmonicity effect and perfect predictions in determining the zero-point vibrational

energies, entropy (S), heat capacity (C) and the enthalpy changes (ΔH) in the temperature range 100–1000 K. The results are tabulated in Table S12 from analysis of results we can observed that thermodynamic parameters increase with respective rise of temperature due to molecular vibrational intensities increase with temperature [97].

**3.12. Sensitivity towards autoxidation mechanism and water**

In order to obtain a clearer picture of the local reactivity of molecule HBFAA, in this work we have also analysed sensitivity of title molecule towards the autoxidation mechanism, by DFT calculation of bond dissociation energies for hydrogen abstraction (H-BDE). Degradation is one of the most important mechanisms for the removal of toxic organic compounds [21, 23, 98, 99].In the same time, it is also known that oxidative reactions are highly important for the degradation of toxic organic compounds [100].Since there is a correlation between autoxidation mechanism and H-BDE, in this work we have decided to employ this approach in order to evaluate to what extent HBFAA could be sensitive towards autoxidation, Figure 4.

According to the results provided in Figure 4, it can be concluded that HBFAA could be highly sensitive towards autoxidation mechanism. Namely, if the H-BDE parameter takes values between 70 and 85 kca/mol, it indicates that the observed molecule could be highly sensitive towards autoxidation mechanism [101, 102]. In the same time, values between 85 to 90 kcal/mol could also be indicative of sensitivity towards autoxidation mechanism, however they should be taken with caution [102].HBFAA has two important locations, with respect to the values of H-BDE. Namely, H-BDE in cases of hydrogen atoms $H_6$ and $H_7$ is having values of ~82 kcal/mol, indicating sensitivity towards autoxidation mechanism. Additionally, hydrogen atom $H_{21}$, belonging to OH group, has the H-BDE value of ~86 kcal/mol, which also indicates possible sensitivity towards autoxidation.

Taking into account the importance of water in terms of resource which frequently accommodates organic pharmaceutical pollutants, in this work we have also calculated radial distribution functions (RDF) after MD simulation, with the purpose to identify atoms with the strongest interactions with water molecules. RDFs of atoms with significant interactions have been provided in Figure 5.

Results of RDF indicate that two hydrogen atoms belonging to OH groups have highly pronounced interactions with water molecules. Both of these hydrogen atoms have very sharp g(r) profiles, with their maximal g(r) values located at distance significantly lower than 2 Å. By comparing RDF of two hydrogen atoms it can be concluded that $H_{22}$ has slightly stronger interactions with water molecules, due to the fact that it's maximal g(r) value is significantly higher than maximal g(r) value of the $H_{21}$. Results presented in Figure 5 also indicate that autoxidation mechanism could hardly occur at the site of hydrogen atom $H_{21}$, as this atom has strong interactions with water molecules probably preventing oxidation at this site. Other atoms with relatively significant interactions with water molecules are oxygen atoms $O_2$ and $O_4$, with $O_4$ having slightly stronger interactions.

**3.13. Charge transfer**

Charge transfer between HBFAA has been investigated within the framework of Marcus semi-empiric approach. Within this approach, charge transfer rates can be calculated according to the following expression [57, 58]:

$$k_{ET} = \frac{4\pi^2}{h} \frac{1}{\sqrt{4\pi\lambda k_B T}} t^2 \exp\left[\frac{-\lambda}{4 k_B T}\right]. \quad (4)$$

In the last equation, $\lambda$ mark the reorganization energies of electrons ($\lambda_-$) and holes ($\lambda_+$), while *t* is the charge transfer integral which is in this work calculated in dimmer splitting approximation. Reorganization energies ($\lambda_i$, where *i* can be "–" or "+") have been calculated according to the following equations (4-6):

$$\lambda_1 = E^0(G^*) - E^0(G^0) \quad (5)$$

$$\lambda_2 = E^*(G^0) - E^*(G^*) \quad (6)$$

$$\lambda_i = \lambda_1 + \lambda_2 \quad (7)$$

In equations (4) – (7), $E^0(G^0)$ and $E^*(G^*)$ denote ground state energies of the neutral and ionic states, respectively, $E^0(G^*)$ denotes energy of the neutral molecule at the optimal ionic geometry and $E^*(G^0)$ denotes energy of the charged state at the optimal geometry of the neutral molecule. The aforementioned approach is widely used for evaluation of potential of molecules to be applied in the area of organic electronics [59].

Reorganization energies and average charge transfer rates of electrons and holes in crystal and amorphous phase have been summarized in Table 10. Average charge transfer rates have been obtained by summarizing charge transfer rates for all considered pairs and then dividing with the total number of considered pairs.

Results in Table 10 indicate that charge transfer rate of holes is one order of magnitude higher in comparison with charge transfer rate of electrons. It can be seen also that an average charge transfer rates are higher in the case when molecular pairs have been extracted from the amorphous phase in comparison with crystal phase, which is to be expected due to the higher amount of orbital overlap.

Figures 6.a-d contain molecular pairs of HBFAA taken from crystal phase, while molecular pair of HBFAA with the highest charge transfers from the amorphous phase has been presented in Figure 6.e. Corresponding charge transfer rates have been summarized in Table 11.

According to Table 11, it can be seen that the highest charge transfer rates in the case of pairs from crystal phase have been calculated for molecular pair illustrated in Figure 6b. Thus, it can be concluded that the highest orbital overlap occurs between OH group connected to benzene from one side and furan side chain from the other side. Concerning the amorphous phase and thanks to the illustration in Figure 6e, it can be stated that the highest orbital overlap occurred between atoms connected to benzene ring, i.e. mainly between OH groups.

## 4. Conclusion

The title compound 2-(6-hydroxy-1-benzofuran-3-yl) acetic acid was synthetized and characterized by FT-IR, FT-Raman, NMR and SCXRD techniques. SCXRD studies and Hirshfeld surface analysis shows the investigated molecule stabilised by O-H···O and C-H···O inter molecular interactions. The optimization of molecular structures, vibrational frequencies, frontier molecular orbitals, NLO and NBO analysis of investigated compound carried out using B3LYP/6-311++G(d,p) method. The complete analysis each vibrational mode were performed; results shows that good in agreement between experimental and

calculated vibrational modes. First order hyperpolarizability of HBFAA is 34.53 times greater than that of standard NLO material. Detailed study of local reactive properties has been performed by obtaining MEP, ALIE and Fukui function surfaces. MEP surface indicated the reactive importance of the unprotonated oxygen, while the lowest ALIE values were located in the near vicinities of benzene and furan rings. Fukui $f^+$ function indicated that electron density increases in the near vicinity of three hydrogen atoms when charge is added to the molecule, while Fukui $f^-$ function indicated that electron density decreased in the near vicinity of unprotonated oxygen atom in the case when charge is removed from the molecule. H-BDE values indicated that molecule HBFAA could be highly sensitive towards autoxidation mechanism at molecular sites of hydrogen atoms $H_6$ and $H_7$. On the other side, MD simulation and calculated RDFs indicated that hydrogen atoms $H_{21}$ and $H_{22}$ have very strong interactions with water molecules, which might be very important for understanding the stability of this molecule in water. The analysis of charge transfer rates enabled us to identify for which orientations of molecule HBFAA the highest charge transfer occurs.

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**Supplementary Material**

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1412028 and can be obtained free of cost on CCDC 12 Union Road, Cambridge CB21 EZ, UK. (Fax: (+44) 1223 336-033: e-mail: data_request@ccdc.cam.ac.uk).

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**Figure caption**

Fig.1.Optimized geometry of 2-(6-hydroxy-1-benzofuran-3-yl) acetic acid (HBFAA)

Fig. 2.MEP and ALIE surfaces of 2-(6-hydroxy-1-benzofuran-3-yl) acetic acid

Fig. 3.Fukui functions of molecule 2-(6-hydroxy-1-benzofuran-3-yl) acetic acid

Fig. 4.H-BDE values in the case of 2-(6-hydroxy-1-benzofuran-3-yl) acetic acid

Fig.5.RDF of 2-(6-hydroxy-1-benzofuran-3-yl) acetic acid

Fig. 6. a) to d) molecular pairs taken from crystal phase, e) molecular pair with the highest charge transfer rates taken from the amorphous phase.

**Tables**

Table 1.Crystallographic data and structure refinement for the title compound.

Table 2.Geometric parameters for hydrogen bonds and other intermolecular contacts operating in the crystal structure.

Table 3. Optimized geometrical parameters of title compound computed at B3LYP/ 6-311++G(d, p) basis sets.

Table 4. Calculated scaled wave numbers, observed IR, Raman bands and assignments of HBFAA.

Table 5. Experimental and theoretical $^{1}$H-NMR chemical shifts (ppm) of the title compound

Table 6. Excitations, CI expansion, energies coefficient (eV), wavelength λ (nm), and oscillator strengths (*f*)) of title compound calculated at TD-DFT/B3LYP/6311++G(d,p) method.

Table 7. The electric dipole moment (μ), polarizability (Δα) and first order hyper polarizability (β) of title compound by B3LYP/6-311G++(d,p).

Table 8.Second-order perturbation theory analysis of Fock matrix in NBO basis corresponding to the intra-molecular bonds of the title compound.

Table 9.NBO results showing the formation of Lewis and non-Lewis orbitals.

Table 10. Reorganization energies and average charge transfer rates ($k_{ET}^{e-}$ for electrons and $k_{ET}^{h+}$ for holes) of HBFAA in crystal and amorphous phases

Table 11. Charge transfer rates for molecular orientations provided in Figure 9.

**Supplementary material**

Scheme 1. Preparation of 2-(6-hydroxy-1-benzofuran-3-yl) acetic acid

Fig. S2.*ORTEP* view of the title molecule (thermal ellipsoids are drawn with 50% probability) with atom numbering scheme for non-hydrogen atoms (crystallography numbers are in brackets).

Fig.S3.Various modes of alignment of molecules in the crystal packing of 2-(6-hydroxy-1-benzofuran-3-yl) acetic acid.

Fig. S4. Hirshfeld surface and Finger print analysis of 2-(6-hydroxy-1-benzofuran-3-yl) acetic acid (HBFAA).

Fig. S5. Infra-Red spectrum of 2-(6-hydroxy-1-benzofuran-3-yl) acetic acid

Fig. S6. Raman spectrum of 2-(6-hydroxy-1-benzofuran-3-yl) acetic acid.

Fig. S7. $^{1}$H-NMR spectrum of 2-(6-hydroxy-1-benzofuran-3-yl) acetic acid.

Fig.S8. HOMO-LUMO plots of 2-(6-hydroxy-1-benzofuran-3-yl) acetic acid.

Fig. S9. Theoretical UV-Visible spectrum of 2-(6-hydroxy-1-benzofuran-3-yl) acetic acid

Table S10. Mulliken atomic charges of title compound calculated at 6-311++G(d,p)

Table S11. Thermo dynamical parameters of title compound calculated by B3LYP/6-311++G(d,p) method.

Table S12. Thermodynamic properties at different temperatures at the B3LYP/6-311++G (d,p) level for title compound.

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Table 1.
Crystallographic data and structure refinement for the title compound.

| | |
|---|---|
| Formula | $C_{10}H_8O_4$ |
| Formula weight | 192.16 |
| Wavelength(Å) | 0.71073 |
| Crystal system | Monoclinic |
| *a* (Å) | 9.2532(14) |
| *b* (Å) | 6.5740(10) |
| *c* (Å) | 14.033(2) |
| *β* (°) | 91.115(15) |
| Volume (Å$^3$) | 853.5(2) |
| Space group | $P2_1/c$ |
| *Z* | 4 |
| T(K) | 298(2) |
| Crystal size (mm$^3$) | 0.36 x 0.20 x 0.16 |
| $\rho_{calcd}$ (g cm$^{-3}$) | 1.495 |
| $\mu$ (mm$^{-1}$) | 0.117 |
| Tmin, Tmax | 0.870, 1.00 |
| $\theta$ range (°) | 2.90 – 25.00 |
| *h* / *k* / *l* indices | –10 / 11, –7/ 4, –16 /16 |
| Reflections collected | 3058 |
| Unique reflection, $R_{int}$ | 1500 [R(int) = 0.0387] |
| GooF | 0.985 |
| *R*1[$I > 2\sigma(I)$] | 0.0465 |
| *wR*2[all data] | 0.1156 |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.153 and -0.161 |

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Table 2
Geometric parameters for hydrogen bonds and other intermolecular contacts operating in the crystal structure.

| D – H ··· A | D − H (Å) | H···A (Å) | D···A (Å) | ∠D− H···A (°) | Symmetry |
|---|---|---|---|---|---|
| O2–H22···O1 | 0.89(2) | 1.74(3) | 2.622(2) | 172(3) | - |
| O4–H21···O1 | 0.86(2) | 2.02(2) | 2.883(2) | 176(2) | x, -1+y, z |
| C6–H7···O2 | 0.9700 | 2.5700 | 3.459(3) | 153.00 | 1+x, y, z |
| C13–H14···O3 | 0.9300 | 2.5900 | 3.515(2) | 176.00 | x, -1+y, z |

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Table 3

Optimized geometrical parameters of title compound computed at B3LYP/ 6-311++G(d, p) basis sets.

| | | | |
|---|---|---|---|
| Bond length (Å) (DFT/XRD) | | | |
| O1-C5 | 1.201/1.208 | O2-C5 | 1.359/1.304 |
| O3-C9 | 1.376/1.362 | O3-C20 | 1.365/1.365 |
| O4-C17 | 1.370/1.367 | C5 –C6 | 1.519/1.482 |
| C6 –C11 | 1.494/1.475 | C9 –C11 | 1.354/1.327 |
| C11-C12 | 1.448/1.429 | C12-C13 | 1.401/1.381 |
| C12 –C20 | 1.401/1.378 | C13 –C15 | 1.386/1.361 |
| C15–C17 | 1.407/1.386 | C17–C18 | 1.393/1.359 |
| C18 –C20 | 1.388/1.367 | | |
| Bond angle (°) (DFT/XRD) | | | |
| C9-O3-C20 | 106.0/105.3 | O1-C5-O2 | 122.7/123.1 |
| O1-C5-C6 | 126.9/124.8 | O2-C5-C6 | 110.3/112.1 |
| C5-C6-C11 | 114.6/114.4 | O3-C9-C11 | 112.3/113.0 |
| C6-C11-C9 | 126.6/127.3 | C6-C11-C12 | 127.7/127.2 |
| C9-C11-C12 | 105.6/105.5 | C11-C12-C13 | 136.0/135.8 |
| C11-C12-C20 | 105.5/106.2 | C13-C12-C20 | 118.3/118.0 |
| C12-C13-C15 | 119.0/118.9 | C13-C15-C17 | 120.8/121.2 |
| O4-C17-C15 | 116.3/116.7 | O4-C17-C18 | 122.2/121.9 |
| C15-C17-C18 | 121.4/121.4 | C17-C18-C20 | 116.2/116.2 |
| O3-C20-C12 | 110.3/109.9 | O3-C20-C18 | 125.6/125.7 |
| C12-C20-C18 | 124.0/124.3 | | |
| Dihedral angles (°) (DFT/XRD) | | | |
| C20-O3-C9-C11 | -0.05/1.0 | C9-O3-C20-C12 | 0.03/0.6 |
| C9-O3-C20-C18 | -179.7/-179.8 | O1-C5-C6-C11 | -6.6/-6.3 |
| O2-C5-C6-C11 | 173.8/173.9 | C5-C6-C11-C9 | 109.8/104.9 |
| C5-C6-C11-C12 | -71.6/-74.9 | O3-C9-C11-C6 | 178.8/179.0 |
| O3-C9-C11-C12 | 0.05/0.9 | C6-C11-C12-C13 | 1.0/0.4 |
| C6-C11-C12-C20 | -178.8/179.4 | C9-C11-C12-C13 | 179.8/-179.5 |
| C9-C11-C12-C20 | -0.02/-0.5 | C11-C12-C13-C15 | 179.6/179.1 |
| C20-C12-C13-C15 | 0.1/0.2 | C11-C12-C20-O3 | -0.003/-0.1 |
| C11-C12-C20-C18 | 179.7/179.7 | C13-C12-C20-O3 | 179.8/179.1 |
| C13-C12-C20-C18 | -0.1/-0.5 | C12-C13-C15-C17 | -0.1/-0.3 |
| C13-C15-C17-O4 | 179.8/179.3 | C13-C15-C17-C18 | 0.1/0.6 |
| O4-C17-C18-C20 | 179.9/179.5 | C15-C17-C18-C20 | -0.04/-0.9 |
| C17-C18-C20-O3 | 179.7/178.7 | C17-C18-C20-C12 | 0.04/0.8 |

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Table 4

Calculated scaled wave numbers, observed IR, Raman bands and assignments of HBFAA

| B3LYP/6-311++G(d,p) | | | ν(IR) | ν(Raman) | Assignments [a] |
|---|---|---|---|---|---|
| ν($cm^{-1}$) | IR intensity | Raman activity | ($cm^{-1}$) | ($cm^{-1}$) | - |
| 3689 | 73.78 | 135.93 | 3451 | - | υOH(100) |
| 3614 | 75.66 | 159.83 | - | - | υOH(100) |
| 3138 | 0.62 | 106.28 | - | - | υCH(99) |
| 3075 | 4.81 | 152.6 | 3073 | 3074 | υCH(15), υCH(84) |
| 3057 | 2.83 | 152.86 | 3065 | - | υCH(90) |
| 3055 | 9.75 | 22.54 | 3054 | 3053 | υCH(13), υCH(77) |
| 2952 | 3.52 | 65.41 | 2950 | 2951 | υasCH2(70) |
| 2919 | 14.13 | 137.48 | 2917 | 2917 | υsCH2(30) |
| 1753 | 273.06 | 7.45 | 1750 | 1754 | υC=O(86) |
| 1602 | 91.89 | 60.77 | - | - | υCC(22), υCC(17) |
| 1573 | 27.19 | 56.71 | 1589 | 1581 | υCC(29), υCC(17), υCC(14) |
| 1563 | 28.62 | 67.27 | - | - | υCC(31) |
| 1459 | 101.69 | 18.14 | 1455 | 1444 | υCC(20), δHCC(16) |
| 1425 | 12.79 | 6.11 | 1429 | 1427 | δOH(22), υCC(21), δHCC(13), δHCC(14) |
| 1398 | 25.41 | 7.72 | 1402 | 1399 | δCH2(86) |
| 1341 | 0.54 | 15.18 | 1341 | 1343 | υCC(21), υCC(11) |
| 1333 | 80.38 | 23.04 | | | υCC(11), τHCCC(13) |
| 1314 | 2.2 | 60.69 | 1312 | 1317 | δOH(), υCO(), δCCO(16) |
| 1280 | 5.7 | 39.42 | 1282 | 1281 | δOH(16), νCO(16), δHCO(10) |
| 1250 | 2.69 | 8.8 | 1245 | 1246 | υCO(19), δHCO(15), δHCC(15) |
| 1242 | 7.03 | 6.28 | 1245 | 1246 | δHCC(12), δOH(28) |
| 1194 | 55.29 | 5.26 | 1194 | 1196 | υCO(14), δHCC(21), δHCO(25) |
| 1167 | 9.91 | 17.29 | 1193 | | γCH2(34), τHCCC(24) |
| 1135 | 202.43 | 3.83 | 1141 | 1140 | υCC(13), δHOC(52) |
| 1119 | 59.76 | 12.67 | - | - | δHCC(16), δHCC(12), υCO(24) |
| 1105 | 14.41 | 3.85 | - | - | υCC(17),δHCC(50) |
| 1088 | 388.88 | 1.51 | - | | υCO(56),δHOC(22) |
| 1070 | 56.38 | 3.6 | - | | υCO(66) |
| 1041 | 18.18 | 10.75 | - | 1040 | Ring breathing mode |
| 924 | 22.18 | 4.09 | - | - | υOC(12), δOC(16), γCCC(24), γCCC(15) |
| 912 | 4.34 | 5.25 | 909 | 912 | γOH(25), γCH2(16),τHCCC(15), τHCCC(11), τHCCC(13), τOCOC(15) |
| 910 | 1.96 | 2.89 | - | - | τHCCC(24), τCCCC(10) |
| 840 | 2.18 | 10.17 | - | - | γCCC(10) |
| 798 | 41.12 | 0.35 | - | - | δCOC(11), τHCCC(16) |
| 793 | 39.89 | 1.25 | - | - | δCOC(12), τHCCC(37) |
| 785 | 13.05 | 0.76 | - | - | τHCCC(26), τHCCC(28) |
| 764 | 11.16 | 2.08 | - | - | τHCOC(44) |
| 751 | 7.88 | 28.59 | 750 | 752 | νCC(14), νCC(11), δCCC(12), |

| | | | | | |
|---|---|---|---|---|---|
| | | | | | γHCOC (15) |
| 726 | 6.54 | 7.65 | - | - | τHCCC(11), τCOCC(14) |
| 702 | 6.24 | 1.65 | - | - | τCOCC(10), τCCCC(11) |
| 630 | 96.23 | 1.84 | - | - | τOCOC |
| 619 | 14.4 | 2.96 | 617 | 619 | δC=O(20), γOH(20), δCOC(20), δCCC(20) |
| 606 | 11.54 | 1.21 | - | - | τCOCC(11), τHCCC(22) |
| 584 | 38.23 | 5.74 | - | - | δC(=O)O(22) |
| 571 | 8.32 | 0.5 | - | 569 | γC=O(18), τCOCC(12), τHCOC(10), τCCOC(44) |
| 507 | 31.87 | 2.65 | - | - | τHOCC(36), τOCOC(25) |
| 470 | 18.14 | 3.21 | - | - | γCCC(14) |
| 454 | 1.43 | 1.22 | - | - | τHCCC(10) |
| 424 | 9.81 | 0.33 | - | - | τHCCC(12), τCCCC(39), τOCCC(18) |
| 375 | 6.05 | 2.2 | - | - | τCCOC(10), τCCCC(14) |
| 357 | 4.2 | 1.15 | - | - | τCCCC(10) |
| 318 | 3.98 | 2.38 | - | - | δOCC(34), δOCC(19) |
| 285 | 51.49 | 2.84 | - | - | τHOCC(39), τCCCC(14), τOCCC(12) |
| 267 | 53.46 | 0.18 | - | - | τHOCC(57), τCCCC(11) |
| 208 | 0.78 | 0.39 | - | - | τCCCC(17),τCCCC(21), τOCCC(26) |
| 195 | 2.12 | 0.62 | - | - | δCH2 |
| 130 | 0.68 | 0.05 | - | - | δCCC(21), τCCCC(17), τOCCC(16) |
| 62 | 1.81 | 2.92 | - | - | τCCCC(39) |
| 41 | 0.04 | 2.59 | - | - | τCCCC(65) |
| 22 | 0.99 | 2.01 | - | - | τCCCC(12) |

[a] ν-stretching; δ-in-plane-deformation; γ-out-plane-deformation; τ-torsion; potential energy distribution is given in brackets (%) in the assignment column.

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Table 5

Experimental and theoretical $^{1}$H-NMR chemical shifts (ppm) of the title compound

| Proton | Experimental | TMS B3LYP/6-311+G(2d,p) GIAO |
|---|---|---|
| 10H | 7.66 | 7.34 |
| 14H | 7.33 | 7.31 |
| 16H | 6.72 | 7.04 |
| 19H | 6.86 | 6.68 |
| 8H | 3.59 | 3.58 |
| 7H | 3.59 | 3.47 |
| 21H(-OH) | 9.50 | 3.67 |
| 21H(-COOH) | 12.4 | 5.62 |

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Table 6

Excitations, CI expansion, energies coefficient (eV), wavelength λ (nm), and oscillator strengths (*f*)) of title compound calculated at TD-DFT/B3LYP/6311++G(d,p) method.

| Excitation | CI expansion | Energy Coefficient (eV) | Wavelength (nm) | Oscillator Strength (*f*) |
|---|---|---|---|---|
| 49→54 | 0.49715 | 5.7595 | 215 | 0.0013 |
| 49→52 | 0.40751 | 5.7132 | 217 | 0.0714 |
| 49→52 | 0.32491 | 5.6374 | 219 | 0.1086 |
| 50→57 | 0.59910 | 5.5982 | 221 | 0.0362 |
| 50→56 | 0.67038 | 5.4519 | 227 | 0.0059 |
| 49→51 | 0.47407 | 5.1034 | 242 | 0.0482 |
| 50→53 | 0.51064 | 4.9802 | 248 | 0.0026 |
| 50→53 | 0.28703 | 4.8668 | 254 | 0.0005 |
| 50→52 | 0.58309 | 4.7989 | 258 | 0.0051 |
| 50→51 | 0.59359 | 4.6052 | 269 | 0.1210 |

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Table 7

The electric dipole moment (μ), polarizability (Δα) and first order hyper polarizability (β) of title compound by B3LYP/6-311G++(d,p)

| Parameter | Value | Parameter | a.u. | esu($x10^{-24}$) | Parameter | a.u. | esu($x10^{-33}$) |
|---|---|---|---|---|---|---|---|
| $\mu_x$ | 0.3598 | $\alpha_{xx}$ | 167.2017 | 24.7792 | $\beta_{xxx}$ | 357.9366 | 3092.3216 |
| $\mu_y$ | 0.3710 | $\alpha_{xy}$ | 10.2899 | 1.5249 | $\beta_{xxy}$ | 113.5759 | 981.2162 |
| $\mu_z$ | -0.4547 | $\alpha_{yy}$ | 134.1571 | 19.8820 | $\beta_{xyy}$ | 96.8169 | 836.4302 |
| $\mu_o$ | 0.6882 | $\alpha_{xz}$ | -11.0167 | 1.6326 | $\beta_{yyy}$ | 4.4224 | 38.2064 |
| | | $\alpha_{yz}$ | 5.0333 | 0.7459 | $\beta_{xxz}$ | -10.1853 | -87.9938 |
| | | $\alpha_{zz}$ | 84.3250 | 12.4969 | $\beta_{xyz}$ | -35.9650 | -310.7124 |
| | | $\alpha_{tot}$ | 128.5612 | 19.0527 | $\beta_{yyz}$ | -33.0978 | -285.9418 |
| | | Δα | 72.2720 | 10.7107 | $\beta_{xzz}$ | 39.7684 | 343.5711 |
| | | | | | $\beta_{yzz}$ | -4.1572 | -35.9152 |
| | | | | | $\beta_{zzz}$ | -72.6130 | -627.3254 |
| | | | | | $\beta_{tot}$ | 520.5224 | 4496.9495 |
| | | | | | | $\beta_{tot} = 4.49x10^{-30}$ esu | |

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Table 8

Second-order perturbation theory analysis of Fock matrix in NBO basis corresponding to the intra-molecular bonds of the title compound

| Donor(i) | Type | ED/e | Acceptor(j) | Type | ED/e | E(2)[a] | E(j)-E(i)[b] | F(ij)[c] |
|---|---|---|---|---|---|---|---|---|
| O1-C5 | σ | 1.99667 | C5-C6 | σ* | 0.07320 | 1.38 | 1.47 | 0.041 |
| O1-C5 | π | 1.99139 | O1-C5 | π * | 0.20007 | 0.71 | 0.40 | 0.016 |
| O2-C5 | σ | 1.99504 | C6-C11 | σ* | 0.01989 | 1.08 | 1.37 | 0.034 |
| O3-C9 | σ | 1.98760 | C6-C11 | σ* | 0.01989 | 3.48 | 1.30 | 0.060 |
| - | σ | | C18-C20 | σ* | 0.02088 | 4.10 | 1.45 | 0.069 |
| O3-C20 | σ | 1.99028 | C12-C13 | σ* | 0.02400 | 1.81 | 1.45 | 0.046 |
| - | σ | | C12-C20 | σ* | 0.02989 | 0.54 | 1.46 | 0.025 |
| - | σ | | C17-18 | σ* | 0.02396 | 0.70 | 1.47 | 0.029 |
| - | σ | | C18-C20 | σ* | 0.02088 | 0.94 | 1.48 | 0.033 |
| C5-C6 | σ | 1.97444 | O1-C5 | σ* | 0.02141 | 1.14 | 1.27 | 0.034 |
| - | σ | | C6-C11 | σ* | 0.01989 | 0.72 | 1.09 | 0.025 |
| - | σ | | C9-C11 | σ* | 0.01822 | 1.20 | 1.27 | 0.035 |
| - | σ | | C9-C11 | π* | 0.23670 | 2.13 | 0.69 | 0.036 |
| C6-C11 | σ | 1.97664 | O2-C5 | σ* | 0.10157 | 2.09 | 0.99 | 0.041 |
| - | σ | | O3-C9 | σ* | 0.01517 | 1.70 | 1.00 | 0.037 |
| - | σ | | C5-C6 | σ* | 0.07320 | 0.73 | 1.02 | 0.025 |
| - | σ | | C9-C11 | σ* | 0.01822 | 2.97 | 1.27 | 0.055 |
| - | σ | | C11-C12 | σ* | 0.03054 | 2.46 | 1.17 | 0.048 |
| - | σ | | C12-C20 | σ* | 0.02989 | 0.97 | 1.22 | 0.031 |
| C9-C11 | σ | 1.97984 | C6-C11 | σ* | 0.01989 | 2.72 | 1.16 | 0.050 |
| - | σ | | C11-C12 | σ* | 0.03054 | 2.77 | 1.25 | 0.053 |
| - | σ | | C12-C13 | σ* | 0.02400 | 5.28 | 1.28 | 0.073 |
| - | σ | | C18-C20 | σ* | 0.02088 | 0.54 | 1.31 | 0.024 |
| C9-C11 | π | 1.88674 | C5-C6 | σ* | 0.07320 | 4.14 | 0.64 | 0.046 |
| - | π | | C9-C11 | π* | 0.23670 | 1.01 | 0.31 | 0.016 |
| - | π | | C12-C20 | π* | 0.45633 | 11.91 | 0.31 | 0.059 |
| C11-C12 | σ | 1.96031 | C9-C11 | σ* | 0.01822 | 2.56 | 1.27 | 0.051 |
| - | σ | | C12-C13 | σ* | 0.02400 | 4.64 | 1.20 | 0.067 |
| - | σ | | C13-C15 | σ* | 0.01193 | 1.16 | 1.23 | 0.034 |
| - | σ | | C18-C20 | σ* | 0.02088 | 3.96 | 1.22 | 0.062 |
| C12-C13 | σ | 1.97142 | C11-C12 | σ* | 0.03054 | 5.12 | 1.21 | 0.070 |
| - | σ | | C12-C20 | σ* | 0.02989 | 3.81 | 1.25 | 0.062 |
| - | σ | | C13-C15 | σ* | 0.01193 | 3.53 | 1.27 | 0.060 |
| C12-C20 | σ | 1.96621 | C6-C11 | σ* | 0.01989 | 5.28 | 1.11 | 0.069 |
| - | σ | | C18-C20 | σ* | 0.02088 | 4.77 | 1.25 | 0.069 |
| C12-C20 | π | 1.61765 | C9-C11 | π* | 0.23670 | 16.64 | 0.28 | 0.064 |
| - | π | | C13-C15 | π* | 0.31042 | 20.86 | 0.29 | 0.070 |
| - | π | | C17-C18 | π* | 0.38606 | 17.04 | 0.27 | 0.061 |
| C17-C18 | σ | 1.97447 | O3-C20 | σ* | 0.02772 | 5.56 | 1.06 | 0.069 |
| - | σ | | C15-C17 | σ* | 0.02401 | 3.89 | 1.26 | 0.063 |
| C17-C18 | π | 1.70456 | C12-C20 | π* | 0.45633 | 22.51 | 0.29 | 0.076 |
| | π | | C13-C15 | π* | 0.31042 | 14.98 | 0.30 | 0.060 |
| | π | | C17-C18 | π* | 0.38606 | 0.62 | 0.29 | 0.012 |
| C18-C20 | σ | 1.97318 | O3-C9 | σ* | 0.01517 | 1.66 | 1.06 | 0.038 |
| - | σ | | O4-C17 | σ* | 0.02241 | 4.35 | 1.06 | 0.061 |
| - | σ | | C12-C20 | σ* | 0.02989 | 4.55 | 1.27 | 0.068 |

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| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| - | σ | | C17-C18 | σ* | 0.02396 | 2.65 | 1.28 | 0.052 |
| LPO1 | σ | 1.97774 | O2-C5 | σ* | 0.10157 | 1.43 | 1.04 | 0.035 |
| - | σ | | C5-C6 | σ* | 0.07320 | 2.47 | 1.07 | 0.046 |
| LPO1 | π | 1.84362 | O2-C5 | σ* | 0.10157 | 34.27 | 0.60 | 0.130 |
| - | π | | C5-C6 | σ* | 0.07320 | 19.45 | 0.63 | 0.101 |
| - | π | | C9-C11 | π* | 0.23670 | 0.58 | 0.31 | 0.012 |
| LPO2 | σ | 1.97781 | O1-C5 | σ* | 0.02141 | 6.73 | 1.26 | 0.082 |
| LPO2 | π | 1.83167 | O1-C5 | π* | 0.20006 | 42.74 | 0.35 | 0.110 |
| LPO3 | σ | 1.97357 | C9-C11 | σ * | 0.01822 | 2.78 | 1.19 | 0.051 |
| - | σ | | C12-C20 | σ * | 0.02989 | 3.65 | 1.14 | 0.058 |
| LPO3 | π | 1.74432 | C9-C11 | π* | 0.23670 | 24.77 | 0.36 | 0.085 |
| - | π | | C12-C20 | π* | 0.45633 | 25.90 | 0.36 | 0.091 |
| LPO4 | σ | 1.97904 | C17-C18 | σ * | 0.02396 | 5.81 | 1.17 | 0.074 |
| LPO4 | π | 1.88100 | C17-C18 | π* | 0.38606 | 27.63 | 0.35 | 0.094 |

[a]E(2) means energy of hyper-conjugative interactions (stabilization energy in kJ/mol)

[b]Energy difference (a.u) between donor and acceptor i and j NBO orbitals

[c]F(i,j) is the Fock matrix elements (a.u) between i and j NBO orbitals

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Table 9

NBO results showing the formation of Lewis and non-Lewis orbitals

| Bond(A-B) | ED/energy | EDA% | EDB% | NBO | s% | p% |
|---|---|---|---|---|---|---|
| σ O1-C5 | 1.99667 | 65.14 | 34.86 | $0.8071(sp^{1.42})O+$ | 41.22 | 58.65 |
| | -1.11547 | - | - | $0.5904(sp^{1.91})C$ | 34.31 | 65.54 |
| π O1-C5 | 1.99139 | 69.62 | 30.38 | $0.8344(sp^{99.99})O+$ | 0.05 | 99.83 |
| | -0.40615 | - | - | 0.5512(99.99)C | 0.04 | 99.46 |
| σ O2-C5 | 1.99504 | 68.35 | 31.65 | $0.8268(sp^{2.02})O+$ | 33.10 | 66.81 |
| | -0.94427 | - | - | $0.5625(sp^{2.69})C$ | 27.07 | 72.71 |
| σ O3-C9 | 1.98760 | 69.23 | 30.77 | $0.8320(sp^{2.31})O+$ | 30.17 | 69.76 |
| | -0.87961 | - | - | $0.5547(sp^{3.22})C$ | 23.63 | 76.06 |
| σ O3-C20 | 1.99028 | 68.28 | 31.72 | $0.8263(sp^{2.08})O+$ | 32.43 | 67.50 |
| | -0.91075 | - | - | $0.5632(sp^{3.21})C$ | 23.70 | 76.06 |
| σ C5-C6 | 1.97444 | 48.43 | 51.57 | $0.6959(sp^{1.59})C+$ | 38.61 | 61.35 |
| | -0.66131 | - | - | $0.7181(sp^{3.02})C$ | 24.87 | 75.06 |
| σ C6-C11 | 1.97664 | 50.07 | 49.93 | $0.7076(sp^{2.28})C+$ | 30.46 | 69.50 |
| | -0.66426 | - | - | $0.7066(sp^{1.91})C$ | 34.32 | 65.66 |
| σ C9-C11 | 1.97984 | 48.63 | 51.37 | $0.6974(sp^{1.37})C+$ | 42.20 | 57.76 |
| | -0.73946 | - | - | $0.7167(sp^{1.94})C$ | 33.98 | 65.97 |
| πC9-C11 | 1.88674 | 48.86 | 51.14 | $0.6990(sp^{1.00})C+$ | 0.00 | 99.92 |
| | -0.28305 | - | - | $0.7151(sp^{1.00})C$ | 0.00 | 99.92 |
| σ C11-C12 | 1.96031 | 49.55 | 50.45 | $0.7039(sp^{2.16})C+$ | 31.63 | 68.33 |
| | -0.65694 | - | - | $0.7103(sp^{2.03})C$ | 33.04 | 66.93 |
| σ C12-C13 | 1.97142 | 52.23 | 47.77 | $0.7227(sp^{1.69})C+$ | 37.19 | 62.78 |
| | -0.69966 | - | - | $0.6912(sp^{1.84})C$ | 35.14 | 64.80 |
| σ C12-C20 | 1.96621 | 50.48 | 49.52 | $0.7105(sp^{2.37})C+$ | 29.65 | 70.30 |
| | -0.68598 | - | - | $0.7037(sp^{1.74})C$ | 36.46 | 63.50 |
| πC12-C20 | 1.61765 | 53.10 | 46.90 | $0.7287(sp^{1.00})C+$ | 0.00 | 99.96 |
| | -0.25719 | - | - | $0.6849(sp^{1.00})C$ | 0.00 | 99.96 |
| σ C17-C18 | 1.97447 | 49.71 | 50.29 | $0.7051(sp^{1.64})C+$ | 37.90 | 62.06 |
| | -0.71844 | - | - | $0.7091(sp^{1.85})C$ | 35.13 | 64.82 |
| πC17-C18 | 1.70456 | 45.07 | 54.93 | $0.6713(sp^{1.00})C+$ | 0.00 | 99.95 |
| | -0.26933 | - | - | $0.7412(sp^{1.00})C$ | 0.00 | 99.95 |
| σ C18-C20 | 1.97318 | 49.53 | 50.47 | $0.7037(sp^{1.87})C+$ | 34.84 | 65.11 |
| | -0.72293 | - | - | $0.7105(sp^{1.53})C$ | 39.54 | 60.43 |
| σ LPO1 | 1.97774 | - | - | $Sp^{0.70}$ | 58.78 | 41.21 |
| | -0.71498 | - | - | - | - | -- |
| πLPO1 | 1.84362 | - | - | $Sp^{99.99}$ | 0.04 | 99.88 |
| | -0.28215 | - | - | - | - | - |
| σ LPO2 | 1.97781 | - | - | $Sp^{1.20}$ | 45.48 | 54.48 |
| | -0.64576 | - | - | - | - | - |
| πLPO2 | 1.83167 | - | - | $Sp^{1.00}$ | 0.00 | 99.94 |
| | -0.35430 | - | - | - | - | - |
| σ LPO3 | 1.97357 | - | - | $Sp^{1.67}$ | 37.50 | 62.47 |
| | -0.58492 | - | - | - | - | - |
| π LPO3 | 1.74432 | - | - | $Sp^{1.00}$ | 0.00 | 99.94 |
| | -0.33746 | - | - | - | - | - |
| σ LPO4 | 1.97904 | - | - | $Sp^{1.23}$ | 44.82 | 55.15 |
| | -0.61369 | - | - | - | - | - |
| π LPO4 | 1.88100 | - | - | $Sp^{1.00}$ | 0.00 | 99.94 |

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| | | | | | |
|---|---|---|---|---|---|
| -0.33072 | - | - | - | - | - |

ED/e is expressed in a.u.

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Table 10

Reorganization energies and average charge transfer rates ($k_{ET}^{e-}$ for electrons and $k_{ET}^{h+}$ for holes) of HBFAA in crystal and amorphous phases

| structure | $\lambda_-$ [eV] | $\lambda_+$ [eV] | $k_{ET}^{e-}$ [$s^{-1}$] | | $k_{ET}^{h+}$ [$s^{-1}$] | |
|---|---|---|---|---|---|---|
| | | | crystal | amorphous | crystal | amorphous |
| HBFAA | 0.64 | 0.43 | $2.256\times10^{11}$ | $7.074\times10^{11}$ | $1.873\times10^{12}$ | $8.950\times10^{12}$ |

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Table 11

Charge transfer rates for molecular orientations provided in Figure 6

| Molecular pairs | $k_{ET}^{e-}$ [$s^{-1}$] | $k_{ET}^{h+}$ [$s^{-1}$] |
|---|---|---|
| a) | $7.329\times10^{9}$ | $8.304\times10^{11}$ |
| b) | $2.989\times10^{11}$ | $2.923\times10^{12}$ |
| c) | $2.538\times10^{11}$ | $1.522\times10^{12}$ |
| d) | $2.538\times10^{11}$ | $1.516\times10^{12}$ |
| e) | $7.187\times10^{12}$ | $8.691\times10^{13}$ |

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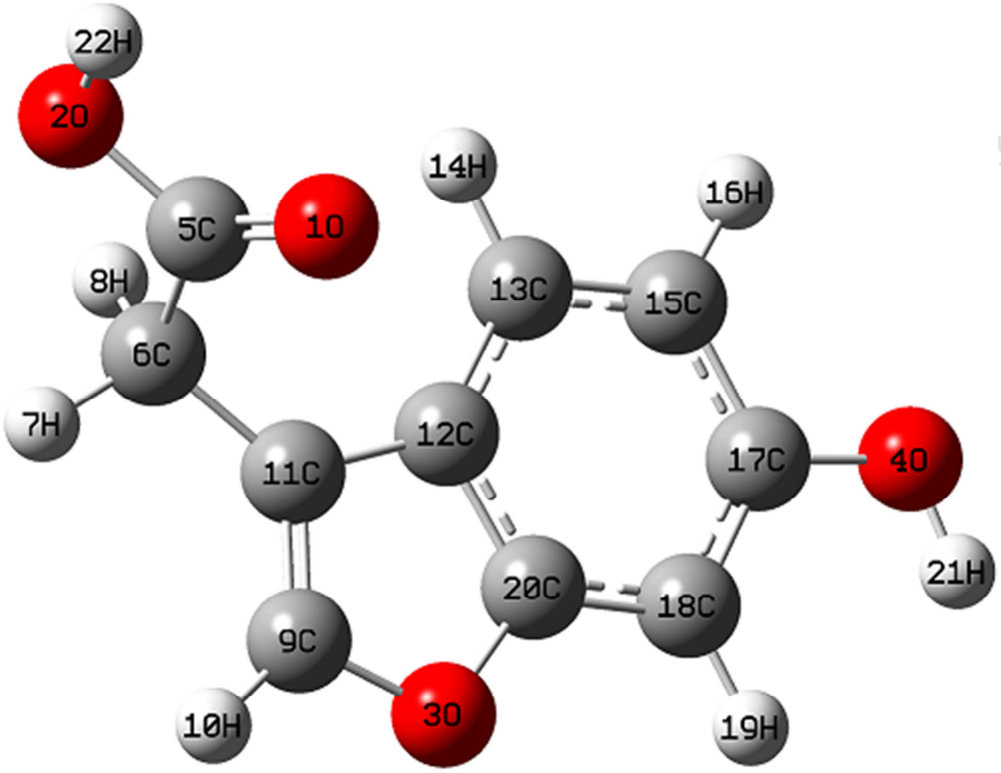



**Fig.1.** Optimized geometry of 2-(6-hydroxy-1-benzofuran-3-yl) acetic acid (HBFAA)

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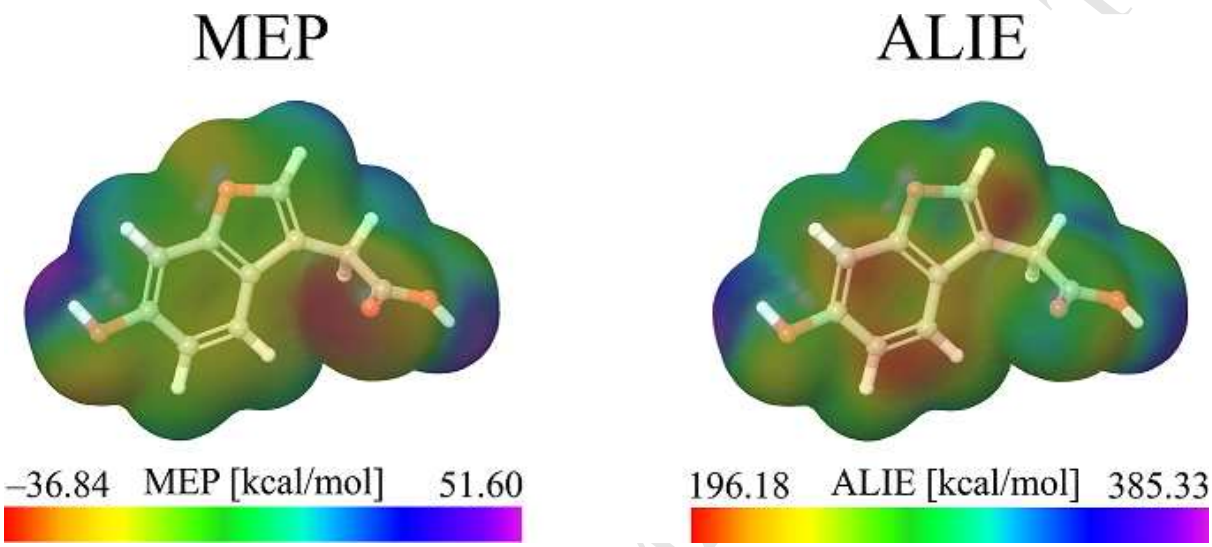



**Fig. 2.** MEP and ALIE surfaces of 2-(6-hydroxy-1-benzofuran-3-yl) acetic acid

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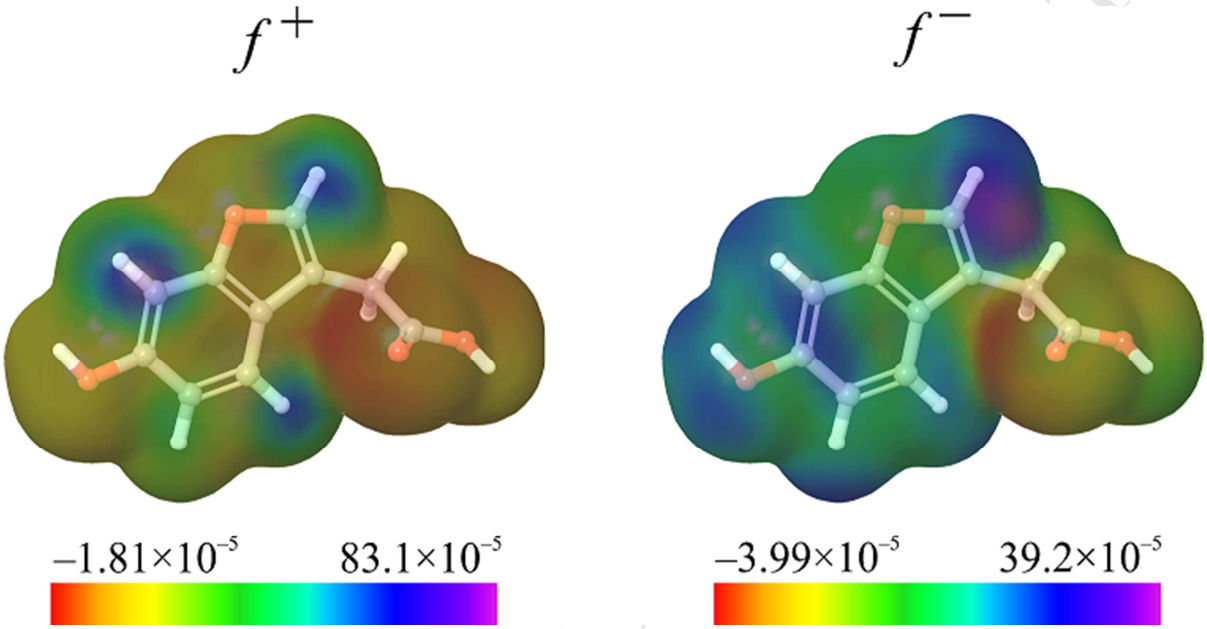



**Fig. 3.** Fukui functions of molecule 2-(6-hydroxy-1-benzofuran-3-yl) acetic acid

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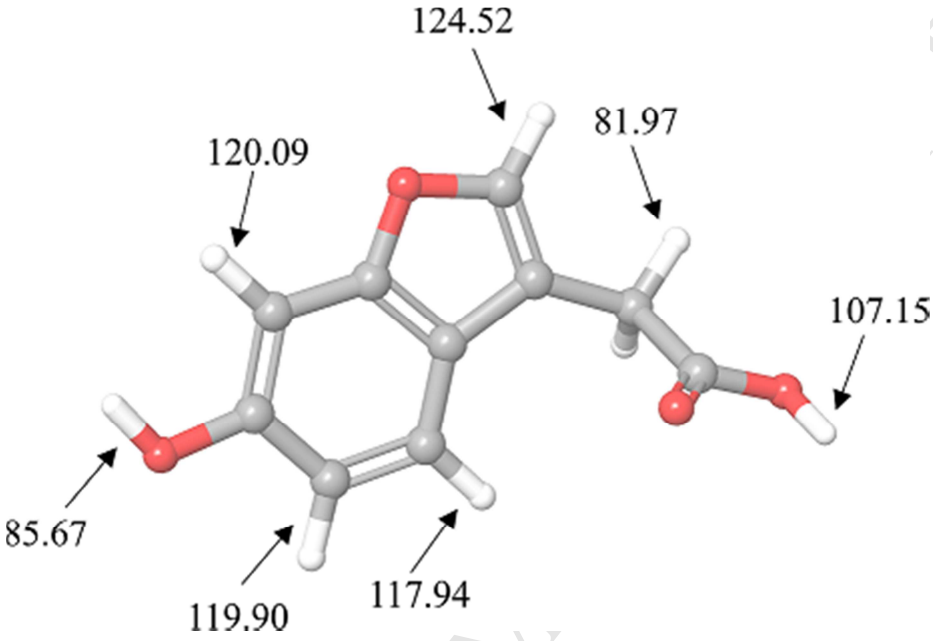



**Fig. 4.** H-BDE values in the case of 2-(6-hydroxy-1-benzofuran-3-yl) acetic acid

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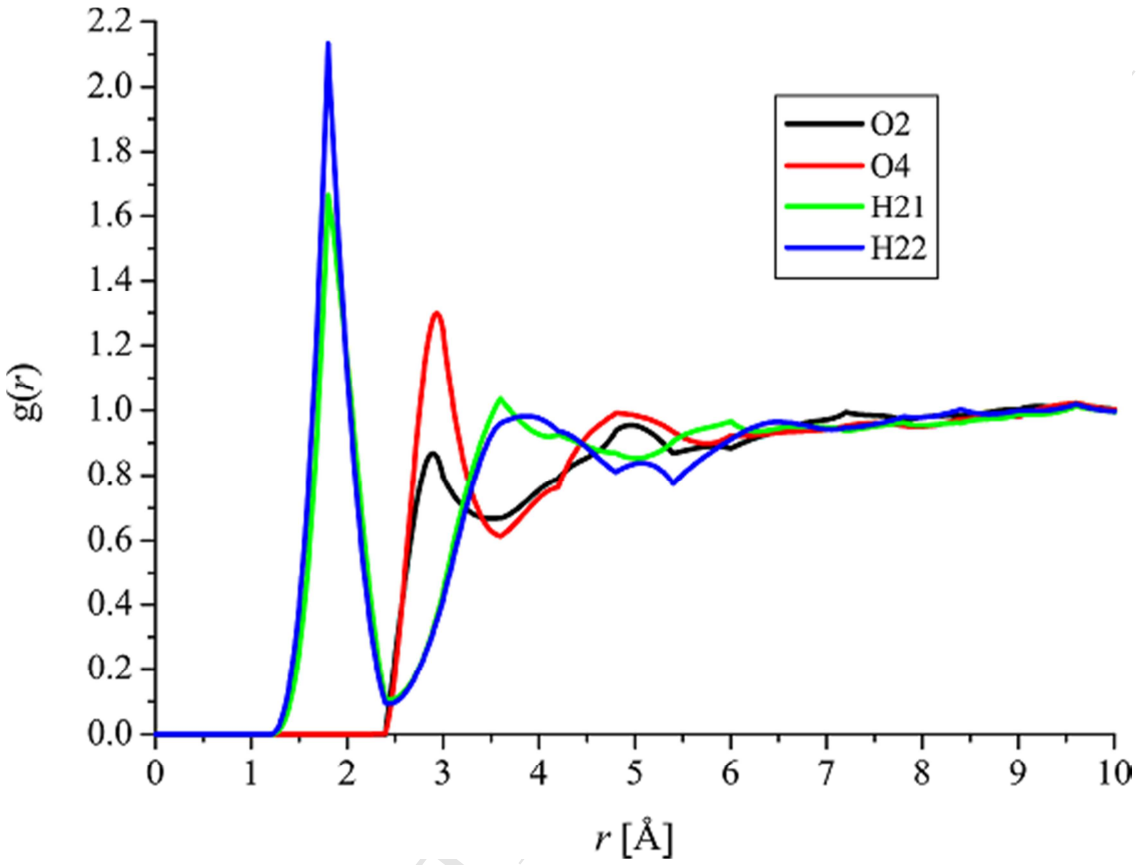



**Fig. 5.** RDF of 2-(6-hydroxy-1-benzofuran-3-yl) acetic acid

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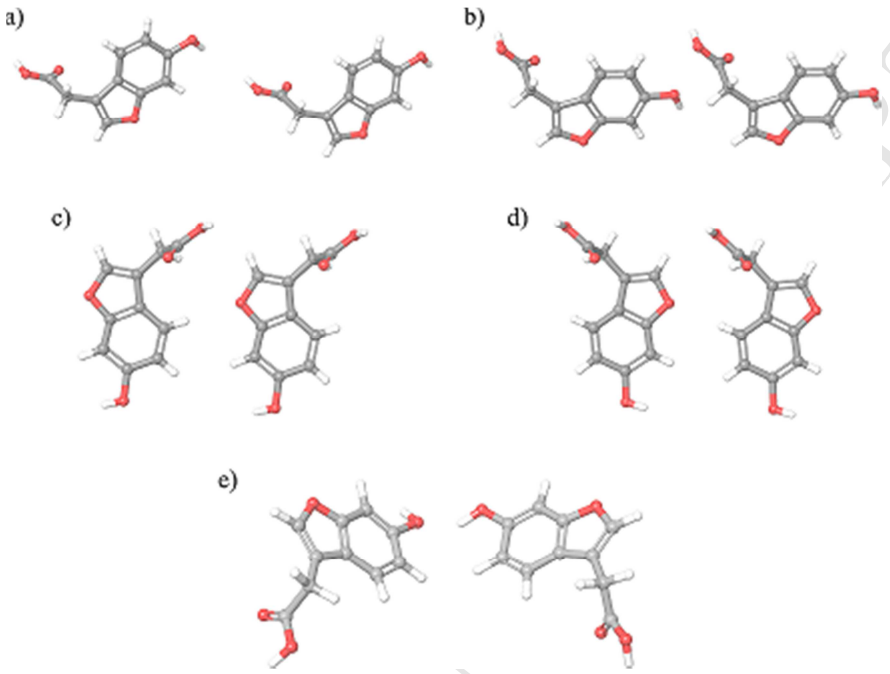



**Fig. 6.** a) to d) molecular pairs taken from crystal phase, e) molecular pair with the highest charge transfer rates taken from the amorphous phase

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Highlights

- Solid state crystal structure and intermolecular contacts are studied by Single crystal X-ray diffraction and Hirshfeld surface analysis.
- The complete vibrational assignments were performed on the basic of the potential energy distribution (PED).
- Most reactive sites are identified.
- MEP, ALIE, BDE and Fukui function have been discussed in detail.
- The analysis of charge transfer rates between title molecules is also done.

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# Synthesis, characterization and computational study of the newly synthetized sulfonamide molecule

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ABSTRACT

A new compound *N*-(2,5-dimethyl-4-nitrophenyl)-4-methylbenzenesulfonamide (NDMPMBS) has been derived from 2,5-dimethyl-4-nitroaniline and 4-methylbenzene-1-sulfonyl chloride. Structure was characterized by SCXRD studies and spectroscopic tools. Compound crystallized in the monoclinic crystal system with $P2_1/c$ space group $a = 10.0549$, $b = 18.967$, $c = 8.3087$, $\beta = 103.18$ and $Z = 4$. Type and nature of intermolecular interaction in crystal state investigated by 3D-Hirshfeld surface and 2D-finger print plots revealed that title compound stabilized by several interactions. The structural and electronic properties of title compound have been calculated at DFT/B3LYP/6-311G++(d,p) level of theory. Computationally obtained spectral data was compared with experimental results, showing excellent mutual agreement. Assignment of each vibrational wave number was done on the basis of potential energy distribution (PED). Investigation of local reactivity descriptors encompassed visualization of molecular electrostatic potential (MEP) and average local ionization energy (ALIE) surfaces, visualization of Fukui functions, natural bond order (NBO) analysis, bond dissociation energies for hydrogen abstraction (H-BDE) and radial distribution functions (RDF) after molecular dynamics (MD) simulations. MD simulations were also used in order to investigate interaction of NDMPMBS molecule with 1WKR and 3ETT proteins protein.

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## 1. Introduction

$SO_2$–NH group is a key constituent of sulfonamide pharmaceuticals, which are promising chemotherapeutic agents used for treatment of various diseases [1]. Sulfa-drugs possess a wide verity of medicinal chemistry applications such as antiprotozoal [2], antibacterial [3], antifungal [4], insecticidal [5], anti-inflammatory [6], carbonic anhydrase inhibitor [7] and rheumatoid arthritis [8]. Recent literature reports indicate that sulphonamides are also applied in the cases of Alzheimer's [9], cancer [10,11] and HIV [12] diseases as well. Besides pharmaceutical applications, sulphonamides are also used as reagents in analytical chemistry for concentration, separation, selective qualitative and quantitative determination of the 3d transition metal cations [13–15]. Sulfonamide compounds have been studied extensively and numerous experimental and computational reports. Xing et al. reported the crystal structure of 4-methyl-*N*-(4-nitrophenyl)benzenesulfonamide [16]. Sarojini et al. reported synthesis, structural, spectroscopic and computational studies of 4-methyl-*N*-(3-nitrophenyl) benzene sulfonamide combining experimental and theoretical approaches [17]. Rajamani et al. investigated electronic absorption, vibrational spectra, nonlinear optical properties, NBO analysis and thermodynamic properties of *N*-(4-nitro-2-phenoxyphenyl) methanesulfonamide molecule within the Hartree-Fock and

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density functional approaches [18]. Govindarasu et al. carried out detailed experimental and computational DFT study of *N*-phenylbenzenesulfonamide [19].

In this paper we report synthesis, detailed spectroscopic and computational characterization of *N*-(2,5-dimethyl-4-nitrophenyl)-4-methylbenzenesulfonamide (NDMPMBS) molecule. In order to uniquely characterize the title compound we have measured FT-IR, Raman and NMR spectra. Spectral data were also computed within DFT approach in order to validate the used level of theory. Computational investigation within DFT approach has proven to be effective tool for investigation of physical and chemical properties of various organic molecules [20–24] and in this study we used it to study both global and local quantum-molecular descriptors of the title compound. Taking into account that organic pharmaceutical molecules such as NDMPMBS represent great threat for water resources [25–30], we have also investigated sensitivity of NDMPMBS towards autoxidation and hydrolysis, in order to gain an insight into its possible degradation properties.

## 2. Material and methods

### 2.1. General remarks

FT-IR spectrum (Fig. 1) was recorded in solid state using KBr disc in the range of 4000–600 $cm^{-1}$ on ATR module ALPHA-T Bruker FT-IR spectrophotometer. FT-Raman spectrum (Fig. 2) was measured for solid sample on Bruker RFS 100/s, Germany using Nd:YAG laser source, excitation wave length 1064 nm with spectral resolution 2 $cm^{-1}$ in the region of 0–4000 $cm^{-1}$.$^{1}$H and $^{13}$C NMR chemical shift values were reported in ppm using TMS as internal standard on Bruker 400 MHz spectrometer.

### 2.2. Synthesis of N-(2,5-dimethyl-4-nitrophenyl)-4-methylbenzenesulfonamide

To a stirred solution of 2,5-dimethyl-4-nitroaniline (0.5 g, 3.01 mmol) in pyridine (5 mL), 4-methylbenzene-1-sulfonyl chloride (0.86 g, 4.51 mmol) was added. The reaction mixture was stirred for 16 h at room temperature. After completion of reaction by TLC, the reaction mixture was diluted with D.M.water and acidified with dilute HCl solution. Solid was filter, washed with D.M.water, MTBE and followed by 1:1 ethyl acetate: hexane. Dried under vacuum to afford (0.67 g, 69%) of *N*-(2,5-dimethyl-4-nitrophenyl)-4-methylbenzene-1-sulfonamide as pale yellow solid (Scheme-1 supporting information). Suitable single crystals were grown by slow evaporation solution growth technique at ambient temperature using chloroform: methanol (1:3) solvent.

### 2.3. X-ray data collection and refinement details

A suitable prism like crystal was selected and mounted on a Bruker APEX-II CCD diffractometer using graphite monochromated MoKa (λ = 0.71073 Å) radiation and detector (CCD). The crystal was kept at 273 (2) K during data collection. The structure was solved using Olex2 software with the olex2. solve [31] structure solution program using Charge Flipping and the structure was refined with the ShelXL [32] refinement package using Least Squares minimization. All the non-hydrogen atoms were revealed in the first difference Fourier map itself and were refined anisotropically. All the hydrogen atoms were positioned geometrically. All H atoms were positioned geometrically, with C–H = 0.96 Å for methyl H, C–H = 0.93 Å for aromatic H, and refined using a riding model with $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl H and $U_{iso}(H) = 1.2U_{eq}(C)$ for aromatic H. The nitrogen bound H atom was located in a difference map and was refined isotropically with the bond length restraint N–H = 0.86 (2) Å. All the geometrical calculations were carried out using the program *PLATON* [33] within the WinGX suite [34]. The molecular and packing diagrams were generated using the software *MERCURY* [35]. The crystallographic data and refinement parameters are summarized in Table 1.

### 2.4. Computational details

Firstly, molecular structure of the title compound was extracted from the single crystal X-ray structure to be used as a starting geometry for geometry optimization. The molecular geometry optimization in gas phase together with vibrational analysis, frontier orbital analysis (HOMO-LUMO), MEP, surface analysis and Mullikan atomic charges calculation were performed at DFT level of theory with B3LYP [36] hybrid exchange-correlation functional and 6-311G++(d,p) (5D, 7 F) basis set, using Gaussian 09 software package [37]. The assignment and PED analysis of wave number were done by GaussView 5.0 program [38] and VEDA4 program [39]. For better agreement of calculated wavenumber number with

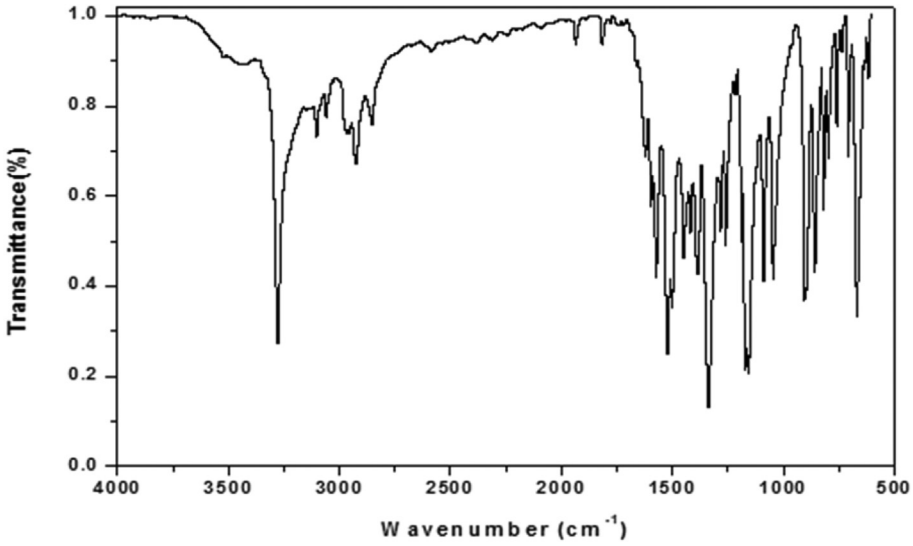



**Fig. 1.** FT-IR spectrum of *N*-(2,5-dimethyl-4-nitrophenyl)-4-methylbenzenesulfonamide.

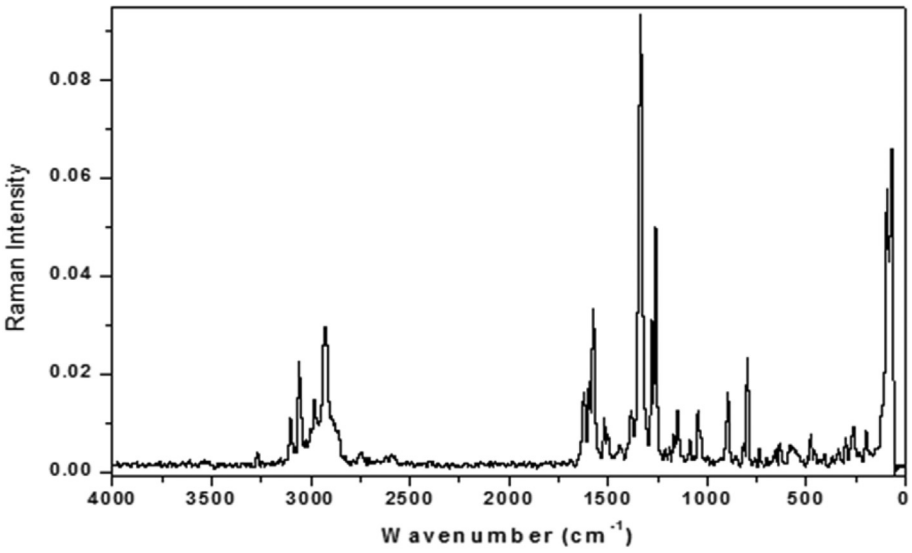



**Fig. 2.** FT-Raman spectrum of *N*-(2,5-dimethyl-4-nitrophenyl)-4-methylbenzene sulfonamide.

**Table 1**
Crystallographic data and structure refinement parameters of NDMPMBS.

| CCDC Number | 1539743 |
|---|---|
| Empirical formula | $C_{15}H_{16}N_2O_4S$ |
| Formula weight | 320.37 |
| Temperature/K | 273.15 |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |
| a/Å | 10.0549 (13) |
| b/Å | 18.967 (2) |
| c/Å | 8.3087 (11) |
| α/° | 90 |
| β/° | 103.184 (4) |
| γ/° | 90 |
| Volume/Å$^3$ | 1542.8 (3) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.3792 |
| μ/mm$^{-1}$ | 0.229 |
| F (000) | 672.8 |
| Crystal size/mm$^3$ | 0.28 × 0.25 × 0.22 |
| Radiation | Mo Kα (λ = 0.71073) |
| 2Θ range for data collection/° | 4.68 to 53.02 |
| Index ranges | $-12 \le h \le 12$, $-23 \le k \le 23$, $-10 \le l \le 10$ |
| Reflections collected | 28527 |
| Independent reflections | 3199 [$R_{int}$ = 0.0493, $R_{sigma}$ = 0.0222] |
| Data/restraints/parameters | 3199/0/206 |
| Goodness-of-fit on F$^2$ | 1.073 |
| Final R indexes [I ≥ 2σ (I)] | $R_1$ = 0.0416, w$R_2$ = 0.1127 |
| Final R indexes [all data] | $R_1$ = 0.0464, w$R_2$ = 0.1188 |
| Largest diff. peak/hole/e Å$^{-3}$ | 0.32/-0.46 |

experimental values, the wave numbers were scaled by a scaling factor 0.9613 [40]. DFT calculations were also performed with Jaguar 9.6 [41] program with B3LYP functional and 6–311++G (d,p), 6-31 + G (d,p), 6-311G (d,p) basis sets for calculations of ALIE, Fukui functions and BDEs, respectively. MD simulations and RDF calculations were performed with Desmond program [42–45]. Both Jaguar and Desmond programs were used as implemented in Schrödinger Materials Science Suite 2017–2 [45]. In case of the MD simulation, one molecule of title compound was placed in the cubic box with approximately 3000 water molecule. OPLS3 force field [42,46–48] was used and the model was of NPT ensemble class. Simulation time was set to 10 ns, temperature to 300 K, pressure to 1.0325 bar, with cut-off radius set to 12 Å. Simple point charge (SPC) model [49] was used for description of solvent. An approach developed by Johnson et al. [50,51], as implemented in Jaguar program, was applied for the investigation of intra molecular non-covalent interactions.

### 2.5. Hirshfeld surfaces

The 3D-Hirshfeld surfaces [52–54] and the corresponding 2D-fingerprint plots ($d_e$ *vs* $d_i$) [55–57], provides summary and quantification of the intermolecular interactions in the crystal structure [52,58], were generated by using CrystalExplorer3.1 [59] and which accepts a structure input file in the CIF format. The $d_{norm}$ values are mapped onto the Hirshfeld surfaces by using a rainbow colour scheme (red-white-blue): where a red colour indicates contacts shorter than sum of van der Waals radii, white colour denotes for contacts around the *vdW* and blue colour specifies contacts longer than sum of van der Waals radii.

## 3. Result & discussion

### 3.1. Molecular and crystal structure

The *ORTEP* view of the molecule of the title compound is shown in Fig. 3. The dihedral angle between the two benzene rings in the title compound is 85.54 (6)°. The nitro group is essentially planar (rmsd = 0.003 Å) and is tilted to the aniline ring by 25.86 (3)°. The atoms around the sulfonamide $S_{37}$ atom in the title compound are arranged in a slightly distorted tetrahedral arrangement as observed generally in sulfonamides. The biggest deviation is in the angle $O_{33}$–$S_{37}$–$O_{34}$ of 119.34 (1)°, followed by 104.14 (2)° of $O_{33}$–$S_{37}$–$N_{31}$. The V shaped molecular conformation is stabilized by intramolecular C–H···O hydrogen bonds involving $H_{18}$ and $O_{34}$ atoms (Fig. 3, Table 2) that encloses to form a S (6) motif. In the crystal, molecules are linked by pairs of N–H···O hydrogen bonds involving amino nitrogen atom $N_{31}$ as the hydrogen bond donor and sulfonyl oxygen atom $O_{33}$ as the acceptor. These two hydrogen bonds form inversion related $R^2_2$ (8) dimers (Fig. 4(a), Table 2). These dimers are linked by C–H···O hydrogen bonds involving $H_{14}$ hydrogen atom and the sulfonyl oxygen atom $O_{34}$ to form a double C (7) chains propagating along the c-axis direction and forming a ribbon like architecture (Fig. 4(a)). Neighbouring ribbons are linked via offset π … π interactions [*Cg* … *Cg* = 3.9058 (19) Å; interplanar

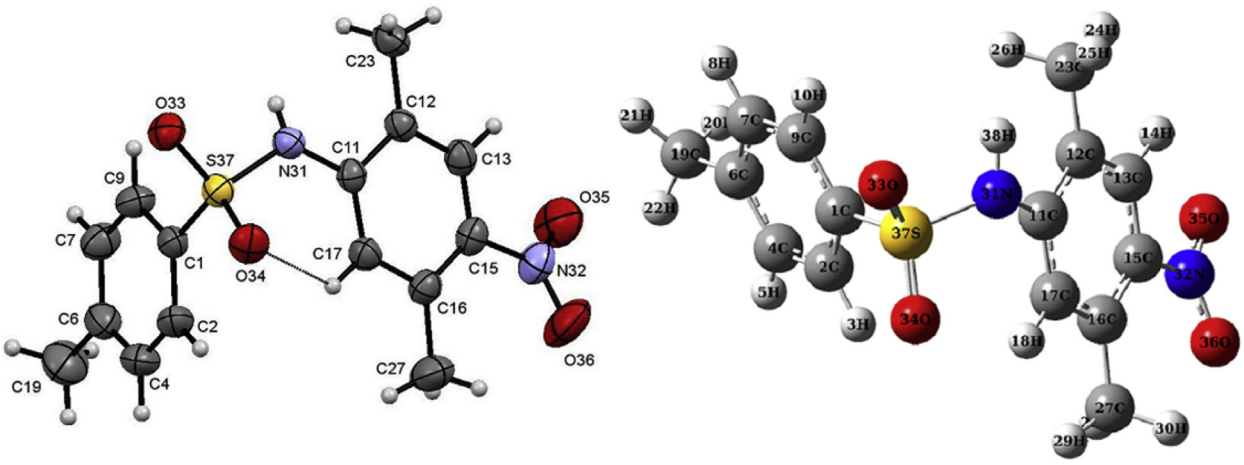



**Fig. 3.** ORTEP diagram of *N*-(2,5-dimethyl-4-nitrophenyl)-4-methylbenzenesulfonamide with thermal ellipsoids drawn at 50% probability with optimized geometry.

**Table 2**
Geometric parameters for hydrogen bonds and other intermolecular contacts (Å, °) operating in the crystal structures of NDMPMBS.

| D-H … A | D-H | H … A | D … A | D-H … A |
|---|---|---|---|---|
| C17–H18···O34[a] | 0.93 | 2.45 | 3.0825 | 125 |
| N31–H38···O33[b] | 0.81 | 2.20 | 2.9772 | 160 |
| C13–H4···O34[c] | 0.93 | 2.38 | 3.2133 | 149 |

[a] Intra.
[b] x,1-y,1-z.
[c] x,y,-1+z.

distance = 3.6104 (19) Å; slippage = 1.490 Å; symmetry code: 1-x,1-y, 1-z] between the nitro aniline rings $C_{11}/C_{12}/C_{13}/C_{15}/C_{16}/C_{18}$ forming a two dimensional sheet parallel to the *ac*-plane, as illustrated in Fig. 4(b).

### 3.2. Hirshfeld surface analysis

The Hirshfeld surfaces of title compound display in Fig. 5(a), the surfaces have been mapped over $d_{norm}$ (A), shape index (B) and curvedness (C) in the range of −0.452 to 1.427 Å, −1.0 to 1.0 Å and −4.0 to 0.4 Å, respectively. Two major interactions are observed, first interaction between sulfonamide $N_{31}$–$H_{38}$ with $O_{33}$ of sulphonamide, which can visualize as dark red areas and labelled as a and a'. Another, interaction between $O_{34}$ of sulfonamide with the $C_{13}$–$H_4$ of nitrobenzene, which can be seen as bright red spots marked as b and b' in Fig. 5(a) and (b), on the $d_{norm}$ mapped surfaces. The upper spike denoted with b (Fig. 5(c)) corresponds to the donor spike ($H_{38}$ atom in $SO_2NH$ group interacting with $O_{33}$ atom of the $SO_2NH$ group), with the lower spike indicate with a corresponding to an acceptor spike ($O_{33}$ atom of the $SO_2NH$ group with $H_{38}$ atom of the $SO_2NH$ group), both are look like sharp spikes with almost same in length and forming inversion dimers that enclose $R^2_2$ (8) loops. Fig. 5(c), depicted H···H contacts appears as spikes, indicate with red circle and the wings encircled with black due to the C···H contacts. From the fingerprint analysis revealed that the H–H (36.5%) and O–H (36.4%) and C–H (17.6%) contacts appears to be a predominant contribution in the crystal packing.

### 3.3. Optimized geometry

Full geometry optimization (shown in Fig. 3) of title compound was carried out for isolated molecules in gas phase at DFT/B3LYP/6–311++G (d,p) method, initially coordinates obtained from X-ray

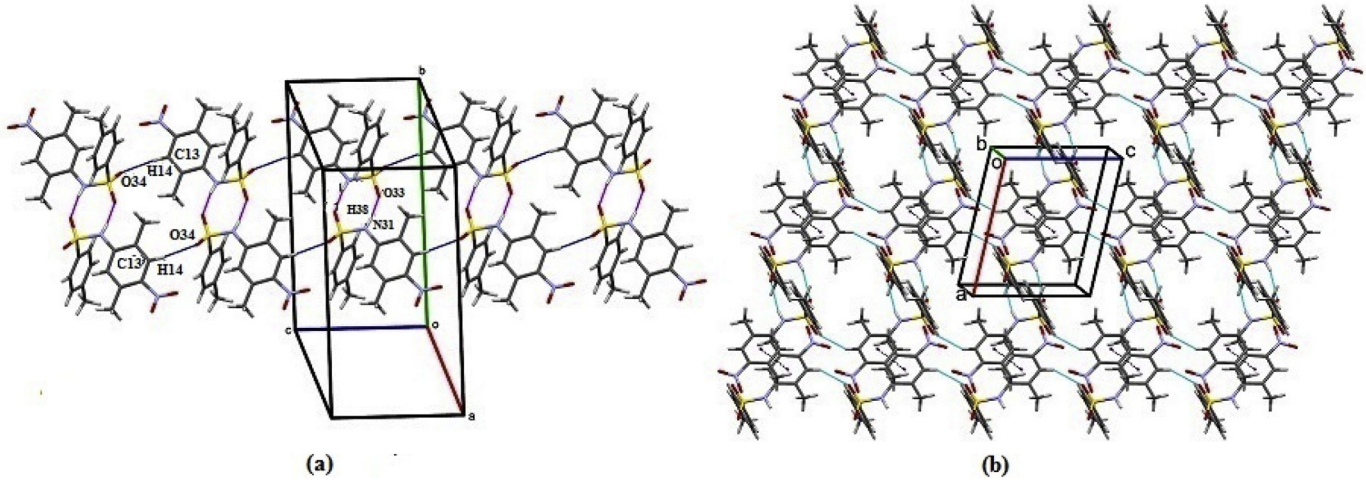
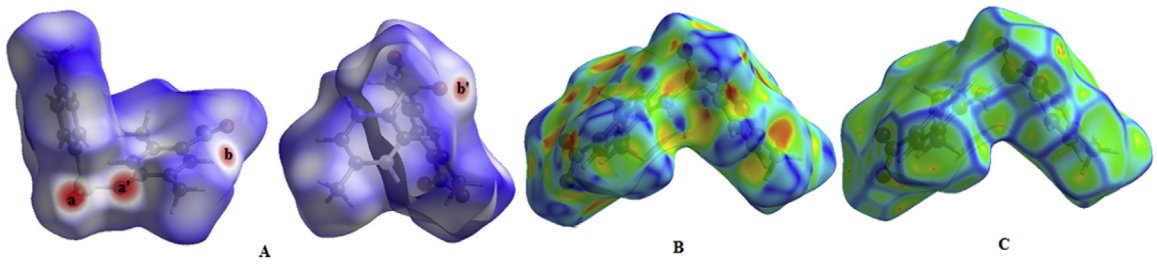
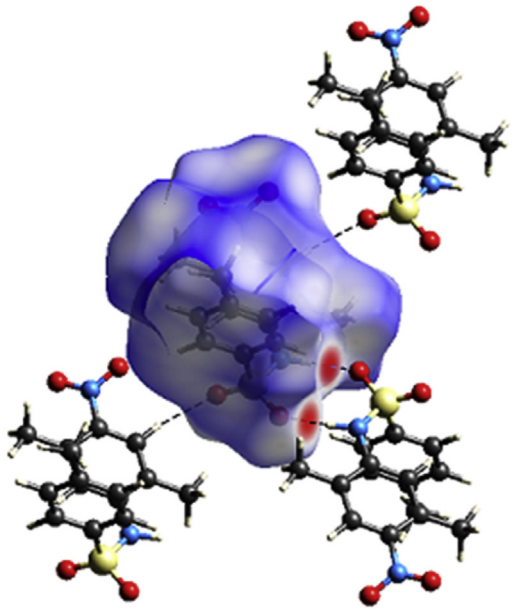


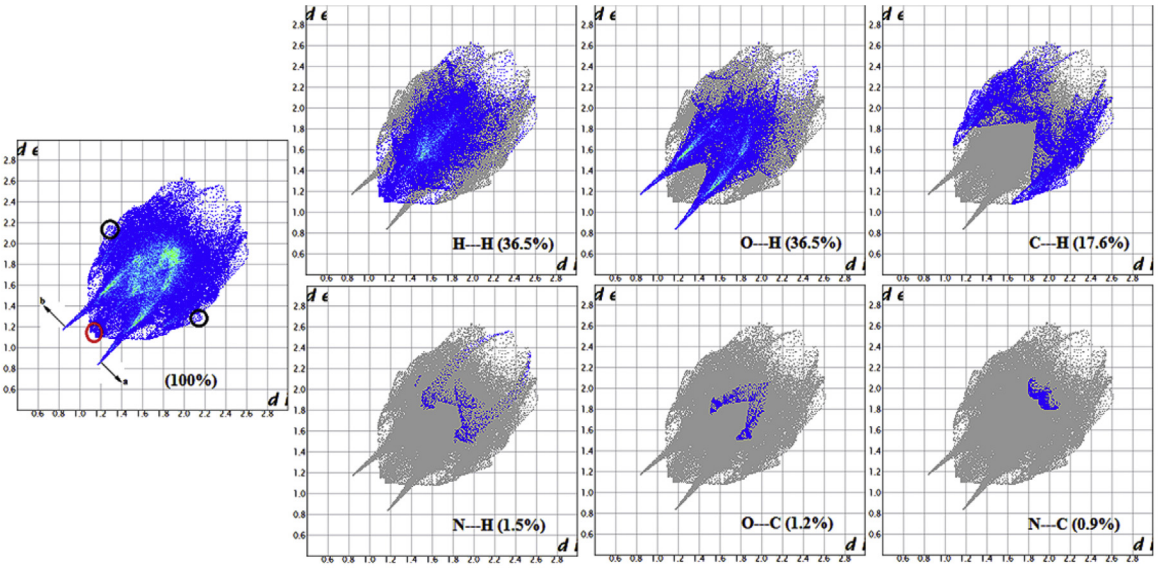

**Fig. 4.** (a) Ribbon like architecture formed via N–H–O and C–H–O hydrogen bonds in the title compound. (b) A view of the crystal packing of the compound displaying two dimensional sheets.




(a) Hirshfeld surfaces of NDMPMBS (A) $d_{norm}$ (B) shape index and (C) curvedness



(b) Hirshfeld surfaces mapped with $d_{norm}$ showing various interactions with surrounding molecules




(c) Finger print plots of NDMPMBS; (a) total surface area (100%), (b) H---H (36.5%), (c) O---H (36.4%), (d) C---H (17.6%), N---H(1.5%), O---C(1.2%) and N---C(0.9%) interactions visualized with percentage of contacts.

**Fig. 5.** (a) Hirshfeld surfaces of NDMPMBS (A) $d_{norm}$ (B) shape index and (C) curvedness. (b) Hirshfeld surfaces mapped with $d_{norm}$ showing various interactions with surrounding molecules. (c) Finger print plots of NDMPMBS; (a) total surface area (100%), (b) H—H (36.5%), (c) O—H (36.4%), (d) C—H (17.6%), N—H (1.5%), O—C (1.2%) and N—C (0.9%) interactions visualized with percentage of contacts.

structure without any constraints. Selected geometrical parameters (bond length (Å), bond angle (°) and torsion angle (°) of investigated compound are listed in Table 3). The comparative study shows a good agreement among the computational and experimental parameters (Supplementary information). The computational geometrical parameters are slightly more than that of experimental values. Because of, the experimental results were based on molecules in the solid state, while the computed values were carried in gas phase for isolated molecule.

### 3.4. Vibrational spectral analysis

The calculated (scaled) wavenumbers, experimental IR, Raman bands and assignments are given in Table 4.

The N–H stretching vibration mode generally measured in region 3500-3300 $cm^{-1}$ [60,61]. In the present case, the bands observed at 3277 $cm^{-1}$ (IR), 3276 $cm^{-1}$ (Raman) and 3488 $cm^{-1}$ (DFT) is assigned as NH stretching vibration mode. The mode (mode no 1) is pure and PED is exactly 100%. The difference between computational and experimental N–H stretching vibration is 171 $cm^{-1}$ for IR and 172 $cm^{-1}$ for Raman, this may due to the N–H–O intermolecular interaction of title molecule in crystal state. The N–H in-plane bending vibration mode is usually expected around 1400 $cm^{-1}$ [17]. In the present case, the bands observed at 1386 $cm^{-1}$ in the IR spectrum, 1384 $cm^{-1}$ in the Raman spectrum and 1391 $cm^{-1}$ for DFT (B3LYP) are assigned to the N–H in plane bending vibration mode, this is good agreement with literature values. The mode number 79 have calculated wave number at 492 $cm^{-1}$ correlate well with experimental Raman spectrum at 493 $cm^{-1}$ assigned as NH out-of-plane bending vibration.

The asymmetric and symmetric stretching modes of the methyl group are expected in the regions 3000 ± 50 $cm^{-1}$ and 2900 ± 45 $cm^{-1}$ [62,63]. For the title compound the stretching modes are assigned at 2981 $cm^{-1}$ (Raman), in the range 2999–2940 $cm^{-1}$ (B3LYP) (asymmetric stretching modes); 2924 $cm^{-1}$ (IR), 2925 $cm^{-1}$ (Raman) and in the region 2929-2895 $cm^{-1}$ (B3LYP) (symmetric stretching modes) as expected. The asymmetric and symmetric deformations vibrations of methyl group generally appear in the region of 1400–1485 $cm^{-1}$ and 1380-1420 $cm^{-1}$, respectively [64–67]. For title compound, the bands calculated at 1449, 1435, 1434, 1432, 1430, 1421 $cm^{-1}$ (B3LYP), experimentally observed at 1448, 1418 $cm^{-1}$ (IR) (asymmetric deformation) and 1367, 1363, 1362 $cm^{-1}$ (B3LYP) (symmetric deformation vibrations), shows good agreement with literature values. For the investigated compound, the rocking modes of methyl group are calculated at 1023, 1021, 1017 and 970 $cm^{-1}$ (B3LYP) and experimentally observed at 970 $cm^{-1}$ in the Raman spectrum, assigned as expected. The $CH_3$ torsion vibrational modes are usually appear in the region 185 ± 65 $cm^{-1}$ [62], the bands assigned at 206, 188, 168 and 28 $cm^{-1}$ (B3LYP).

The stretching vibration modes of aromatic nitro group are expected in range, 1570-1485 $cm^{-1}$ (asymmetric stretching) and 1370-1320 $cm^{-1}$ (symmetric stretching) [68]. For in case of investigated compound, these modes are assigned at 1521, 1502 $cm^{-1}$ (IR), 1520, 1502 $cm^{-1}$ (Raman), 1541, 1505 $cm^{-1}$ (B3LYP) (asymmetric stretching modes); 1300 $cm^{-1}$ (IR and Raman), 1305 $cm^{-1}$ (DFT) (symmetric stretching modes). Both the modes show high IR intensity and Raman activity. The $NO_2$ deformation modes (scissoring, out-of-plane wagging, in-plane rocking and torsion) are expected in the regions 855 ± 40, 760 ± 30, 540 ± 30 and 70 ± 20 $cm^{-1}$ respectively [62]. The bands at 858, 734 $cm^{-1}$ in IR spectrum, 857, 734 $cm^{-1}$ in Raman spectrum and 847 and 732 $cm^{-1}$ (DFT) are assigned as deformation modes of $NO_2$ group of title compound. The reported values of the $NO_2$ deformations modes are 809, 727, 524 $cm^{-1}$ (experimentally), 800, 727, 534 $cm^{-1}$ (DFT) [69].

The asymmetric and symmetric stretching vibrational modes fall in region 1330-1295 $cm^{-1}$ and 1150-1125 $cm^{-1}$, respectively for $SO_2$ group [70]. In the present case, the bands computed at 1267 and 1082 $cm^{-1}$ (DFT), experimentally observed at 1260, 1086 $cm^{-1}$ in the IR spectrum and 1260 and 1085 $cm^{-1}$ in the Raman spectrum are assigned as $SO_2$ asymmetric and symmetric stretching modes. The $SO_2$ stretching mode is not pure, but it contains contribution from other modes. Although the region of the $SO_2$ scissoring (560 ± 40 $cm^{-1}$) and that of $SO_2$ wagging vibration mode (500 ± 55 $cm^{-1}$) partly overlap, the two vibrations appear separately [62]. The DFT calculation of these bands at 567 $cm^{-1}$ and 515 $cm^{-1}$, observed at 566 $cm^{-1}$ and 515 $cm^{-1}$ in the Raman spectrum assigned as wagging and scissoring, respectively. The twisting vibrational mode of $SO_2$ is fall in region 400 ± 50 $cm^{-1}$ and rocking vibrational mode at around 350 $cm^{-1}$ [62]. For the present case, these modes are computed at 426 $cm^{-1}$ and 255 $cm^{-1}$, respectively.

The SN stretching vibration modes are expected in region 905 ± 30 $cm^{-1}$ [62] and in present study, the bands observed at 798 $cm^{-1}$ (IR), 797 $cm^{-1}$ (Raman) and 801 $cm^{-1}$ (B3LYP) assigned as these modes. The PED is 33% with IR intensity (145.02) and Raman activity (44.11) respectively. From the references the CN stretching vibration modes are fall in the region 1275 ± 55 $cm^{-1}$ [62], for the title compound the vibrational modes expected at 1337, 1017 $cm^{-1}$(IR), 1336, 1015 $cm^{-1}$ (Raman) and 1349, 1225, 1017 $cm^{-1}$ (theoretically). The stretching vibration modes for CS generally lie in the region 930-670 $cm^{-1}$ [71]. The CS stretching vibrational wave number for title compound calculated at 629 $cm^{-1}$ and experimentally observed at 632 $cm^{-1}$ (IR and Raman) as expected [71], PED of 21% and with high IR intensity (147.45) and low Raman activity (19.42).

The C–H stretching vibrational modes of substituted benzene ring are generally observed in the region 3000-3100 $cm^{-1}$ [62]. In present case, the C–H modes are assigned at 3102, 3084, 3059 $cm^{-1}$ (IR) and 3101, 3077, 3059, 3045 $cm^{-1}$ (Raman) and 3088, 3087, 3086, 3075, 3050, 3046 $cm^{-1}$ (B3LYP) as expected. The stretching vibration modes (2–7) are pure with PED contribution around 100%. The in-plane and out-of-plane aromatic CH deformation

**Table 3**
Geometrical parameters of the NDMPMBS.

| | | | |
|---|---|---|---|
| **Bond length (Å) DFT/XRD** | | | |
| C1–C2 | 1.393/1.386 | S37–N31 | 1.706/1.636 |
| C1–C9 | 1.394/1.386 | C11–N31 | 1.410/1.414 |
| C2–C4 | 1.391/1.380 | C11–C17 | 1.397/1.390 |
| C4–C6 | 1.399/1.382 | C12–C11 | 1.411/1.400 |
| C6–C7 | 1.401/1.385 | C12–C13 | 1.386/1.381 |
| C7–C9 | 1.390/1.376 | C15–N32 | 1.472/1.467 |
| C1–S37 | 1.794/1.756 | C15–C16 | 1.406/1.387 |
| S37–O33 | 1.457/1.435 | C16–C17 | 1.396/1.392 |
| S37–O34 | 1.456/1.423 | | |
| **Bond angle (°) DFT/XRD** | | | |
| C1–S37–O33 | 108.510/108.80 | S37–C1–C2 | 119.732/120.56 |
| C1–S37–O34 | 107.940/108.54 | S37–C1–C9 | 119.139/118.75 |
| S37–N31–H38 | 109.049/111.41 | C2–C1–C9 | 121.127/120.69 |
| O33–S37–O34 | 122.550/119.34 | C1–C2–C4 | 118.954/118.86 |
| O33–S37–N31 | 102.979/104.14 | C2–C4–C6 | 121.265/121.53 |
| O34–S37–N31 | 107.449/108.40 | C4–C6–C7 | 118.424/118.42 |
| N31–S37–C1 | 106.296/106.95 | | |
| **Torsion angle (°) DFT/XRD** | | | |
| O33–S37–C1–C2 | −155.788/-134.76 | N31–S37–C1–C9 | −85.795/-65.94 |
| O33–S37–C1–C9 | 24.365/45.99 | S37–C1–C2–C4 | −179.096/-178.98 |
| O34–S37–C1–C2 | −20.975/-3.45 | C9–C1–C2–C4 | 0.746/0.3 |
| O34–S37–C1–C9 | 159.178/177.30 | S37–C1–C9–C7 | 179.146/179.23 |
| N31–S37–C1–C2 | 94.050/113.31 | | |

**Table 4**
Calculated scaled wave numbers, observed IR and Raman bands and assignment of NDMPMBS.

| B3LYP/6–311++G (d,p) | | | IR | Raman | Assignments[a] |
|---|---|---|---|---|---|
| $\nu(cm^{-1})$ | IRI | RA | $\nu(cm^{-1})$ | $\nu(cm^{-1})$ | |
| 3448 | 46.4581 | 91.8182 | 3277 | 3276 | νNH(100) |
| 3088 | 0.5718 | 96.5058 | 3102 | 3101 | νCHII(74) |
| 3087 | 3.3703 | 9.074 | – | – | νCHII(69) |
| 3086 | 0.9234 | 42.5747 | 3084 | – | νCHI(90) |
| 3075 | 1.4139 | 82.2193 | – | 3077 | νCHI(93) |
| 3050 | 7.0118 | 78.9474 | 3059 | 3059 | νCHI(95) |
| 3046 | 9.4734 | 104.0429 | – | 3045 | νCHI(93) |
| 2999 | 15.0176 | 55.4886 | – | 3000 | νasyCH3 |
| 2995 | 10.2853 | 57.2905 | – | – | νasyCH3 |
| 2990 | 11.0976 | 68.4502 | – | – | νasyCH3 |
| 2986 | 5.5996 | 78.0916 | – | 2981 | νasyCH3 |
| 2964 | 15.5323 | 86.467 | – | – | νasyCH3 |
| 2940 | 13.0716 | 65.2499 | – | – | νasyCH3 |
| 2929 | 11.5999 | 210.3946 | 2924 | 2925 | νsyCH3 |
| 2909 | 16.7402 | 282.9166 | – | – | νsyCH3 |
| 2895 | 20.7788 | 210.3411 | – | – | νsyCH3 |
| 1596 | 72.8545 | 123.5693 | – | 1595 | νPhII(25) |
| 1571 | 23.4981 | 71.5686 | 1572 | 1573 | νPhI(30), δPhI(10) |
| 1549 | 2.4327 | 6.3037 | – | – | νPhI(27), δPhI(13) |
| 1541 | 130.8072 | 150.8671 | 1521 | 1520 | νasyNO2(11), νPhII(23) |
| 1505 | 223.5909 | 57.7494 | 1502 | 1502 | νasyNO2(30) |
| 1469 | 69.7658 | 12.3407 | – | – | δCHII(26) |
| 1463 | 9.1238 | 1.7324 | 1453 | – | δCHI(20) |
| 1449 | 11.8096 | 3.2022 | 1448 | – | δasyCH3(29) |
| 1435 | 11.8435 | 6.6691 | – | – | δasyCH3(30), τCH3(13) |
| 1434 | 14.2335 | 9.1215 | – | – | δasyCH3(40), τCH3(12) |
| 1432 | 10.021 | 9.273 | – | – | δasyCH3(58), τCH39110 |
| 1430 | 22.3058 | 5.4629 | – | – | δasyCH3(27) |
| 1421 | 8.0846 | 7.661 | 1418 | – | δasyCH3(53), τCH3(16) |
| 1391 | 21.8701 | 1.2362 | 1386 | 1384 | δHNC (39), δasCH3 (12), νPhII(12) |
| 1372 | 8.3958 | 1.4436 | – | – | δCH(10), PhI(17) |
| 1367 | 7.9481 | 17.2254 | – | – | δsyCH3(53) |
| 1363 | 10.179 | 8.8532 | – | – | δHNC (10), δsyCH3(41) |
| 1362 | 3.3186 | 22.9263 | – | – | δsyCH3(28) |
| 1349 | 30.6472 | 12.2288 | 1337 | 1336 | νCN(10), PhII(18) |
| 1305 | 479.1206 | 466.0533 | 1301 | 1300 | νsyNO2(36), δNO2(11) |
| 1289 | 20.1009 | 4.1237 | – | – | νPhII(12) |
| 1283 | 3.887 | 11.5492 | 1283 | – | δCHI(13), νPhI(14) |
| 1278 | 2.8038 | 3.9597 | 1278 | 1278 | δCHI(13), νPhI(10) |
| 1267 | 92.2633 | 5.4774 | 1260 | 1260 | νSO2(24), νCHII(16) |
| 1236 | 57.3095 | 122.7941 | – | – | νSO2(27), νCHII(26) |
| 1225 | 159.3669 | 260.7209 | – | – | νPhII(13), νCN(14) |
| 1181 | 2.706 | 17.4604 | – | – | δPhI(12), νCC(39) |
| 1165 | 9.701 | 2.0068 | – | – | δCHII(13) |
| 1160 | 4.3426 | 4.3912 | 1156 | 1151 | δCHI(17), CC(10) |
| 1124 | 5.4554 | 10.3407 | – | 1124 | δPhII(10), νCN(13), νCC(12) |
| 1095 | 6.9218 | 0.1308 | 1089 | 1089 | δCH(15), νPhI(14) |
| 1082 | 228.657 | 57.5833 | 1086 | 1085 | νSO2(27), νCS(12) |
| 1036 | 49.2109 | 12.0904 | – | – | νSO2(17), νPhI(18) |
| 1023 | 21.2059 | 4.1252 | – | – | δCH3(16) |
| 1021 | 25.9912 | 3.4665 | – | – | δCH3(16) |
| 1017 | 138.9511 | 52.8199 | – | – | δCH3(11), νCN(13), νCC(15) |
| 1017 | 1.868 | 0.872 | 1017 | 1015 | δCH3(11), νCN(13) |
| 1006 | 23.1045 | 23.1076 | – | – | τHCCC(20) |
| 991 | 8.8863 | 2.0952 | – | – | δPhI(22) |
| 971 | 5.1592 | 7.7547 | – | – | νPh(11), τHCCC(19) |
| 970 | 0.1598 | 0.2327 | – | 971 | δCH3(10), δCH3(10), τHCCC(36) |
| 954 | 0.0298 | 0.3556 | – | – | δCHI(23) |
| 935 | 0.3507 | 0.3669 | – | – | δCHI(18), τPhI(10) |
| 896 | 33.6547 | 0.3834 | 895 | 895 | δCHII(40) |
| 879 | 5.5845 | 1.8665 | – | – | δCHII(43) |
| 847 | 2.6101 | 23.6678 | 858 | 857 | δNO2(30) |
| 818 | 0.179 | 0.262 | 818 | 817 | δCHI(26) |
| 801 | 145.0279 | 44.1127 | 798 | 797 | νSN(33) |
| 795 | 53.2133 | 13.1022 | – | – | δCHI(24) |
| 780 | 38.8255 | 9.2131 | – | – | δNO2(25), δCC(19), δPhII(19) |
| 777 | 6.191 | 57.6339 | – | – | δPhI(30) |
| 732 | 5.1162 | 1.4291 | 734 | 734 | δNO2 |
| 712 | 6.0197 | 4.593 | 706 | – | δNO2 |
| 697 | 19.2976 | 7.6921 | – | 698 | τPhII(16) |
| 688 | 3.337 | 1.0984 | – | 684 | τPhI(31) |
| 635 | 17.125 | 15.7566 | – | – | νPhII(15) |
| 629 | 147.4525 | 19.4248 | 632 | 632 | νCC(14), δPhI(10), νCS(21) |

**Table 4** (*continued*)

| B3LYP/6–311++G (d,p) | | | IR | Raman | Assignments[a] |
|---|---|---|---|---|---|
| $\nu$(cm$^{-1}$) | IRI | RA | $\nu$(cm$^{-1}$) | $\nu$(cm$^{-1}$) | |
| 621 | 2.5455 | 6.1092 | 615 | – | νPhI(36) |
| 584 | 14.7141 | 0.8446 | – | – | τHCCC(12), δCCCC(14) |
| 567 | 80.959 | 10.0026 | – | 566 | δSO2 wag (10) |
| 537 | 88.1423 | 7.5126 | – | – | δONC(14) |
| 515 | 78.0052 | 2.5205 | – | 515 | δSO2 sci (14) |
| 492 | 25.7815 | 14.2137 | – | 493 | δNHCC(54) |
| 474 | 2.3793 | 3.7152 | – | – | δCCCC(15) |
| 457 | 1.7323 | 10.4594 | – | – | νCC(10), δPhII(17) |
| 443 | 10.9643 | 2.065 | – | – | τPhII(24), δCCCC(12) |
| 426 | 6.5447 | 2.3866 | – | – | δSO2(28), δCCC(10) |
| 409 | 0.3637 | 1.7107 | – | – | δCCC(11) |
| 398 | 0.0749 | 0.0283 | – | – | τPhI(28), τHCCC(12) |
| 383 | 0.0748 | 1.8542 | – | – | δONC(10), δCCC(15) |
| 355 | 1.4186 | 0.4892 | – | – | δNSC(12) |
| 320 | 1.1514 | 0.8876 | – | – | δNSC(11), δCCCC(10) |
| 316 | 1.0446 | 0.3568 | – | – | δCCC(49) |
| 306 | 1.7845 | 0.1186 | – | 301 | νCN(12), δPhII(13) |
| 275 | 2.1131 | 5.4593 | – | – | νCS(32) |
| 255 | 3.0132 | 3.4884 | – | – | δSO2 rock (10), νCS(12), δOSN(10) |
| 244 | 1.7079 | 2.4539 | – | – | δCCN(14), δOSN(19) |
| 227 | 0.6907 | 3.3657 | – | 227 | νPhII(10), δCCC(20), νSN(14) |
| 212 | 1.7256 | 1.5674 | – | – | δNCC(42), δOSN(10) |
| 206 | 0.7871 | 0.4177 | – | – | τCH3(25), δCCCC(14) |
| 188 | 1.3078 | 1.3333 | – | – | τCH3(11), δNCCC(15), δNSC(14) |
| 168 | 0.5755 | 0.8188 | – | – | τCH3(18), δNSC(10) |
| 156 | 0.7665 | 0.569 | – | – | δSCC(56), δONCS(24) |
| 142 | 0.3113 | 0.1023 | – | – | τPhII(12), δNCCC(12) |
| 101 | 3.3054 | 1.2104 | – | – | δCNS(31), δCCN(23) |
| 91 | 1.9723 | 0.6841 | – | 92 | τPhII(13) |
| 57 | 2.9088 | 1.2039 | – | – | τPhII(21) |
| 34 | 0.0972 | 1.5942 | – | – | τNO2(53) |
| 28 | 0.1761 | 0.9245 | – | – | τCH3(34) |
| 26 | 0.0845 | 3.4964 | – | – | τNO2(22) |
| 19 | 1.3962 | 6.4671 | – | – | τNO2(10) |

[a] ν-stretching; δ-in-plane deformation and out-of-plane deformation; τ-torsion; 2,5-dimethyl 4-nitrophenyl and tosyl ring are represented as PhI and PhII; potential energy distribution is given in brackets (%) in the assignment column.

modes are expected above and below 1000 cm$^{-1}$ [62] and for in the case of investigated compound these modes assigned at 1283, 1278, 1260, 1156, 1089 cm$^{-1}$ (IR), 1278, 1260, 1089 cm$^{-1}$ (Raman), 1283, 1278, 1267, 1236, 1095 cm$^{-1}$ (B3LYP) (in-plane deformation) and at 895, 818 cm$^{-1}$ (IR), 895, 817 cm$^{-1}$ (Raman), 896, 818 cm$^{-1}$ (B3LYP) (out-of-plane deformation). The aromatic ring stretching vibrational modes expected in the region 1615-1260 cm$^{-1}$ [62]. For the investigated compound, the bands experimentally observed at 1572, 1502, 1386, 1278 cm$^{-1}$ (IR), 1595, 1573, 1502, 1384, 1278 cm$^{-1}$ (Raman) and in the range of 1596–1278 cm$^{-1}$ (B3LYP) assigned as these modes.

### 3.5. NMR spectral analysis

NMR spectroscopy is one of the important and valuable tool for identification of structural and functional groups of the molecules. $^{13}$C and $^{1}$H NMR chemical shifts values of title compound were recorded in DMSO solvent (TMS as internal standard), calculated in DMSO at GIAO method [72] using DFT/6-311G++(d,p) basic set, which provide information about the number of different types of carbon atoms and the number of different types of protons present in the molecule, respectively. The $^{13}$C and $^{1}$H NMR spectra are given in Fig. 6(a) and (b). Correlated results of experimental and calculated $^{13}$C and $^{1}$H NMR chemical shifts values are given in Table 5.

The result in Table 5 shows that the range of $^{13}$C NMR chemical shift of typical organic molecule usually is > 100 ppm [73,74] the accuracy ensures reliable interpretation of spectroscopic parameters. In $^{13}$C NMR spectrum, upfield signal observed at 16.92, 19.68 and 20.95 ppm and calculated at 16.85, 24.07, 22.09 ppm was assigned to methyl carbon atoms at $C_{23}$, $C_{27}$ and $C_{19}$. The signals for aromatic carbons (tosyl ring and nitrobenzene ring) were observed at 126.57–145.12 ppm and calculated at 124.86–154.11 ppm for DFT. The $C_{15}$ carbon of nitrobenzene ring appears 145.12 ppm due to nitro substitution, calculated as 150.35 ppm. The signal at $C_1$ and $C_6$ carbons of tosyl ring appears at 137.31 ppm (147.51 ppm) and 139.89 ppm (154.11 ppm) (experimental/calculated) due to methyl group as well as sulfonyl group substitution. The signal at 143.59 ppm is assigned as $C_{11}$ carbon of nitrobenzene ring due to amine group substitution, which was calculated at 149.61 ppm, show good agreement.

The title compound have 16 protons occur in three regions, out of which 9 protons attached to methyl groups, one protons is attached nitrogen (N–H proton) and 6 protons are aromatic protons. The 9 methyl protons are occur in the upfield region at δ 2.04, 2.37, 2.42 ppm (experimental) and calculated at 2.01, 2.35, 2.64 ppm, shows good agreement. The N–H proton observed experimental at 10.01 ppm and computed at 6.07 ppm. The phenyl ring protons are observed around at 7.20–7.82 ppm (experimental) which shows good agreement with calculated value 7.45–8.17 ppm.

### 3.6. Electronic spectra and frontier molecular orbital analysis

Electronic spectra of title compound calculated in DMSO as well as methanol solution by TD-DFT/PCM model using B3LYP/6-311G++(d,p) basic set (Table 6). The electronic spectra of the title

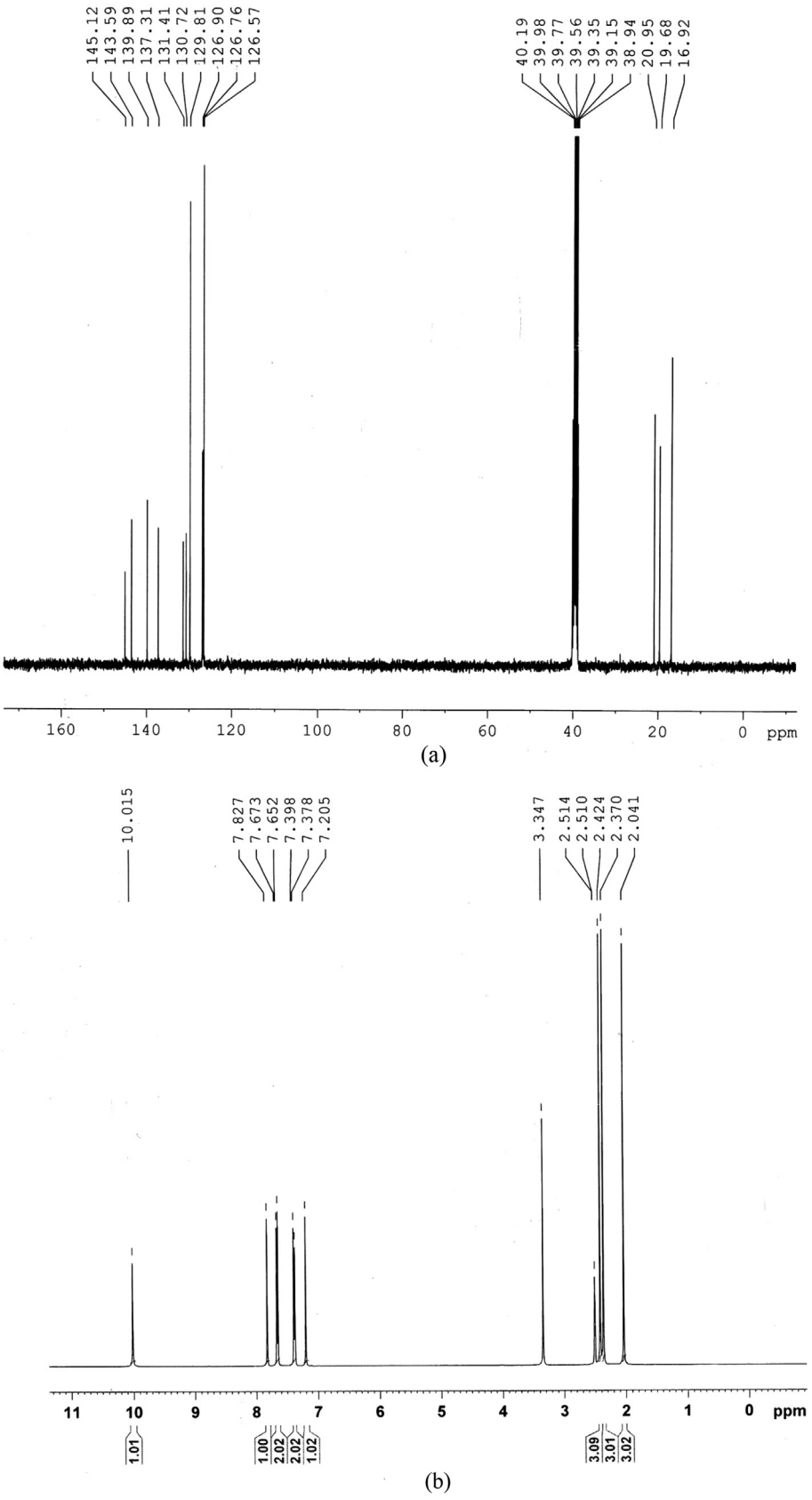



**Fig. 6.** $^{13}C$ NMR (a) and $^{1}H$ NMR (b) spectrum of *N*-(2,5-dimethyl-4-nitrophenyl)-4-methylbenzenesulfonamide.

**Table 5**
Experimental and calculated ($^{13}$C and $^{1}$H) NMR chemical shifts (ppm) of NDMPMBS.

| Atom | Experimental (ppm) | TMS B3LYP/6-311 + G (2d,p) GIAO (ppm) |
|---|---|---|
| **$^{13}$C-NMR** | | |
| C23 | 16.92 | 16.85 |
| C27 | 19.68 | 24.07 |
| C19 | 20.95 | 22.09 |
| C17 | 126.57 | 124.86 |
| C13 | 126.76 | 133.47 |
| C12 | 126.90 | 131.86 |
| C2, C9 | 129.81 | 131.04 |
| C4, C7 | 130.72 | 134.71 |
| C16 | 131.41 | 144.83 |
| C1 | 137.31 | 147.19 |
| C6 | 139.89 | 154.11 |
| C11 | 143.59 | 149.61 |
| C15 | 145.12 | 150.35 |
| **$^{1}$H-NMR** | | |
| H24–H26 | 2.04 | 2.01[a] |
| H20–H22 | 2.37 | 2.35[a] |
| H28–H30 | 2.42 | 2.64[a] |
| H5, H8 | 7.38 | 7.45[a] |
| H18 | 7.20 | 8.10 |
| H3, H10 | 7.66 | 7.82[a] |
| H14 | 7.82 | 8.17 |
| H38 | 10.01 | 6.07 |

[a] Average.

compound (in Figure S2 and S3 supporting information) illustrate an electronic absorption band with maxima at 349 nm (DMSO) and 347 nm (methanol), is due to the electronic transition from the ground state to the first excited state. It is mainly described by one-electron excitation from the HOMO (characterizes by the ability of electron donating) to LUMO (characterizes by the ability of electron accepting). Diagrammatic representation of HOMO-LUMO proved in Fig. 7, HOMO (MO 84) is confined on –NH–$SO_2$ group and delocalized over nitrobenzene; LUMO (MO 85) is confined on nitro group, delocalized on benzene ring of nitrobenzene. Consequently, HOMO→LUMO transition implies an electron cloud transfer from –$SO_2$ group to nitro group through the benzene ring of title compound. In case of title compound, the calculated energy values of HOMO and LUMO are −7.01 eV and −2.7 eV, respectively and the energy separation between HOMO and LUMO is 4.31 eV.

In order to understand the chemical reactivity of title compound, global reactivity parameters were calculated DFT method.

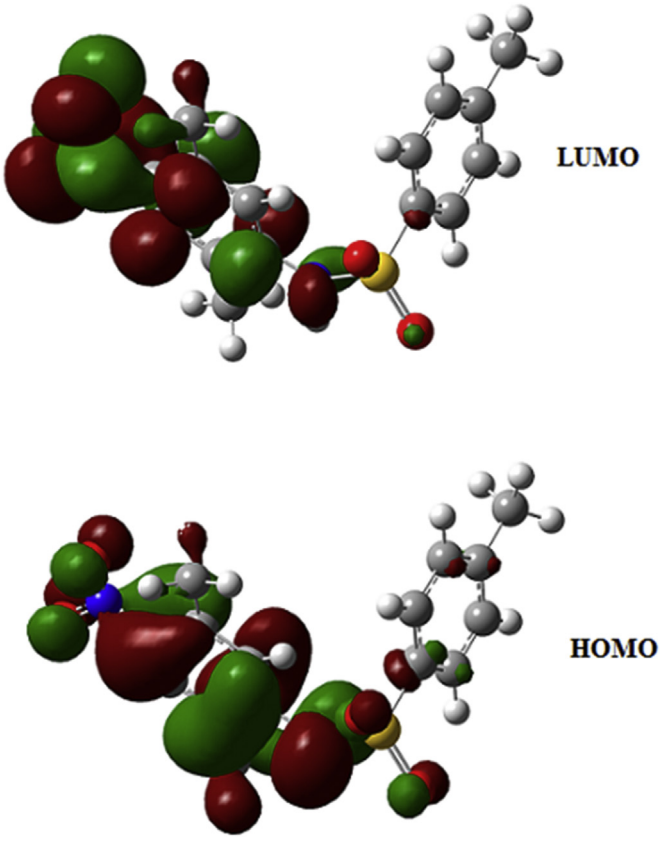



**Fig. 7.** HOMO-LUMO plots of *N*-(2,5-dimethyl-4-nitrophenyl)-4-methylbenzene sulfonamide.

Single point calculation was performed at DFT at 6–311++G (d,p) method. The difference in energies gave the vertical ionization potential (I) and vertical electron affinity (A) defined by equations, $I = E_{N-1} - E_N$, $A = E_N - E_{N+1}$, where $E_{N+1}$, $E_N$ and $E_{N-1}$ are the energies of the N+1, N and N-1 electron systems respectively [75]. The magnitude of global reactivity descriptor values as tabulated in Table 7 were calculated with the help of energies of Ionization potential (I) and electronic affinity (A) utilizing equations provided in the supplementary material.

**Table 6**
Theoretical electronic absorption spectra of title compound (absorption wavelength λ (nm), excitation energies E (eV) and oscillator strengths (*f*)) using TD-DFT/B3LYP/6311++G (d,p) method.

| Excitation | CI expansion | Energy Coefficient (eV) | Wavelength (nm) | Oscillator Strength (*f*) |
|---|---|---|---|---|
| **DMSO** | | | | |
| 84 → 85 | 0.68391 | 3.5498 | 349 | 0.3372 |
| 80 → 85 | 0.23487 | 3.7555 | 330 | 0.0277 |
| 82 → 85 | −0.12971 | | | |
| 83 → 85 | 0.63785 | | | |
| 80 → 85 | 0.61136 | 3.9266 | 315 | 0.0317 |
| 82 → 85 | −0.12639 | | | |
| 83 → 85 | −0.25811 | | | |
| 84 → 85 | 0.15724 | | | |
| **Methanol** | | | | |
| 84 → 85 | 0.68231 | 3.5631 | 347 | 0.3240 |
| 80 → 85 | 0.24398 | 3.7605 | 329 | 0.0255 |
| 82 → 85 | −0.12914 | | | |
| 83 → 85 | 0.63440 | | | |
| 80 → 85 | 0.60688 | 3.9277 | 315 | 0.0330 |
| 82 → 85 | −0.12481 | | | |
| 83 → 85 | −0.26620 | | | |
| 84 → 85 | 0.16292 | | | |

### 3.7. Local reactivity properties of NDMPMBS – MEP and ALIE surfaces, Fukuifunction surfaces and non-covalent interactions

In order to locate possibly important reactive sites of the newly synthetized NDMPMBS molecule, in this study we have also investigated frequently used quantum-molecular descriptors such as MEP, ALIE and Fukui functions. Values of the aforementioned quantities have been mapped to the electron density surface in order to visualize their distribution within NDMPMBS molecule, Figs. 8–10.

We begin with the identification of possibly important reactive (electrophilic and nucleophilic) sites by the molecular electrostatic potential (MEP) surface, which is a very useful descriptor in studies of biological recognition and hydrogen-bonding interactions [76,77]. The pictorial representation with rainbow colour scheme of electrostatic potential for title compound has been shown in Fig. 8, in the range of −6.012 a. u. to +6.012 a. u. The darkest red colour denotes electron rich regions (V(r) <-6.012 a. u.) that could be sensitive towards electrophilic attacks. According to Fig. 8 these regions are localized over oxygen atoms $O_{33}$ and $O_{34}$ (belonging to sulfonyl group) and oxygen atoms $O_{35}$ and $O_{36}$ (belonging to the nitro group). The darkest blue colour indicates electron poor regions (V(r) > +6.012 a. u.), and therefore the molecule sites that could be sensitive towards the nucleophilic attacks.

Also, the electrostatic potential mapped over the $d_{norm}$ surface of the neighbouring molecules (Figure S4 supporting information) clearly showed that the electrostatic potential on the hydrogen bond donors and acceptors in the neighbouring molecules are to one another (red spots close to H-acceptor and blue spots close to H-bond donors), thus provide further evidence to the $R^2_2$ (8) hydrogen bond pattern formed by N–H–O hydrogen bonds (Figure S4 supporting information). indicates the occurrence of $N_{31}$–$H_{38}$–$O_{33}$, $C_{13}$–$H_{14}$–$O_{34}$ and $C_{17}$–$H_{18}$–$O_{34}$ interactions in title compound. ALIE surface is even more reliable tool than MEP for the identification of molecule sites sensitive towards electrophilic attacks, since ALIE values show molecule areas where electrons are least tightly bound [78–81]. Representative ALIE surface (Fig. 9) of NDMPMBS molecule emphasizes the importance of oxygen atoms $O_{35}$ and $O_{36}$, when it comes to the sensitivity to electrophilic attacks. These molecule sites are characterized by the lowest ALIE values of ~217 kcal/mol. Intramolecular noncovalent interactions have also been visualized in Fig. 9. Two noncovalent interactions were formed between oxygen and hydrogen atoms ($O_{34}$–$H_{18}$ and $O_{36}$–$H_{30}$), with very similar strength of ~0.015 electron/bohr$^3$.

The importance of oxygen atoms $O_{35}$ and $O_{36}$ from the aspect of reactivity has been also confirmed by Fukui functions as well, Fig. 10. Fukui functions give information about the changes in electron density as a consequence of charge addition or removal. Purple color in Fig. 10(a) gives information about where electron density increased after the charge addition, while negative color in Fig. 10(b) gives information where electron density decreased after the charge addition. According to the results presented in Fig. 10(a), electron density could increase in the near vicinity of oxygen atoms $O_{36}$ and $O_{37}$ after the charge addition. On the other side, results in Fig. 10(b) indicate that electron density decreases in the near vicinity of oxygen atoms $O_{33}$ and $O_{34}$ after the charge removal.

**Table 7**
The energy values of global reactivity descriptors (Ionization potential (IP), electron affinity (EA), electro negativity (χ), chemical potential (μ), global hardness (η), global softness (σ) and global electrophilicity (ω)) for title compound.

| Parameter | Value (eV) |
|---|---|
| Ionization potential (IP) | 8.48 |
| Electron affinity (EA) | 1.09 |
| Electronegativity (χ) | 4.78 |
| Chemical potential (μ) | −4.78 |
| Global hardness (η) | 3.69 |
| Global softness (σ) | 0.13 |
| Electrophilicity index (ω) | 3.09 |

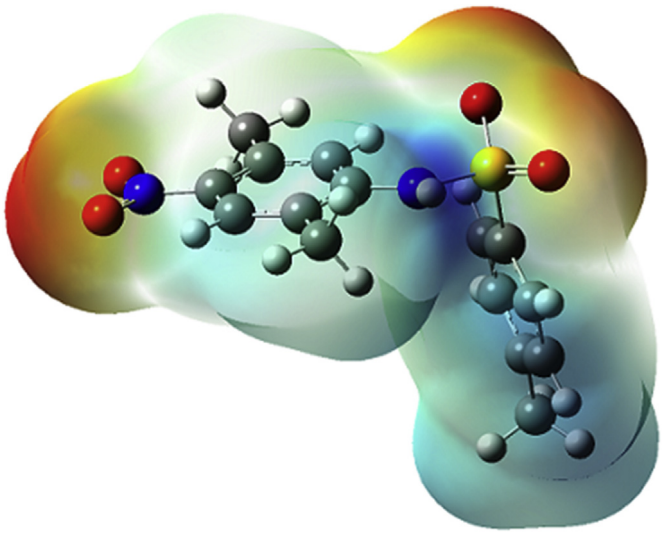


**Fig. 8.** MEP plot of *N*-(2,5-dimethyl-4-nitrophenyl)-4-methylbenzenesulfonamide.

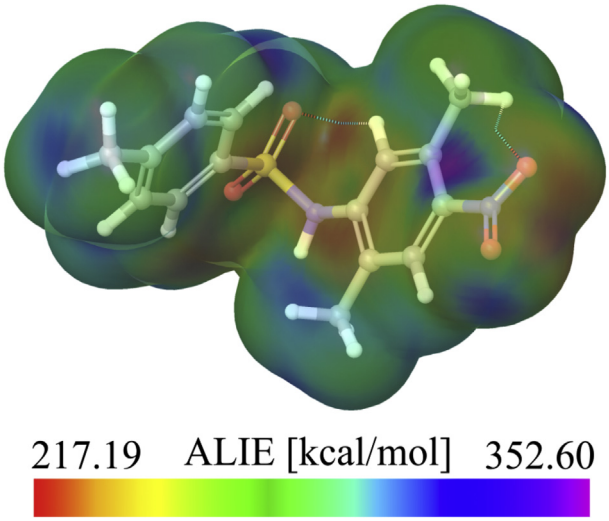



**Fig. 9.** Representative of ALIE surface of *N*-(2,5-dimethyl-4-nitrophenyl)-4-methylbenzenesulfonamide.

### 3.8. Nonlinear optical properties

Nonlinear optical materials occupy a foremost function in nonlinear optics and in particular they have a great impact on information technology and industrial applications. NLO properties find applications in optical communication, telecommunications, optical phase conjugation, frequency mixing, optical mixing, dynamic image processing, signal processing and second harmonic wave generation [82–84]. Total dipole moment ($\mu_o$), anisotropy of the polarizability ($\alpha_{tot}$), mean polarizibility ($\Delta\alpha$), and first-order hyperpolarizibilitiy($\beta$) of NDMPMBS were calculated at DFT/B3LYP/6-311G++(d,p) method and listed in Table 8. The dipole moment and mean polarizability of the title compound are 2.2670

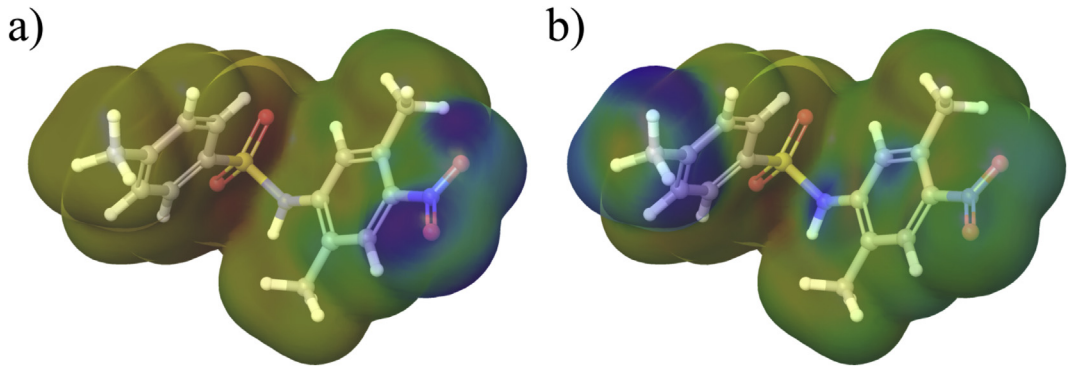



**Fig. 10.** Fukui functions of *N*-(2,5-dimethyl-4-nitrophenyl)-4-methylbenzenesulfonamide.

Debye and 7.4165 × $10^{-24}$ esu. The is first-order hyperpolarizibilitiy(β) of NDMPMBS calculated and is found to be 12.02 × $10^{-30}$ esu which is 92.46 times greater than that of the standard NLO material urea (0.13 × $10^{-30}$ esu) [85]. The highest value of first-order hyperpolarizibilitiy(β) may be due transfer of π-electron cloud from donor (sulphonamide group) to acceptor (nitro group) which makes molecule highly polarized and the possibility of intra molecular charge transfer (ICT).

### 3.9. NBO analysis

The natural bond orbital (NBO) calculations were performed using NBO 3.1 program [86] as executed in the Gaussian09 suite at the B3LYP/6–311++G (d,p) (5D, 7 F) basic set which offers a suitable basis for examining the various interactions in both filled and virtual orbital spaces that could enhance the analysis of inter and intramolecular interactions. The second-order Fock-matrix was carried out to evaluate the donor–acceptor interactions in the NBO basis [87,88]. In NBO analysis large E (2) value shows the intensive interaction between electron-donors and electron-acceptors, and greater the extent of conjugation of the whole system, the possible intensive interaction are given in Tables 9 and 10.

The strong interaction $n_3(O_{35}) \rightarrow \pi^*(N_{32}–O_{36})$ has the highest E (2) value 155.95 kJ/mol and an another interaction has been in $n_1(N_{31}) \rightarrow \pi^*(C_{11}–C_{17})$ with an energy of 23.39 kJ/mol. Table 10 gives the occupancy of electrons and p-character in significant NBO natural atomic hybrid orbital. Almost, a very close to pure p-character was observed in π-bonding of $C_{11}–C_{17}$, $N_{32}–O_{36}$ and lone pairs of $n_2O_{33}$, $n_2O_{34}$, $n_2O_{35}$, $n_3O_{35}$, $n_2O_{36}$, $n_1N_{31}$.

### 3.10. Mulliken atomic charge analysis

The Mulliken atomic charges of investigated compound calculated at DFT/B3LYP/6-31 + G (d,p) method in gaseous state are given in Table 11. It is based on the linear combination of atomic orbitals and therefore the wave function of the molecule are obtained from Mulliken population analysis [89]. The charge distribution on the molecule has an important role in the application of quantum chemistry calculations for the molecular system.

From the analysis of Table 11, hydrogen atoms of title compound shows atomic charges with positive values in the range of 0.138–0.308 and but some H atoms exhibit more positive atomic charges $H_{38}$ (0.308), $H_{14}$ (0.247) and $H_{18}$ (0.266) comparative other hydrogen atoms and possess acidic nature. Due to the presence of more negative atomic charges values on oxygen atom $O_{33}$ (−0.131), $O_{34}$ (−0.100) and nitrogen atom $N_{31}$ (−0.215), net positive atomic charge values on hydrogen atom $H_{38}$ (0.308), $H_{14}$ (0.247) and $H_{18}$ (0.266) may support the formation of hydrogen bonding $N_{31}–H_{38}–O_{33}$, $C_{13}–H_{14}–O_{34}$ and $C_{17}–H_{18}–O_{34}$.

### 3.11. Sensitivity towards autoxidation and stability in water

Modern water purification methods in the case of organic pharmaceutical pollutants are based on the oxidation reactions [90–92]. In terms of computational molecular modelling techniques, the concept of bond dissociation energies (BDE) can be useful for predicting molecule's weak spots where degradation could start. Particularly, bond dissociation energies for hydrogen abstraction (H-BDE) resemble the molecule's sensitivity towards autoxidation mechanism [93–95], while in the same time BDEs for the remaining single acyclic bonds can be very useful for predicting

**Table 8**
The electric dipole moment (μ), polarizability (Δα) and first order hyper polarizability (β) of title compound by B3LYP/6-311G++(d,p).

| Parameter | Value | Parameter | a.u. | esu (×$10^{-24}$) | Parameter | a.u. | esu (×$10^{-33}$) |
|---|---|---|---|---|---|---|---|
| $\mu_x$ | −1.7249 | $\alpha_{xx}$ | 265.9277 | 39.4104 | $\beta_{xxx}$ | 966.0397 | 8345.9067 |
| $\mu_y$ | 1.1390 | $\alpha_{xy}$ | 13.2483 | 1.9633 | $\beta_{xxy}$ | 718.7733 | 6209.6981 |
| $\mu_z$ | 0.9312 | $\alpha_{yy}$ | 217.2198 | 32.1919 | $\beta_{xyy}$ | 322.1631 | 2783.2636 |
| $\mu_o$ | 2.2670 | $\alpha_{xz}$ | −24.6687 | 3.6559 | $\beta_{yyy}$ | 29.1894 | 252.1759 |
| | | $\alpha_{yz}$ | 1.0165 | 0.1506 | $\beta_{xxz}$ | −137.3283 | 1186.4203 |
| | | $\alpha_{zz}$ | 214.6588 | 31.8124 | $\beta_{xyz}$ | −28.2303 | 243.89 |
| | | $\alpha_{tot}$ | 232.6021 | 34.4716 | $\beta_{yyz}$ | −24.3833 | 210.6546 |
| | | Δα | 50.0441 | 7.4165 | $\beta_{xzz}$ | −120.6461 | 1042.2978 |
| | | | | | $\beta_{yzz}$ | 4.6938 | 40.5511 |
| | | | | | $\beta_{zzz}$ | 77.0165 | 665.3686 |
| | | | | | $\beta_{tot}$ | 1391.7089 | 12023.3906 |
| | | | | | $\beta_{tot} = 12.02 \times 10^{-30}$ esu | | |

**Table 9**
Second-order perturbation theory analysis of Fock matrix in NBO basis corresponding to the intramolecular bonds of the title compound.

| Donor(i) | Type | ED/e | Acceptor(j) | Type | ED/e | E (2)[a] | E(*j*)-E(i)[b] | F (i,j)[c] |
|---|---|---|---|---|---|---|---|---|
| C1–C2 | σ | 1.97716 | C1–C9 | σ* | 0.02400 | 3.90 | 1.27 | 0.063 |
| _ | – | | C2–C4 | σ* | 0.01496 | 2.13 | 1.30 | 0.047 |
| _ | – | | O33–S37 | σ* | 0.14580 | 0.58 | 0.99 | 0.022 |
| C1–C9 | σ | 1.97704 | C1–C2 | σ* | 0.02395 | 3.89 | 1.28 | 0.063 |
| _ | – | | C7–C9 | σ* | 0.01480 | 2.18 | 1.30 | 0.048 |
| _ | – | | O34–S37 | σ* | 0.15553 | 0.61 | 0.99 | 0.023 |
| C2–C4 | σ | 1.97568 | C1–C2 | σ* | 0.02395 | 2.83 | 1.25 | 0.053 |
| _ | – | | C1–S37 | σ* | 0.20548 | 3.50 | 0.86 | 0.051 |
| _ | – | | C4–C6 | σ* | 0.02239 | 2.55 | 1.27 | 0.051 |
| _ | – | | C6–C19 | σ* | 0.01388 | 3.33 | 1.11 | 0.054 |
| C4–C6 | σ | 1.97692 | C2–C4 | σ* | 0.01496 | 2.33 | 1.27 | 0.049 |
| _ | – | | C6–C7 | σ* | 0.02266 | 2.53 | 1.26 | 0.050 |
| _ | – | | C6–C19 | σ* | 0.01388 | 1.31 | 1.11 | 0.034 |
| C6–C7 | σ | 1.97678 | C4–C6 | σ* | 0.02239 | 2.52 | 1.26 | 0.050 |
| _ | – | | C6–C19 | σ* | 0.01388 | 1.27 | 1.11 | 0.034 |
| _ | – | | C7–C9 | σ* | 0.01480 | 2.34 | 1.27 | 0.049 |
| C7–C9 | σ | 1.97587 | C1–C9 | σ* | 0.02400 | 2.88 | 1.25 | 0.054 |
| _ | – | | C1–S37 | σ* | 0.20548 | 3.38 | 0.87 | 0.051 |
| _ | – | | C6–C7 | σ* | 0.02266 | 2.54 | 1.27 | 0.051 |
| _ | – | | C6–C19 | σ* | 0.01388 | 3.28 | 1.12 | 0.054 |
| C11–C17 | σ | 1.97383 | C11–C12 | σ* | 0.03083 | 3.62 | 1.25 | 0.060 |
| _ | – | | C11–N31 | σ* | 0.03005 | 0.93 | 1.12 | 0.029 |
| _ | – | | C12–C23 | σ* | 0.01497 | 3.23 | 1.11 | 0.054 |
| C11–C17 | π | 1.63339 | C11–C17 | π* | 0.37633 | 0.76 | 0.28 | 0.013 |
| _ | – | | C12–C13 | π* | 0.30516 | 15.53 | 0.29 | 0.061 |
| _ | – | | C15–C16 | π* | 0.41191 | 21.46 | 0.28 | 0.075 |
| C12–C13 | σ | 1.97050 | C11–C12 | σ* | 0.03083 | 3.03 | 1.25 | 0.055 |
| _ | – | | C11–N31 | σ* | 0.03005 | 4.14 | 1.12 | 0.061 |
| _ | – | | C12–C23 | σ* | 0.01497 | 1.70 | 1.11 | 0.039 |
| C15–C16 | σ | 1.97351 | C13–C15 | σ* | 0.01906 | 3.79 | 1.27 | 0.062 |
| _ | – | | C16–C17 | σ* | 0.01780 | 2.11 | 1.28 | 0.047 |
| _ | – | | C16–C27 | σ* | 0.01377 | 1.71 | 1.12 | 0.039 |
| N32–O36 | σ | 1.99561 | C13–C15 | σ* | 0.01906 | 0.80 | 1.62 | 0.032 |
| _ | – | | C15–N32 | σ* | 0.09523 | 0.55 | 1.36 | 0.025 |
| N32–O36 | π | 1.98387 | C15–C16 | π* | 0.41191 | 3.35 | 0.46 | 0.039 |
| _ | – | | N32–O36 | π* | 0.63887 | 7.42 | 0.31 | 0.052 |
| LP N31 | σ | 1.80373 | C1–S37 | σ* | 0.20548 | 7.63 | 0.47 | 0.053 |
| _ | – | | C11–C17 | π* | 0.37633 | 23.39 | 0.33 | 0.082 |
| _ | – | | O34–S37 | σ* | 0.15553 | 3.69 | 0.57 | 0.042 |
| LP O33 | σ | 1.98241 | C1–S37 | σ* | 0.20548 | 0.81 | 0.96 | 0.026 |
| _ | – | | O34–S37 | σ* | 0.15553 | 2.20 | 1.07 | 0.045 |
| LP O33 | π | 1.81651 | C1–S37 | σ* | 0.20548 | 17.99 | 0.45 | 0.081 |
| _ | – | | N31–S37 | σ* | 0.27315 | 8.97 | 0.40 | 0.055 |
| LP O34 | σ | 1.98051 | C1–S37 | σ* | 0.20548 | 0.77 | 0.96 | 0.026 |
| _ | – | | O33–S37 | σ* | 0.14580 | 2.08 | 1.07 | 0.043 |
| LP O34 | π | 1.81923 | C1–S37 | σ* | 0.20548 | 17.63 | 0.45 | 0.080 |
| _ | – | | N31–S37 | σ* | 0.27315 | 10.34 | 0.40 | 0.059 |
| LP O35 | σ | 1.9813 | C15–N32 | σ* | 0.09523 | 4.27 | 1.09 | 0.062 |
| _ | – | | N32–O36 | σ* | 0.63887 | 2.27 | 1.21 | 0.047 |
| LP O35 | π | 1.89823 | C15–N32 | σ* | 0.09523 | 11.51 | 0.58 | 0.073 |
| _ | – | | N32–O36 | σ* | 0.05723 | 19.09 | 0.70 | 0.104 |
| LP O35 | n | 1.46754 | N32–O36 | π* | 0.63887 | 155.95 | 0.14 | 0.136 |
| LP O36 | π | 1.90136 | C15–N32 | σ* | 0.09523 | 10.94 | 0.58 | 0.071 |
| _ | – | – | N32–O35 | σ* | 0.05831 | 19.69 | 0.70 | 0.106 |

[a] E (2) means energy of hyper-conjugative interactions (stabilization energy in kJ/mol).
[b] Energy difference (a.u) between donor and acceptor i and j NBO orbitals.
[c] F (i,j) is the Fock matrix elements (a.u) between i and j NBO orbitals.

where degradation mechanism could start.

Since majority of pharmaceutical pollutants eventually end up in the water resources, it is also of great importance for predictions of degradation properties to understand the stability of molecules in water. This can be done thanks to the molecular dynamics (MD) simulations and radial distribution functions (RDF), which are very useful for the identification of atoms with pronounced interactions with water molecules. The results regarding BDEs are presented in Fig. 11, while Fig. 12 contains information on the most important RDFs.

Results presented in Fig. 11 indicate the absence of H-BDE values lower than at least 90 kcal/mol. This indicates that the title

**Table 10**
NBO results showing the formation of Lewis and non-Lewis orbitals.

| Bond (A-B) | ED/e[a] | EDA% | EDB% | NBO | s% | p% |
|---|---|---|---|---|---|---|
| σC1-C2 | 1.97716 | 51.40 | 48.60 | 0.7169 ($sp^{1.61}$)C+ | 38.33 | 61.63 |
| _ | −0.74770 | – | – | 0.6971 ($sp^{1.97}$)C | 33.65 | 66.30 |
| σC1-C9 | 1.97704 | 51.34 | 48.66 | 0.7165 ($sp^{1.63}$)C+ | 38.05 | 61.91 |
| _ | −0.74669 | – | – | 0.6975 ($sp^{1.97}$)C | 33.66 | 66.29 |
| σC2-C4 | 1.97568 | 50.33 | 49.67 | 0.7094 ($sp^{1.81}$)C+ | 35.52 | 64.44 |
| _ | −0.72622 | – | – | 0.7048 ($sp^{1.86}$)C | 35.00 | 64.96 |
| σC4-C6 | 1.97692 | 49.28 | 50.72 | 0.7020 ($sp^{1.85}$)C+ | 35.03 | 64.93 |
| _ | −0.72233 | – | – | 0.7121 ($sp^{1.94}$)C | 34.00 | 65.96 |
| σC6-C7 | 1.97678 | 50.68 | 49.32 | 0.7119 ($sp^{1.95}$)C+ | 33.84 | 66.12 |
| _ | −0.72114 | – | – | 0.7023 ($sp^{1.86}$)C | 34.97 | 64.99 |
| σC7-C9 | 1.97587 | 49.65 | 50.35 | 0.7046 ($sp^{1.85}$)C+ | 35.09 | 64.87 |
| _ | −0.72850 | – | – | 0.7096 ($sp^{1.80}$)C | 35.66 | 64.30 |
| σC11-C17 | 1.97383 | 51.47 | 48.53 | 0.7174 ($sp^{1.71}$)C+ | 36.88 | 63.08 |
| _ | −0.73082 | – | – | 0.6966 ($sp^{1.97}$)C | 33.65 | 66.30 |
| πC11-C17 | 1.63339 | 47.40 | 52.60 | 0.6885 ($sp^{99.99}$)C+ | 0.01 | 99.99 |
| _ | −0.28039 | – | – | 0.7252 ($sp^{99.99}$)C | 0.01 | 99.95 |
| σC12-C13 | 1.97050 | 50.80 | 49.20 | 0.7127 ($sp^{1.86}$)C+ | 35.00 | 64.96 |
| _ | −0.72910 | – | – | 0.7014 ($sp^{1.80}$)C | 35.76 | 64.20 |
| σC15-C16 | 1.97351 | 50.44 | 49.56 | 0.7102 ($sp^{1.60}$)C+ | 38.44 | 61.52 |
| _ | −0.73156 | – | – | 0.7040 ($sp^{2.03}$)C | 33.01 | 66.95 |
| σN32-O36 | 1.99561 | 49.06 | 50.94 | 0.7004 ($sp^{2.15}$)N+ | 31.66 | 68.23 |
| _ | −1.08213 | – | – | 0.7138 ($sp^{3.13}$)O | 24.18 | 75.68 |
| πN32-O36 | 1.98387 | 39.14 | 60.86 | 0.6256 ($sp^{99.99}$)N+ | 0.02 | 99.72 |
| _ | −0.45651 | – | – | 0.7801 ($sp^{99.99}$)O | 0.06 | 99.71 |
| n1 N31 | 1.80373 | – | – | $sp^{14.60}$ | 6.41 | 93.56 |
| _ | −0.32731 | – | – | – | – | – |
| n1 O33 | 1.98241 | – | – | $sp^{0.32}$ | 75.47 | 24.50 |
| _ | −0.82036 | – | – | – | – | – |
| n2 O33 | 1.81651 | – | – | $sp^{99.99}$ | 0.08 | 99.61 |
| _ | −0.31360 | – | – | – | – | – |
| n1 O34 | 1.98051 | – | – | $sp^{0.33}$ | 75.20 | 24.76 |
| _ | −0.81948 | – | – | – | – | – |
| n2 O34 | 1.81923 | – | – | $sp^{99.99}$ | 0.11 | 99.58 |
| _ | −0.31566 | – | – | – | – | – |
| n1O35 | 1.98139 | | | $sp^{0.32}$ | 75.71 | 24.28 |
| _ | −0.81272 | – | – | – | – | – |
| n2 O35 | 1.89823 | – | – | $sp^{99.99}$ | 0.25 | 99.64 |
| _ | −0.29882 | – | – | – | – | – |
| n3O35 | 1.46754 | – | – | $sp^{99.99}$ | 0.07 | 99.73 |
| _ | −0.28319 | – | – | – | – | – |
| n2O36 | 1.90136 | – | – | $sp^{99.99}$ | 0.41 | 99.48 |
| _ | −0.30047 | – | – | – | – | – |

[a] ED/e is expressed in a. u.

**Table 11**
Mulliken atomic charge of title compound by DFT/B3LYP/6-311G (d,p).

| Atoms | Atomic charges | Atoms | Atomic charges |
|---|---|---|---|
| S37 | 0.134 | H3 | 0.208 |
| N31 | −0.215 | H5 | 0.182 |
| N32 | −0.203 | H8 | 0.184 |
| O33 | −0.131 | H10 | 0.249 |
| O34 | −0.100 | H14 | 0.247 |
| O35 | 0.013 | H18 | 0.266 |
| O36 | 0.004 | H20 | 0.185 |
| C1 | 0.204 | H21 | 0.151 |
| C2 | −0.285 | H22 | 0.156 |
| C4 | −0.610 | H24 | 0.175 |
| C6 | 0.496 | H25 | 0.182 |
| C7 | −0.495 | H26 | 0.153 |
| C9 | −0.164 | H28 | 0.195 |
| C11 | −0.199 | H29 | 0.138 |
| C12 | 0.955 | H30 | 0.212 |
| C13 | −0.442 | H38 | 0.308 |
| C15 | −2.057 | | |
| C16 | 1.860 | | |
| C17 | −0.683 | | |
| C19 | −0.479 | | |
| C23 | −0.471 | | |
| C27 | −0.326 | | |

molecule is not sensitive towards the autoxidation mechanism. Namely, all of the H-BDE values are much higher than the desired threshold of 90 kcal/mol, with the lowest H-BDE values calculated for hydrogen atoms of methyl groups, thanks to which it is expected that the title molecule is stable in the presence of oxygen. The lowest BDE value of the rest of the single acyclic bonds have been calculated in the case of N—S bond, with BDE value of just 41 kcal/mol, indicating that degradation could start precisely by breaking of this bond. Other significantly low BDE values have been calculated in the cases of C—N bond (N belonging to the $NO_2$ group) and C—S bond, with BDE values of around 70 kcal/mol, indicating that detachment of benzene or $NO_2$ group could occur during the degradation.

Calculations of RDFs indicate that six atoms of NDMPMBS have high and sharp RDF curves. However, five of six of the aforementioned atoms have their maximal g($r$) values located at distances of around 4 Å. Certainly, the most important RDF has been calculated in the case of hydrogen atom $H_{38}$, with its maximal g($r$) value located at distance of 2 Å, which indicates significant interactions with water molecules. This hydrogen atom with the most important RDF curve is located adjacent to the bond with the lowest BDE value, indicating that the influence of water could be of importance for the degradation of NDMPMBS.

### 3.12. Drug likeness and molecular docking

Drug likeness properties associated to the Lipinski's rule of five [96,97] for the newly synthetized NDMPMBS molecule have been calculated and summarized in Table 12. According to all parameters provided in Table 12 it can be concluded that newly synthetized NDMPMBS molecule could be considered as a candidate for practical applications in some pharmaceutical formulation. Namely, the AlogP value is 3.67, which is far below the desired threshold of 5. In the same time, prospective drug candidates should have less than 5 and 10 HBD and HBA, respectively. These prerequisites are also fulfilled by the NDMPMBS molecule. Ghose et al. [98], have stated that the molar refractivity should be in the range between 40 and 130, while PSA should take values less than 140 $Å^2$. Inspection of Table 12 clearly indicates that these criteria are satisfied by the NDMPMBS molecule, including the criteria by Veber et al. [99], for the number of rotatable bonds, which should be lower than 10. NDMPMBS molecule is also very close to satisfy the Congreeve's rule of three [100]. Namely, the Congreeve's rule of three is just slightly violated by the NDMPMBS molecule in terms of somewhat higher AlogP value and one more rotatable bond.

Drug likeness parameters motivated us to further investigate NDMPMBS molecule from the aspect of pharmaceutical properties. In order to identify in which direction NDMPMBS molecule could exhibit its biological activity we have employed the Prediction of Activity Spectra for Substances (PASS) online software [101], which screens the biologically activity spectrum of the potential drug candidates taking into account the large training set. The results concerning the predicted biological activities have been summarized in Table 13, where Pa represents the probability for molecule to be active, while Pi represents the probability for molecule to be inactive. Table 13 contains information about activities that are higher than 0.7.

According to the screening of biological activities by PASS it can be seen that NDMPMBS molecule has significantly high probabilities to be active as inhibitor of arylsulfatesulfotransferase and

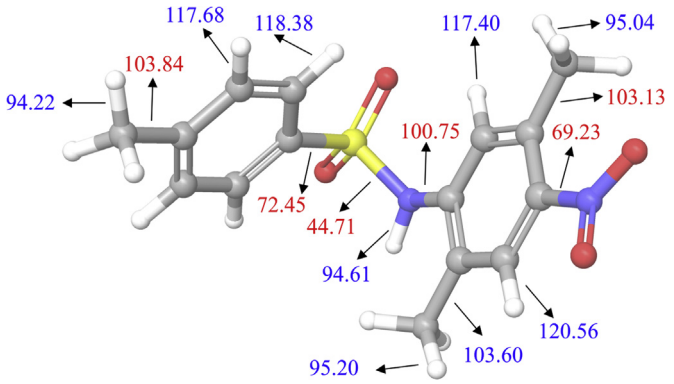



**Fig. 11.** BDE of all single acyclic bonds of *N*-(2,5-dimethyl-4-nitrophenyl)-4-methylbenzenesulfonamide.

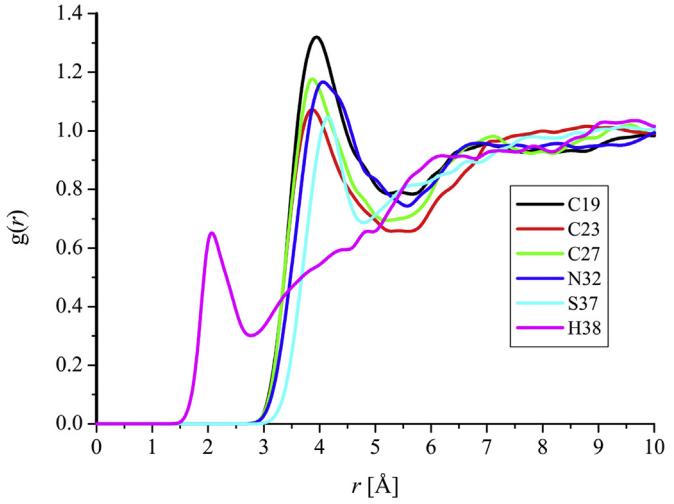



**Fig. 12.** RDF's of atoms of *N*-(2,5-dimethyl-4-nitrophenyl)-4-methylbenzenesulfonamide with significant interactions with water.

**Table 12**
Drug likeness parameters for the NDMPMBS molecule.

| Descriptor | Value |
|---|---|
| Hydrogen Bond Donor (HBD) | 1 |
| Hydrogen Bond Acceptor (HBA) | 2 |
| Mass | 320.40 |
| AlogP | 3.67 |
| Polar surface area (PSA) [Å2] | 97.69 |
| Molar refractivity | 85.34 |
| Number of atoms | 38 |
| Number of rotatable bonds | 4 |

polyporopepsin. Since probabilities for these two activities are very similar, we have decided to investigate how NDMPMBS molecule binds to the representatives of proteins related to arylsulfate-sulfotransferase and polyporopepsin. Using the RCSB protein databank and taking into account the arylsulfatesulfotransferase and polyporopepsin inhibitor acitivites we have chosen to investigate docking of NDMPMBS to proteins with PDB IDs: 1WKR and 3ETT, respectively.

Molecular docking has been performed with Autodock4 tools, while preparation of ligand and proteins has been performed with AutoDock tools [102]. After being imported from the protein databank, proteins have been firstly prepared by the set of the

**Table 13**
PASS predicted biological activities of NDMPMBS.

| Pa | Pi | Activity |
|---|---|---|
| 0.889 | 0.004 | Arylsulfate sulfotransferase inhibitor |
| 0.888 | 0.007 | Polyporopepsin inhibitor |
| 0.860 | 0.005 | Glutamyl endopeptidase II inhibitor |
| 0.850 | 0.003 | Phospholipid-translocating ATPase inhibitor |
| 0.766 | 0.011 | Omptin inhibitor |
| 0.757 | 0.010 | Venombin AB inhibitor |
| 0.744 | 0.003 | Antiprotozoal (Coccidial) |
| 0.758 | 0.023 | Benzoate-CoA ligase inhibitor |
| 0.731 | 0.004 | Aspergillopepsin I inhibitor |
| 0.724 | 0.011 | 2-Hydroxymuconate-semialdehyde hydrolase inhibitor |
| 0.734 | 0.056 | Ubiquinol-cytochrome-c reductase inhibitor |

actions including: removal of water molecules, addition of hydrogen atoms and addition of charges according to Gasteiger-Marsili approach. Protein sites which contained docked molecules from the experimentally obtained results were used as a target search space for docking studies. Fig. 13 contains illustration of the docked NDMPMBS molecule to the surface of the two selected proteins, while binding energies of several representative docking modes have been summarized in Table 14.

Results provided in Fig. 13 and Tables 12–14 indicate great potential of the newly synthesized NDMPMBS molecule for application in pharmaceutical applications. Fig. 13 and Table 14 illustrate that NDMPMBS molecule binds to 1WKR and 3ETT proteins with significantly high binding energies. In both cases binding energy of the most representative docking mode had the value of −7.20 kcal/

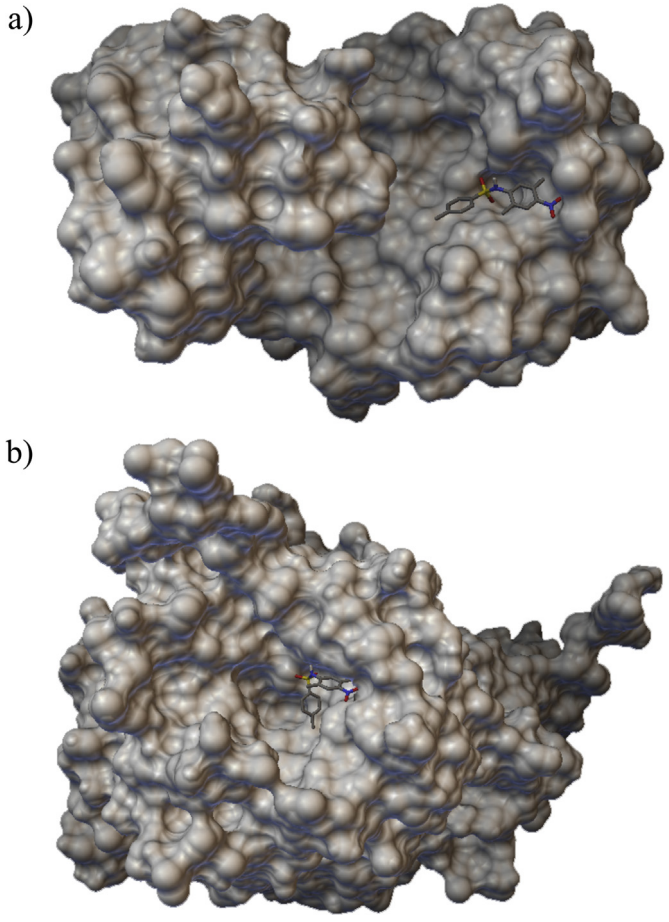



**Fig. 13.** Docked NDMPMBS molecule at the surface of a) 1WKR and b) 3ETT proteins.

**Table 14**
The binding energies of several modes for docking of NDMPMBS against 1WKR and 3ETT

| Mode | Binding energy with 1WKR (kcal/mol) | Binding energy with 3ETT (kcal/mol) |
|---|---|---|
| 1 | −7.20 | −7.20 |
| 2 | −6.96 | −7.12 |
| 3 | −6.90 | −7.12 |
| 4 | −5.77 | −7.01 |
| 5 | −5.76 | −6.97 |
| 6 | −5.70 | −6.85 |
| 7 | −5.62 | −6.78 |
| 8 | −5.61 | −6.66 |
| 9 | −5.46 | −6.97 |
| 10 | −5.45 | −6.79 |

mol. However, the remaining docking modes in the case of 3ETT protein had higher magnitudes of binding energies than in the case of 1WKR protein. Thus, the molecular docking results indicate that the newly synthetized molecule could be considered as a candidate with significant activity against the bacterial arylsulfatesulfotransferase catalytic intermediate (3ETT).

## 4. Conclusion

*N*-(2,5-dimethyl-4-nitrophenyl)-4-methylbenzenesulfonamide has been synthesized and characterized by single crystal X-ray diffraction, FT-IR, FT-Raman, $^{1}H$ and $^{13}C$ NMR. The molecular conformation is stabilized by $C_{17}—H_{18}—O_{34}$ intra-molecular hydrogen bond that encloses to form a S (6) motif. The vibrational spectroscopic studies of title compound were investigated experimentally (FT-IR and FT-Raman) and theoretically. The complete assignment of normal mode of vibrations was done by potential energy distribution analysis. Computationally predicted geometrical parameters are good in agreement with the experimental SCXRD data. HOMO is confined on $-NH-SO_2$ group and delocalized over nitrobenzene; LUMO is confined on nitro group, delocalized on benzene ring of nitrobenzene which gives charge transfer process in the molecular system. The most electrophilic sites are oxygen atoms of sulfonyl group as well as nitro group and neucleophilic sites are amine hydrogen as well as other hydrogen atoms. The is first-order hyperpolarizibilitiy($\beta$) of NDMPMBS calculated and is found to be $12.02 \times 10^{-30}$ esu which is 92.46 times that of the standard NLO material urea. ALIE surfaces and Fukui functions indicate that oxygen atoms $O_{35}$ and $O_{36}$ could be important reactive centres of the NDMPMBS molecule. H-BDE values indicate that NDMPMBS molecule is not sensitive towards the autoxidation, however BDE of the N—S bond has very low value of just 41 kcal/mol, indicating that degradation mechanism could start with the breaking of this bond. Analysis of RDFs indicate that hydrogen atom $H_{38}$ has pronounced interactions with water molecules, which could be also of importance for the degradation of NDMPMBS molecule, since $H_{38}$ is adjacent to the weakest single acyclic bond. Drug likeness parameters indicate high potential of the title molecule for the practical pharmaceutical applications.

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## Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.molstruc.2017.10.028.

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# Formulations and Analytical Method Developments for Poor Soluble Drugs: A Review on Applications of Nano Chemistry

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**Abstract-** In this review, various approaches for nano-formulations for poor soluble and low permeable drugs are focused, advantages and future scope for the nono formulations in pharmaceutical industries are elaborated. For the manufacture of new medicines new manufacturing technology is needed. In the pharmaceutical formulations pellets dosage forms gives the improved results compare to tablet dosage forms. According to ICH BCS (BIOPHARMACEUTICS CLASSIFICATION SYSTEM) drugs class four, Low solubility, Low permeability drugs. Improved use of Low solubility, Low permeability drugs pelletized formulation at Nano level is proposed. Nano level pelletized drug formulations gives the better results compared to normal, micro level pelletized drug formulations.

**Key words-** Analytical method development, Nano-formulation, and Nano-chemistry

## 1. INTRODUCTION

Our daily life is depends on quality of the food we eat, the medicine we use the water we drink, and the air we breathe. The compound which is interacts with a biological organism to produce a biological response that may be favorable or harmful. Favorable is known as medicine, harmful is known as poison. Due to expressed development in the field of science and technology new medications are rapidly coming in to the market for new syndrome. For the manufacture of new medicines new manufacturing technology is needed. In the pharmaceutical formulations pellets dosage forms gives the improved results compare to tablet dosage forms. These dosage forms summarized in terms of safety, purity, efficacy and stability. Final pharmaceutical pellets dosage forms comprises an active pharmaceutical ingredient (API) combined with a varying number of excipients. Some of the Active pharmaceutical ingredients are Low solubility, Low permeability nature (BCS class four). To overcome the low solubility, low permeability problem we are proposing nano level formulations methodology. Very few researchers are worked on the Nano technology applications for drug molecules, even though not related to Nano pelletized formulations. Nano pelletized formulations gives the improved results in controlling of various types of diseases compare to normal, micro level formulations. Due to this reason we are concentrating on nano level pelletized formulations, and its analytical method development. Our ultimate aim is "Best medication for Healthier world" with lesser price.

## 2. OBJECTIVES

- Our daily life is mainly depends on quality of the air, water, food medicine, without these we are unable to assume our life.
- The compound which is interacts with a biological system to produce a biological response that may be Beneficial is known as medicine, harmful is known as poison.
- Manufacturing of medicines are regulated by Food and Drug administration (FDA): International conference on harmonization (ICH): Current good manufacturing practices (cGMP): Pre-approval Inspections (PAIS): World health organization (WHO), ultimate aim is quality of medicines for healthier world.
- The pharmacopeias (USP, B.P, IP, and E.P) necessities for a pharmaceutical dosage form may be summarizing in terms of safety, purity, efficacy and stability.
- Final pharmaceutical formulations comprises an active pharmaceutical ingredient (API) combined with a varying number of excipients.
- The word "Pellet" describes a variety of systematically produced, geometrically defined agglomerates obtained from various starting materials utilizing different processing conditions.

- Pellets have various therapeutic advantages over traditional single units, such as tablets and powder-filled capsules.
- According to ICH BCS (BIOPHARMACEUTICS CLASSIFICATION SYSTEM) drugs class four, Low solubility, Low permeability drugs.
- Improved use of Low solubility, Low permeability drugs pelletized formulation at Nano level is proposed.
- Nano level pelletized drug formulations gives the better results compared to normal, micro level pelletized drug formulations.
- In house Analytical methods have to be developed and validated for the Analysis of nano level drug formulations.
- Our ultimate aim is to produce the best medicines for healthier world with lesser cost.

## 3. IMPORTANCE OF THE PROPOSED AREA IN THE PRESENT CONTEXT

With the aim of producing "Quality medicines in low prices for healthier world", we are reviewing of Nano level pelletized formulations for low solubility, Low permeability drug materials. According ICH these are BCS (BIOPHARMACEUTICS CLASSIFICATION SYSTEM) drugs class four. Very lesser number of researchers doing the research work related to Nano technology applications to drugs formulations, but not doing pelletized formulations in Nano level. These formulations gives the effective medicines with lesser side effects compare to normal, micro level formulations. Nano level pelletized formulations advantages as follows.

- Solubility of the drugs can be increases.
- Permeability of the drug in biological matter can be increases.
- Lesser amount of drug dosage is required to control the disease.
- Side effects are less compare to normal and micro level drug dosage formulations.
- Consumption of drugs dosage frequency is less.

Due to above advantages proposed Review i.e Nano level Pelletized formulations place important role in invention of Medicines.

The compound which is interacts with a biological organism to produce a biological response that may be favorable or harmful. favorable is known as medicine, harmful is known as poison. for example, penicillin reacts with bacterial cause to kill them.

Penicillin

Penicillin is a medicine for Humans due to it interacts with bacteria and kills them. In case of bacteria it is a (biological system) poison.

The articulated development in the field of science and technology utilized as on date merged with relatively stringent new regulations, namely federal drug authority, latestly called as food and drug administration (FDA):International conference on harmonization (ICH): Current good manufacturing practices(cGMP): Pre-approval Inspections(PAIS):World health organization(WHO), like organizations are now serving as a legal binding specifically for the pharmaceutical formulations and drug analysis.

## 4. ROLE OF API'S IN DRUG FORMULATIONS

APIs are core active substances mixed with a carrier in any medication. When any of the active substance is not easily absorbed by the human body; the substance is dissolved into or mixed with an excipient so that the human body easily receives it. Further these actives are used as medications.

4.1. According to ICH BCS (BIOPHARMACEUTICS CLASSIFICATION SYSTEM) drugs class four, Low solubility, Low permeability drugs. Consider example for API(Active pharmaceutical Ingredient)

- ACECLOFENAC ($C_{16}H_{13}Cl_2NO_4$), chemically [(2-{2, 6-dichlorophenyl) amino} phenylacetooxyacetic acid],
- Acyclovir (ACV): It also known as acyclovir is an antiviral medication. It is primarily used for the treatment of virus infections, chickenpox, and shingles.

*4.2. Pellets*

The word "Pellet" has been used to exemplify a variety of systematically produced, geometrically defined agglomerates obtained from various starting materials utilizing different processing conditions. Pellets range in size, typically, between 0.5 – 2.0 mm, though other sizes could be prepared.

4.3. Low solubility, Low permeability drugs pelletized formulations in Nano level, are useful as better medications for various types of diseases. Very few researchers did the work on Nano technology applications for drug molecules, even though not related to Nano pelletized formulations. So we are concentrating on the Nano level pelletized formulations for BCS drugs class four. These

formulations are use full for the society to control the various types' diseases with lesser side effects. Our ultimate aim is "Best medication for Healthier world" with lesser price.

*4.4. Analytical Method Development:* In house Analytical method is useful for the Analysis of Nano level formulated drugs to check the dissolution profile, Assay, stability of the various dosage forms; the method must be validated according to ICH guidelines, Parameters for approval

## 5. RESEARCH AND DEVELOPMENT IN THE SUBJECT

Review subject, Nano level pelletized formulations, literature reveals that

- Nano suspension drug delivery system (DDS) was firstly developed in 1994 for the poorly soluble drugs.
- Pharmaceutical medicinal products "curcumin nano crystal" have a significant role in treatment of various types diseases such as cancers of pancreas or colon or even multiple myeloma, psoriasis or myelodys plastic syndromes (Goel et al., 2008., Liu et al., 2013).
- In recent times all drugs with low solubility like curcumin can be approached by Nano crystal methods,
- One more important study in the field of Nano-formulated curcumin was done by Agarwal et al in 2007 (Garodia et al., 2007). In a study, curcumin was encapsulated with more than 97.5% potency in PLGA and PEG. It has been proved that nano-formulated curcumin represents more efficacy and faster cellular uptake than free curcumin in vitro.

Literature survey reveals that very lesser number of researchers did the work on Nano level pelletized formulations, but it reveals that excellent scope is present on this work because advantages are more on Nano level pelletized formulations

## 6. CONCLUSION

In order to be classified as a "nano pharmaceutical", we suggest the drug product has to meet two major criteria. First, nano engineering has to play a major role in the manufacturing process. Second, the nano material used has to be either essential for the therapeutic activity or has to confer additional and unique properties to the active drug entity. Above literature reviles that Worldwide very less research work is going on Nano level pelletized formulations.

Nano level pelletized drug formulations gives the better results compared to normal, micro level pelletized drug formulations.

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RESEARCH ARTICLE

# One-Pot Synthesis of Triazolo-Heterolignans: Biological Evaluation and Molecular Docking Studies as Tubulin Inhibitors

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**Abstract:** ***Background*:** The anti-mitotic activity of podophyllotoxin derivative targeting tubulin enzyme proved them as strong polymerization inhibitors. The introduction of heteroatom along with different heteroaryl systems in naturally obtained lignans created a latitude for design of bioactive components. A novel one-pot sequential propargylation/cycloaddition reaction strategy has been followed to synthesize triazolo-heterolignans.

***Objective*:** To screen anti-proliferative activity of novel heterolignans and to determine their mode of action

***Method*:** SRB assay, Cytotoxicity evaluation, PI uptake for analysis of cell cycle, caspase-3 activity, Western blot analysis and Immunofluorescence and molecular docking studies.

***Results*:** SRB assay of synthesised compounds were provided compound **3a** and **5f** to be highly active among the synthesized compounds. The Compound **3a** showed cell cycle arrest at G2/M phase and **5f** arrest the cells at G1 phase. Compound **5f** displayed caspase 3 mediated apoptotic effect at lower levels. Compound **3a** and **5f** displayed microtubule disassembly inhibition same as paclitaxel and found to be occupying colchicine binding site of tubulin, both ligands were depicted π-cation interaction with Lys352 residue and triazole ring accommodated at the lactone binding site.

***Conclusion*:** A novel one-pot sequential propargylation/cycloaddition reaction has been developed for the synthesis of triazolo-heterolignans. Compound **3a** and **5f** were displayed good cytotoxic activities and found to inhibit microtubule disassembly. The importance of triazole ring of heterolignans has been studied by molecular docking experiments and results were compared.

**Keywords:** Heterolignan, one-pot synthesis, cycloaddition, anti-proliferative, tubulin inhibitor, molecular docking.

## 1. INTRODUCTION

The discovery of bioactive lignans from plant sources against cancer created a new platform to design promising drug like candidates [1, 2]. Few of the lignans or its derivatives became essential drugs for cancer chemotherapy [3, 4]. Podophyllotoxin (**I**) is one of the natural lignans found to be the best ancient anti-neoplastic agent which has produced excellent drugs such as etoposide (**IA**) and teniposide (**IB**) for combating different carcinomas (Fig. **1a**) [5]. The anti-mitotic activity of podophyllotoxin derivative targeting tubulin enzyme proved them as strong polymerization inhibitors. The multifold anti-cancer activity of podophyllotoxin derivatives has drawn the attention of medicinal chemists to explore more synthetic analogs by altering its basic ring system [6]. The introduction of heteroatom along with different heteroaryl systems in naturally obtained lignans created a latitude for design of bioactive components (**II**) [7, 8]. Heterolignans with significant biological activity have been reported by the replacement of 1,3 dioxalo phenyl group with different heteroycles such as thiophene (**III**), oxazole (**IV**) and indole (**V**) [8-13]. In addition, replacement of lactone ring of podophyllotoxin [13] with triazole moiety is also investigated [14]. The heterolignans are one of the leading synthetic subclass of natural carbolignans afforded the potent bioactive agents like azatoxin (**V**) [7]. Based on the reports we have drawn attention to study the effect of series of synthesized compounds towards tubulin inhibitory activity of novel triazolo-heterolignans, comprising of heterocycle (in place of 1,3 dioxalo phenyl) and triazole (as substitute to the lactone) (Fig. **1b**). The validated *insilico* docking studies indicated that, triazole-heterolignan derivatives found to be favourable at tubulin active site when compared with lactone. Herein, we report a novel one-pot sequential propargylation/cycloaddition reaction strategy for the synthesis of triazolo-heterolignans, their biological evaluation and molecular docking studies as tubulin inhibitors.

In continuation of our interest on the synthesis of heterocycles using 1-aryl propargyl alcohols [15-18], we envisaged that the propargylation of thiophenyl azide **1** with propargylic alcohol **2** followed by 1,3 –dipolar cycloaddition reaction would lead to the desired triazolothienolignans (**3**). Firstly, the reaction of thiophenyl azide (**1,** prepared from known alcohol)[16] with 1,3-diphenylprop-2-yn-1-ol (**2a**) was studied. Based on previous work [15-21], propargylation reaction was carried out using *p*TSA to give the propargylated azide (**Int A**, 89%), which upon heating at 80°C in acetonitrile provided the 6-benzyl-3,4-diphenyl-4,8-dihydrothieno[2,3-d][1,2,3]triazolo[1,5-a]pyridine (**3a**) with 89% yield (Scheme **1**). Delightfully, the above two reactions were accomplished in one-pot to obtain **3a** in 76% yield. Similarly, diversely substituted propargylic alcohols **2b** to **2f** having different substitutions at R and $R^1$ were

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Anti-Cancer Agents in Medicinal Chemistry

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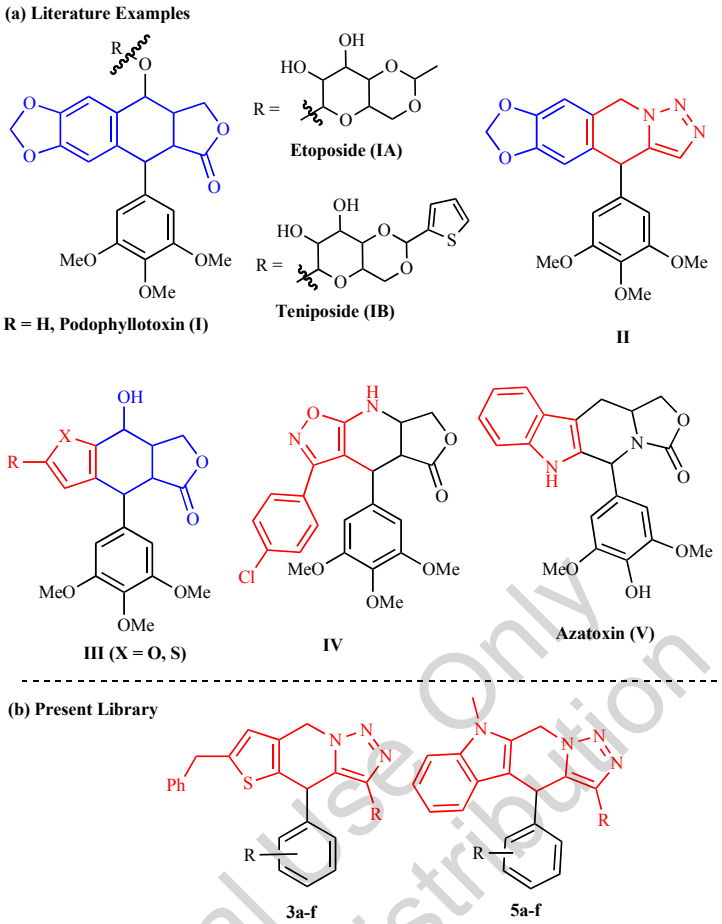



**Fig. (1).** Bioactive Lignan, heterolignans and triazoloheterolignans.

treated with azide **1** under the above optimized conditions to furnish the triazolothienolignans derivatives **3b-3f** in good yield (75-82%, Scheme **1**).

In the second case, 2-(azidomethyl)-*1H*-indole (**4**) [22] was used as substrate to accomplish the targeted triazole-indololignans. The reactions of **4** with propargylic alcohols **2a-2f** were also successful in providing the corresponding triazoloindolyl analogs **5a-5f** in good yield (78-85%) *via* the developed one-pot sequential propargylation/cycloaddition reactions (Scheme **2**).

## 2. EXPERIMENTAL DETAILS

The detailed synthetic procedures with spectral interpretations, biological testing protocol and docking methods were provided here.

### 2.1. Materials and Methods

All reactions were carried out under inert atmosphere in oven-dried glassware. Reagents and solvents were used without further purification, unless otherwise stated. All reactions were magnetically stirred and monitored by thin-layer chromatography carried out on silica plates using UV-light and anisaldehyde for visualization. Column chromatography was performed on silica gel (60–120 and 100-200 mesh) using hexanes and ethyl acetate as eluent. Evaporation of solvents were conducted under reduced pressure at temperatures less than 45°C. $^{1}$H and $^{13}$C NMR spectra were recorded in $CDCl_3$ and DMSO-d6 solvent on a 300 MHz, 400 MHz and 500 MHz NMR spectrometer. Chemical shifts δ and coupling constants J are given in ppm (parts per million) and Hz (hertz) respectively.

### 2.2. Synthesis

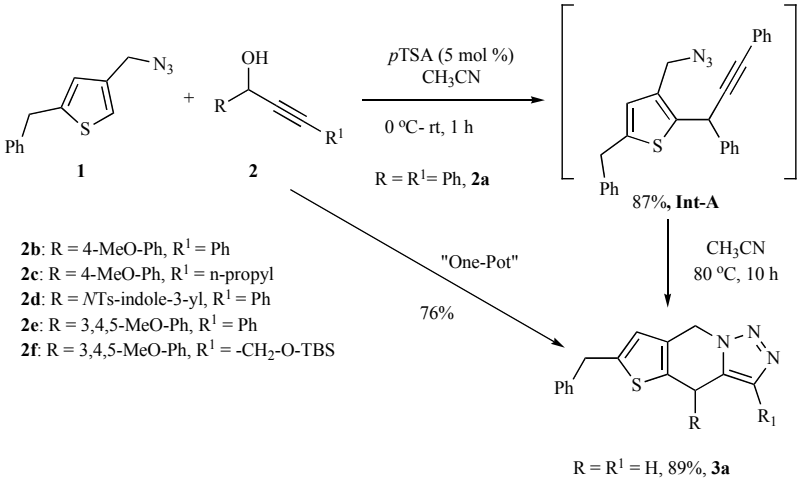
#### *4-(Azidomethyl) 2-benzyl thiophene (1)*

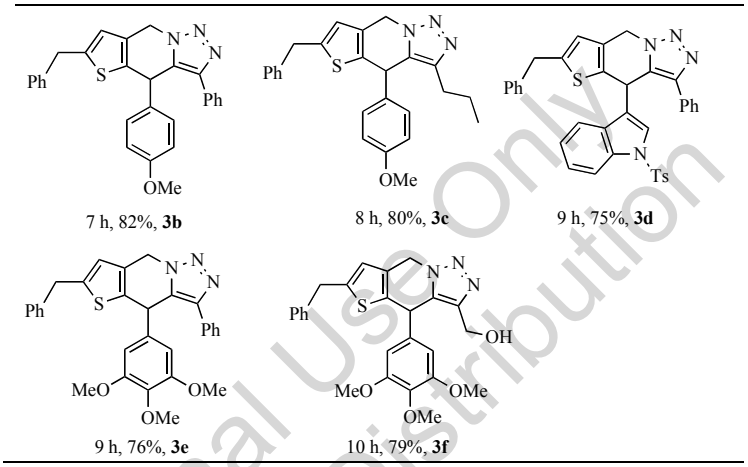
To the mixture of triphenylphosphine (1.9 g, 7.3 mmol) in THF (10 mL) was added diisopropyl azodicarboxylate (1.4 mL, 7.3 mmol), at 0°C and was maintained for 30 min at same temperature. To the reaction mixture was added (5-benzylthiophen-3-yl) methanol [19] (1 g, 4.9 mmol) in THF (10 mL) followed by the addition of DPPA (4.2 mL, 24.0 mmol) at 0°C. The reaction mixture was maintained at room temperature for 3 h. After complete consumption of alcohol (monitored by TLC), water was added to the reaction mixture and extracted with EtOAc (2 x 10 mL). The combined orgonic layer was washed with brine solution and dried over sodium sulfate. The organic layer was evaporated under reduced pressure and purified by column chromatography to give desired compound-as a colorless liquid, 0.96 g, 86% yield, $R_f$ = 0.7 (hexanes: EtOAc = 9:1); $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.33 (m, 2H), 7.19 (m, 3H), 7.04 (dt, J = 1.5, 0.8 Hz, 1H), 6.74 (d, J = 1.2 Hz, 1H), 4.24 (s, 2H), 4.12 (s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 145.8, 139.9, 135.7, 128.6, 126.6, 125.3, 122.3, 49.9, 36.3; IR (KBr): 2910, 2095, 1769, 1451, 1248, 1100, 698 cm-1.

#### *3-(Azidomethyl)-5-benzyl--2-(1,3-diphenylprop-2-yn-1-yl)thiophene (Int-A)*

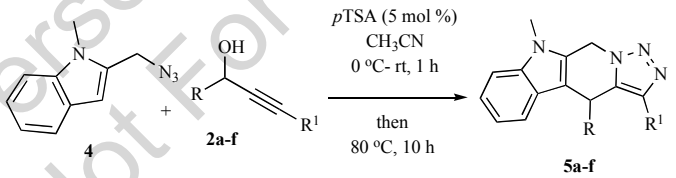
160 mg, 87% yield, Pale yellow semi solid; $R_f$ = 0.3 (hexanes: EtOAc = 9:1); $^{1}$H NMR (500 MHz, $CDCl_3$): δ 7.38 (dd, *J* = 5.1, 4.3, 3.7 Hz, 4H), 7.27 (dd, *J* = 10.7, 4.3 Hz, 2H), 7.22 (ddd, *J* = 7.5, 5.7, 4.3 Hz, 5H), 7.20-7.13 (m, 4H), 6.55 (d, *J* = 25.4 Hz, 1H), 5.37 (s, 1H), 4.20 (dd, *J* = 32.6, 13.9 Hz, 2H), 3.98 (s, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 142.7, 140.8, 140.2, 139.6, 131.7, 131.3, 128.7,

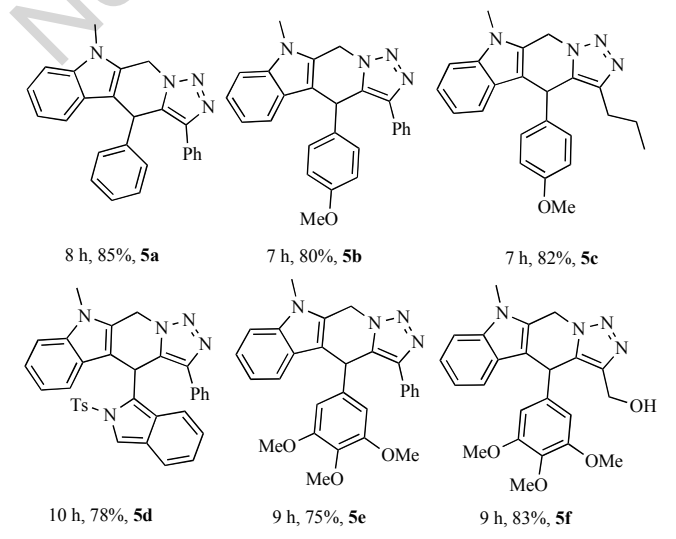
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**Scheme 1.**




**Scheme 2.** Synthesis of triazolo-indololignan **5a-f**.

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128.7, 128.6, 128.2, 127.6, 127.4, 126.8, 126.6, 122.9, 88.8, 84.6, 47.7, 36.9, 36.1; IR (KBr): 3020, 2922, 2101, 1734, 1458, 1216, 757 $cm^{-1}$; MS (ESI): *m/z* 420 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{27}H_{21}N_3NaS$ $(M+Na)^+$: 442.1348, found: 442.1370.

### *2.2.1. General procedure for the synthesis of triazole-thienolignans 3a to 3f*

To a stirred solution of azide (1.0 mmol) and propargylic alcohol (1.0 mmol) in 10 mL of acetonitrile was added *p*TSA (5 mol%) at $0^oC$, stirred at room temperature for 1 - 2 h, then the reaction mixture was heated to $80^oC$ for 7 - 10 h. After the completion of reaction (monitored by TLC), The reaction mixture was concentrated under reduced pressure. Purified by column chromatography on silica gel (EtOAc: *n*-hexane) to give the corresponding triazoles.

#### *6-Benzyl-3,4-diphenyl-4,8-dihydrothieno[2,3-d][1,2,3]triazolo[1,5-a]pyridine (3a)*

162 mg, 89% yield, White solid; $R_f$ = 0.4 (hexanes: EtOAc = 7:3); mp 166-168$^oC$; $^1H$ NMR (300 MHz, $CDCl_3$): δ 7.50 (dd, *J* = 7.9, 1.6 Hz, 2H), 7.35-7.28 (m, 2H), 7.26 (dd, *J* = 4.9, 2.6 Hz, 4H), 7.21 (dd, *J* = 4.1, 2.3 Hz, 3H), 7.18 (dd, *J* = 5.2, 3.0 Hz, 2H), 7.02 (dd, *J* = 7.7, 1.7 Hz, 2H), 6.60 (s, 1H), 5.75-5.49 (m, 3H), 4.39-3.76 (m, 2H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 146.2, 143.0, 141.7, 139.3, 134.9, 131.0, 130.9, 129.1, 128.7, 128.6, 128.3, 127.7, 127.6, 127.2, 127.1, 126.8, 122.0, 47.0, 40.6, 36.3; IR (KBr): 3453, 3052, 2922, 2855, 1734, 1457, 759 $cm^{-1}$; MS (ESI): *m/z* 420 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{27}H_{22}N_3S$ $(M+H)^+$: 420.1534, found: 420.1557.

#### *6-Benzyl-4-(4-methoxyphenyl)-3-phenyl-4,8-dihydrothieno[2,3-d][1,2,3]triazolo[1,5-a]pyridine (3b)*

160 mg, 82% yield, Light brown solid; $R_f$ = 0.3 (hexanes: EtOAc = 7:3); mp 88-90$^oC$; $^1H$ NMR (500 MHz, $CDCl_3$): δ 7.52 (dd, *J* = 8.2, 1.2 Hz, 2H), 7.33 – 7.26 (m, 4H), 7.26 (s, 1H), 7.25 – 7.20 (m, 3H), 6.99 – 6.88 (m, 2H), 6.78 – 6.68 (m, 2H), 6.59 (s, 1H), 5.70 – 5.48 (m, 3H), 4.05 (q, *J* = 16.0 Hz, 2H), 3.72 (s, 3H); $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 158.8, 146.1, 142.9, 139.3, 135.4, 133.9, 131.3, 130.9**,** 128.7, 128.6, 128.3, 128.2, 127.7, 127.2, 127.0, 126.8, 121.9, 114.4, 55.2, 47.0, 39.8, 36.3; IR (KBr): 3030, 2920, 2843, 1609, 1506, 1251, 758, 701 $cm^{-1}$; MS (ESI): *m/z* 450 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{28}H_{24}N_3OS$ $(M+H)^+$: 450.1640, found: 450.1655.

#### *6-Benzyl-4-(4-methoxyphenyl)-3-propyl-4,8-dihydrothieno[2,3-d][1,2,3]triazolo[1,5-a]pyridine (3c)*

145 mg, 80% yield, White solid; $R_f$ = 0.3 (hexanes: EtOAc = 7:3); mp 124-126$^oC$; $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.35-7.28 (m, 2H), 7.23 (dd, *J* = 8.1, 6.7 Hz, 3H), 7.11-6.92 (m, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 6.60 (s, 1H), 5.51 (ddd, *J* = 37.8, 16.8, 3.5 Hz, 2H), 5.28 (dd, *J* = 11.1, 7.6 Hz, 1H), 4.05 (d, *J* = 9.8 Hz, 2H), 3.79 (s, 3H), 2.49-2.29 (m, 1H), 2.27-2.11 (m, 1H), 1.56-1.44 (m, 1H), 1.37 (ddt, *J* = 13.6, 8.8, 6.9 Hz, 1H), 0.77 (t, *J* = 7.4 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 159.1, 146.3, 143.6, 139.4, 135.4, 133.6, 131.0, 128.8, 128.7, 128.6, 127.2, 126.8, 121.8, 114.3, 55.3, 46.6, 39.4, 36.4, 27.1, 22.0, 13.8; IR (KBr): 2920, 2853, 1730, 1605, 1507, 1247, 1032, 751, 704 $cm^{-1}$; MS (ESI): *m/z* 416 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{25}H_{25}N_3OSNa$ $(M+Na)^+$: 438.1611, found: 438.1649.

#### *6-Benzyl-3-phenyl-4-(1-tosyl-1H-indol-3-yl)-4,8-dihydrothieno[2,3-d][1,2,3]triazolo[1,5-a]pyridine (3d)*

200 mg, 75% yield, White solid; $R_f$ = 0.4 (hexanes: EtOAc = 7:3); mp 97-99$^oC$; $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.3 Hz, 1H), 7.50-7.44 (m, 2H), 7.41-7.36 (m, 2H), 7.34-7.27 (m, 3H), 7.27-7.21 (m, 3H), 7.21-7.14 (m, 4H), 7.14-7.09 (m, 1H), 7.03 (dd, *J* = 16.0, 7.9 Hz, 3H), 6.61 (s, 1H), 5.92 (t, *J* = 3.0 Hz, 1H), 5.66 (d, *J* = 3.1 Hz, 2H), 4.03 (q, *J* = 16.1 Hz, 2H), 2.29 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 146.2, 144.8, 142.9, 139.2, 135.2, 134.7, 132.9, 130.6, 129.8, 129.6, 128.7, 128.6, 128.2, 128.1, 127.6 , 127.5, 127.0, 126.8, 126.5, 125.1, 124.1, 123.4, 122.0, 121.7, 119.1, 113.8, 47.0, 36.3, 32.1, 21.6; IR (KBr): 2919, 2853, 1731, 1368, 1175, 976, 754, 696 $cm^{-1}$; MS (ESI): *m/z* 613 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{36}H_{29}N_4O_2S_2$ $(M+H)^+$:613.1732, found:613.1734.

#### *6-Benzyl-3-phenyl-4-(3,4,5-trimethoxyphenyl)-4,8-dihydrothieno[2,3-d][1,2,3]triazolo [1,5-a]pyridine (3e)*

170 mg, 76% yield, White solid; $R_f$ = 0.4 (hexanes: EtOAc = 7:3); mp 176-178$^oC$; $^1H$ NMR (500 MHz, $CDCl_3$): δ 7.59 – 7.46 (m, 2H), 7.34 – 7.29 (m, 4H), 7.28 – 7.26 (m, 1H), 7.26 – 7.22 (m, 3H), 6.64 (s, 1H), 6.17 (s, 2H), 5.67 – 5.48 (m, 3H), 4.09 (d, J = 7.8 Hz, 2H), 3.74 (s, 3H), 3.64 (s, 6H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 153.5, 146.2, 143.2 , 139.3 , 137.4, 136.8, 134.4, 131.0, 128.7, 128.6, 128.4, 127.9, 127.7, 127.6, 126.8, 122.0, 104.4, 60.8, 56.1, 47.03, 40.49, 36.4; IR (KBr): 3006, 2922, 2845, 1593, 1458, 1125, 756 $cm^{-1}$; MS (ESI): *m/z* 510 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{30}H_{28}N_3O_3S$ $(M+H)^+$:510.1851, found:510.1867.

#### *6-Benzyl-4-(3,4,5-trimethoxyphenyl)-4,8-dihydrothieno[2,3-d][1,2,3]triazolo[1,5a] pyridin-3-yl)methanol (3f)*

170 mg, 83% yield, White solid; $R_f$ = 0.2 (hexanes: EtOAc = 6:4); mp 159-161$^oC$; $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.32 (dd, J = 7.8, 6.4 Hz, 2H), 7.26 (d, J = 2.2 Hz, 1H), 7.25 – 7.21 (m, 2H), 6.63 (s, 1H), 6.32 (s, 2H), 5.67 – 5.27 (m, 3H), 4.57 (d, J = 13.1 Hz, 1H), 4.30 (d, J = 12.9 Hz, 1H), 4.14 – 4.01 (m, 2H), 3.83 (s, 3H), 3.77 (s, 6H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 153.7, 146.6, 142.8, 139.3, 137.8, 136.2, 134.2, 132.2, 128.7, 128.6, 127.3, 126.9, 121.8, 104.8, 60.9, 56.2, 46.7, 40.2, 36.4; IR (KBr): 3369, 2923, 2851, 1732, 1593, 1461, 1126, 756 cm-1; MS (ESI):m/z464 $(M+H)^+$; HRMS (ESI): m/z calcd for $C_{25}H_{26}N_3O_4S$ $(M+H)^+$:464.1644, found:464.1643

### *2.2.2. General Procedure for the Synthesis of Triazolo-indololignans 5a to to 5f*

To a stirred solution of azide [22] (1.0 mmol) and propargylic alcohol (1.0 mmol) in 10 mL of acetonitrile was added *p*TSA (5 mol%) at $0^oC$, stirred at room temperature for 1 - 2 h, then the reaction mixture was heated to $80^oC$ for 7 - 10 h. After the completion of reaction (monitored by TLC), The reaction mixture was concentrated under reduced pressure. Purified by column chromatography on silica gel (EtOAc: *n*-hexane) to give the corresponding triazole.

#### *2-(Azidomethyl)-1-methyl-1H-indole (4)*

80 mg, 70% yield, Brown colour semi solid; $R_f$ = 0.6 (hexanes: EtOAc = 9:1; $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.62-7.58 (m, 1H), 7.32 (dd, *J* = 8.3, 0.8 Hz, 1H), 7.25 (ddd, *J* = 8.2, 5.6, 1.2 Hz, 1H), 7.12 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 6.54 (s, 1H), 4.46 (s, 2H), 3.75 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 138.2, 132.9, 127.0, 122.4 , 121.0, 119.8, 109.3, 103.3, 46.9, 29.8; IR (KBr): 3056, 2923, 2091, 1467, 1318, 1206, 734 $cm^{-1}$; MS (ESI): *m/z* 187 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{10}H_{11}N_4$ $(M+H)^+$:187.0978, found:187.0989.

#### *9-Methyl-3,4-diphenyl-9,10-dihydro-4H-[1,2,3]triazolo[1',5':1,6]pyrido[3,4-b]indole (5a)*

170 mg, 85% yield, White solid; $R_f$ = 0.4 (hexanes: EtOAc = 6:4); mp 240-242$^oC$; $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.58-7.54 (m, 2H), 7.47 (d, *J* = 7.9 Hz, 1H), 7.36-7.27 (m, 4H), 7.23 (t, *J* = 7.6 Hz, 1H), 7.17-7.10 (m, 4H), 7.08 (dt, *J* = 12.1, 4.6 Hz, 2H), 5.95-5.71 (m, 3H), 3.81 (s, 3H); $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 143.4, 141.7, 138.3, 133.3, 131.1, 128.6, 128.3, 127.7, 127.0, 126.9, 124.8, 122.4, 120.0, 119.0, 109.7, 109.2, 44.5, 37.9, 29.9; IR (KBr): 3406, 2920, 2853, 1733, 1464, 1183, 755 $cm^{-1}$; MS (ESI): *m/z* 377 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{25}H_{21}N_4$ $(M+H)^+$:377.1761, found:377.1794.

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***4-(4-Methoxyphenyl)-9-methyl-3-phenyl-9,10-dihydro-4H-[1,2,3]triazolo[1',5':1,6] pyrido[3,4-b]indole (5b)***

180 mg, 82% yield, White solid; $R_f$ = 0.3 (hexanes: EtOAc = 7:3); mp 220-222°C; $^1$H NMR (400 MHz, $CDCl_3$): δ 7.61 – 7.56 (m, 2H), 7.45 (d, J = 7.9 Hz, 1H), 7.38 – 7.27 (m, 4H), 7.25 – 7.20 (m, 1H), 7.09 – 6.99 (m, 3H), 6.66 (d, J = 8.8 Hz, 2H), 5.87 (d, J = 2.3 Hz, 2H), 5.74 (t, J = 2.8 Hz, 1H), 3.79 (s, 3H), 3.67 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 158.43, 143.2, 138.3, 133.9, 133.5, 131.1, 128.8, 128.3, 127.7, 126.8, 124.8, 122.4, 119.9, 119.1, 114.0, 109.9, 109.2, 55.2, 44.5, 37.1, 29.8; IR (KBr); 2957, 2928, 1611, 1511, 1468, 1221, 745 cm$^{-1}$; MS (ESI): *m/z* 407 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{26}H_{23}ON_4$, 407.1866 $(M+H)^+$: found 407.1867.

***4-(4-Methoxyphenyl)-9-methyl-3-propyl-9,10-dihydro-4H-[1,2,3]triazolo[1',5':1,6]pyrido[3,4-b]indole (5c)***

165 mg, 82% yield, White solid; $R_f$ = 0.4 (hexanes: EtOAc = 6:4); mp 202-204°C; $^1$H NMR (400 MHz, $CDCl_3$): δ 7.32 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.20 (dd, *J* = 12.1, 4.3 Hz, 2H), 7.14-7.07 (m, 2H), 6.99 (td, *J* = 7.3, 0.9 Hz, 1H), 6.83-6.74 (m, 2H), 5.75 (ddd, *J* = 49.0, 16.5, 3.5 Hz, 2H), 5.38 (t, *J* = 3.4 Hz, 1H), 3.77 (s, 3H), 3.75 (d, *J* = 3.5 Hz, 3H), 2.48-2.28 (m, 2H), 1.50 (dtt, *J* = 13.7, 8.9, 6.8 Hz, 1H), 1.34 (tdd, *J* = 13.6, 11.4, 6.9 Hz, 1H), 0.80 (t, *J* = 7.4 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 158.6, 144.0, 138.4, 133.5, 132.9, 129.2, 127.1, 125.1, 122.3, 119.8, 119.3, 114.1, 109.1, 109.1, 55.2, 44.0, 37.0, 29.8, 27.2, 22.1, 13.8; IR (KBr): 2930, 1610, 1510, 1468, 1251, 1033, 746 cm$^{-1}$; MS (ESI): *m/z* 373 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{23}H_{25}ON_4$, 373.2022 $(M+H)^+$; found 373.2026.

***5-Methyl-3-phenyl-4-(1-tosyl-1H-indol-3-yl)-5,10-dihydro-4H-[1,2,3]triazolo[1',5':1,6] pyrido[4,3-b]indole (5d)***

240 mg, 78% yield, White solid; $R_f$ = 0.3 (hexanes: EtOAc = 6:4); mp 285-287°C; $^1$H NMR (300 MHz, $CDCl_3$+DMSO-$d_6$): δ 8.06 (s, 1H), 7.95 (s, 1H), 7.75 (d, J = 7.2 Hz, 2H), 7.64 (d, J = 8.3 Hz, 1H), 7.46 (d, J = 8.1 Hz, 2H), 7.38 (dd, J = 13.6, 7.8 Hz, 4H), 7.10 (dt, J = 15.4, 8.8 Hz, 4H), 6.92 (dd, J = 15.8, 7.8 Hz, 2H), 6.66 (d, J = 7.9 Hz, 1H), 6.40 (s, 1H), 6.13 (dd, J = 40.7, 17.3 Hz, 2H), 3.86 (s, 3H), 2.31 (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$+DMSO-$d_6$): δ 149.7, 147.5, 143.1, 139.7, 139.3, 135.7, 134.7, 133.2, 133.1, 132.5, 132.2, 131.3, 130.1, 129.3, 128.0, 126.9, 125.5, 124.3, 124.0, 123.6, 118.2, 114.2, 110.9, 49.30, 34.8, 34.1, 26.3; IR (KBr); 3019, 2924, 2856, 1731, 1457, 1318, 1175, 754 cm$^{-1}$; MS (ESI): *m/z* 570 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{34}H_{28}N_5O_2S$ $(M+H)^+$:570.1958, found:570.2008.

***9-Methyl-3-phenyl-4-(3,4,5-trimethoxyphenyl)-9,10-dihydro-4H-[1,2,3]triazolo[1',5':1,6] pyrido[3,4-b]indole (5e)***

190 mg, 75% yield, White solid; $R_f$ = 0.3 (hexanes: EtOAc = 3:7); mp 247-249°C; $^1$H NMR (400 MHz, $CDCl_3$): δ 7.54 (dd, J = 8.1, 1.4 Hz, 2H), 7.44 (d, J = 7.9 Hz, 1H), 7.35 (tdd, J = 8.6, 4.9, 3.8 Hz, 4H), 7.29 – 7.26 (m, 1H), 7.17 – 7.03 (m, 1H), 6.26 (s, 2H), 5.86 (d, J = 2.7 Hz, 2H), 5.73 (t, J = 2.7 Hz, 1H), 3.82 (s, 3H), 3.70 (s, 3H), 3.60 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 153.2, 143.7, 138.4, 137.1, 133.3, 131.3, 128.3, 128.1, 128.0, 127.3, 125.0, 122.5, 120.0, 119.2, 109.3, 109.0, 105.2, 60.7, 56.1, 44.4, 37.8, 30.0; IR (KBr): 3019, 2920, 2850, 1734, 1467, 1214, 749 cm$^{-1}$; MS (ESI): *m/z* 467 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{28}H_{27}O_3N_4$, 467.2077 $(M+H)^+$: found, 467.2074.

***(9-Methyl-4-(3,4,5-trimethoxyphenyl)-9,10-dihydro4H[1,2,3]triazolo[1',5':1,6]pyrido [3,4-b]indol-3-yl)methanol (5f)***

185 mg, 83% yield, White solid; $R_f$ = 0.2 (hexanes: EtOAc = 3:7); mp 234-236°C; $^1$H NMR (300 MHz, $CDCl_3$+DMSO-$d_6$): δ 7.36 (d, J = 8.2 Hz, 1H), 7.18 (dd, J = 18.5, 7.8 Hz, 2H), 6.96 (t, J = 7.4 Hz, 1H), 6.50 (s, 2H), 5.83 (dt, J = 16.8, 10.0 Hz, 2H), 5.61 (s, 1H), 4.51 (d, J = 12.6 Hz, 1H), 4.21 (d, J = 12.6 Hz, 1H), 3.81 (s, 3H), 3.71 (s, 6H), 3.69 (s, 3H)**;** $^{13}$C NMR (75 MHz, $CDCl_3$+DMSO-$d_6$): δ 157.9, 148.1, 143.1, 141.8 , 141.6, 138.9, 133.0, 129.8, 126.9, 124.4, 123.8, 114.1, 112.6, 110.3, 65.2, 60.9, 60.0, 48.8, 42.0, 34.8; IR (KBr): 3407, 2920, 2852, 1732, 1463, 1181, 758 cm$^{-1}$; MS (ESI): m/z 421 $(M+H)^+$; HRMS (ESI): m/z calcd for $C_{23}H_{25}N_4O_4$ $(M+H)^+$:421.1876, found:421.1872.

## 2.3. Biology

### *2.3.1. Cell Culture*

Cancer cells were maintained in DMEM medium supplemented with 10% fetal bovine serum (FBS), 0.1% streptomycin-penicillin, 1% non-essential amino acids and 1% sodium pyruvate. Cells were incubated at 37°C in a 5% $CO_2$ humidified atmosphere and maintained at sub confluency by passaging regularly with trypsin-EDTA.

### *2.3.2. Cytotoxicity Evaluation*

The synthesized test compounds were evaluated for cytotoxicity in four different human cancer cell lines (DU145, Hela, MCF7 and HepG2). A standard SRB assay is used for the determination of cytotoxicity of the synthesized compounds [23]. The sensitivity of the cancer cells to the test compound was expressed in terms of $IC_{50}$, a value defined as the concentration of compound that produced 50% reduction as compared to the control absorbance. $IC_{50}$ values are indicated as means ±SD of three independent experiments.

### *2.3.3. PI Uptake for Analysis of Cell Cycle*

Cell death induced by selected compounds was determined as a measure of PI uptake. Cells were harvested after treatment with compounds at desired concentration and fixed in 70% ethanol at -20 °C for overnight. All cells in the form of a pellet resuspended in PI solution (RNase -0.1 mg/mL, Triton X 100-0.05%, PI-50 µg/mL) and incubated for 1h in dark at room temperature. The excess PI solution was washed away by repeated washings with DPBS. The resultant PI uptake was analyzed by fluorescence activated cell sorting (FACS Calibur System; BD Bio-science, Erembodegem, Belgium) in a FL-2 fluorescence detector (10000 events were recorded for each condition). Flow cytometry data was analyzed using FCS express 4 software (De Novo Software, Los Angeles, CA).

### *2.3.4. Determination of Caspase-3 Activity*

Caspase-3 activity is measured by treating the MCF7 cells with selected compounds using specific fluorogenic substrate Ac-DEVD-AMC. DMSO and paxcitaxel were taken as negative and positive controls respectively. After 48 h treatment, harvested cells were lysed directly in caspase lysis buffer (50 mM HEPES, 5mM CHAPS, 5 mM DTT, pH 7.5). The lysates were incubated with the respective substrate (Ac-LEHD-AMC) in 20mM HEPES (pH 7.5), 0.1% CHAPS, 2mM EDTA and 5 mM DTT at 37°C for 2 h. The release of AMC was analyzed by a fluorimeter using an excitation/emission wavelength of 380/460 ηm, which is directly proportional to caspase-3 activity, respectively. The observed fluorescence values were normalized with total protein concentration estimated by Bradford method and the relative caspase activity was calculated as the ratio of values between mock treated (DMSO) and treated cells.

### *2.3.5. Western Blot Analysis*

Soluble and insoluble protein fraction of compounds treated cells lysates were collected as per the protocol previously explained (Kumar *et al*). Protein samples were separated on 10% SDS-PAGE gel and transferred to a nitrocellulose membrane. The membrane was blocked in 5% BSA for 1h at room temperature, and probed with primary antibodies for β-Tubulin (1:2000), GAPDH (1:2000). The membranes were exposed to HRP conjugated secondary anti-

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**Table 1. Anti-cancer activity of compounds.**

| Compound | Hela | MCF-7 | DU145 | HepG2 |
|---|---|---|---|---|
| | $IC_{50}$ | $IC_{50}$ | $IC_{50}$ | $IC_{50}$ |
| **3a** | 14.58 | 11.46 | 9.42 | 19.28 |
| 3b | 92.50 | 79.86 | 12.82 | 90.31 |
| 3c | 75.65 | 82.79 | 15.25 | 78.07 |
| 3d | 29.23 | 27.70 | 13.45 | 26.97 |
| 3e | 85.54 | 66.63 | >100 | 88.50 |
| 3f | 91.72 | 81.98 | >100 | 68.52 |
| 5a | >100 | 79.48 | >100 | 87.48 |
| 5b | 78.94 | 85.30 | 63.00 | 92.78 |
| 5c | 76.32 | 89.97 | 46.30 | >100 |
| 5d | 71.12 | 85.42 | 60.10 | 75.30 |
| 5e | 81.56 | 82.21 | 73.90 | 85.87 |
| **5f** | 22.35 | 12.92 | 25.66 | 69.59 |
| **Paclitaxel** | 2.09 | 2.84 | 2.50 | 1.99 |
| **Podophyllotoxin** | 7.58 | - | 2.89 | 2.27 |

bodies for 2 h at room temperature and protein expression was detected by using enhanced chemi luminescence (ECL) Western blotting detection reagent (Syngene, GBOX, UK).

### *2.3.6. Immunofluorescence*

Compound treated cells were washed in DPBS and fixed in freshly prepared 3% (w/v) paraformaldehyde (PFA) for 15 min at room temperature. The cells were then permeabilized in 1% (v/v) Triton X-100 for 15 min at room temperature. Cells were then processed for labelling indirect immunofluorescence using the β-Tubulin antibody. The tubulin epitope was visualized with fluorescein isothiocyanate (FITC) - conjugated goat anti-mouse IgG secondary antibody. For each incubation step cells were washed with DPBS. The cover slips were mounted on glass slides with mounting medium containing DAPI. The fluorescent staining pattern was viewed in a confocal laser-scanning microscope (Olympus, Japan).

## 2.4. Docking Methods

The X-ray crystallographic structure of tubulin polymer with colchicine active site (PDB: 1SA0) was attributed from protein data bank [24]. The chain (β-subunit) of tubulin was selected for current docking interpretations, it has prepared and minimized by protein preparation wizard. All the ligands were sketched with 2D-skechter and prepared with Ligprep [25, 26]. The receptor grid around colchicine was generated using Glide module. The extra precision docking protocol of Glide was employed for present docking studies and they were analyzed using Maestro11.1 [27].

# 3. RESULTS AND DISCUSSION

## 3.1. Anti-Proliferative Activity

Having the successful development of methodology to the synthesis of triazolo-heterolignans, next we evaluated their cytotoxic activity against a panel of four different human cancer cells including HeLa (cervical), MCF-7 (breast), DU-145 (prostate) and HEPG-2 (liver) cells using SRB assay [28]. The cytotoxicity results against the tested cell lines are summarized in Table **1**. Among the tested ones, compound **3a**, **3b**, **3c** and **3d** were found to inhibit prostate cancer cell line at lower micromolar concentrations (<20 μM). Compound **3a** and **5f** showed activity $IC_{50}$ <12.92 μM against MCF-7 breast cancer cells. Therefore, compound **3a** having phenyl substitution displayed better anti-cancer activity among the triazolo-thienolignans **3a** to **3f**. With respect to active compounds **3b** and **3d**, phenyl group on triazole ring might significant for maintaining the cytotoxicity, while *n*-propyl group in compound **3c** lowered the potency. Whereas, compound **3e** & **3f** having trimethoxy substitution were found to be inactive. In case of indololignan analogs, reversed interpretations were observed and the compound **5f** found to be active among the triazolo-indololignans **5a** to **5f**. It may be due to the difference in orientation of heterocyclic ring, thiophene/indole. This was studied in molecular docking simulations.

## 3.2. Effect of Compound 3a and 5f on Cell Life Cycle

From the test results, compounds **3a** and **5f** were exhibited good cytotoxic activity with $IC_{50}$ values ranging between 9.42 μM to 25 μM across the four cell lines. Further, the effect of **3a** and **5f** was studied on cell cycle progression of MCF-7 cells. Compound **3a** showed cell cycle arrest at G2/M phase (33%/28.3%) and **5f** arrest the cells at G1 phase (65.2%/58.3%) compared to the control cells treated with DMSO (Fig. **2**).

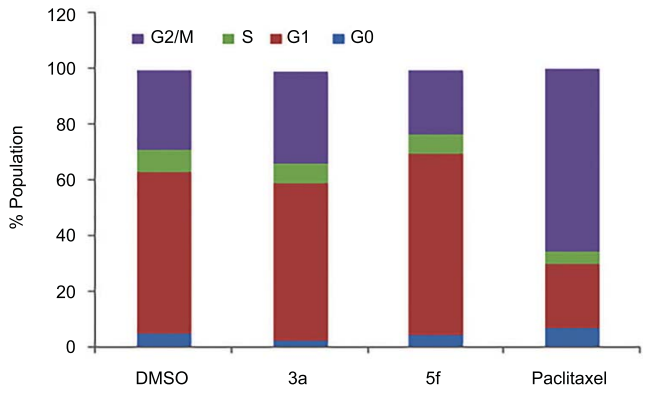



**Fig. (2).** Effect of **3a** and **5f** on cell cycle progression of MCF-7 breast cancer cells.

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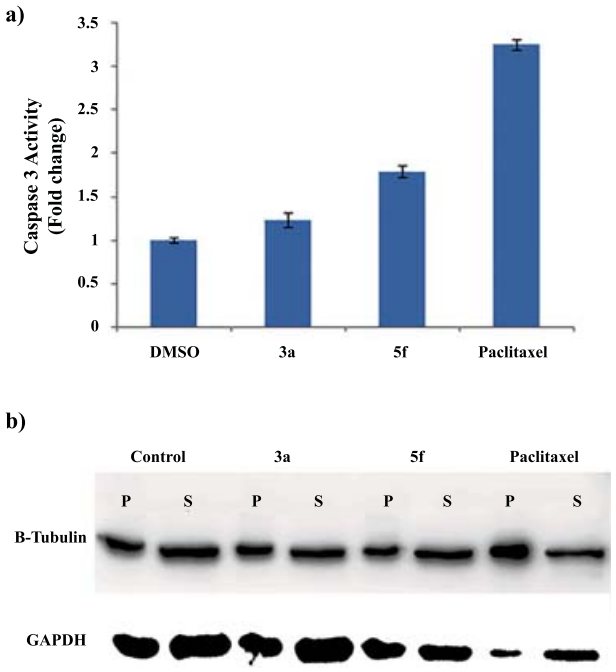



**Fig. (3). a**) Effect of **3a** and **5f** on Caspase 3 activity, **b**) β-Tubulin assay by immunofluorescence and western blot.

### 3.3. Effect of Compound 3a and 5f on Caspase

Further, to evaluate the mode of action, the effect of **3a** and **5f** was investigated on cell proliferation and caspase 3 mediated cell death in MCF-7 cells. It was observed that caspase 3 activity was increased in MCF-7 cells when treated with **3a** and **5f.** In caspase assays, paclitaxel was used as positive control. Interestingly, in **3a** treated cells, the caspase 3 activity is increased but not significant as paclitaxel, whereas in **5f** treated cells caspase3 is significantly activated (Fig. **3a**). Therefore, we sought to understand the specific property of the selected compounds. As series of test compounds prepared based on chemical scaffold that inhibit tubulin polymerization, the effect of **3a** and **5f** was determined on tubulin polymerization in *in vivo* in MCF-7 cells. In this study, after cells exposed to **3a** and **5f** for 48 h, the levels of soluble and insoluble fractions of β-Tubulin in the total cell lysates were analyzed. From these results, **3a** and **5f** treated cells have increased insoluble of β-Tubulin when compared to controls and as similar as paclitaxel (Fig. **3b**).

### 3.4. Tubulin Inhibition Studies

To determine the effect of these **3a** and **5f** on β-Tubulin polymerization in *in vivo*, we also performed immunofluorescence using β-Tubulin specific antibody. For nuclear staining, DAPI counterstain was used to stain nucleus. Results indicate that both the compounds are affecting microtubule disassembly like paclitaxol positive control. Of the two tested compounds, **5f** is more effective in stabilizing the microtubule polymer and inhibiting it from disassembly (Fig. **4**). Due to inhibition of microtubule disassembly, chromosomes are unable to achieve a metaphase spindle configuration leading to prolonged mitotic phase during cell division. This further blocks the progression of mitosis leading to mitotic arrest and triggers apoptosis for cancer cell death or arrest the division of proliferating cells.

## 4. MOLECULAR DOCKING STUDIES

The validated molecular docking studies of **3a** and **5f** were carried out and compared with podophyllotoxin (**I**) structure. Compound **3a** is accommodated at recognized site of colchicine and it has also been observed that triazole moiety is exactly mapped with the lactone ring of podophyllotoxin when overlapped. The phenyl ring on triazole of **3a** is accommodated opposite to the keto group of lactone ring of podophyllotoxin. The substituted thiophene ring

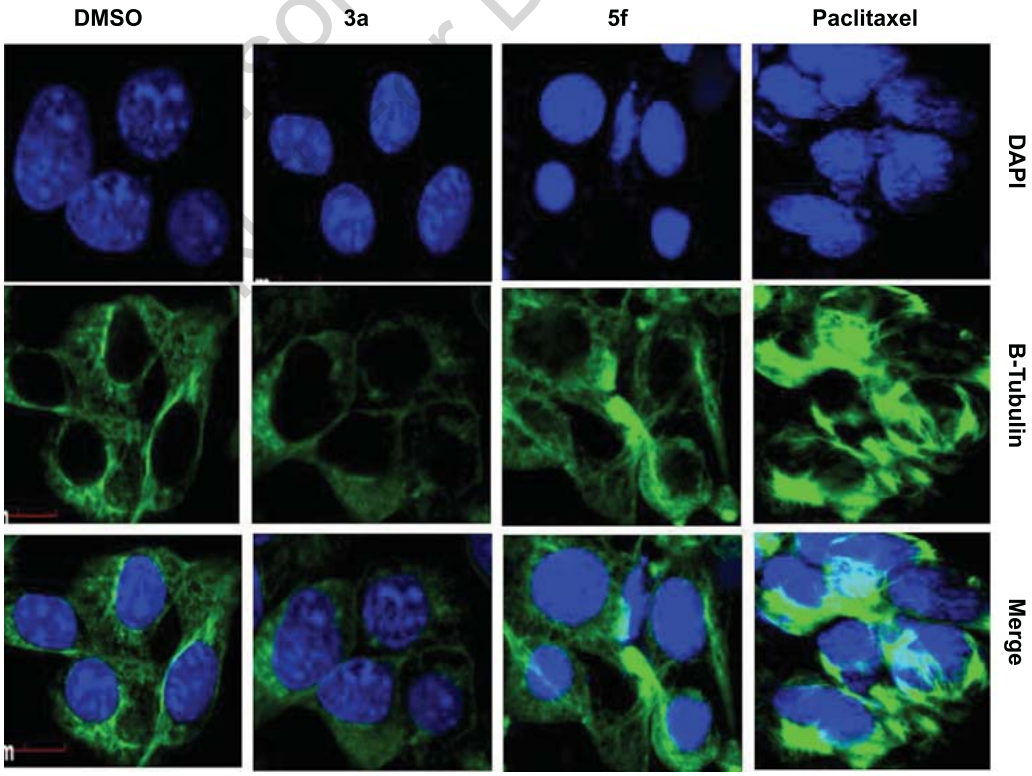



**Fig. (4).** Effect of **3a** & **5f** on β-Tubulin polymerization in DU145 prostate cancer cells.

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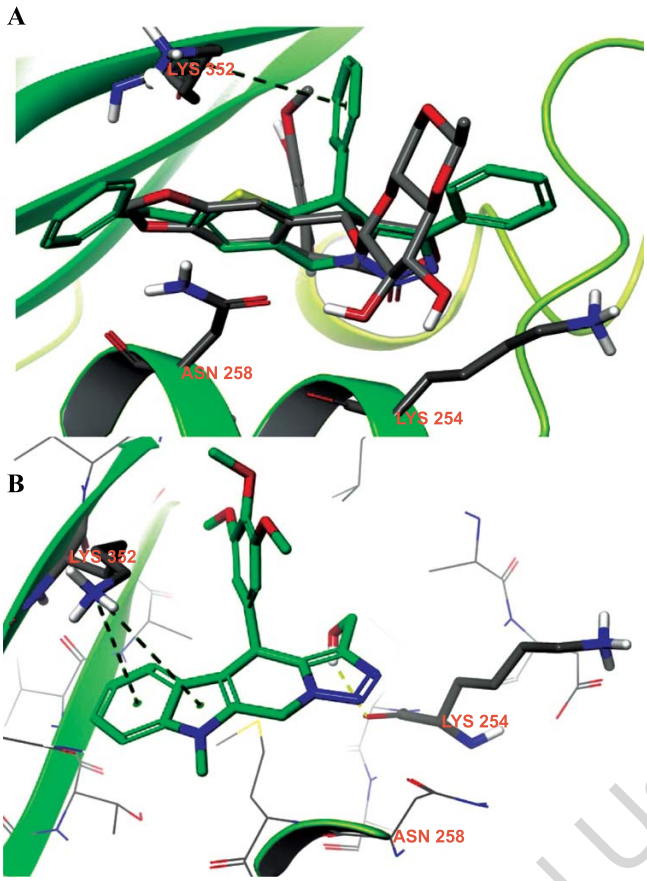



**Fig. (5). a**) Overlap of **3a** with podophyllotoxin; **b**) **5f** at colchicine binding site of β-Tubulin polymer; green thick sticks indicate active compounds and macromodel sticks indicate active site residues. Green dotted line indicates π-cation and yellow dotted line indicate hydrogen bond.

of **3a** occupied at dioxalane binding position (Fig. **5a**). The axial phenyl ring established the π-cation interaction with Lys352. With respect to the compound **5f**, the hydroxy methyl of triazole found to be making hydrogen bond with backbone of Lys254. The presence of indole nucleus is responsible for contributing two π-cation interactions with Lys352. Whereas, the axial trimethoxy phenyl ring of **5f** not made any interactions with active site residues (Fig. **5b**). In addition, we also deliberated the alignment of inactive compounds **3f** and **5a** with their counter parts **5f** and **3a**. The dissimilar binding mode of inactive **3f** and **5a** at colchicine binding pocket is noticed, when they were overlapped with active **3a** and **5f** (see supporting information). Further, compound **5f** has been overlaid with triazole based podophyllotoxin **II** along with podophyllotoxin (**I**). The binding position of triazole of both **5f** and **II** were occupied lactone imperative site (Figs. **6** & **7**).

## CONCLUSION

In conclusion, a novel one-pot sequential propargylation/ cycloaddition reaction has been developed for the synthesis of triazolo-heterolignans. The anti-proliferative activity of triazole-thienolignans (**3a-3f)** and indololignans (**5a-5f)** against four different cancer cell lines has been carried out and found that **3a** and **5f** exhibited moderate cytotoxic activity. The slight caspase 3 mediated apoptotic effect of compound **5f** has been noticed. Additionally, these compounds found to be inhibiting microtubule disassembly. The molecular docking studies indicated that, compound **3a** and **5f** accommodated within the active site of tubulin and triazole ring of both **3a** and **5f** occupied the lactone binding site of podophyllotoxin.

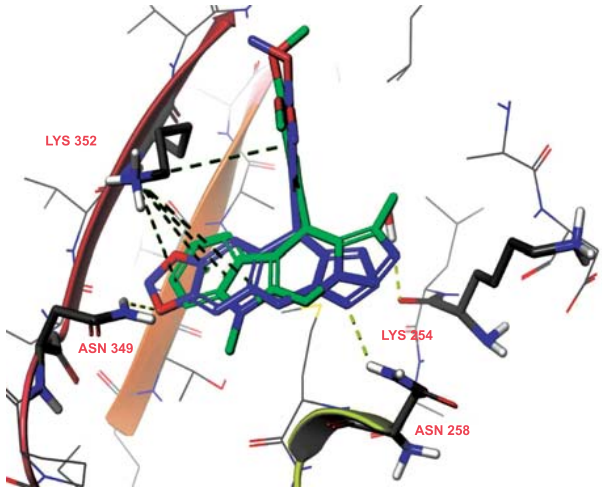



**Fig. (6).** Overlap of **5f** with Compound **II** (blue sticks) at colchicine binding site of β-Tubulin polymer; green thick sticks indicate **5f** compounds and macromodel sticks indicates active site residues. Green dotted line indicates π-cation and yellow dotted line indicates hydrogen bond.

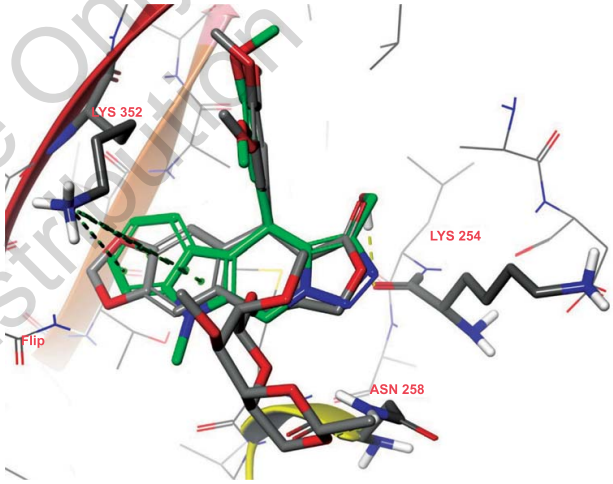



**Fig. (7).** Overlap of **5f** with Podophyllotoxin (macromodel thick sticks) at colchicine binding site of β-Tubulin polymer; green thick sticks indicate **5f** compounds and macromodel sticks indicates active site residues. Green dotted line indicates π-cation and yellow dotted line indicates hydrogen bond.

## ETHICS APPROVAL AND CONSENT TO PARTICIPATE

Not applicable.

## HUMAN AND ANIMAL RIGHTS

No Animals/Humans were used for studies that are the basis of this research.

## CONSENT FOR PUBLICATION

Not applicable.

## CONFLICT OF INTEREST

The authors declare no conflict of interest, financial or otherwise.

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## SUPPLEMENTARY MATERIAL

The additional figures and spectral data is provided in supplementary information.

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# The Biblical Allusions in John Milton's Paradise Lost

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**Abstract**

*This paper tries to trace out some of the ALLUSIONS that are found in the PASSAGES of Paradise Lost to REFERENCES in the BIBLE. A list of important quotations is taken from "Paradise Lost" by John Milton that would help me to support the statements. All of the important quotes from "Paradise Lost" listed here correspond, at least in some way, to the topic above and by themselves can give great ideas for an essay by offering quotes about the theme of Biblical Allusions in "Paradise Lost."*

**Keywords: Milton-Paradise Lost-Biblical Allusions.**

## Introduction

John Milton was a very important English poet, author of the monumental Paradise Lost (1667), which was one of the great literary masterpieces of the seventeenth century, which was also to have a major influence on literature in his country, and especially on the romantic poets. He was born in 1608 on Cheapside Street in London. Born into a cultured, religious bourgeois family, Milton is intended to take holy orders, but a trip to Italy after his mother's death together with reading the Italian poets Torquato Tasso (1544 - 1595) and Dante (1265 - 1321) would make him want to become a writer.

After studying at Cambridge, he decides against all odds to abandon the all-ready mapped out career in either the church or even at a university to be able to dedicate him to the art of writing. Some say today that already then Milton would have a sense he would leave the world the gift of his production. In any case, at this point, he would retire instead to the family home and would spend a lot of his time reading Greek and Latin classics, as well as studying political and religious history. It is then also he would start writing his first poems.

During the 1640s John Milton wrote a series of political pamphlets. Some would be against the church, both the Catholic and the Protestant, always as a fierce advocate of the freedom of worship.

Others would for the freedom of the press and for the right to divorce and civil liberty, becoming the foremost speaker of his day.

He published his first collection of poems in 1646. He composed the ten books of Paradise Lost between 1658 and 1663. He had first prearranged the work as early as 1640, expecting to write a tragedy titled Adam Unparadised. Paradise Lost was first published in 1667 even though it had been written almost 10 years before. Milton was getting blind by the time he started work on it. To help him with his writing he would get assistants, and most notably the English metaphysical poet Andrew Marvell (1621-1678). A second edition embellished with minor revisions would follow in 1674.

The present paper tries to ground how Milton has used the Biblical Allusions as influential theme in his remarkable epic Paradise Lost.

The poem concerns the Biblical story of the Fall of Man and tells the story of Lucifer, the fallen angel the temptation of Adam and Eve by the fallen angel Satan. More specifically, the poem deals with the Christian view on the origin of man and refer to the temptation of Adam and Eve by Satan as well as their eventual expulsion from the Garden of Eden. The way in which they are rendered by Milton in "Paradise Lost" offers a new reading of the biblical Adam and Eve. Understandably, a great deal of critical and scholarly attention has been devoted to deconstructing Milton's versions of the biblical characters Adam and Eve in "Paradise Lost." A kind of theological settlement through poetry on the origin of man, the work gets its inspiration as much from the Bible for its content as from Virgil's (70 - 19 BC) twelve-book Latin epic poem Aeneid for its form.

Milton's intent, expressed clearly in the epic poem's opening lines, was to "justify the ways of God to men" (Book I, l. 26) that Milton wished to justify where he succeed in fulfilling his purpose to the maximum extent. The Biblical account of the fall in the Book of Genesis, with his epic poem, Paradise Lost, John Milton adds a lot of detail about the complete story of Man, the beginning of Satan, his rise and Man's Fall. Although the ideas for Paradise Lost came from a few pages in the Book of Genesis, Milton's account kept readers wondering what was going to happen next. Because he was going against the church already with Paradise Lost, it was more intriguing for him to take the same ideas in the Bible and extend them into more detail, making Satan look like the Hero and succeeding at what he wanted to do. Satan, the perfect angel, banished from nothing to the pits of Hell, with no chance of return, conjures up a plan to get revenge, building a legacy and an army to overthrow those who put him there.

Then God created the Son, the angels, Man, Heaven, Earth and everything else. Milton faced a difficult task with creating tension about what would happen since God already knew. In Paradise Lost, God is almost emotionless or aloof; he embodies pure reason and pure justice, and every response he gives seems to be cold. In Genesis God is wise and known as the creator and is more the narrator of what is happening than in Milton's epic. Also, He is referred to as Lord God, instead of God, as Milton refers to Him. So, in close the start and fall Man to summarize the creation and reason for human nature are "God gave Man free will, from Man's free will, sin and death came into the world."

## Biblical Allusions

Blind Milton might be when he wrote "Paradise Lost," but to him, the Bible remained an open book. After reading his "Paradise Lost," any one shall appreciate the exactness of his knowledge in using the allusions form the Bible. No doubt there were passages and certain sections of passages of the Scriptures over which Milton had long brooded as being especially suitable for his great project. A study of the allusions emphasizes the specialized theme of Paradise Lost. It is not to look for a balanced treatment of Christianity or of religion.

Genesis is used in great detail for the story of the Fall and the Creation and the early history of the race and Israel. Isaiah alludes to a good many times. The allusion is made to the world-wide extension of the blessing given to Abraham and his seed. Ezekiel furnishes a useful source, especially in the passages about the wheels and eyes instinct with spirit, from which Milton enriches his description of the war in Heaven. The Apocalypse is a very valuable basis for his descriptions of Heaven and Hell.

Every decade of the book of Psalms contributes references. To him, as to the Christian Church in his own and other ages, the Book of Psalms was a treasure-house of devotional and inspirational

writings. It is perhaps surprising to find 360, more than 25% of the whole body of references in this single book. Similarly, there are more references to the theology of the Pauline Epistles than to the life or teachings of Jesus Christ in the Gospels. The single page of Jude's Epistle has more references than the whole of the Gospel according to St. Mark. For Milton, in writing this poem must have had a special fascination in first and last pages of the Bible.

There are hundreds of allusions in Paradise Lost, many of them to the Bible. Rather than list every single possible allusion- which would probably take a few years, some of the more important ones are listed below.

| | | |
|---|---|---|
| Jesus Christ | | (1.4) |
| Moses | | (1.8; 1.338) |
| Adam and Eve | | (1.29) |
| Genesis | 2:17 | (1.32) |
| Leviathan, from Isaiah | 27:1 and Job 41:34 | (1.201) |
| Exodus | 10:13-5 | (1.338) |
| 1 Kings | 11:1-9 | (1.383-91) |
| 2 Samuel | 12: 26-27 | (1.396) |
| 2 Chronicles | 34:4-5 | (1.418) |
| Genesis | 11:4 | (1.694) |
| Psalms | 2:4 | (2.191) |
| 1 Kings | 12:11 | (2.701) |
| Revelations | 21:19 | (2.1050) |
| Genesis | 6:4 | (3.463; 11.573-627) |
| Genesis | 11:1-9 | (3.466-7) |
| Genesis | 28.17 | (3.510-5) |
| Exodus | 28:17-24 | (3.597) |
| Revelation | 12:3-12 | (4.1-5) |
| 1 Corinthians | 11:15 | (4.308) |
| Psalms | 2:6-7 | (5.603) |
| 2 Timothy | 4:7 | (6.30) |
| Genesis | 2: 19 | (6.76) |
| 2 Kings | 19:37 | (6.365) |
| Matthew | 3:17, 17:5 | (6.728) |
| Mark | 1:11 | (6.728) |
| Ezekiel | 10: 9-10 | (6.749-59) |
| Proverbs | 8: 25-30 | (7.7-12) |
| Genesis | 2:19-20 | (8.350). |
| Genesis | 2:18 | (8.445) |
| 1 Peter | 3:7 | (9.383) |
| Song of Solomon | 6:2 | (9.442) |
| Romans | 2:14 | (9.654) |
| 1 Timothy | 2:14 | (9.916) |
| Samson and Delilah | | (9.1059-60) |
| Luke | 10:18 | (10.84) |
| Isaiah | 61:10 | (10.222) |
| Luke | 1:28 | (11.158) |
| Genesis | 32:1-2 | (11.214) |
| Ezekiel | 40:2 | (11.377) |

## The Direct References that Milton had taken for his Paradise Lost from the Old Testament

| | |
|---|---|
| Genesis | 360 |
| Exodus | 99 |
| Leviticus | 7 |
| Numbers | 19 |
| Deuteronomy | 21 |
| Joshua | 12 |
| **Total** | **518** |

| | |
|---|---|
| Judges | 11 |
| 1 Samuel | 23 |
| 2 Samuel | 8 |
| 1 Kings | 37 |
| 2 Kings | 39 |
| 1 Chronicles | 7 |
| 2 Chronicles | 2 |
| Ezra | 4 |
| Nehemiah | 2 |
| Esther | 2 |
| **Total** | **135** |

| | |
|---|---|
| Job | 32 |
| Psalms | 90 |
| **Total** | **122** |

| | |
|---|---|
| Proverbs | 9 |
| Ecclesiastes | 5 |
| **Total** | **14** |

| | |
|---|---|
| Isaiah | 50 |
| Jeremiah | 14 |
| Ezekiel | 37 |
| Daniel | 5 |
| **Total** | **106** |

| | |
|---|---|
| Hosea | 5 |
| Amos | 3 |
| Micah | 1 |
| Habakkuk | 2 |
| Zechariah | 3 |
| **Total** | **14** |

Total Allusions to Old Testament = 909

## The Direct References that Milton had taken for his Paradise Lost from the New Testament

| | |
|---|---|
| Matthew | 55 |
| Mark | 9 |
| Luke | 36 |
| John | 45 |
| Acts | 20 |
| **Total** | **165** |

| | |
|---|---|
| Romans | 61 |
| 1 Corinthians | 23 |
| 2 Corinthians | 7 |
| Galatians | 13 |
| Ephesians | 19 |
| Philippians | 13 |
| Colossians | 10 |
| 1 Thessalonians | 7 |
| 2 Thessalonians | 1 |
| 1 Timothy | 4 |
| 2 Timothy | 2 |
| Hebrews | 32 |
| **Total** | **192** |

| | |
|---|---|
| James | 5 |
| 1 Peter | 11 |
| 2 Peter | 11 |
| 1John | 10 |
| Jude | 14 |
| **Total** | **51** |

| | |
|---|---|
| Revelation | 82 |
| **Total** | **82** |

Total Allusions to New Testament = 490

**Putting all allusions together to the Bible 909 + 490= 1399**

## Conclusion

And of course, the entire poem is one gigantic allusion to the book of Genesis, from which the story of Adam and Eve is taken. Likewise, Milton has taken many references from both Old Testament and New Testament as shown above.

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# Representation of Indian Tradition and Culture in the Select Novels of RK Narayan

Abstrct

Ripuram krishnaswamy Iyer Narayanaswami was born in Chennai on 10th October1906 in a middle class South Indian family.All the works of Narayan are located in the imaginary place called 'Malgudi' which is located in south India. South Indian tradition and culture are greatly highlighted in the works of Narayan.As India is a vast country, we find cultural differences from place to place. South Indian tradition and culture may have slight contrast with the other parts of the nation. Though many festivals are celebrated together, variations in celebrations are clearly noticed. The beauty of India lies in similarity in the differences. On the other hand as the novels are written during 1935 to 1952 we can also see age old Indian customs and strong rooted religious believes. Since education was not spread and limited to some sect of people before British and during British, superstitious believes were very much believed. Social evils like unto uchbility, gender discrimination and caste systems are also portrayed in his works.

Key Words:Malgudi, Religion, Education, gender discrimination, untouchbility.

## Introduction

RK Narayan, who was labeled "a small town ironist" always concentrated on gentle humor, weaknesses, and life style of south Indian people. Narayan also addressed the fundamental questions regarding human existence, social evils, sensitive believes and human relations. Narayan also portrayed philosophical touch of Hindu Dharma, Karma and its relevance in

everyday life.Gandhian philosophy is one of the chief concepts in the works of Narayan.Gandhian philosophy shows more impact on finding solutions to Hidhu religious issues. He strongly believesin Gandhian philosophy which did not satisfy the contemporary writers like Mulk Raj Anand and Raja Rao.

In the early novel of Narayan "The man Eater of Malgudi", we can see the orthodox Hindu religious believes and caste mark on the forehead of Nataraj. He symbolizes the strong rooted mystery of Hindu religion. *"I hung up a framed picture of goddess Lakshmi poised on her lotus, holding the bounties of earth in her forehands, and through her grace I did not do badly".*( The man Eater of Malgudi page 7) Natarajdoes prayers to the sun in the early morning and also hangs up the frame of goddess Lakshmi in his parlor. The traditional approach of Narayan is depicted here. His believes in Hindu darma , Indian epics, Puranas, myths and mythologies. He takes the Ramanaya andthe Mahabharata for references and solutions for contemporary issues.

Narayan's thirdnovel "The Dark Room"published in 1938 portrays the southern family culture in the contemporary society. Husband is the head of the family and wife is expected to walk in the footsteps of the husband. Woman is always expected to have lot of patience and always Sita character from the Ramayan is depicted. At the end of the novel Savitri shows modern ideology by thinking of leaving the family and deciding to spend rest of her life in the service of God.

*She at one stage is determined that ' She would dedicate her life to the service of God, numb her senses and memory, forget the world, and spend the rest of the years thus and die, no husband, home or children".*( The Dark Room, page 146)Thus religion is chosen as the last and ultimate source for solace and peace.

The Guide is the ultimate depiction of Hindu religion, swami and saints in Indian colorful society with the distinctive humor. Superstitions, duplicities, believes and stupidities are greatly captured in this novel. Malgudi is portrayed as the combined place of traditionalism and modernism with the character like Rossie, a classical dancer. "*What must happen must happen, no power on earth or heaven can change its course list as no one can change thecourse of that river".* (page15)

The guide also is a satirical humor on Hindu blind believes. Raju, the main character in the novel is worshipped as saint as he is found sitting under a tree alone after release from jail. The local communities believe that he has lot of powers and provide him food and other needs. His meaningless words are positively taken by them with lot of philosophy.

In his recent novel published in 1990 The World of Nagaraj, the character is differently portrayed. Nagarj prefers to spend much of his time writing letters, drinking coffee and doing some leisurely accounting for a friend.Nagaraj is a mild mannered man with a fragile character from a wealthy aristocrat family. He strongly observes the self-imposed calmness and prepares his soul for te silence of death. “You are like Lakshmana, who stood behind Rama, his elder brother, all the time without a murmur or doubt. (The World of Nagaraj page27) This shows the influence of Hindu epics on Narayan and Indian society. MeenakshiMukharjee says “RK Narayan successfully achieves the vision through Malgudi”. The indian joint family system also gets changed in the novel as Nagaraj, his mother and wife Sita are left to themselves as his elder brother settles down in village saying that he needs to take care of fields.

Conclusion

Narayan’s characters in Malgudi represent age old Indian tradition and set the modern ideology with the influence of western culture in the later novels. Early novels show the fragrance of Indian soil, vedas, puranas and epics. The later characters are very much westernized with modern ideology. The spirit of questioning the existing social evils like social inequalities, superstitious believes, untouchbility and caste system are questioned. The thought of questioning is the big change in his early novels to later novels.

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# Microwave assisted synthesis and anti-Inflammatory activity evaluation of Pyrazole derivatives

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**Abstract. Microwave promoted easy, efficient and environment friendly procedure has been devised for the synthesis of a series of pyrazole derivatives in high yields by the reaction of chalcones with phenyl hydrazine hydrochloride under catalyst free, solvent free conditions. The newly synthesized compounds were characterized by NMR ( $^{1}H$ and $^{13}C$), Mass, IR and C, H, N analyses. *In vitro* anti-inflammatory activity of the synthesized compounds was investigated against inhibition of Albumin Denaturation and Membrane Stabilization test methods. Majority of the compounds showed good activity when compared with the standard drugs.**

***Keywords — microwave irradiation, pyrazole derivatives, chalcones, anti-inflammatory activity***

## I. INTRODUCTION

Pyrazole refer to both to class of simple aromatic ring organic compound of heterocyclic diazole series characterized by a 5- member ring structure composed of three carbon atom and two nitrogen atom in the adjacent position and to unsaturated parent compound. These are important organic compounds for pharmaceutical [1] and agrochemical industry [2]. Numerous compounds containing pyrazole moiety are known to exhibit anti-hyperglycemic [3], analgesic [4], anti-inflammatory [5], antipyretic [6], antibacterial [7], antimicrobial [8], antihypertensive [9] and antidepressant [10] activities. They are also used as herbicides [11] and dyestuffs [12]. Pyrazole is a multipurpose lead compound developed by chemical architecture for effective molecules which are biologically active. Several synthetic routes are accorded to the development of pyrazole containing reactions to afford a novel molecule which is an enormous opportunity in the field of medicinal chemistry.[13a-l]

In recent years, microwave assisted organic syntheses have gained enormous attention of the chemists due to their advantages such as shorter reaction times, cleaner products, operational simplicity, higher yields and being a potential alternative to accomplish the effective synthesis of heterocyclic bioactive compounds. [14] Solvent-free reaction condition has been demonstrated to be an efficient technique for various organic reactions. It often leads to a remarkable decrease in reaction time, increased yields, easier workup, enhancement of regio and stereo selectivity of reaction matches with the green chemistry protocol.[15]

Paracetamol is a relatively COX-2 selective, non-steroidal anti-inflammatory drug (NSAID) with analgesic and antipyretic properties. But the continuous use of Paracetamol can cause diarrhea, vomiting, skin rash, dizziness and bitterness in the mouth. Hence there is a need for developing superior anti-inflammatory with better safety profile.

Motivated by the afore-mentioned literature and in continuation of our studies towards developing new methods for the synthesis of pyrazole derivatives having good anti-inflammatory activity[16], we envision our approach towards the design and synthesis of novel structurally diverse series of pyrazole derivatives for their anti-inflammatory activity.

## II. EXPERIMENTAL DETAILS

The reactions were carried out in a round bottom 50 mL flask fitted with reflux condenser, a dropping funnel and in Nitrogen atmosphere. A magnetic stirrer cum hot plate was used for stirring and heating the reaction mixtures. Rota evaporator was used for removing the solvent from the reaction mixture. All the solvents and reagents were dried and purified before use by adopting the standard procedures and techniques. Progress of the reaction and purity of the compounds were monitored by thin layer chromatography (TLC) on aluminium sheet of silica gel 60F254, E-Merck, Germany using iodine as visualizing agent. Melting points (mp) were determined in open capillary tubes using a calibrated thermometer by Guna Digital Melting Point apparatus, expressed in degrees centigrade (°C) and are


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uncorrected. $^1$H NMR spectra was recorded as solutions in $CDCl_3$ on a Bruker AMX/ VARIAN 400 MHz spectrometer operating at 400 MHz. The $^1$H chemical shifts were expressed in parts per million (ppm) with reference to tetramethylsilane (TMS). The following abbreviations were used while presenting the NMR data: **s** = singlet, **d** = doublet, **t** = triplet, **q** = quartet and **m** = multiplet. All the chemicals used in the present work were obtained from Sd. Fine Chem. Ltd., Boisar, India and Qualigens, Mumbai and were used after purifying them by following the established procedures.

***Preparation of pyrazole derivatives (5a-j)***

In the first step, to a cold solution (below 10°C) of paracetamol (**1**) (0.01 mol), 4-methoxybenzaldehyde (**2b**) (0.01 mol) in ethanol and a chilled solution of NaOH (10 mL of 30% solution) were added. Then the reaction mixture was allowed to stir for 12h. It was diluted with water (100 mL) and acidified with Conc. HCl. The product obtained was filtered, washed with water and recrystallized from ethanol to get pure chalcone (**3a**).

In the second step, a mixture of the chalcone (**3a**) (0.01 mol) and phenyl hydrazine hydrochloride (**4**) (0.01 mol) were taken in flat-bottomed flask and irradiated with microwave radiations in a microwave oven at 490 Watts. The reaction mixture was heated consecutively two times for 2-3 min period each time followed by a 1 min cooling interval between irradiations. To avoid the continuous overheating of the reactants, this method was proposed. In order to maintain the homogeneity of the irradiating field throughout the reaction, the reaction mixture was kept under stirring. The progress of the reaction was monitored by TLC on silica gel using ethyl acetate-hexane (8:2 v/v). After complection of the reaction, the solvent was removed under reduced pressure to get the crude product. The resulting crude product was purified by column chromatography on silica gel (100-200 mesh) using ethyl acetate-hexane (1:1) as eluent to get pure 4-(5-(4-methoxyphenyl)-1-phenyl-4,5-dihydro-1H-pyrazol-3-ylamino)phenol (**5a**). The remaining compounds **5b-j** were prepared by adapting to the above described procedure. The synthetic protocol for the title compounds is presented in **Scheme 1**.

***Physical, analytical and spectral data for the compounds (5a-j)***

4-(5-(4-methoxyphenyl)-1-phenyl-4,5-dihydro-1H-pyrazol-3-ylamino)phenol (**5a**): Yield: 87%; solid. M.P. 80-81 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 9.29 (s, 1H, -OH), 8.88 (s, 1H, Ar-NH), 7.46-6.74 (m, 9H, Ar-H), 3.89 (t, 1H, pyrazole-C-H), 3.48 (s, 3H, $OCH_3$), 2.14 (m, 1H, pyrazole-$CH_2$), 0.88 (m, 1H, pyrazole-$CH_2$); $^{13}$C NMR spectrum (100 MHz, $CDCl_3$): $\delta$ 157.4 (C-22), 146.5 (C-10), 143.6 (C-3), 142.5 (C-13), 134.8 (C-19), 131.5 (C-7), 129.8 (C-15, C-17), 125.2 (C-20, C-24), 121.2 (C-16), 116.7 (C-8, C-12), 115.7 (C-9, C-11), 114.6 (C-14, C-18), 114.0 (C-21, C-23), 54.5 (C-25), 50.3 (C-5), 38.7 (C-4); IR (KBr) ($\nu_{max}$ cm$^{-1}$): 3336 (OH), 3217 (NH), 1585 (C=N); LCMS (m/z, %): 360 ($M+H^+$, 100); Anal. Calcd for $C_{22}H_{21}N_3O_2$: C, 73.52; H, 5.89; N, 11.69; %; found: C, 73.60; H, 5.82; N, 11.76%.

(E)-4-(1-phenyl-5-styryl-4,5-dihydro-1H-pyrazol-3-ylamino)phenol (**5b**): Yield: 91%; solid. M.P. 142-146 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 9.29 (s, 1H, -OH), 8.88 (s, 1H, Ar-NH), 7.57-6.70 (m, 14H, Ar-H), 6.25 (d, 1H, Ar-**CH**=CH), 6.12 (d, 1H, Py-**CH**=CH), 3.83 (t, 1H, pyrazole-C-H), 2.14 (m, 1H, pyrazole-$CH_2$), 0.88 (m, 1H, pyrazole-$CH_2$); $^{13}$C NMR spectrum (100 MHz, $CDCl_3$): $\delta$ 148.5 (C-10), 145.6 (C-3), 143.8 (C-13), 136.4 (C-21), 134.4 (C-20), 132.7 (C-7), 129.5 (C-15, C-17), 128.8 (C-19), 128.6 (C-23, C-25), 128.5 (C-22, C-26), 127.9 (C-24), 120.8 (C-16), 117.7 (C-8, C-12), 116.7 (C-9, C-11), 114.3 (C-14, C-18), 50.8 (C-5), 37.3 (C-4); IR (KBr) ($\nu_{max}$ cm$^{-1}$): 3339 (OH), 3227 (NH), 1593 (C=N); LCMS (m/z, %): 356 ($M+H^+$, 100); Anal. Calcd for $C_{23}H_{21}N_3O$: C, 77.72; H, 5.96; N, 11.82%; found: C, 77.78; H, 5.85; N, 11.89%.

4-(1,5-diphenyl-4,5-dihydro-1H-pyrazol-3-ylamino)phenol (**5c**): Yield: 93%; solid. M.P.270-272 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 9.29 (s, 1H, -OH), 8.88 (s, 1H, Ar-NH), 7.53-6.68 (m, 14H, Ar-H), 3.89 (t, 1H, pyrazole-C-H), 2.14 (m, 1H, pyrazole-$CH_2$), 0.88 (m, 1H, pyrazole-$CH_2$); $^{13}$C NMR spectrum (100 MHz, $CDCl_3$): $\delta$ 147.5 (C-10), 143.6 (C-3), 142.8 (C-13), 135.4 (C-19), 131.7 (C-7), 129.8 (C-15, C-17), 127.6 (C-21, C-23), 127.5 (C-20, C-24), 126.2 (C-22), 121.5 (C-16), 117.0 (C-8, C-12), 116.2 (C-9, C-11), 114.3 (C-14, C-18), 54.8 (C-25), 50.7 (C-5), 38.6 (C-4); IR (KBr) ($\nu_{max}$ cm$^{-1}$): 3344 (OH), 3216 (NH), 1592 (C=N); LCMS (m/z, %): 330 ($M+H^+$, 100); Anal. Calcd for $C_{21}H_{19}N_3O$: C, 76.57; H, 5.81; N, 12.76%; found: C, 76.64; H, 5.78; N, 12.83%.

4-(5-(4-nitrophenyl)-1-phenyl-4,5-dihydro-1H-pyrazol-3-ylamino)phenol (**5d**): Yield: 85%; solid. M.P.207-208 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 9.29 (s, 1H, -OH), 8.88 (s, 1H, Ar-NH), 8.29-6.70 (m, 13H, Ar-H), 3.89 (t, 1H, pyrazole-C-H), 2.14 (m, 1H, pyrazole-$CH_2$), 0.88 (m, 1H, pyrazole-$CH_2$); $^{13}$C NMR spectrum (100 MHz, $CDCl_3$): $\delta$ 150.6 (C-19), 147.5 (C-10), 144.6 (C-22), 143.5 (C-3), 142.9 (C-13), 131.8 (C-7), 128.5 (C-15, C-17), 122.8 (C-21, C-23), 121.2 (C-20, C-24), 120.6 (C-16), 117.9 (C-8, C-12), 116.0 (C-9, C-11), 114.1 (C-14, C-18), 50.5 (C-5), 38.6 (C-4); IR (KBr) ($\nu_{max}$ cm$^{-1}$): 3351 (OH), 3220 (NH), 1593 (C=N); LCMS (m/z, %): 375 ($M+H^+$, 100); Anal. Calcd for $C_{21}H_{18}N_4O_3$: C, 67.37; H, 4.85; N, 14.96%; found: C, 67.44; H, 4.92; N, 14.90%.

4-(5-(4-chlorophenyl)-1-phenyl-4,5-dihydro-1H-pyrazol-3-ylamino)phenol (**5e**): Yield: 90%; solid. M.P.179-180 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 9.29 (s, 1H, -OH), 8.88 (s, 1H, Ar-NH), 7.56-6.65 (m, 13H, Ar-H), 3.89 (t, 1H, pyrazole-C-H), 2.14 (m, 1H, pyrazole-$CH_2$), 0.88 (m, 1H, pyrazole-$CH_2$); $^{13}$C NMR spectrum (100 MHz, $CDCl_3$): $\delta$ 147.5 (C-10), 143.6 (C-3), 142.6 (C-13), 140.2 (C-19), 133.7 (C-7), 131.6 (C-22), 129.8 (C-15, C-17), 127.3 (C-21, C-23), 126.8 (C-20, C-24), 121.9 (C-16), 117.2 (C-8, C-12),


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116.1 (C-9, C-11), 114.0 (C-14, C-18), 50.2 (C-5), 38.6 (C-4); IR (KBr) ($\nu_{max}$ $cm^{-1}$): 3349 (OH), 3225 (NH), 1596 (C=N); LCMS (m/z, %): 364 ($M+H^+$, 100); Anal. Calcd for $C_{21}H_{18}ClN_3O$: C, 69.32; H, 4.99; N, 11.55%; found: C, 69.42; H, 4.93; N, 11.60%.

4-(5-(4-fluorophenyl)-1-phenyl-4,5-dihydro-1H-pyrazol-3-ylamino)phenol (**5f**): Yield: 94%; solid. M.P.215-217 °C; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 9.29 (s, 1H, -OH), 8.88 (s, 1H, Ar-NH), 7.30-6.56 (m, 13H, Ar-H), 3.89 (t, 1H, pyrazole-C-H), 2.14 (m, 1H, pyrazole-$CH_2$), 0.88 (m, 1H, pyrazole-$CH_2$); $^{13}C$ NMR spectrum (100 MHz, $CDCl_3$): $\delta$ 167.6 (C-22), 147.4 (C-10), 144.6 (C-3), 142.7 (C-13), 137.1 (C-19), 133.5 (C-7), 129.9 (C-15, C-17), 128.0 (C-20, C-24), 121.2 (C-16), 117.5 (C-8, C-12), 116.2 (C-9, C-11), 115.6 (C-21, C-23), 114.1 (C-14, C-18), 50.3 (C-5), 37.8 (C-4); IR (KBr) ($\nu_{max}$ $cm^{-1}$): 3363 (OH), 3234 (NH), 1597 (C=N); LCMS (m/z, %): 348 ($M+H^+$, 100); Anal. Calcd for $C_{21}H_{18}FN_3O$: C, 72.61; H, 5.22; N, 12.10%; found: C, 72.68; H, 5.15; N, 12.16%.

4-(5-(3,5-dichlorophenyl)-1-phenyl-4,5-dihydro-1H-pyrazol-3-ylamino)phenol (**5g**): Yield: 83%; solid. M.P.167-168 °C; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 9.29 (s, 1H, -OH), 8.88 (s, 1H, Ar-NH), 7.60-6.57 (m, 12H, Ar-H), 3.89 (t, 1H, pyrazole-C-H), 2.14 (m, 1H, pyrazole-$CH_2$), 0.88 (m, 1H, pyrazole-$CH_2$); $^{13}C$ NMR spectrum (100 MHz, $CDCl_3$): $\delta$ 147.6 (C-10), 145.4 (C-19), 143.6 (C-3), 142.8 (C-13), 136.3 (C-21, C-23), 131.8 (C-7), 129.9 (C-15, C-17), 127.8 (C-22), 125.9 (C-20, C-24), 121.2 (C-16), 117.2 (C-8, C-12), 116.1 (C-9, C-11), 114.3 (C-14, C-18), 49.2 (C-5), 38.6 (C-4); IR (KBr) ($\nu_{max}$ $cm^{-1}$): 3350 (OH), 3222 (NH), 1590 (C=N); LCMS (m/z, %): 398 ($M+H^+$, 100); Anal. Calcd for $C_{21}H_{17}Cl_2N_3O$: C, 63.33; H, 4.30; N, 10.55%; found: C, 63.38; H, 4.25; N, 10.61%.

4-(5-(2-nitrophenyl)-1-phenyl-4,5-dihydro-1H-pyrazol-3-ylamino)phenol (**5h**): Yield: 92%; solid. M.P.183-184 °C; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 9.29 (s, 1H, -OH), 8.88 (s, 1H, Ar-NH), 8.17-6.72 (m, 13H, Ar-H), 3.89 (t, 1H, pyrazole-C-H), 2.14 (m, 1H, pyrazole-$CH_2$), 0.88 (m, 1H, pyrazole-$CH_2$); $^{13}C$ NMR spectrum (100 MHz, $CDCl_3$): $\delta$ 166.4 (C-22), 147.5 (C-10), 144.2 (C-24), 143.5 (C-3), 142.9 (C-13), 136.5 (C-19), 134.1 (C-21), 133.7 (C-7), 129.9 (C-15, C-17), 125.7 (C-20), 122.5 (C-23), 120.9 (C-16), 117.2 (C-8, C-12), 116.3 (C-9, C-11), 114.0 (C-14, C-18), 45.2 (C-5), 37.5 (C-4); IR (KBr) ($\nu_{max}$ $cm^{-1}$): 3342 (OH), 3219 (NH), 1590 (C=N); LCMS (m/z, %): 375 ($M+H^+$, 100); Anal. Calcd for $C_{21}H_{18}N_4O_3$: C, 67.37; H, 4.85; N, 14.96%; found: C, 67.42; H, 4.90; N, 14.90%.

4-(1-phenyl-5-(4-(trifluoromethyl)phenyl)-4,5-dihydro-1H-pyrazol-3-ylamino)phenol (**5i**): Yield: 86%; solid. M.P.177-179 °C; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 9.29 (s, 1H, -OH), 8.88 (s, 1H, Ar-NH), 7.65-6.68 (m, 13H, Ar-H), 3.89 (t, 1H, pyrazole-C-H), 2.14 (m, 1H, pyrazole-$CH_2$), 0.88 (m, 1H, pyrazole-$CH_2$); $^{13}C$ NMR spectrum (100 MHz, $CDCl_3$): $\delta$ 147.7 (C-10), 144.5 (C-19), 143.6 (C-3), 142.4 (C-13), 133.7 (C-7), 129.9 (C-15, C-17), 129.0 (C-22), 124.9 (C-25), 123.6 (C-20, C-24), 122.8 (C-21, C-23), 120.8 (C-16), 117.3 (C-8, C-12), 116.4 (C-9, C-11), 114.0 (C-14, C-18), 50.5 (C-5), 38.6 (C-4); IR (KBr) ($\nu_{max}$ $cm^{-1}$): 3345 (OH), 3224 (NH), 1587 (C=N); LCMS (m/z, %): 398 ($M+H^+$, 100); Anal. Calcd for $C_{22}H_{18}F_3N_3O$: C, 66.49; H, 4.57; N, 10.57; found: C, 66.55; H, 4.51; N, 10.62%.

4-(1-phenyl-5-(pyridin-4-yl)-4,5-dihydro-1H-pyrazol-3-ylamino)phenol (**5j**): Yield: 91%; solid. M.P.156-157 °C; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 9.25 (s, 1H, -OH), 8.86 (s, 1H, Ar-NH), 8.35-6.88 (m, 13H, Ar-H), 3.89 (t, 1H, pyrazole-C-H), 2.14 (m, 1H, pyrazole-$CH_2$), 0.88 (m, 1H, pyrazole-$CH_2$); $^{13}C$ NMR spectrum (100 MHz, $CDCl_3$): $\delta$ 148.2 (C-19), 147.5 (C-10), 147.0 (C-21, C-23), 143.4 (C-3), 140.7 (C-13), 132.6 (C-7), 129.9 (C-15, C-17), 123.5 (C-20, C-24), 120.4 (C-16), 117.2 (C-8, C-12), 116.1 (C-9, C-11), 114.0 (C-14, C-18), 51.0 (C-5), 38.2 (C-4); IR (KBr) ($\nu_{max}$ $cm^{-1}$): 3325 (OH), 3223 (NH), 1595 (C=N); LCMS (m/z, %): 331 ($M+H^+$, 100); Anal. Calcd for $C_{20}H_{18}N_4O$: C, 72.71; H, 5.49; N, 16.96; found: C, 72.75; H, 5.43; N, 16.99%.

### *In vitro* Anti-inflammatory activity

*In vitro* anti-inflammatory activity of the synthesized compounds **5a-j** was investigated against inhibition of Albumin Denaturation [17] and Membrane Stabilization test methods [18].

### (a) Inhibition of Albumin Denaturation

All the synthesized compounds **5a-j** were evaluated for their anti-inflammatory activity with respect to inhibition of Albumin Denaturation method. The reaction mixture consisting of test compounds at different concentrations and 1% aqueous solution of bovine albumin fraction. $p^H$ of the reaction mixture was adjusted using small amount of 1N HCl to 7. The samples were incubated at 37° C for 20 min and then heated at 57° C for 20 min. After cooling the samples, the turbidity was measured spectrophotometrically at 660 nm. The experiment was performed in triplicate. Percent inhibition of protein denaturation was calculated as follows.

Percentage inhibition=($Abs_{control}$–$Abs_{sample}$)X 100/ $Abs_{control}$

Denaturation of protein is a well documented cause of inflammation. Phenyl butazone and flufenamic acids (anti-inflammatory drugs) have shown a dose dependent ability to thermally induced protein denaturation.

### (b) Membrane Stabilization test

#### *Preparation of red Blood cells (RBCs) Suspension*

Fresh human blood (10 mL) was collected and transferred to the heparinized centrifuged tubes. The tubes were centrifuged at 3000 rpm for 10 min and were washed three times with equal volume of normal saline. The volume of the blood was measured and reconstituted as10% v/v suspension with saline.

#### *Heat Induced Hemolysis*


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The reaction mixture (2 mL) consisting of 1mL of test drug solution and 1 mL of 10% RBCs suspension, instead of the drug only, saline was added to the control test tube [16]. Salicylic acid was taken as a standard drug. All the centrifuge tubes containing reaction mixture were incubated in a water bath at 56° C for 30 min. At the end of the incubation, the tubes were cooled under running tap water. The reaction mixture was centrifuged at 2500 rpm for 5 min and the absorbance of the supernatants was taken at 560 nm. The experiment was performed in triplicates. Per cent membrane stabilization activity was calculated by the formula.

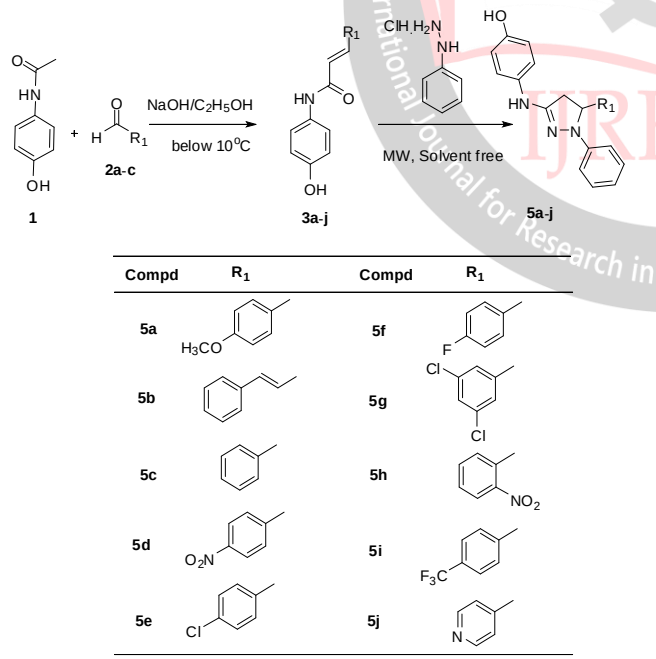
Percentage inhibition= ($Abs_{control}$–$Abs_{sample}$) X 100/ $Abs_{control}$

***Statistical Analysis***

The anti-inflammatory activity were screened by Carregeenan rat paw Oedema, Cotton pellet (*in vivo*) and Albumin Denaturation , Membrane Stabilization (*in vitro*) was compared *versus* negative control group by one way Analysis of Variance (ANOVA) with Dunnets post-test a value of $p< 0.05$ was considered significant.

## III. RESULTS AND DISCUSSION

In this letter, we report an efficient and environmentally benign protocol for the synthesis of pyrazole derivatives (**5a-j**) by the reaction of chalcones (**3a-j**) (0.01 mol) with phenyl hydrazine hydrochloride (**4**) (0.01 mol) under solvent-free conditions at room temperature using microwave radiation at 490W (**Scheme 1**).




**Scheme 1. Synthesis of biologically active pyrazole derivatives**

The chemical structure of the title compounds **5a-j** were characterized by spectral data ($^1$H and $^{13}$C NMR, IR and LC-MS), elemental analysis and the results were presented in experimental section. The proton signals at 8.88-8.86 and 9.29-9.25 are due to Ar-NH and OH protons for the compound (**5a-j**). The $^1$H NMR spectra of the compounds (**5a-j**) gave signals due to Ar-H in the range of 8.29-6.56 ppm. The proton signals at 3.89 is due to C-H proton of pyrazole ring for the compounds (**5a-j**). The methylene protons of pyrazole ring gave two multiplets at $\delta$ 2.14 and $\delta$ 0.88 respectively for the compounds (**5a-j**). $^{13}$C NMR chemical shift for C-H and $CH_2$ carbon of pyrazole ring were observed at 38,6-37.3 and 51.0-45.2 for the compounds **5a-j.** IR absorptions in the regions 3363-3325, 3234-3216 and 1597-1585 $cm^{-1}$ were assigned to OH, NH and C=N stretching vibrations respectively for the compounds **5a-j**. In their mass spectra, $M^{+\cdot}$ ions were observed in the expected m/z values.

***In vitro anti inflammatory activity***

*In vitro* anti-inflammatory activity of the tested compounds (**5a-j**) were evaluated with Albumin denaturation method and Membrane test methods. Phenyl butazone, flufenamic acid and salicylic acid are used as standard reference drugs for the study. The experiment was performed in triplicate and the results were presented in **Table 1** and **Table 2**. The title compounds **(5a-j)** showed moderate to good anti-inflammatory activity ranging from 39-75 % (Albumin denaturation method) and 41-79% (Membrane test methods), where as flufenamic acid and starting compound exhibited 79% and 57% respectively in Albumin denaturation method and salicylic acid and starting compound exhibited 85% and 62% respectively in Membrane test method. Especially the compounds compounds **5d**, bearing with 4-nitrophenyl moiety; **5f**, incorporated with 4-fluorophenyl moiety and **5j**, bearing with pyridinyl group showed potent anti-inflammatory activity compared to other derivatives.

It was observed that the position of the substituent on terminal benzene ring of pyrazole moiety has profound effect on the activity. The para position on the terminal benzene ring is the favorable site for the higher potency. Evidently, the compound **5d** with $NO_2$ and **5f** with **F** at para position, exhibiting highest inhibitory activity in the two methods. The presence of pyridine as substituent also exhibits high inhibitory activity in the two methods when compared with standard drugs. The remaining compounds were found to have moderate to good activity.

**Table 1: *In vitro* Anti-inflammatory activity of the title compounds (5a-j) by Inhibition of Albumin Denaturation method**

| Compounds | Dose (mg/mL) | Mean OD | SD | %Inhibition |
|---|---|---|---|---|
| **NC** | RO Water | 2.385 | 0.043 | - |
| **PC1** | 100 | 0.954[b] | 0.010 | 60.432 |
| **PC2** | 200 | 0.504[b] | 0.005 | 79.363 |
| **SC** | 0.2 | 1.045[b] | 0.022 | 57.676 |
| **5a** | 0.2 | 1.521[b] | 0.009 | 39.235 |
| **5b** | 0.2 | 1.236[b] | 0.005 | 43.242 |
| **5c** | 0.2 | 1.151[b] | 0.006 | 54.474 |


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| | | | | |
|---|---|---|---|---|
| **5d** | 0.2 | 0.624 [b] | 0.025 | 75.328 |
| **5e** | 0.2 | 1.014 [b] | 0.008 | 62.743 |
| **5f** | 0.2 | 0.737 [b] | 0.010 | 74.137 |
| **5g** | 0.2 | 1.114 [b] | 0.009 | 56.948 |
| **5h** | 0.2 | 1.197 [b] | 0.019 | 53.754 |
| **5i** | 0.2 | 0.823 [b] | 0.007 | 68.203 |
| **5j** | 0.2 | 0.687 [b] | 0.015 | 74.272 |

NC = Phenyl Butazone; PC = Flufenamic acid; [b] $p<0.05$

**Table 2: *In vitro* Anti-inflammatory activity of the title compounds (5a-j) by Membrane Stabilization test method**

| Compounds | Dose (mg/mL) | Mean OD | SD | % Inhibition |
|---|---|---|---|---|
| **NC** | RO Water | 2.430 | 0.133 | - |
| **PC1** | 100 | 0.912 [b] | 0.025 | 62.713 |
| **PC2** | 200 | 0.373 [b] | 0.042 | 85.253 |
| **SC** | 0.2 | 0.962 [b] | 0.076 | 61.921 |
| **5a** | 0.2 | 1.395 [b] | 0.008 | 41.045 |
| **5b** | 0.2 | 1.203 [b] | 0.011 | 45.933 |
| **5c** | 0.2 | 1.333 [b] | 0.324 | 42.152 |
| **5d** | 0.2 | 0.730 [b] | 0.015 | 76.625 |
| **5e** | 0.2 | 0.706 [b] | 0.016 | 70.964 |
| **5f** | 0.2 | 0.656 [b] | 0.026 | 79.720 |
| **5g** | 0.2 | 1.153 [b] | 0.010 | 52.898 |
| **5h** | 0.2 | 1.295 [b] | 0.007 | 47.701 |
| **5i** | 0.2 | 0.814 [b] | 0.026 | 66.545 |
| **5j** | 0.2 | 1.687 [b] | 0.040 | 77.042 |

PC = Salicylic acid; [b] $p<0.05$

## IV. CONCLUSION

In conclusion, we demonstrated here an efficient, environmentally benign protocol for the formation of *pyrazole derivatives* in high yields through an intermediate chalcone under solvent free condition in the presence of microwave irradiation at room temperature. *In vitro* anti-inflammatory screening results of **5a-j** showed that most of the derivatives exhibits good inhibitory activity in the two methods. **5d**, bearing with 4-nitrophenyl moiety; **5f**, incorporated with 4-fluorophenyl moiety and **5j**, bearing with pyridinyl group showed potent anti-inflammatory activity compared to other derivatives.

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ARTICLE




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# Microwave Mediated Michaelis-Arbuzov Reaction to Synthesize Bioactive Phenylphosphonate Derivatives Under Solvent Free Condition

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## ABSTRACT

Microwave assisted easy, efficient, and environment friendly process has been devised for the synthesis of phosphonates within minutes *via* microwave-assisted Michaelis-Arbuzov reaction. The desired products were obtained in excellent yields and in high purity under solvent-free and catalyst-free conditions. The structure all the synthesized compounds was confirmed by spectral and CHN analysis. *in vitro* Antibacterial and antifungal activity of these compounds was also analyzed. Majority of the title compounds showed good inhibition towards bacteria and fungi.

## KEYWORDS

Microwave, Phosphonates, Michaelis-Arbuzov reaction, Antibacterial activity and antifungal activity.

## INTRODUCTION

Organophosphorus compounds particularly phosphonates have been played a key role in biologically active compounds [1]. Phosphonates feature tetrahedral phosphorus centersare structurally closely related to phosphorous acid [2]. Phosphonates and phosphonic acids are organophosphorus compounds containing C–PO(OH)$_2$ or C–PO(OR)$_2$ groups (where R = alkyl, aryl). Many commercially important phosphonates compounds includes glyphosate (1) (active molecule of herbicide "Roundup"), ethephon (2), a widely used plant growth regulator, tiludronate (3) as anti-inflammatory as well as anti-rheumatismal agent. Bisphosphonates are popular drugs for treatment of osteoporosis. In biology and medicinal chemistry, phosphonate groups are used as stable bioisoteres for phosphate, such as antiviral nucleotide analogue, Tenofovir, one of the cornerstones of anti-HIV therapy [3]. Many synthetic phosphonates are now widely used as herbicides [4], stimulants for the latex production of *Hevea brasiliensis* [5], pesticides [6], detergents [7], reagents for Wittig-Horner reactions [8], antibacterial [9], antiviral [10] and anti-tumor agents [11,12].

Phosphonates have traditionally been accessed through the Arbuzov reaction [13-16]; a double SN$^2$ process between an alkyl halide and a trialkylphosphite, and this remains the most commonly employed route today. However, due to the resistance of aryl groups to nucleophilic attack, the classic

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Arbuzov reaction was essentially limited to the preparation of alkyl phosphonates. The synthesis of aryl phosphonates represents one early challenge. In this regard, transition-metal catalyzed Arbuzov reaction has gained remarkable success [17-21].

On the other hand, microwave-assisted organic synthesis has been given away to provide a number of advantages than the standard heating techniques such as clean reactions, improved reaction yields and shortened reaction times, easy work-ups and/or solvent free reaction conditions [22-25]. Keglevich *et al.* [26] also synthesized arylphosphonates by microwave-assisted Arbuzov reaction of triethylphosphite and aryl bromides in the presence of $NiCl_2$ as catalyst under solvent-free conditions.

As part of our research in the development of new methodologies for the synthesis of bioactive phosphonates, we synthesized a series of phenylphosphonate derivatives *via* Michaelis-Arbuzov reaction using microwave irradiation tech-nique under solvent free condition. All the synthesized compounds were characterized by various spectrophotometric methods and screened for their antibacterial and antifungal activities. Majority of the compounds showed good inhibition towards bacteria and fungi.

## EXPERIMENTAL

All the chemicals used in the present work were obtained from Sd. Fine Chem. Ltd., India; Qualigens, Mumbai and used after purifying them by following the established procedures.

**Characterization:** The reactions were carried out in a 100 mL round bottom flask holding condenser in nitrogen atmosphere. A magnetic agitator cum hot plate was used for stirring and heating the reaction mixtures. Rota evaporator was used for removing the solvent from the reaction mixture. All the chemicals were dehydrated before use by adopting the standard procedures and techniques. Rota evaporator was used for removing the solvent from the reaction mixture. Thin layer chromatography (TLC) on aluminium sheet of silica gel was used to check the development of the reaction and purity of the compounds by iodine as visualizing agent. All microwave-assisted irradiation experiments were conducted using single-mode microwave synthesis apparatus. The $^{31}P$ (161.9 MHz), $^{1}H$ (400 MHz) and $^{13}C$ (100 MHz) NMR spectra were recorded on Bruker AMX spectrometer. Chemical shifts were referenced to TMS ($^{1}H$ and $^{13}C$ NMR) and 85 % $H_3PO_4$ ($^{31}P$ NMR) and DMSO-$d_6$ was used to dissolve the samples. API 2000 Perkin-Elmer Mass spectrometer was used to record mass spectra. Bruker IFS 55 (Equinox) FTIR spectrometer in KBr was used to record IR spectra. Microanalytical data were obtained from University of Hyderabad, Hyderabad, India.

**Synthesis of 4-chloro-*N*-(substituted) benzenesulfonamide (3a-i):** To a stirred solution of 4-chlorobenzene-1-sulfonyl chloride (1) (0.2 mmol) and pyridin-3-amine (**2a**) (0.2 mmol) in dehydrated tetrahydrofuran (40 mL); triethylamine was added at 10 ºC with stirring for about 15 min. It was stirred further at ambient temperature for 4 h. TLC was used for monitoring the progress of the synthetic route and rota-evaporator on the way to eliminate the solvent to obtain crude product. By means of ethyl acetate- *n*-hexane (8:2) as eluent, the product was purified using column chromatography to afford 4-chloro-*N*-(pyridin-3-yl)benzenesulfonamide (**3a**). Similar experimental route was used to synthesize of left over compounds (**3b-i**).

**Conventional synthesis of phenylphosphonate derivatives (5a-i):** 4-Chloro-*N*-(substituted) benzenesulfonamide derivatives (**3a-i**) (0.01 mol) and trimethylphosphite (**4**) (0.02 mol) in THF were mixed together and stirred for 3-5 h at reflux temperature. TLC was used to check the progress of the process. After completion of the reaction, triethylamine hydrochloride salt was filtered off and the solvent was removed in a rota-evaporator. Finally column chromatography was used to get pure phenylphosphonate derivatives (**5a-i**) using ethyl acetate: *n*-hexane (6:4) as eluent.

**Microwave assisted synthesis of phosphonates (5a-i):** 4-Chloro-*N*-(substituted) benzenesulfonamide derivatives (**3a-i**) (0.01 mol) and trimethylphosphite (**4**) (0.02 mol) were mixed together and microwave radiated at 420 W under room temperature for about 12-30 min. TLC was used to check the progress of the reaction. After completion of the reaction, triethylamine hydrochloride salt was filtered off and the solvent was removed in a rota-evaporator. Finally, column chromatography was used to get pure phenylphosphonate derivatives (**5a-i**) by means of ethyl acetate:*n*-hexane (6:4) as eluent.

**Spectral data**

Dimethyl 4-(*N*-pyridin-3-ylsulfamoyl)phenylphosphonate (5a): Yield: 90 %; semi-solid. $^{31}P$ NMR spectrum (DMSO-$d_6$): δ 18.5 ppm; $^{1}H$ NMR spectrum (400 MHz, DMSO-$d_6$): δ 10.35 (s, 1H, NH), 8.35-7.20 (m, 8H, Ar-H), 3.65 (s, 6H, $OCH_3$); $^{13}C$ NMR spectrum (100 MHz, DMSO-$d_6$): δ 145.1 (C-1′), 141.5 (C-2), 141.2 (C-5), 138.8 (C-4′), 137.5 (C-2′), 131.4 (C-4, C-6), 126.8 (C-3, C-7), 124.7 (C-5′), 122.8 (C-6′), 52.5 (C-10, C-12); IR (KBr, $\nu_{max}$, $cm^{-1}$): 3269 (NH), 1468 (P-car), 1332,1183 ($SO_2$), 1225 (P=O), 1018 (P-O-C aliph.), 905 (S-N). LC-MS (*m/z*, %): 343 ($M+H^+$,100); Anal. calcd (found) % for $C_{13}H_{15}N_2O_5PS$: C, 45.61 (45.69); H, 4.42 (4.48); N, 8.18 (8.12).

**Dimethyl 4-(*N*-thiazol-2-ylsulfamoyl)phenylphosphonate (5b):** Yield: 89 %; semi-solid. $^{31}P$ NMR spectrum (DMSO-$d_6$): δ 20.2 ppm; $^{1}H$ NMR spectrum (400 MHz, DMSO-$d_6$): δ 11.94 (s, 1H, NH), 8.36-6.70 (m, 6H, Ar-H), 3.65 (s, 6H, $OCH_3$); $^{13}C$ NMR spectrum (100 MHz, DMSO-$d_6$): δ 171.7 (C-2′), 141.5 (C-2), 141.2 (C-5), 137.0 (C-4′), 131.4 (C-4, C-6), 126.8 (C-3, C-7), 112.1 (C-5′), 52.5 (C-10, C-12). IR (KBr, $\nu_{max}$, $cm^{-1}$): 3283 (NH), 1479 (P-car), 1338, 1186 ($SO_2$), 1228 (P=O), 1018 (P-O-C aliph.), 907 (S-N); LC-MS (*m/z*, %): 349 ($M+H^+$, 100). Anal. calcd. (found) % for $C_{11}H_{13}N_2O_5PS_2$: C, 37.93 (37.99); H, 3.76 (3.82); N, 8.04 (8.00).

**Dimethyl 4-(*N*-(1-methyl-2,6-dioxo-1,2,3,6-tetrahydropyrimidin-4-yl)sulfamoyl)phenylphosphonate (5c):** Yield: 87 %; semi-solid. $^{31}P$ NMR spectrum (DMSO-$d_6$): δ 23.4 ppm; $^{1}H$ NMR spectrum (400 MHz, DMSO-$d_6$): δ 11.36 (s, 1H, urea-NH), 8.35 (d, 2H, Ar-H), 7.88 (d, 2H, Ar-H), 4.35 (d, 2H, ethylene-H), 3.69 (s, 6H, $OCH_3$), 3.24 (s, 3H, N-$CH_3$), 2.13 (s, 1H, NH); $^{13}C$ NMR spectrum (100 MHz, DMSO-$d_6$): δ 163.2 (C-2′), 142.9 (C-2), 142.1 (C-5), 162.3 (C-6′), 161.7 (C-4′), 131.4 (C-4, C-6), 126.8 (C-3, C-7), 75.5 (C-7'), 52.5 (C-10, C-12), 28.0 (C-8′). IR (KBr, $\nu_{max}$, $cm^{-1}$): 3345, 3284 (NH), 1469 (P-car), 1338, 1181 ($SO_2$), 1232 (P=O), 1021 (P-O-C aliph.), 908 (S-N); LC-MS (*m/z*, %): 390 ($M+H^+$,100); Anal. calcd. (found) % for $C_{13}H_{16}N_3O_7PS$: C, 40.11 (40.19); H, 4.14 (4.18); N, 10.79 (10.85).

**Dimethyl 4-(*N*-thiomorpholinosulfamoyl)phenylphosphonate (5d):** Yield: 93 %; semi-solid. $^{31}$P NMR spectrum (DMSO-$d_6$): δ 22.7 ppm; $^{1}$H NMR spectrum (400 MHz, DMSO-$d_6$): δ 8.35 (d, 2H, Ar-H), 8.08 (d, 2H, Ar-H), 3.69 (s, 6H, $OCH_3$), 3.58 (t, 4H, methylene-H), 2.46 (t, 4H, methylene-H); $^{13}$C NMR spectrum (100 MHz, DMSO-$d_6$): δ 142.9 (C-2), 142.1 (C-5), 131.4 (C-4, C-6), 126.8 (C-3, C-7),52.5 (C-10, C-12), 49.3 (C-2′, C-6′), 26.9 (C-3′, C-5′). IR (KBr, $\nu_{max}$, cm$^{-1}$): 1464 (P-car), 1335, 1186 ($SO_2$), 1221 (P=O), 1018 (P-O-C aliph), 903 (S-N); LC-MS (*m/z*, %): 352 (M+H$^+$, 100). Anal. calcd. (found) % for $C_{12}H_{18}NO_5PS_2$: C, 41.02 (41.09); H, 5.16 (5.10); N, 3.99 (4.05).

**Dimethyl 4-(4-Methylpiperazin-1-ylsulfonyl)phenylphosphonate (5e):** Yield: 90 %; semi-solid. $^{31}$P NMR spectrum (DMSO-$d_6$): δ 23.2 ppm; $^{1}$H NMR spectrum (400 MHz, DMSO-$d_6$): δ 8.35 (d, 2H, Ar-H), 8.08 (d, 2H, Ar-H), 3.69 (s, 6H, $OCH_3$), 3.12 (t, 4H, methylene-H), 2.48 (t, 4H, methylene-H), 2.15 (s, 3H, N-$CH_3$); $^{13}$C NMR spectrum (100 MHz, DMSO-$d_6$): δ 142.9 (C-2), 142.1 (C-5), 131.4 (C-4, C-6), 126.8 (C-3, C-7), 53.7 (C-3′, C-5′), 52.5 (C-10, C-12), 46.0 (C-2′, C-6′), 45.5 (C-7′). IR (KBr, $\nu_{max}$, cm$^{-1}$): 1466 (P-car), 1332, 1183 ($SO_2$), 1226 (P=O), 1018 (P-O-C aliph.), 905 (S-N); LC-MS (*m/z*, %): 349 (M+H$^+$, 100). Anal. calcd. (found) % for $C_{13}H_{21}N_2O_5PS$: C, 44.82 (44.89); H, 6.08 (6.02); N, 8.04 (8.09).

**Dimethyl 4-(*N*-(6-nitrobenzo[*d*]thiazol-2-yl)sulfamoyl)-phenylphosphonate (5f):** Yield: 91 %; semi-solid. $^{31}$P NMR spectrum (DMSO-$d_6$): δ 24.3 ppm; $^{1}$H NMR spectrum (400 MHz, DMSO-$d_6$): δ 12.26 (s, 1H, NH), 8.58-8.08 (m, 7H, Ar-H), 3.69 (s, 6H, $OCH_3$); $^{13}$C NMR spectrum (100 MHz, DMSO-$d_6$): δ 142.9 (C-2), 142.1 (C-5), 131.4 (C-4, C-6), 126.8 (C-3, C-7), 174.1 (C-2′), 131.3 (C-4′), 119.1 (C-5′), 144.3 (C-6′), 121.3 (C-7′), 117.3 (C-8′), 159.3 (C-9′), 52.5(C-10, C-12). IR (KBr, $\nu_{max}$, cm$^{-1}$): 3292 (NH), 1477 (P-car), 1339, 1186 ($SO_2$), 1235 (P=O), 1024 (P-O-C aliph.), 909 (S-N); LC-MS (*m/z*, %): 444 (M+H$^+$, 100). Anal. calcd. (found) % for $C_{15}H_{14}N_3O_7PS_2$: C, 40.63 (40.69); H, 3.18 (3.11); N, 9.48 (9.54).

**Dimethyl 4-(*N*-benzo[*d*]thiazol-2-ylsulfamoyl)phenylphosphonate (5g):** Yield: 92 %; semi-solid. $^{31}$P NMR spectrum (DMSO-$d_6$): δ 18.7 ppm; $^{1}$H NMR spectrum (400 MHz, DMSO-$d_6$): δ 11.94 (s, 1H, NH), 8.58-7.50 (m, 8H, Ar-H), 3.69 (s, 6H, OCH3); $^{13}$C NMR spectrum (100 MHz, DMSO-$d_6$): δ 142.9 (C-2), 142.1 (C-5), 131.4 (C-4, C-6), 126.8 (C-3, C-7),172.3 (C-2′), 131.3 (C-4′), 122.4 (C-5′), 124.9 (C-6′), 125.7 (C-7′), 117.7 (C-8′), 152.9 (C-9′), 52.5(C-10, C-12). IR (KBr, $\nu_{max}$, cm$^{-1}$): 3274 (NH), 1465 (P-car), 1330, 1182 ($SO_2$), 1223 (P=O), 1018 (P-O-C aliph.), 902 (S-N); LC-MS (*m/z*, %): 399 (M+H$^+$, 100). Anal. calcd. (found) % for $C_{15}H_{15}N_2O_5PS_2$: C, 45.22 (45.28); H, 3.80 (3.74); N, 7.03 (7.08).

**Dimethyl 4-(*N*-(6-methoxybenzo[*d*]thiazol-2-yl)sulfamoyl)phenylphosphonate (5h):** Yield: 93 %; semi-solid. $^{31}$P NMR spectrum (DMSO-$d_6$): δ 21.6 ppm; $^{1}$H NMR spectrum (400 MHz, DMSO-$d_6$): δ 11.92 (s, 1H, NH), 8.58-7.12 (m, 7H, Ar-H), 3.73 (s, 3H, $OCH_3$), 3.69 (s, 6H, $OCH_3$); $^{13}$C NMR spectrum (100 MHz, DMSO-$d_6$): δ 172.3(C-2′), 154.7 (C-6′), 142.9 (C-2), 142.1 (C-5), 131.4 (C-4, C-6), 126.8 (C-3, C-7), 132.3 (C-4′), 113.8 (C-7′), 117.6 (C-8′), 105.8 (C-5′), 143.7 (C-9′), 54.8 (C-11′), 52.5 (C-10, C-12). IR (KBr, $\nu_{max}$, cm$^{-1}$): 3263 (NH), 1461 (P-car), 1330, 1184 ($SO_2$), 1220 (P=O), 1017 (P-O-C aliph.), 904 (S-N); LC-MS (*m/z*, %): 429 (M+H$^+$, 100). Anal. calcd. (found) % for $C_{16}H_{17}N_2O_6PS_2$: C, 44.86 (44.91); H, 4.00 (3.94); N, 6.54 (6.59).

**Dimethyl 4-(*N*-naphthalen-1-ylsulfamoyl)phenylphosphonate (5i):** Yield: 95 %; semi-solid. $^{31}$P NMR spectrum (DMSO-$d_6$): δ 23.8 ppm; $^{1}$H NMR spectrum (400 MHz, DMSO-$d_6$): δ 10.53 (s, 1H, NH), 8.58-6.86 (m, 11H, Ar-H), 3.69 (s, 6H, $OCH_3$); $^{13}$C NMR spectrum (100 MHz, DMSO-$d_6$): δ 142.9 (C-2), 142.1 (C-5), 131.4 (C-4, C-6), 126.8 (C-3, C-7), 141.5 (C-2′), 132.8 (C-8′), 128.9 (C-7′), 126.9 (C-10′), 126.2 (C-6′), 125.3 (C-5′), 124.9 (C-3′), 120.7 (C-4′), 119.5 (C-9′), 108.4 (C-11′), 52.5 (C-10, C-12). IR (KBr, $\nu_{max}$, cm$^{-1}$): 3274 (NH), 1462 (P-car), 1328, 1180 ($SO_2$), 1215 (P=O), 1012 (P-O-C aliph.), 901 (S-N);LC-MS (*m/z*, %): 392 (M+H$^+$, 100). Anal. calcd. (found) % for $C_{18}H_{18}NO_5PS$: C, 55.24 (55.28); H, 4.64 (4.59); N, 3.58 (3.63).

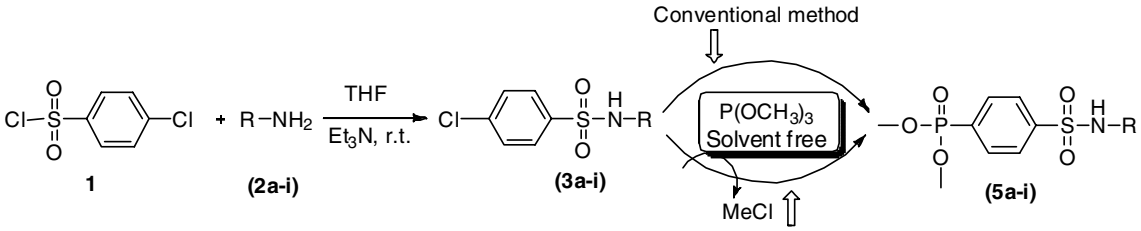
**Antibacterial and antifungal assays:** Antimicrobial activity of title compounds was tested by agar disc-diffusion method [27-29]. Sterile filter paper discs (6 mm diameter) moistened with the test compound solution in DMSO of specific concentrations 50 µg and 100 µg/disc were carefully placed on the agar culture plates that had been previously inoculated separately with the microorganisms. The plates were incubated at 37 ºC and the diameter of growth inhibition zones was measured after 24 h in case of bacteria and after 48 h in case of fungi. Penicillin was used as a reference antibacterial agent. Gresiofulvin was used as a reference antifungal agent. The test compounds, penicillin and gresiofulvin were dissolved in DMSO at concentrations of 50 and 100 µg/mL. Zone of inhibition is the area on an agar plate where growth of any microorganism is prevented by an antibiotic usually placed on the agar surface. If the test organism is susceptible to the antibiotic, the microorganisms will not grow.

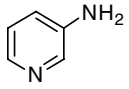
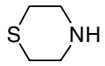
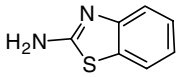
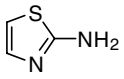
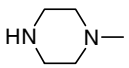
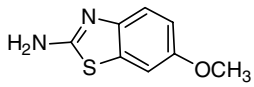
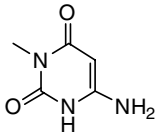
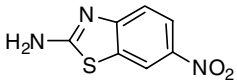
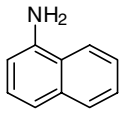
**Minimum inhibitory concentration:** Minimum inhibitory concentration (MIC) was evaluated using micro-broth-dilution method. MIC was determined by taking the minimum concentration at which there were observed no visually detectable bacteria/fungal growth. Specifically, 0.1 mL of standardized inoculum ($1.2 \times 10^7$ c.f.u/mL) was added to each test tube. The tubes were incubated aerobically at 37 ºC for 24 h for bacterial activity and 48-72 h for fungal activity. Control was maintained for each test sample. The lowest concentration (highest dilution) of test compound that produced no visible signs of microbial growth (no turbidity) when compared with the control tubes were regarded as MICs.

## RESULTS AND DISCUSSION

Synthesis of substituted phenylphosphonates (**5a-i**) was accomplished by reacting 4-chloro-*N*-(substituted) benzenesulfonamide derivatives (0.01 mmol) (**3a-i**) (which were synthesized by the reaction of 4-chlorobenzene-1-sulfonyl chloride (**1**) (0.2 mmol) and various amines (**2a-i**) (0.2 mmol) in THF in presence of triethylamine as base with trimethylphosphite (**4**) (0.02 mmol) using conventional and microwave irradiation techniques (**Scheme-I**) in high yields (73-95 %) in short period of time (12-30 min) under solvent free conditions (Table-1).

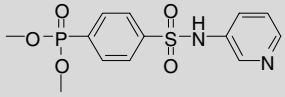
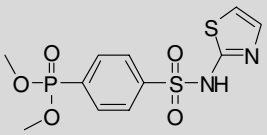
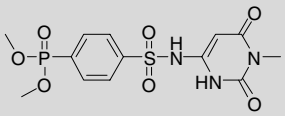
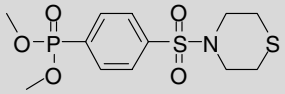
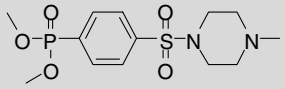
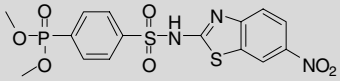
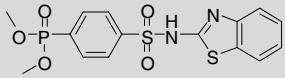
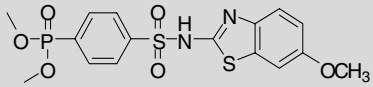
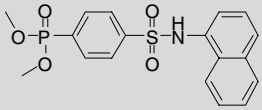
The structures of all the synthesized compounds were confirmed by NMR ($^{31}$P, $^{1}$H, $^{13}$C), IR, mass and CHN analysis. $^{31}$P




| Compd | R-NH$_2$ | Compd | R-NH$_2$ | Compd | R-NH$_2$ |
|---|---|---|---|---|---|
| **5a** |  | **5d** |  | **5g** |  |
| **5b** |  | **5e** |  | **5h** |  |
| **5c** |  | **5f** |  | **5i** |  |

**Scheme-I:** Synthesis of phenylphosphonate derivatives (**5a-i**)

TABLE-1
SYNTHESIS OF COMPOUNDS (**5a-i**) UNDER VARIOUS CONDITIONS

| Compd. | Structure | Conventional method[a] | | Microwave irradiation method[b] | |
|---|---|---|---|---|---|
| | | Time (h) | Yield[c] (%) | Time (h) | Yield[c] (%) |
| **5a** |  | 5 | 58 | 30 | 73 |
| **5b** |  | 4 | 61 | 20 | 77 |
| **5c** |  | 5 | 63 | 26 | 79 |
| **5d** |  | 4.5 | 65 | 24 | 80 |
| **5e** |  | 3 | 62 | 12 | 86 |
| **5f** |  | 3.5 | 68 | 16 | 74 |
| **5g** |  | 4.5 | 71 | 27 | 88 |
| **5h** |  | 4 | 80 | 19 | 95 |
| **5i** |  | 4 | 69 | 18 | 82 |

[a]Reaction of 4-chloro-N-(substituted)benzenesulfonamide derivatives and trimethylphosphite in THF at reflux temperature; [b]Reaction of 4-chloro-N-(substituted)benzenesulfonamide derivatives and trimethylphosphite without solvent under microwave irradiation at optimum temperature; [c]Isolated yield.

NMR signals appeared in the region δ 24.3-18.5 ppm for all the compounds (**5a-i**). $^{1}$H NMR spectra of the compounds (**5a-i**) gave signals for aromatic protons in the range of 8.58-6.70 ppm. The methyl protons of P-O-$CH_3$ showed singlet in the region δ 3.69-3.65 ppm for the compounds (**5a-i**). In $^{13}$C NMR spectra of compounds (**5a-i**), P-O-$CH_3$ was resonated at δ 52.5 ppm for the compounds (**5a-i**). In IR spectra, the bands in the region 1479-1461, 1235-1215 and 1024-1012 $cm^{-1}$ for P-car, P=O and P-O-C aliph. stretching frequencies. In mass spectra of the compounds, molecular ions were found in the accepted *m/z* values.

**Antibacterial activity:** All the synthesized compounds were assayed for their antibacterial activity against the growth of two Gram positive bacteria namely *Staphylococcus aureus*, *Bacillus subtilis* and two Gram negative bacteria such as *Escherichia coli*, *K. pneumoniae* at two different concentrations 50 and 100 µg/mL by agar well diffusion method. The standard drug, penicillin was used as reference for the comparison of the antibacterial activity. The diameter of zone of inhibition (mm) are represented in Table-1. Some analogues of this series were found to equipotent with the standard drug while some of them have comparable potency.

Especially, compound **5f**, bearing with 6-nitrobenzothiazolyl moiety and compound **5b** bearing with thiazol-2-yl group and compound **5c** incorporated with 1-methyl-2,6-dioxo-1,2,3,6-tetrahydropyrimidin-4-yl moiety were found to be most potent among all the title compounds. Zone of inhibition (ZOI) of compound **5f** is in the range 7.2-15.3 mm against Gram positive bacteria and 8.1-14.2 mm against Gram negative bacteria. The compound **5b** exhibited ZOI in the range 6.8-14.9 mm against Gram positive bacteria and 7.9-14.1 mm against Gram negative bacteria. The compound **5c** exhibited ZOI in the range 7.1-14.3 mm against Gram positive bacteria and 7.7-13.6 mm against Gram negative bacteria.The standard drug exhibited ZOI in the range 7.4-16.2 mm and 8.7-15.3 mm, respectively against Gram positive and Gram negative bacteria. The remaining compound exhibited modest activity. The results are shown in Table-2.

**Antifungal activity:** Two pathogenic fungi such as *Curvularia lunata* and *Aspergillus niger* were used to study the antifungal activity of synthesized compounds at two different concentrations 50 and 100 µg/mL using poison plate technique. Standard fungicide, gresiofulvinwas used for the comparison of antifungal activity. All the compounds showed moderate to good antifungal activity.

Especially, compounds **5c** bearing with 1-methyl-2,6-dioxo-1,2,3,6-tetrahydropyrimidin-4-yl moiety and **5f**, bearing with 6-nitrobenzothiazolyl moiety, **5d** bearing with thiomorpholine group were found to be most potent among all the title compounds. Zone of inhibition (ZOI) was found in the range 9.9-20.3 mm

TABLE-2
ANTIBACTERIAL AND ANTIFUNGAL ACTIVITY OF PHOSPHONATE DERIVATIVES (**5a-i**)

| Compd. | Zone of inhibition (mm) | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Antibacterial Activity | | | | | | | | Antifungal activity | | | |
| | *S. aureus* | | *B. subtilis* | | *E. coli* | | *K. pneumoniae* | | *C. lunata* | | *A. niger* | |
| | 50 µg/mL | 100 µg/mL | 50 µg/mL | 100 µg/mL | 50 µg/mL | 100 µg/mL | 50 µg/mL | 100 µg/mL | 50 µg/mL | 100 µg/mL | 50 µg/mL | 100 µg/mL |
| **5a** | 10.1 | 12.4 | 6.8 | 8.3 | 7.4 | 10.2 | 9.6 | 11.5 | 10.7 | 17.3 | 7.2 | 16.9 |
| **5b** | 11.9 | 14.9 | 6.8 | 8.8 | 7.9 | 11.8 | 10.5 | 14.1 | 9.5 | 15.2 | 8.4 | 16.1 |
| **5c** | 11.5 | 14.3 | 7.1 | 8.4 | 7.7 | 11.1 | 10.8 | 13.6 | 12.4 | 20.3 | 9.9 | 18.7 |
| **5d** | 9.2 | 11.8 | 6.1 | 8.2 | 7.0 | 9.8 | 8.6 | 11.9 | 11.2 | 18.0 | 8.6 | 17.1 |
| **5e** | 10.3 | 13.5 | 6.4 | 8.6 | 7.2 | 10.8 | 9.5 | 12.3 | 8.4 | 13.6 | 7.2 | 15.3 |
| **5f** | 12.1 | 15.3 | 7.2 | 9.2 | 8.1 | 11.8 | 11.0 | 14.2 | 11.8 | 18.7 | 8.9 | 17.9 |
| **5g** | 7.4 | 10.3 | 5.1 | 8.0 | 5.4 | 7.9 | 8.8 | 11.9 | 5.8 | 12.5 | 6.2 | 11.3 |
| **5h** | 6.9 | 9.1 | 4.5 | 5.6 | 6.0 | 7.7 | 8.4 | 10.7 | 6.0 | 13.1 | 7.0 | 12.1 |
| **5i** | 7.9 | 11.0 | 6.3 | 8.5 | 6.3 | 8.5 | 9.7 | 12.4 | 7.3 | 13.5 | 7.6 | 15.2 |
| Penicillin | 12.3 | 16.2 | 7.4 | 10.5 | 8.7 | 12.6 | 12.3 | 15.3 | – | – | – | – |
| Gresiofulvin | – | – | – | – | – | – | – | – | 12.8 | 21.2 | 10.2 | 18.9 |

TABLE-3
MIC VALUES OF THE SYNTHESIZED SULFONAMIDE DERIVATIVES (**5a-i**)

| Compd. | Minimum inhibitory concentration (µg/mL) | | | | | |
|---|---|---|---|---|---|---|
| | Bacterial strains | | | | Fungal strains | |
| | *S. aureus* | *B. subtilis* | *E. coli* | *K. pneumoniae* | *C. lunata* | *A. niger* |
| **5a** | 75 | 60 | 45 | 55 | 60 | 55 |
| **5b** | 20 | 25 | 40 | 35 | 40 | 25 |
| **5c** | 25 | 30 | 45 | 35 | 20 | 15 |
| **5d** | 59 | 64 | 59 | 44 | 20 | 30 |
| **5e** | 25 | 45 | 30 | 35 | 55 | 60 |
| **5f** | 15 | 20 | 25 | 15 | 15 | 20 |
| **5g** | 85 | 90 | 75 | 70 | 70 | 80 |
| **5h** | 75 | 80 | 65 | 70 | 85 | 60 |
| **5i** | 90 | 75 | 55 | 65 | 25 | 35 |
| Penicillin | 5 | 10 | 10 | 10 | – | – |
| Gresiofulvin | – | – | – | – | 5 | 10 |

for **5c**, 8.9-18.7 mm for **5f** and 8.6-18.0 for compound **5d** against the fungal strains where as the standard drug exhibited ZOI in the range 10.2-21.2 mm. The remaining compound exhibited moderate activity against all fungal strains. The results are presented in Table-2.

Minimum inhibitory concentration (MIC) was evaluated using micro-broth-dilution method [21]. The compounds **5f**, **5b** and **5c** exhibited the lower MIC values in the range of 15-45 µg/mL against bacteria and compounds **5c**, **5f** and **5d** showed lower MIC values in the range of 15-30 µg/mL against fungal strains (Table-3).

## Conclusion

In outline, we have demonstrated the synthesis of substituted phenylphosphonates (**5a-i**) by the reactions of 4-chloro-*N*-(substituted)benzene sulfonamide derivatives (**3a-i**) with trimethylphosphite under solvent free condition using microwave irradiation. Mild, non-hazardous and environment friendly reaction conditions, excellent yield in short reaction time are major advantages of this technique. The compounds **5f**, **5c** and **5b** showed promising antibacterial activity when compared with the remaining title compounds and were closer to standard drug. The compounds **5c**, **5f** and **5d** showed potent antifungal activity against the two tested fungal strains when compared with the remaining compounds. The remaining compounds exhibited reasonable activity against both bacterial and fungal strains.

## ACKNOWLEDGEMENTS

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ARTICLE

# Microwave-Assisted Synthesis and Anti-inflammatory Activity Evaluation of α-Aminophosphonates

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## ABSTRACT

In the present report, an expeditious green synthetic approach was developed for the synthesis of α-aminophosphonates **5(a-j)** in good yields through one-pot three component reaction (Kabachnik-Fields reaction) in solvent-free conditions under microwave irradiation. The newly synthesized compounds were characterized by IR, NMR ($^{1}$H, $^{13}$C and $^{31}$P), mass and C, H, N analysis. The synthesized compounds were screened for their anti-inflammatory activity using rat paw edema method. Most of the compounds from the series showed significant ($p < 0.05$) anti-inflammatory activity.

## KEYWORDS

α-Aminophosphonates, Microwave irradiation, Sulphadiazine, Antimicrobial activity.

## INTRODUCTION

The area of drug discovery and drug development has experienced significant advances with the introduction of combinatorial chemistry approaches. This innovative technology of producing libraries of structurally related compounds is particularly beneficial in the step of lead optimization. Lead optimization involves structural modifications of a "lead" compound that has demonstrated desired biological or pharmacological activities and/or reduce unwanted side effects.

During the past few years, cyclooxygenases (COX-1 and COX-2) have been introduced as novel targets for anti-inflammatory and cancer treatment [1]. Currently, there is an increasing body of evidence stating that targeting COX enzymes, especially COX-2 isoform, is an effective approach for the prevention or treatment of inflammation and various types of cancers. Nimesulide is a relatively COX-2 selective, non-steroidal anti-inflammatory drug (NSAID) with analgesic and antipyretic properties. But continuous use of nimesulide can cause diarrhea, vomiting, skin rash, dizziness and bitterness in mouth. Hence there is a need for developing superior anti-inflammatory with better safety profile.

The α-aminophosphonates, structural analogues of natural amino acids have received wide attention in medicinal, bioorganic and organic chemistry. They are reported to possess antitumor [2], anti-inflammatory [3] and antibiotic [4] activities.

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Their potential as good enzyme inhibitors [5], herbicides [6], peptide mimetics [7], fungicides [8], insecticides [9] plant growth regulators [10] *etc*. is also well documented. The assortment of possibilities of practical use of α-aminophosphonates has stimulated considerable interest toward α-aminophosphonate chemistry. Various synthetic protocols have been described for the synthesis of α-aminophosphonates. The nucleophilic addition of phosphites to imines (Kabachnik-Fields reaction) represents a convenient route for their preparation. A variety of Brønsted acid [11] or Lewis acids like $ZnCl_2$ [12], $BF_3$-$Et_2O$ [13], $CdI_2$/benzene [14], $CdI_2$/microwave [15]. One-pot syntheses of α-aminophosphonates have been carried out in organic solvents using lanthanide triflate [16], $InCl_3$ [17], $ZrCl_4$ [18], $In(OTf)_3/MgSO_4$ [19], $GaI_3$ [20], $BiCl_3$ [21], $Cu(OTf)_2$ [22], $SbCl_3/Al_2O_3$ [23]. Moreover, water [24] and ionic liquid [25] turned to be a kind of promising medium for such three component syntheses of α-aminophosphonates. Solvent-free transformations of phosphite to α-aminophosphonates could be accomplished in the presence of $LiClO_4$_$Et_2O$ [26,27], TFA [28], $LiClO_4$ [29], metal triflate [30], $Na_2CaP_2O_7$ [31], $ZrOCl_2{\cdot}8H_2O$, $ZrO(ClO_4)_2{\cdot}6H_2O$ [32] and TsCl [33].

Although, these approaches are satisfactory for three component, one-pot synthesis of α-aminophosphonates, nevertheless the utilization of toxic solvents, undesirable reaction conditions, expensive reagents, lengthened reaction times, costly catalysts and formation of side products limit the exercise of these approaches. The development of a simple and inexpensive procedure for one-pot synthesis of α-aminophosphonates is needed. Further, in recent years microwave irradiation [34-36] technique was playing a prominent role to promote one-pot synthesis of α-aminophosphonates and provide a number of advantages over the standard heating techniques such as improved reaction yield, shorten the reaction time and easy work-up procedure. For the most part, microwave assisted solvent-free reaction provides an opportunity to work with open vessels thus avoiding the development of high pressure and provide a possibility of up scaling the reaction on a preparative scale and helps the induction of the reaction under dry conditions. Overview of literature and to overcome the former drawbacks, we familiarized to explore the preparation of novel α-aminophosphonates under conventional as well as microwave assisted methods using solvent-free conditions.

## EXPERIMENTAL

All the chemicals are procured from Sigma-Aldrich, Merck and Lancaster were used as such without further purification. All solvents used for spectroscopic and other physical studies were reagent grade and were further purified employing the reported methods. The melting points were determined in open capillary tubes on a Guna Digital melting point apparatus and are uncorrected. IR spectra ($\nu_{max}$, $cm^{-1}$) were recorded as KBr pellets using Perkin-Elmer spectrophotometer at APL Research centre, Hyderabad. The $^1H$ NMR, $^{13}C$ NMR and $^{31}P$ NMR spectra were recorded on Bruker AMX 300 MHz NMR spectrometer operating at 300 MHz for $^1H$ NMR, 75.4 MHz for $^{13}C$ NMR and 161.9 MHz for $^{31}P$ NMR. All compounds were dissolved in DMSO-$d_6$ and chemical shifts were referenced to TMS ($^1H$ NMR and $^{13}C$ NMR) and 85 % $H_3PO_4$ ($^{31}P$ NMR) and mass spectra were recorded on API 2000 Perkin-Elmer PE-SCIEX Mass spectrometer. Micro-analytical data were obtained from University of Hyderabad, Hyderabad, India.

**Preparation of *N*-(4-amino-2-phenoxy phenyl)methanesulfonamide (2):** In the first step, to a mixture of nimesulide (5 g, 16.2 mmol) and tin (3.13 g) was added conc. HCl (20 mL) and the mixture was heated on a water bath at 90 °C for 3 h. After the completion of the reaction, the mixture was poured into ice water and the solid separated was filtered. After basification the crude product obtained was purified by re-crystallization from methanol and chloroform mixture to give the desired product as light brown solid; mp 198 °C; IR (KBr, $\nu_{max}$, $cm^{-1}$): 3412, 1572, 1487, 1215 and 1154; $^1H$ NMR (200 MHz, DMSO-$d_6$) δ 9.2 (s, 1H), 7.4 (m, 2H), 7.3 (d, *J* 8.6 Hz, 1H), 7.2 (m, 2H), 6.8 (d, *J* 8.6 Hz, 1H), 6.5 (s, 1H), 3.5 (br s, 2H), 3.1 (s, 3H); Mass (*m/z*) 279.1 ($M^+$, 100 %); Elemental analysis found C, 56.25; H, 5.07; N, 10.26; $C_{13}H_{14}N_2O_3S$ requires C, 56.10; H, 5.07; N, 10.06 [37].

### Procedure for the synthesis of a-aminophosphonates 5a-j

**Conventional method:** A mixture of N-(4-amino-2-phenoxy phenyl)methanesulfonamide (**2**, 0.005 mol) in ethanol, diethylphosphite (**3**, 0.005 mol) and 3-nitrobenzaldehyde (**4a**, 0.005 mol) were taken in flat-bottomed flask and stirred the reaction mixture vigorously at 40 °C for 4 h. The reaction progress was monitored by TLC on silica gel using ethyl acetate-hexane (7:3 v/v). After completion of the reaction, the solvent was removed under reduced pressure to get the crude product. The resulting crude product was purified by column chromatography on silica gel (100-200 mesh) using ethyl acetate-hexane (1:1) as eluent to afford pure diethyl (4-fluorophenyl)(4-(methylsulfonamido)-3-phenoxyphenylamino)methylphosphonate (**5a**). The other compounds **5b-j** were prepared by adapting to the above described procedure.

**Microwave irradiation method:** A mixture of N-(4-amino-2-phenoxy phenyl)methanesulfonamide (**2**, 0.005 mol), diethylphosphite (**3**, 0.005 mol) and 3-nitrobenzaldehyde (**4a**, 0.005 mol) were taken in flat-bottomed flask and irradiated with microwave radiations using catalyst systems (CATA-4R) at 490 Watts. The reaction mixture was heated successively twice for 2-3 min period each time followed by a 1 min cooling interval between irradiations. This method was intended to avoid continuous overheating of reactants. The reaction mixtures were kept under stirring to maintain the homogeneity of the irradiating field throughout the reaction. By monitoring with TLC, the reaction was stopped after 3-6 min. The obtained crude products were recrystallized from ethyl acetate to afford pure **5a-j** as solids with 80.9-90.6 % yield.

### Physical, analytical and spectral data for the compounds (5a-j)

**Diethyl (4-fluorophenyl)(4-(methylsulfonamido)-3-phenoxyphenylamino)methylphosphonate (5a):** Yield: 91 %; semi solid. $^{31}P$ NMR spectrum (DMSO-$d_6$): δ 18.5 ppm; $^1H$ NMR spectrum (400 MHz, DMSO-$d_6$): δ 8.41 (s, 1H, $SO_2$-**NH**), 7.66-7.21 (m, 9H, Ar-H), 6.53 (d, 1H, Ar-H), 6.48 (d, *J* = 6.8 Hz, 1H, Ar-H), 6.33 (s, 1H, Ar-H), 5.32 (s, 1H, C-NH), 4.54 (d, 1H, P-CH), 3.86 (m, 4H, O-**$CH_2$**$CH_3$), 2.89 (s, 3H, $SO_2$**$CH_3$**), 1.25 (t, 6H, O-$CH_2$**$CH_3$**); $^{13}C$ NMR spectrum (100

MHz, DMSO-$d_6$): δ 161.9, 157.8, 141.5, 136.5, 132.8, 129.7, 127.6, 122.5, 121.5, 119.9, 118.3, 114.3, 113.6, 101.9, 64.4, 55.8, 37.9, 16.5; IR (KBr, $\nu_{max}$, $cm^{-1}$): 3407 (-NH), 3296 (NH), 1227 (P=O); LCMS (*m/z*, %): 523 ($M+H^+$, 100); Anal. calcd. for $C_{24}H_{28}N_2O_6PSF$: C, 55.17; H, 5.40; N, 5.36 %; found: C, 55.54; H, 5.38; N, 5.42 %.

**Diethyl (4-(methylsulfonamido)-3-phenoxyphenylamino)(3-nitrophenyl)methylphosphonate (5b):** Yield: 91 %; semi solid. $^{31}P$ NMR spectrum (DMSO-$d_6$): δ 17.2 ppm; $^1H$ NMR spectrum (400 MHz, DMSO-$d_6$): δ 8.52 (s, 1H, $SO_2$-**NH**), 8.18-7.23 (m, 9H, Ar-H), 6.53 (d, 1H, Ar-H), 6.48 (d, *J* = 6.8 Hz, 1H, Ar-H), 6.33 (s, 1H, Ar-H), 5.31 (s, 1H, C-NH), 4.53 (d, 1H, P-CH), 3.86 (m, 4H, O-$CH_2CH_3$), 2.89 (s, 3H, $SO_2$**$CH_3$**), 1.24 (t, 6H, O-$CH_2CH_3$); $^{13}C$ NMR spectrum (100 MHz, DMSO-$d_6$): δ 157.8, 148.5, 141.5, 139.3, 136.5, 134.5, 130.4, 127.6, 122.6, 122.5, 121.5, 122.1, 119.9, 118.3, 113.6, 101.9, 64.4, 55.9, 37.9, 16.6; IR (KBr, $\nu_{max}$, $cm^{-1}$): 3399 (NH), 3285 (NH), 1227 (P=O); LCMS (*m/z*, %): 550 ($M+H^+$, 100); Anal. calcd. for $C_{24}H_{28}N_3O_8PS$: C, 52.45; H, 5.14; N, 7.65 %; found: C, 52.52; H, 5.20; N, 7.62 %.

**Diethyl (4-chloro-3-nitrophenyl)(4-(methylsulfonamido)-3-phenoxyphenylamino)methylphosphonate (5c):** Yield: 90 %; semi solid. $^{31}P$ NMR spectrum (DMSO-$d_6$): δ 17.7 ppm; $^1H$ NMR spectrum (400 MHz, DMSO-$d_6$): δ 8.53 (s, 1H, $SO_2$-**NH**), 7.81-7.23 (m, 8H, Ar-H), 6.53 (d, 1H, Ar-H), 6.48 (d, *J* = 6.8 Hz, 1H, Ar-H), 6.33 (s, 1H, Ar-H), 5.32 (s, 1H, C-NH), 4.55 (d, 1H, P-CH), 3.86 (m, 4H, O-$CH_2CH_3$), 2.89 (s, 3H, $SO_2$**$CH_3$**), 1.23 (t, 6H, O-$CH_2CH_3$); $^{13}C$ NMR spectrum (100 MHz, DMSO-$d_6$): δ 157.8, 148.2, 141.5, 137.6, 136.5, 134.7, 131.5, 127.6, 124.1, 123.4, 122.5, 121.5, 119.9, 118.3, 113.6, 101.9, 64.4, 55.7, 37.9, 16.4; IR (KBr, $\nu_{max}$, $cm^{-1}$): 3399 (NH), 3285 (NH), 1227 (P=O); LCMS (*m/z*, %): 584 ($M+H^+$, 100), 586 (M+1, 26.6 %), 586 (M+2, 36.8 %); Anal. calcd. for $C_{24}H_{27}N_3O_8PSCl$: C, 49.36; H, 4.66; N, 7.20 %; found: C, 49.42; H, 4.58; N, 7.24 %.

**Diethyl(4-hydroxy-3-nitrophenyl)(4-(methylsulfonamido)-3-phenoxyphenylamino)methylphosphonate (5d):** Yield: 87 %; semi solid. $^{31}P$ NMR spectrum (DMSO-$d_6$): δ 18.1 ppm; $^1H$ NMR spectrum (400 MHz, DMSO-$d_6$): δ 10.12 (s, 1H, -OH), 8.50 (s, 1H, $SO_2$-**NH**), 7.85-7.20 (m, 8H, Ar-H), 6.52 (d, 1H, Ar-H), 6.43 (d, *J* = 6.8 Hz, 1H, Ar-H), 6.35 (s, 1H, Ar-H), 5.30 (s, 1H, C-NH), 4.53 (d, 1H, P-CH), 3.85 (m, 4H, O-$CH_2CH_3$), 2.87 (s, 3H, $SO_2$**$CH_3$**), 1.23 (t, 6H, O-$CH_2CH_3$); $^{13}C$ NMR spectrum (100 MHz, DMSO-$d_6$): δ 157.8, 156.2, 141.5, 138.4, 136.5, 135.8, 130.7 127.6,, 123.5, 122.5, 122.1, 121.5, 119.9, 118.3, 113.6, 101.9, 64.4, 55.6, 37.7, 16.4; IR (KBr, $\nu_{max}$, $cm^{-1}$): 3399 (NH), 3285 (NH), 1227 (P=O); LCMS (*m/z*, %): 566 ($M+H^+$, 100); Anal. calcd. for $C_{24}H_{28}N_3O_9PS$: C, 50.97; H, 4.99; N, 7.43 %; found: C, 50.92; H, 4.95; N, 7.48 %.

**Diethyl (3-bromo-4-fluorophenyl)(4-(methylsulfonamido)-3-phenoxyphenylamino)methylphosphonate (5e):** Yield: 92 %; semi solid. $^{31}P$ NMR spectrum (DMSO-$d_6$): δ 17.9 ppm; $^1H$ NMR spectrum (400 MHz, DMSO-$d_6$): δ 8.52 (s, 1H, $SO_2$-**NH**), 7.65-7.21 (m, 8H, Ar-H), 6.53 (d, 1H, Ar-H), 6.48 (d, *J* = 6.8 Hz, 1H, Ar-H), 6.33 (s, 1H, Ar-H), 5.31 (s, 1H, C-NH), 4.51 (d, 1H, P-CH), 3.86 (m, 4H, O-$CH_2CH_3$), 2.88 (s, 3H, $SO_2$**$CH_3$**), 1.22 (t, 6H, O-$CH_2CH_3$); $^{13}C$ NMR spectrum (100 MHz, DMSO-$d_6$): δ 166.3, 157.8, 141.5, 136.5, 134.6, 132.5, 128.4, 127.6, 122.5, 121.5, 119.9, 119.2, 118.3, 113.6, 110.7, 101.9, 64.4, 55.7, 37.9, 16.5; IR (KBr, $\nu_{max}$, $cm^{-1}$): 3399 (NH), 3285 (NH), 1227 (P=O); LCMS (*m/z*, %): 601 ($M+H^+$, 100), 599 (M-2, 96.7 %), 602 (M+1, 26.9 %); Anal. calcd. for $C_{24}H_{27}N_2O_6PSBrF$: C, 47.93; H, 4.53; N, 4.66 %; found: C, 47.89; H, 4.57; N, 4.62 %.

**Diethyl (4-chlorophenyl)(4-(methylsulfonamido)-3-phenoxyphenylamino)methylphosphonate (5f):** Yield: 90 %; semi solid. $^{31}P$ NMR spectrum (DMSO-$d_6$): δ 17.6 ppm; $^1H$ NMR spectrum (400 MHz, DMSO-$d_6$): δ 8.51 (s, 1H, $SO_2$-**NH**), 7.66-7.21 (m, 9H, Ar-H), 6.53 (d, 1H, Ar-H), 6.48 (d, *J* = 6.8 Hz, 1H, Ar-H), 6.33 (s, 1H, Ar-H), 5.33 (s, 1H, C-NH), 4.54 (d, 1H, P-CH), 3.86 (m, 4H, O-$CH_2CH_3$), 2.87 (s, 3H, $SO_2$**$CH_3$**), 1.23 (t, 6H, O-$CH_2CH_3$); $^{13}C$ NMR spectrum (100 MHz, DMSO-$d_6$): δ 157.8, 141.5, 136.5, 135.1, 134.2, 129.9, 129.4, 127.6, 122.5, 121.5, 119.9, 118.3, 113.6, 101.9, 64.4, 55.7, 37.6, 16.4; IR (KBr, $\nu_{max}$, $cm^{-1}$): 3399 (NH), 3285 (NH), 1227 (P=O); LCMS (*m/z*, %): 539 ($M+H^+$, 100), 541 (M+2, 38); Anal. calcd. for $C_{24}H_{28}N_2O_6PSCl$: C, 53.48; H, 5.24; N, 5.20 %; found: C, 53.52; H, 5.20; N, 5.15 %.

**Diethyl (2,4-dichlorophenyl)(4-(methylsulfonamido)-3-phenoxyphenylamino)methylphosphonate (5g):** Yield: 91 %; semi solid. $^{31}P$ NMR spectrum (DMSO-$d_6$): δ 18.4 ppm; $^1H$ NMR spectrum (400 MHz, DMSO-$d_6$): δ 8.54 (s, 1H, $SO_2$-**NH**), 7.75-7.23 (m, 8H, Ar-H), 6.53 (d, 1H, Ar-H), 6.48 (d, *J* = 6.8 Hz, 1H, Ar-H), 6.33 (s, 1H, Ar-H), 5.33 (s, 1H, C-NH), 4.56 (d, 1H, P-CH), 3.86 (m, 4H, O-$CH_2CH_3$), 2.88 (s, 3H, $SO_2$**$CH_3$**), 1.24 (t, 6H, O-$CH_2CH_3$); $^{13}C$ NMR spectrum (100 MHz, DMSO-$d_6$): δ 157.8, 141.5, 140.6, 136.5, 134.7, 132.6, 131.3, 129.5, 128.4, 127.6, 125.3, 122.5, 121.5, 119.9, 118.3, 113.6, 101.9, 64.4, 56.1, 38.2, 16.8; IR (KBr, $\nu_{max}$, $cm^{-1}$): 3399 (NH), 3285 (NH), 1227 (P=O); LCMS (*m/z*, %): 573 ($M+H^+$, 100), 573 (M+2, 70); Anal. calcd. for $C_{24}H_{27}N_2O_6PSCl_2$: C, 50.27; H, 4.75; N, 4.89 %; found: C, 50.35; H, 4.84; N, 4.95 %.

**Diethyl (2-hydroxyphenyl)(4-(methylsulfonamido)-3-phenoxyphenylamino)methylphosphonate (5h):** Yield: 87 %; semi solid. $^{31}P$ NMR spectrum (DMSO-$d_6$): δ 18.0 ppm; $^1H$ NMR spectrum (400 MHz, DMSO-$d_6$): δ 10.15 (s, 1H, -OH), 8.45 (s, 1H, $SO_2$-**NH**), 7.63-6.95 (m, 9H, Ar-H), 6.53 (d, 1H, Ar-H), 6.48 (d, *J* = 6.8 Hz, 1H, Ar-H), 6.33 (s, 1H, Ar-H), 5.29 (s, 1H, C-NH), 4.49 (d, 1H, P-CH), 3.87 (m, 4H, O-$CH_2CH_3$), 2.88 (s, 3H, $SO_2$**$CH_3$**), 1.22 (t, 6H, O-$CH_2CH_3$); $^{13}C$ NMR spectrum (100 MHz, DMSO-$d_6$): δ 158.4, 157.8, 141.5, 136.5, 129.5, 129.2, 127.6, 124.2, 122.7, 122.5, 121.5, 119.9, 118.4, 118.3, 113.6, 101.9, 64.4, 55.4, 37.7, 16.3; IR (KBr, $\nu_{max}$, $cm^{-1}$): 3399 (NH), 3285 (NH), 1227 (P=O); LCMS (*m/z*, %): 521 ($M+H^+$, 100); Anal. calcd. for $C_{24}H_{28}N_3O_8PS$: C, 55.38; H, 5.62; N, 5.38 %; found: C, 55.45; H, 5.70; N, 5.32 %.

**Diethyl (4-(methylsulfonamido)-3-phenoxyphenylamino)(thiophen-2-yl)methylphosphonate (5i):** Yield: 90 %; semi solid. $^{31}P$ NMR spectrum (DMSO-$d_6$): δ 16.8 ppm; $^1H$ NMR spectrum (400 MHz, DMSO-$d_6$): δ 8.52 (s, 1H, $SO_2$-**NH**), 7.66-6.92 (m, 8H, Ar-H), 6.53 (d, 1H, Ar-H), 6.48 (d, *J* = 6.8 Hz, 1H, Ar-H), 6.33 (s, 1H, Ar-H), 5.31 (s, 1H, C-NH), 4.50 (d, 1H, P-CH), 3.86 (m, 4H, O-$CH_2CH_3$), 2.89 (s, 3H, $SO_2$**$CH_3$**), 1.24 (t, 6H, O-$CH_2CH_3$); $^{13}C$ NMR spectrum (100

MHz, DMSO-$d_6$): δ 157.8, 141.5, 140.3, 136.5, 129.3, 128.3, 127.6, 126.3, 122.5, 121.5, 119.9, 118.3, 113.6, 101.9, 64.4, 55.8, 37.7, 16.4; IR (KBr, $\nu_{max}$, $cm^{-1}$): 3399 (NH), 3285 (NH), 1227 (P=O); LCMS (*m/z*, %): 511 ($M+H^+$, 100); Anal. calcd. for $C_{22}H_{27}N_2O_6PS_2$: C, 51.75; H, 5.33; N, 5.49 %; found: C, 51.82; H, 5.27; N, 5.56 %.

**Diethyl (4-(methylsulfonamido)-3-phenoxyphenyl-amino)(5-nitrothiophen-2-yl)methylphosphonate (5j):** Yield: 91 %; semi solid. $^{31}P$ NMR spectrum (DMSO-$d_6$): δ 17.1 ppm; $^1H$ NMR spectrum (400 MHz, DMSO-$d_6$): δ 8.53 (s, 1H, $SO_2$-**NH**), 7.95-6.96 (m, 7H, Ar-H), 6.53 (d, 1H, Ar-H), 6.48 (d, *J* = 6.8 Hz, 1H, Ar-H), 6.33 (s, 1H, Ar-H), 5.33 (s, 1H, C-NH), 4.54 (d, 1H, P-CH), 3.86 (m, 4H, O-$CH_2CH_3$), 2.86 (s, 3H, $SO_2$**$CH_3$**), 1.22 (t, 6H, O-$CH_2CH_3$); $^{13}C$ NMR spectrum (100 MHz, DMSO-$d_6$): δ 157.8, 152.1, 149.9, 141.5, 136.5, 129.3, 128.4, 127.6, 122.5, 121.5, 119.9, 118.3, 113.6, 101.9, 64.4, 55.8, 37.8, 16.5; IR (KBr, $\nu_{max}$, $cm^{-1}$): 3399 (NH), 3285 (NH), 1227 (P=O); LCMS (*m/z*, %): 556 ($M+H^+$, 100); Anal. calcd. for $C_{22}H_{26}N_3O_8PS_2$: C, 47.56; H, 4.72; N, 7.56 %; found: C, 47.52; H, 4.78; N, 7.62 %.

**Anti-inflammatory activity:** Anti-inflammatory activity was determined by carrageenan induced paw edema method. A either sex of rats weighing 150-200 g were divided into 6 groups (n = 6) and they were fasted with free access to water at least 16 h. Group-I received 1 % sodium CMC (negative control), Group-II received diclofenac sodium and nimesulide at a dose of 40 mg/kg (positive control) and Group-III to VI were given the compounds **5a-j** (40 mg/kg). All the compounds **5a-j** were given in oral route. After 30 min, 0.1 mL of 1 % carrageenan suspension in normal saline was injected into the subplantar region of the left hind paw of each rat to induce edema. The edema volumes of the injected paw measured with the help of plethysmograph at the interval of 1, 2, 3 and 4 h. The difference between the paw volumes of treated animals were compared with that of the control group and the mean edema volume was calculated. Percentage inhibition was calculated as per the formula,

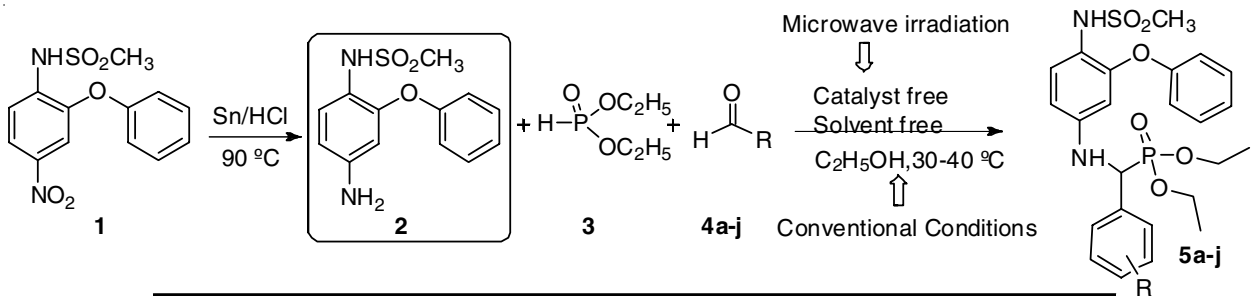
$$\text{Inhibition } (\%) = \left( \frac{V_o - V_t}{V_o} \right) \times 100$$

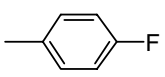
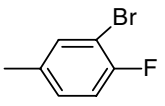
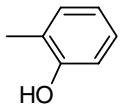
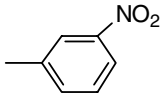
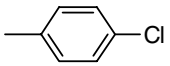
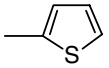
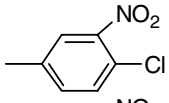
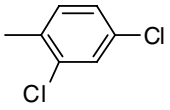
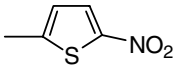
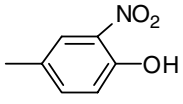
where $V_o$ = volume of the paw control at time t, $V_t$ = volume of the paw of drug treated at time t.

## RESULTS AND DISCUSSION

A series of α-aminophosphonates (**5a-j**) were conveniently synthesized by equimolar quantities of *N*-(4-amino-2-phenoxy phenyl)methanesulfonamide (**2**) which is previously prepared from nimesulide (**1**, 0.005 mol) on reduction, diethylphosphite (**3**, 0.005 mol) and various aldehydes (**4a-j**) (0.005 mol) through Kabachinic-Field reaction under conventional and microwave irradiation methods using neat reaction conditions was depicted in **Scheme-I**. The physical data of the title compounds are given in Table-1.

The chemical structure of the title compounds **5a-j** are supported by spectral data ($^{31}P$, $^1H$ and $^{13}C$ NMR, IR and LC-MS), elemental analysis and the results are presented in Experimental section. $^{31}P$ NMR signals were observed in the region 18.5-16.8 ppm [38] for all the compounds **5a-j**. The $^1H$ NMR spectra gave signals due to Ar-H in the range of δ 8.18-6.33 ppm. The proton signals in the range of 8.53-8.41, 5.32-5.30 and 4.55-4.53 ppm were due to $SO_2$-NH, C-NH and P-CH respectively. The methylene protons of P-O-$\underline{CH_2}CH_3$ gave a multiplet and methyl protons of P-O-$CH_2\underline{CH_3}$ resonated as a




| Compd | R | Compd | R | Compd | R |
|---|---|---|---|---|---|
| 5a |  | 5e |  | 5h |  |
| 5b |  | 5f |  | 5i |  |
| 5c |  | 5g |  | 5j |  |
| 5d |  | | | | |

**Scheme-I**: Microwave assisted synthesis of α-aminophosphonates (**5a-j**)

TABLE-1
COMPARISON OF CONVENTIONAL/MICROWAVE CONDITIONS OF THE SYNTHESIZED COMPOUNDS **5a-j**

| Compd. | Conventional conditions | | Microwave conditions | |
|---|---|---|---|---|
| | Time (h) | Yield (%) | Time (min) | Yield (%) |
| **5a** | 4 | 80.2 | 7 | 90.6 |
| **5b** | 3 | 78.3 | 5 | 86.2 |
| **5c** | 5 | 75.6 | 9 | 89.7 |
| **5d** | 3 | 81.2 | 6 | 85.5 |
| **5e** | 6 | 77.3 | 12 | 89.1 |
| **5f** | 4 | 70.3 | 8 | 80.9 |
| **5g** | 3 | 75.2 | 5 | 85.2 |
| **5h** | 4 | 80.5 | 7 | 87.2 |
| **5i** | 3 | 84.2 | 6 | 88.5 |
| **5j** | 6 | 78.9 | 10 | 85.9 |

triplet in the region δ 3.86-3.84 and δ 1.25-1.22 respectively. $^{13}$C NMR chemical shift for P-CH was observed in the region 56.1-55.4 ppm. IR absorptions in the regions 3399-3380, 3285-3256 and 1227-1220 cm$^{-1}$ were assigned to $SO_2$-NH, NH and P=O stretching vibrations respectively for the compounds **5a-j**. In their mass spectra, $M^{+\cdot}$ ions were observed in the expected *m/z* values.

**Anti-inflammatory activity:** In order to identify the potential anti-inflammatory agents among the newly synthesized compounds was evaluated for their *in vivo* anti-inflammatory activity using carrageenan-induced paw edema method [39] in rats. Considering the fact that carrageenan-induced paw edema assay is a biphasic event involving the release of histamine and serotonin as the mediators of inflammation in the first phase which normally lasts for about 2 h after the carrageenan injection followed by the second phase which generally operates between 2 and 4 h after the carrageenan injection and involves prostaglandins as the mediators for the inflammation, thus any anti-inflammatory activity in the second phase of this biphasic event can be attributed to the inhibition of prostaglandin synthesis.

The results shown in Table-2 revealed that most of the compounds showed significant anti-inflammatory activity 3 h and 4 h after carrageenan injection with as many as 5 compounds showing more than 80 % inhibition after 3 h (as compared to the reference drugs 88.34 and 85.88 %) and 7 compounds showing more than 80 % inhibition after 4 h (as compared to the references drug 91.57 and 88.20 %). The compounds **5d** (R = 4-F), 5e (R = 3-Br, 4-F), **5g** (R = 3,4-Cl), **5f** (R = 4-Cl) and **5b** (R = 3-$NO_2$, 4-Cl) showed remarkable anti-inflammatory activity ranging from 87.73 to 84.04 % comparable to the reference drug diclofenac sodium (88.34 %) and nimesulide (85.88 %) 3 h after carrageenan injection. The compounds **5j** (R = 5-nitrothiophen-2-yl), **5a** (R = 3-$NO_2$), **5i** (R = 5-nitrothiophen-2-yl), **5c** (R = 3-$NO_2$, 4-OH) and **5h** (R = 4-OH) showed appreciable anti-inflammatory activity ranging from 79.75 to 74.84 % 3 h after carrageenan injection. After 4 h of carrageenan injection, the compounds **5d** (R = 4-F), **5e** (R = 3-Br, 4-F), **5g** (R = 3,4-Cl), **5f** (R = 4-Cl), **5b** (R = 3-$NO_2$, 4-Cl), **5a** (R = 3-$NO_2$) and **5j** (5-nitrothiophen-2-yl) showed anti-inflammatory activity ranging from 91.01 to 80.33 % inhibition comparable to diclofenac sodium (91.57 %) and nimesulide (88.20 %). The remaining compounds showed anti-inflammatory activity ranging from 78.08 to 75.84 % inhibition 4 h after carrageenan injection. It is difficult to draw a correlation between the anti-inflammatory activity and the substituents present on the aromatic rings in 1 or 2 as the anti-inflammatory activity seems to be independent of the nature of substituents. The excellent anti-inflammatory inhibition exhibited by these compounds, 4 h after carrageenan injection suggested that these compounds do not get easily metabolized in the body.

## Conclusion

In conclusion, a new series of α-aminophosphonates has been prepared and fully assigned by analytical and spectral data. The present investigation showed significant anti-inflammatory action to all compound of the series when compared against vehicle treated control. The results were found to be equipotent with diclofenac. The anti-inflammatory effect was found to be most significant at 3 and 4 h. Overall looking at duration of action and percent inhibition, the sustained and momentous action was reported with **5d**, **5e**, **5g**, **5f**, **5b**, **5a** and **5j**. Hence the present series could be developed as a novel class of anti-inflammatory agents.

TABLE-2
MEAN PAW VOLUME (mL) AND % INHIBITION OF COMPOUNDS **5a-j**

| Compd. | Mean paw volume (mL) ± SEM | | | | Inhibition of edema (%) | | | |
|---|---|---|---|---|---|---|---|---|
| | 1 h | 2 h | 3 h | 4 h | 1 h | 2 h | 3 h | 4 h |
| Control | 1.03 ± 0.12 | 1.32 ± 0.16 | 1.63 ± 0.09 | 1.78 ± 0.20 | – | – | – | – |
| Diclofenac | 0.08 ± 0.02* | 0.17 ± 0.05* | 0.19 ± 0.03* | 0.15 ± 0.05* | 92.23 | 87.12 | 88.34 | 91.57 |
| Nimesulide | 0.12 ± 0.02* | 0.26 ± 0.06* | 0.23 ± 0.06* | 0.21 ± 0.06* | 88.34 | 80.30 | 85.88 | 88.20 |
| **5a** | 0.29 ± 0.10* | 0.34 ± 0.10* | 0.35 ± 0.08* | 0.35 ± 0.10* | 71.84 | 74.24 | 78.52 | 80.33 |
| **5b** | 0.20 ± 0.10* | 0.25 ± 0.06* | 0.26 ± 0.06* | 0.25 ± 0.06* | 80.58 | 81.06 | 84.04 | 85.95 |
| **5c** | 0.24 ± 0.10* | 0.35 ± 0.06* | 0.39 ± 0.07* | 0.39 ± 0.06* | 76.69 | 73.48 | 76.07 | 78.08 |
| **5d** | 0.10± 0.03* | 0.22 ± 0.06* | 0.20 ± 0.01* | 0.16 ± 0.06* | 90.29 | 83.33 | 87.73 | 91.01 |
| **5e** | 0.11 ± 0.03* | 0.20 ± 0.06* | 0.21 ± 0.06* | 0.18 ± 0.06* | 89.32 | 84.84 | 87.11 | 89.88 |
| **5f** | 0.17 ± 0.04* | 0.22 ± 0.08* | 0.24 ± 0.09* | 0.26 ± 0.05* | 83.49 | 83.33 | 85.27 | 85.39 |
| **5g** | 0.16 ± 0.06* | 0.19± 0.14* | 0.22 ± 0.10* | 0.22 ± 0.07* | 84.46 | 85.60 | 86.50 | 87.64 |
| **5h** | 0.28 ± 0.08* | 0.39 ± 0.07* | 0.41 ± 0.09* | 0.43 ± 0.09* | 72.81 | 70.45 | 74.84 | 75.84 |
| **5i** | 0.23 ± 0.10* | 0.37 ± 0.05* | 0.39 ± 0.07* | 0.40 ± 0.08* | 77.66 | 71.96 | 76.07 | 77.52 |
| **5j** | 0.26 ± 0.08* | 0.28 ± 0.10* | 0.33 ± 0.08* | 0.35 ± 0.07* | 74.75 | 78.78 | 79.75 | 80.33 |

Test compounds = 40 mg/kg. reference standard, diclofenac sodium = 40 mg/kg.
*Significantly different compared to respective control values, $P < 0.01$.
[a]Values are expressed as mean ± SEM (number of animals = 6) and analyzed by ANOVA.
[b]Values in parentheses (percentage anti-inflammatory activity, %).

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## Editorial……

It is heartening to note that our journal is able to sustain the enthusiasm and covering various facets of knowledge. It is our hope that IJMER would continue to live up to its fullest expectations savoring the thoughts of the intellectuals associated with its functioning .Our progress is steady and we are in a position now to receive evaluate and publish as many articles as we can. The response from the academicians and scholars is excellent and we are proud to acknowledge this stimulating aspect.

The writers with their rich research experience in the academic fields are contributing excellently and making IJMER march to progress as envisaged. The interdisciplinary topics bring in a spirit of immense participation enabling us to understand the relations in the growing competitive world. Our endeavour will be to keep IJMER as a perfect tool in making all its participants to work to unity with their thoughts and action.

The Editor thanks one and all for their input towards the growth of the **Knowledge Based Society**. All of us together are making continues efforts to make our predictions true in making IJMER, a Journal of Repute

**Dr.K.Victor Babu**
**Editor-in-Chief**

# SIMULATION STUDY OF ADVANCED INVERTING AMPLIFIER FOR LOW POWER BIOMEDICAL APPLICATIONS

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**Abstract**
In this paper, Simulation study of Advanced Inverting Amplifier for Low Power Biomedical Applications using 45 nm technology node is proposed using Cascode Operational transconductance amplifier .The proposed structure uses carbon nanotube field effect transistor. It is observed that the proposed Amplifier is also consuming low power of 188 µW. There is no need of negative feedback and feedback resistor. Further the proposed Amplifier consumes very low power and simple circuitry. Furthermore, the proposed advanced inverting amplifier is electronically tunable. It can be used for Low Power Biomedical Applications due to low power , low voltage and low amplitude of signal.

**Index Terms**— CMOS, CNTFET, COTA, Power consumption, Inverting Amplifier

## I. INTRODUCTION

Cascode Operational transconductance amplifier (COTA) is a new class of O.T.A. It has improved gain (due to Band output resistance) and bandwidth due to reduced Miller capacitance [5]. In order to ensure further improvement in Cascode COTA performance, Carbon Nanotube Field Effect Transistors (CNTFETs) based Circuits that promise to deliver much better performance than existing CMOS based Cascode Operational transconductance amplifiers is proposed [6]. CNTFET technology can easily club with the bulk CMOS technology on a single chip and utilizes the same infrastructure at 45 nm [7].

## II. DESIGN OF ADVANCED INVERTING AMPLIFIER:-

The amplifiers designed using operational amplifier haves serious limitations. Negative Feedback used in operational amplifier based Inverting Amplifier, an external Feedback Resistor is required. This feedback connection between the output and the inverting input terminal forces the differential input voltage towards zero. This closed-loop inverting amplifier uses negative feedback to accurately control the overall gain of the amplifier, but at a cost in the reduction of the amplifiers gain. But in proposed Cascode Operational transconductance amplifier based Advanced Inverting Amplifier, there is no need of negative feedback and feedback resistor. Further the proposed Amplifier consumes very low power and simple circuitry. Furthermore, the proposed advanced inverting amplifier is electronically tunable [1-4].



Figure 1.Multi wall CNTs

The R-C band stop filter is similar to a band pass filter in which the shunt arm is replaced by the series arm and the series arm is replaced by the shunt one.

Flexibility and tunability are the big advantages of OTAs. The output current io of the ideal COTA can be expressed by equation (1)

$$io = gm\ (vp - vn)$$

Where gm is the transconductance, vp and vn are positive and negative input terminals respectively. The ideal OTA has infinite output resistance. All of io flows in the external capacitive load and none flows in the OTA's own output resistance .Towards increasing the OTA output resistance, the current mirrors are cascoded. Cascode amplifier configuration improves gain due to Band output resistance and bandwidth due to reduced Miller capacitance.

## III.PROPOSED COTA BASED ADVANCED INVERTING AMPLIFIER

The Cascode Operational transconductance amplifier (COTA) circuit is used to design inverting amplifier. The proposed inverting amplifier is simulated using 0.9 V at 45 nm.

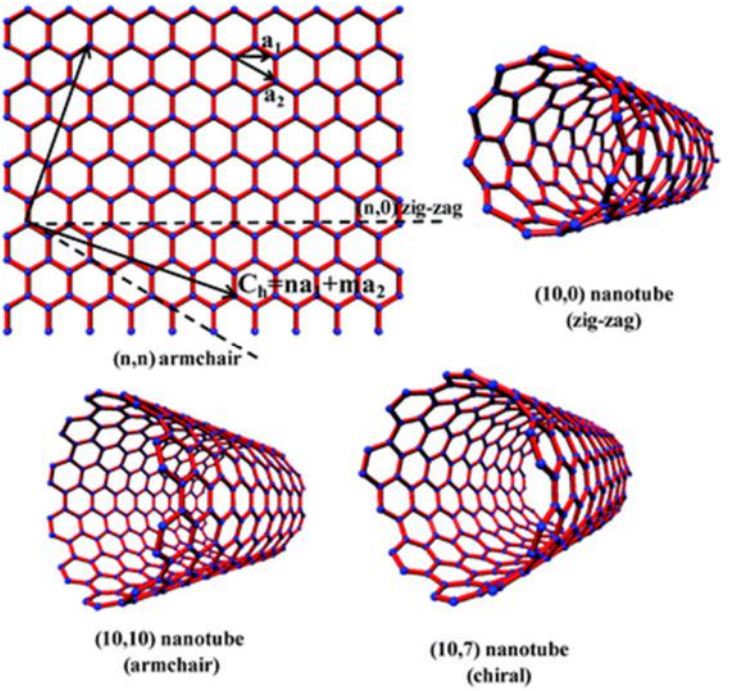



Figure 2. Different configurations of Single wall CNT

The carbon nanotubes exist in two forms: (i) Single wall carbon nanotube (SWCNT) and (ii) multiwall carbon nanotube as shown in Figure 1(a). SWCNT are actually tubes of graphite that are normally capped at the ends. They can be visualized as a layer of graphite rolled into a seamless cylinder [8-9]. Their diameter is around 1nm and length a few microns. They are superior to MWCNT, however, are costlier. MWCNT appear like a coaxial assembly of SWCNTs, like a coaxial cable. They diameter of MWCNT ranges from 5-50 nm and the inter layer spacing is 3.4Å. They are easy to produce in large quantity. However, the structure is complex and the structural imperfections may diminish their unique properties [10]. The wrapping of graphite sheets in SWCNT can be represented by a pair of indices (n, m), called as the chirality vector or roll-up vector, as shown in Figure 1(b). There are three types of SWCNTs based on the chiral vector and chiral angle (θ).

Figure 3. shows the schematics of one of the important application of CNT, that is, carbon nanotube field effect transistor (CNTFET). In a CNTFET, the channel is made up of parallel combination of SWCNTs. The source and drain regions are highly doped regions and the CNT channel is undoped. The important advantages of CNTFET include 1D ballistic transport of charge carriers, high mobility, large drive current and very low power consumption [11].

Nanotube diameter and chiral angles are given as [12-22]

$$d_t = \frac{\sqrt{3}a_{c-c}\sqrt{m^2 + mn + n^2}}{\pi}$$

$$\theta = \tan^{-1}\frac{\sqrt{3}n}{2m + n}$$

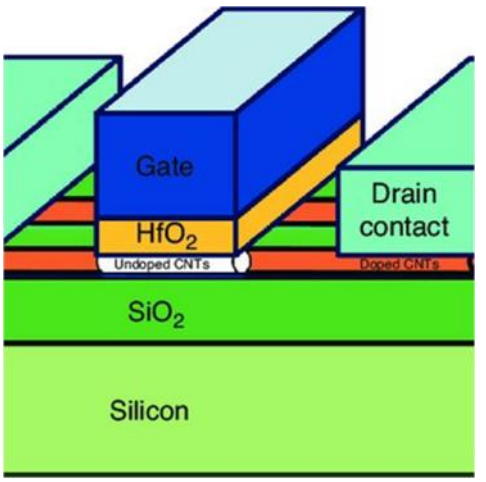



Figure 3. Schematic of a CNTFET

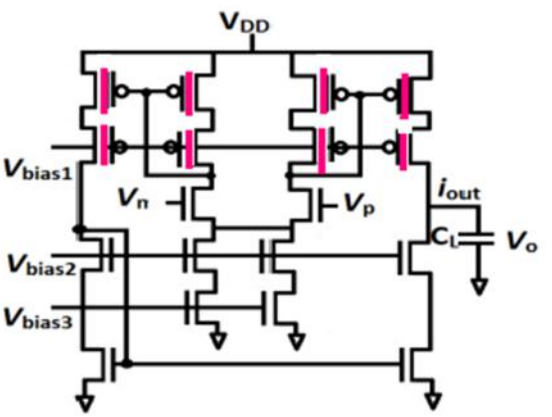



Figure 4. COTA [9]

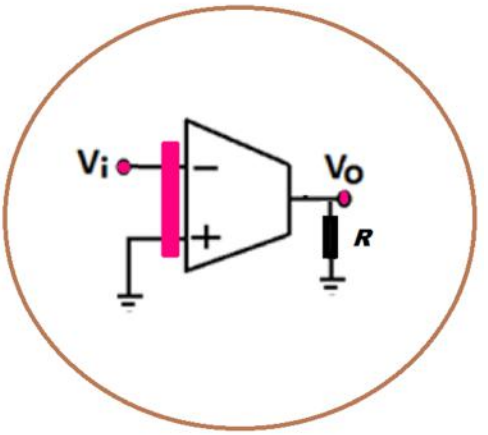



Figure 5. Advanced inverting amplifier

In inverting amplifier the output is exactly 180 degree out of phase with respect to input (i.e. if you apply a positive voltage, output will be negative). Output is an inverted (in terms of phase) amplified version of input. It is shown from the frequency response characteristics of Inverting Amplifier that the amplification can be performed successfully over the designed range with a reasonable accuracy.

It is observed that the proposed Amplifier is also consuming low power of 188 µW. It can be used for Low Power Biomedical Applications due to low power , low voltage and low amplitude of signal.

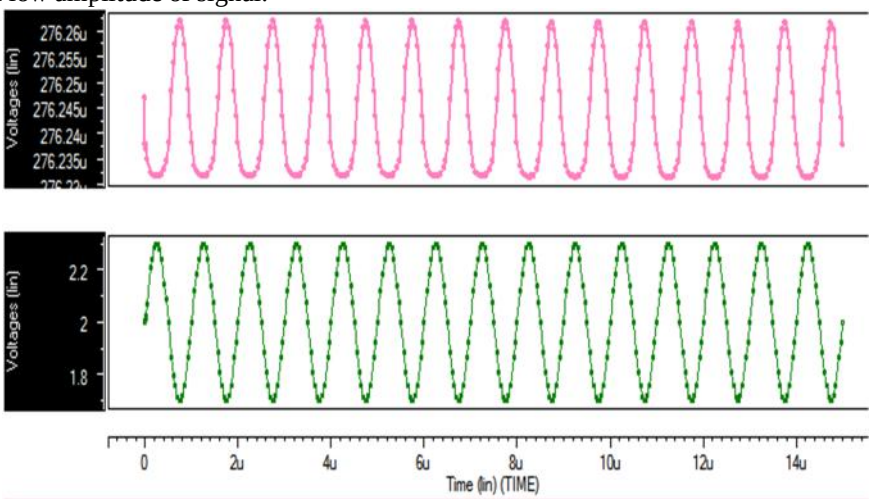



Figure 6. Frequency response of Proposed Inverting amplifier

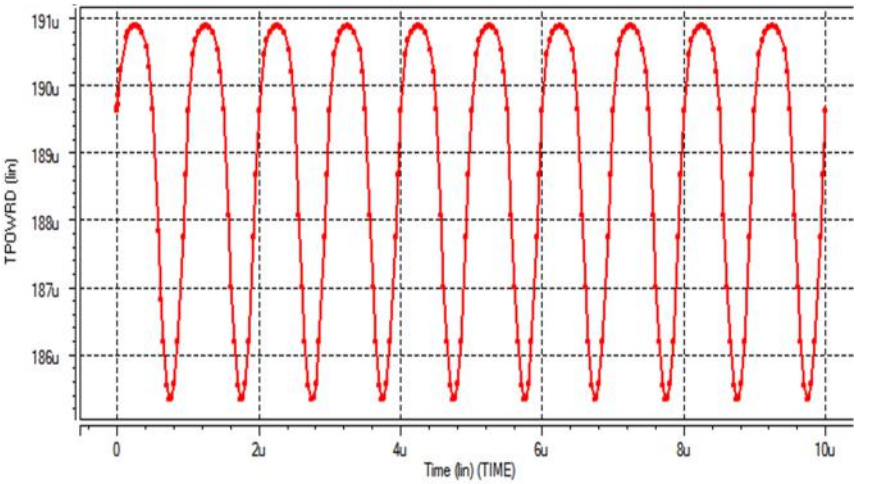



Figure 7. Average Power of Proposed Inverting amplifier

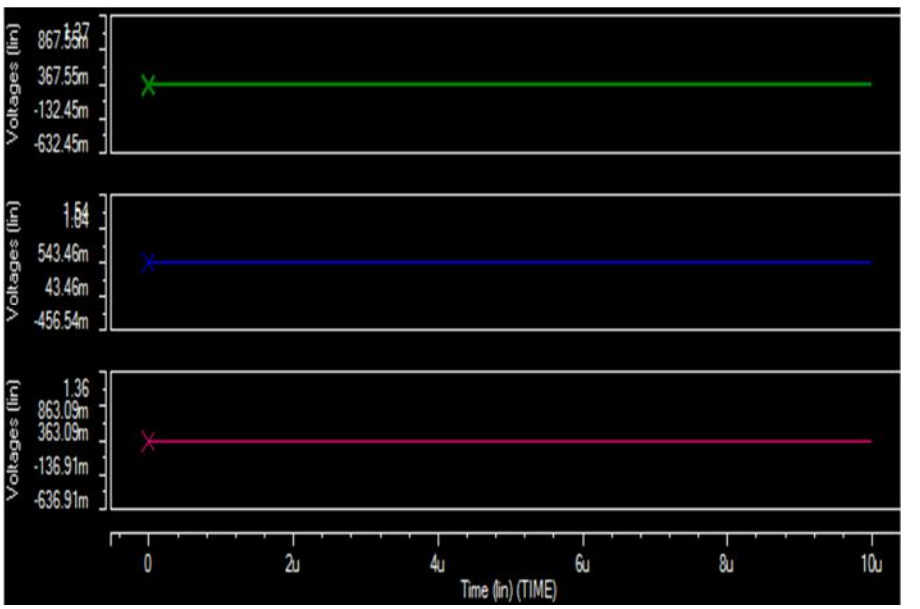



Figure 8. Biasing Voltages used in Proposed Inverting amplifier

## IV. CONCLUSION

In this work, Simulation study of Advanced Inverting Amplifier for Low Power Biomedical Applications is proposed. The proposed structure uses carbon nanotube field effect transistor. The proposed Amplifier is also consuming low power of 188 µW. It can be used for Low Power Biomedical Applications.

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# ROLE OF VOLUNTARY ORGANIZATIONS IN COMMUNITY MOBILIZATION

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## Abstract

Emergences of a force, called voluntary organization, in urban and rural area have contributed towards structural change of the society where they are pertinent. The prime motive of these organizations is helping the society for uplifting the standard of life. These organizations are also expected to be the communication bridge between government and citizens. Community mobilization is a process which helps in monitoring good governance though local group intervention. The study is based on the role of voluntary organization in community mobilization; this will attempt to study the nature and functioning of voluntary organizations e.g. NGOs. Further the study will be carried on the responses of community particularly, women of Assam. In this context, the study analyses the impact of voluntary organizations in rural development.The study has been carried out in Ambikapur, Sadiya under Tinsukia District of Assam. In the study, what was the role of a single voluntary organization in community mobilization was analyzed through observation method. Survey data and project documentation were used as source of the study. In the study it was found that the organization was partially successful in motivating the community women towards upliftment of life. The sustainability of community organization is uncertain for future generations due to lacking of financial support, resource management etc. This study will attempts to analyses the following questions. Therefore change is needed in the structure of the community organization.

- How voluntary organization build rapport with the community people special women groups
- The Role of voluntary organization in increasing participation of the women group in community building
- Sustainability of organization in long run.

**Key words:** Voluntary Organization, Community mobilization, Assam, Women groups

## Introduction:

In recent times, response to the need of the society and to fulfill the demands arising out of population changes, several groups or group of individuals are voluntarily forming organizations with a definite goal. These organizations are also known as non-governmental organization. These are popularly called so, because they are free from governmental control in their functioning. It is also argued that this 'third sector' fights for the enlargement of people's choices as well as encourage 'people friendly' grassroots movement (Biswajit Ghosh, 2012). With the spirit of voluntarism and innovative intervention attempts to develop the society into next level through alleviation of poverty, hunger and diseases. These organizations' credibility is their friendly attitudes towards common people, disadvantaged groups and environments. These organizations are also means of communication between service provider and common people as their work primarily based on grass root level even in remote areas. In the implementation of the participatory democracy, these voluntary organizations played a significant role in mobilizing people toward the value of equity. Only these organizations can contextualized the issues of common masses on various aspects of life. As these organizations work on ground level they can make intimate contact with the common people. To address the issues like health, social or environmental, people engaged themselves together and make an effort for the welfare of a community is understood as community mobilization. It facilitates change by empowering individual community member ( Somnath Chattopadhyay, Udai Pareek, 1984 )

The year 2001 was declared as International Year of Volunteers (IYV) by 52$^{nd}$ session of UN General Assembly. This year was announced as IYV to recognize the work done in the past in the field of human rights, community development by the group of individuals voluntarily. These Voluntary Organizations/ Non-Governmental Organizations played a significant role in developmental arena during the 19$^{th}$ centuries. In India, Gandhian philosophy promotes volunteerism in social welfare actions. Prior to independence also there was a tradition of voluntary actions in India (Abdul Rashid Khan, 2006). After independence, with the emergence of NGOs, perception on development was changed. To enable the people to participate in economic growth programmes, initiated by government for community development efforts in rural areas. National government and Aid agencies approached NGOs to assist in the

implementation of community development welfare programmes. On the basis of origin and activity content, Indian NGOs are typologied as developmental, environmental, philanthropic, vocational, training, research advocacy or emergency aid ( Michael M. Cernea, 1997).

The study has been carried out in Ambikakur, Sadiya under Tinsukia District. Ambikapur is 45km far away from Sadiya town centre. There are various communities like Deori, Moran, Kachari tribe inhabit. The major sources of income for the people of the region are mainly farming, poultry farming, weaving. The study area is outskirt of Tinsukia District, only single public transport travel from Sadiya to Ambikapur. No single public amenities are there to fulfill the basic needs of the people. In 2006 a NGO intervened the study area to mobilize the community people. The NGO is North-East Affected Area Development Society (NEADS) which was founded in 1985 by a group of young enterprising people of Jorhat, led and guided by Mr. Girin Chetia (Present Director cum Chief Functionary) at the village of Dhekiakhowa. Their dream was to work together for greater impact at the grassroot developmental stage to reduce disaster risks, poverty and social exclusion. Girin Chetia, being a developmental activist, who was associated earlier and experienced for a number of years with National Institute for bank Management (NIBM), Peoples Institute for Development and Training (PIDT), Society For Rural Urban & Tribal Initiative (SRUTI) and Oxfam India Trust, together with his volunteers group felt the need to establish a social organization which will work in the affected areas for socially excluded families and marginalized communities for their holistic capacity development across the region. NEADS is one of Assam's oldest and pioneer Non-Government Organization in the field of development. As a registered organization under Societies Registration Act 1860, NEADS began to work since the year 1987. During the early years, the organization started its intervention in the geographically remote and vulnerable pockets of the district in the field of awareness generation and capacity building on livelihood opportunities, mobilization of affected communities to participate in decisions which affect their lives and strengthening traditional flood coping mechanism among the peoples of Brahmaputra plains to mitigate miseries of recurrent flood. Since 1998 onwards, NEADS began to look beyond from its existing based area of Jorhat and expanded the remit to support development work in other districts of Upper Assam, and also responded to humanitarian crisis caused by

emergency flood many a times since its inception. The organization currently have its programmatic intervention in five districts of Upper Assam region and which has impacted the lives of many individuals, groups and communities, by rendering services in the aspects of social and economic development. Today, with its presence in more than five hundred villages of vulnerable pockets, NEADS is working in the thematic focus on Disaster Risk Reduction and Humanitarian Response, Water, Sanitation & Hygiene (WASH), Vulnerable Livelihood, Education and Children, Gender Justice & Development in its intervention in its operational areas.

**Methodology:**

This study is a qualitative descriptive case study of a NGOs called *NEADS*. The study attempted to explain the functioning of an eight year project lead by *NEADS*. The study is based on both primary and secondary sources; the secondary data were collected from project reports, annual reports of the NGO (NEADS). The primary information was collected from the field visit in the surrounding areas of Ambikapur, Sadiya Block Division. Qualitative data were collected from observation method, personal interviews and focussed group discussion with the community people, NGO workers. Analytical method was used in interpreting the results. Among the all respondent female respondents are more than the male.

**Limitation of the study:**

There are certain limitations during the study, time constraint is one of among them. On the other hand, targeted population of the NGO intervention is about 8347, so it is impossible to visit door to door to collect information from all the community member. Further transportation and communication is one of the biggest bottleneck while visiting the fields.

**Discussion:**

*NEADS* intervened the study area of Ambikapur, Kukuramora, and Ghurmora which stands on a grassy plain, nearly surrounded by forested foothills of Himalayan mountains, on the right bank of the main stream of the Brahmaputra river. The widest point of any river all over the world at the point of creation of mighty river Brahmaputra with the joining of three rivers namely—Siang, Dibang and Lohit river. It has been the strategic importance for controlling trade with the hills and for checking

armed intrusions by the hill tribes on the plains during Ahom and succeeding British rule in the area. Great Assam earthquake of 1950 destroyed the old Sadiya town, changed its topography beyond recognition and repair and contributed to today its being one of the most deprived areas of Assam and its communities most vulnerable. The organization targeted 28 villages of Sadiya Subdivision. The total numbers of targeted household were 1868 and total targeted population is 8,347. Their project targeted tenure is 10 year and it was sponsored by Action Aid, which is an international non-governmental organization fighting against poverty and injustice worldwide. This worldwide organization work in around 45 countries with local partner organization, communities and individual groups. ActionAid was founded as a charity in 1972, and throughout the history they have innovated and evolved approach to better address the structural drivers of poverty and injustice. In the 1990s, they adopted a human rights based approach to development, which we continue to apply. In 2003, they established theActionAid International Federation, comprising members in every region of the world, and headquartered in South Africa.

The Core Programme Thrust Areas of the *Neads* in the study areas were :

**Education and Child Development:**

The prime objective of the organization in the study area was to promote primary education and child development for all the children age group 3-14 years. As there was no single school established by the government and community groups. The organization initiated to establish primary school through community participation for the growth and foundation of the children. The organization focused on community involvement in education so that they can identify local education issues and able to develop strategies to resolve barrier that impede access and retention and compromise quality(Jane P. Preston, 2013). Secondly the organization focused on teachers training exposure because training of the teachers plays an important role in an education. Rightful training only can guide the students toward evolution and advancement in potentiality, caliber, skill of the children ( Wafula Lorna, 2012 ). Quality education drive is another pertinent initiative taken by the organization which targeted qualitative growth of children. Under the education system by following traditional education system of India e.g. Pathsala, promoted production and innovation for self-reliance. For demonstration and mobilizing the community people for education of the children the organization

established a model school in the study area, where teaching is not limited only curriculum, their education system extended towards value education, knowledge of nutrition supplement, health, grooming of behaviour. It Initiated training and support for extracurricular learning, set up Joyful Learning Centre, libraries for Children in villages. Provided Training to educated youth to become JLCC volunteer facilitators. Created an opportunities for children to expedite in other parts of Assam. Initiated learning exchange programme between JLCC members, organized sports and cultural events for children, promoted Child Parliament.

**Food Security and Livelihood:**

**U**nder this trust area organization tried to bridge the gap between citizen and government on various issues like land, labour and agriculture. Therefore, community was mobilized to survey land and other resources in the study area. To tackle the slow production of the agricultural product and storage of seeds (grain) for rapid cultivation, the organization trained the community for seed preservation and established a community grain bank, where more than hundred samples of rice grain were preserved. Traditionally women of the North East India are the key participant in the labour force of the agricultural sector. More than 80% works in the paddy field are done by the women alone. So the organization felt the need to promote women producers group in the study area and also formed women agriculture producer group. For the demonstration and to motivate community towards production process a model farm was created at community centre. Bamboo plantation and nursery was also developing at the community centre. On the other hand poultry farming was encouraged to mobilize women towards economic empowerment, also goat farming unit were created among the women group.

**Community Health:**

To keep people healthy, the organization had initiated certain health promotion and disease prevention programmes. They try to empower community people by engaging them in certain programmes where community people are taught to choose healthy behaviour and make changes that reduce the risk of developing chronic disease and other morbidities. Community member are encouraged to explore at their own pace, health exhibits and information presented in a highly visible, easily

accessible, interactive learning environment (Anita Chandra, Joie D. Acosta, Katherine Grace Carman, Tamara Dubowitz, Laura Leviton, Laurie T. Martin, Carolyn Miller, Christopher Nelson, Tracy Orleans, Margaret Tait, Matthew D. Trujillo, Vivian L. Towe, Douglas Yeung and Alonzo L. Plough, 20016). The organization arranged health camps by qualified doctors, nurses and paramedics and community health worker to help the community to get healthcare free of cost. A drive of malaria prevention with homeopathy was also taken by the organization. World Health Organization stated that homoeopathy is the second most used medical system internationally which is a nontoxic form of alternative medicine and can be combined with classical treatment methods for avoiding the risk of adverse effects. Innumerous scientific researchers have been carried out to sustain homoeopathy as a complete scientific system to combat antagonism. Establishment of classical homeopathic drugs for malaria can prove as a next generation therapy, as homeopathy doesn't give any scope of resistance. The most important and significant aspect of homeopathic medicines is that they are developed after direct proving on human beings and not on animals. Each homeopathic medicine is therefore more akin to human nature and human system ( Rajan, Aswathy and Ravichandran, Ramanibai and Bagai, Upma, 2017 ).

**Promoting Community Based Institution / Peoples Organization:**

One of the most overlooked forms of violence in today's society is violence against women. Violence against women in the north eastern state of Assam has become a cause for severe concern as like all over India, women in Assam too have been facing violence in the domestic and public spheres. Assam registered second-highest number of incidents of crime against women in the entire country. According to the NCRB report of 2012, Assam tops the rate of cognizable crimes against women in India in 2012 at 89.54%. This high incidence of crime against women is a matter of great concern. The data available with the National Crime Records Bureau (NCRB) shows that most of the cases are related to kidnapping, rape and cases of domestic violence under section 498 (A) of the Indian Penal Code (IPC). Despite various legal provisions in the state to protect women against domestic abuse, women are still victims of domestic violence, dowry, rape, kidnapping and other forms of atrocities, both physical and mental. To promote gender justice in the study area the organization executed certain programmes like leadership training, legal aid training, training on functioning of local bodies. For the maintenance

of balance and check on functioning of governmental policies, implementation of the act, certain platform were formed such as *Sanmilita Nari Adhikar Surksha Mancha*. This forum has established a network of communities based women volunteers working for a gender just society and work in a collective approach to prevent violence through counseling support, community sensitization and mobilization ( Adittya Vatta, B. N. Borthakur, 2017 ). Women of the study area were also encouraged to participate in political process. They were trained on values and rights of their life.

**Policy implication:**

The organization successfully implemented the project in the study area. The project implication helps community people to take part in micro decision making process in local bodies and Panchayats. Even the local administration of the sub –division seeks help from this community people and various forums of the women. By establishing educational institution and community learning centre, it helps to promote education and awareness among community people. As there was no school in the study area, children were denied the fundamental rights e.g. right to education. After the establishment of school by the organization, initially enrolment number was quite depressing but later slowly number increased to a reasonable extent. There were around 65 students in 2016 (Adittya Vatta, B. N. Borthakur, 2017). Community learning centre and school established by the organization helped to enhance knowledge of craft and other skill. It also helped children in expressing the creativity by using waste material and other easily available resources. The initiative of the organization helped in promoting amusing environment of the study area, it helped in abolishing intoxication among young generation. Dropout rate among the children was also decreasing slowly in the study area. The children were trained to communicate with each other without hesitation through intra-personal communication method, which considerably developed their personality and attitude toward each other. Four centrally located Joyful Learning Community Centres were created and it was run by the children and community themselves. Trained JLCC students have started teaching younger children, this initiative of the organization helped children in participation and accomplishment of JLCC in larger platforms. It also enhanced confidence and brought changes in attitude of JLCC children, public speaking and

communication skill amongst JLCC students also improved through this initiatives.

The organization had successfully formed women forums in grass root level. These forums were committed to achieve gender equality by standing against gender based violence, and tried to create a gender sensitive society. These forums helped in maintaining balance in terms of work and power relation between men and women by participating and representing equally in decision making process. These forum provided counseling and support to the women who are victimized in both public and private sphere. Women forum tried to solve cased based on gender violence by their own at first, if the case is much critical then only they seek legal intervention. Several trafficked victim women were rescued from railway station, bus stoppage by these women forum. To support those rescued women a self-help group was created and they were given training on different skills like weaving, tailoring, embroidery etc. Even women of these forums equally participated in production process and market. Women Forum has been able to bring changes in the area like bus service started to Ambikapur with pressure from Mahila Mancha, assurance by SDO to improve road condition, PHC functioning, short term hostel started for girl students at Chapakhowa, Sadiya. Twenty one women's agriculture producer groups were engaged in regular farming. Their profit – started from capital Rs.1, 82,210/- to capital – 2, 50,692/- till 2013. Twenty community grain banks were formed. This idea of grain bank became popular among community people later. The starting stock was 296.44 quintal paddy. Apparently it increased to 1520.20 quintal stock. Demonstration of possibility of agriculture in sandy soil was successful. Community Centre land was developed as a forest despite of sandy soil. Family kitchen gardens became a regular feature in every household.

The organization in the study area helps community to keep monitoring on the functioning of the Public Health Centre to promote healthy life. They are also mobilized by the organization to check on regularization of Public Distribution system to assure food security of the community people. 25117 people received job card under National Rural Employment Guarantee Act (NREGA) which provides a legal Guarantee of 100 days of wage employment in a financial year. Regular monitoring of MGNREGA by community was materializedby the intervention of the organization. Regular participation of community in Gram Sabha ensured

after the mobilization through various discussion and participatory activities.

**Conclusion:**

The voluntary organizations are considered to be part of the alternative development paradigm. Voluntary organization established itself as a medium for the delivery of economic and social development. It also promoted the very notion of participation and democracy in order to improve civil society (S. Abbar Zaidi, 1999). In contrast to government, the caricature of voluntary organization has been extremely laudatory,where they are viewed by many official agencies and members of the public as more ancient and cost-effective service providers than governments, giving better value-for-money, especially in reaching poor people'(Edwards and Hulme, 1996). This voluntary organization, NEADS in the study area have influenced the lives of the community people through their humanitarian aid, development projects and advocacy campaigns. This organization has dramatically increased the ability of the people in terms of growth and development. It resulting in higher level of involvement of the people at almost all the sphere e.g. Panchayats, community decision, land resources etc (Gina Oramae Lewis, 2016). But the sustainability of the project of this organization cannot be overstated. There are certain factors affecting it's sustainability. The challenges faced by NEADS pose peculiar issues of concern for all concerned stakeholders on how to remain operational for the foreseeable future (Lynda Khamisi Shivairo, Susan Were, 2017). The factors affecting the organization in smooth functioning are:

Border area conflict: as the study area is situated in the border of Assam and Arunachal, time to time conflict between people of both the state take place which imbalances the peace among the people. Smuggling of drugs and women is the prominent issues but the state failed to address those issues.

Rapid Climate Variation: The study area is very prone to flood, every year flood submerge all the resources and livelihoods of the people. It creates distress and makes people's life in very precarious condition.

Lack of political will: as the region is isolated from mainstream and far away from major towns, the absence of political will for the prosperity of the region as well as the people is apparent. Lack of political

awareness among the people is also one of the reasons behind negligence of the power holders.

Geographic isolation and Remote landscape: geographically also the study area is isolated and remote by nature. For the smooth functioning and suitability of the organization need skillful community workers, due to its remoteness many worker refuse to work and monitoring from far away is not possible all the time.

Subsequently the project run by the NEADS in the study area is stagnant in present days; along with the other factors above mentioned, resource generation is also a significant challenge for the organization. Supports from funding agency are also very limited to run the project efficiently. More or the less this organization is unable to generate strong leaders among the community people to sustain the project run by the organization. The focus was more on the project mode which led catastrophe to the organization. Still there are many gaps in mobilization of community toward self, sustainable and subsistent life. Project sustainability is a challenging endeavour because it can only be determined long after the completion of the project by which time there are no resources to allocate for any further review or remedial action if need be (Okoth, A., 2016).

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# వ్యవహారిక భాషోద్యమ ఊతం - గిడుగు 'బాలకవి శరణ్యం'

**డా. గోపవరం పద్మప్రియ**
అసిస్టెంట్ ప్రొఫెసర్ (తెలుగు)
డి.కె.ప్రభుత్వ స్వయం ప్రతిపత్తి
మహిళా కళాశాల, నెల్లూరు

ఈనాడు మనం అనుభవిస్తున్నసాంఘీక, సాహిత్య స్వేచ్ఛ వెనుక మనమూహించలేనంత ఉద్యమ నేపథ్యం కన్పిస్తుంది .సాంఘీక దురాచారాల నిర్మూలనకు ,స్త్రీవికాసం కొరకు రాజా రామ్మోహన్ రాయ్, కందుకూరి వీరేశలింగం లాంటివారు ఎంత పోరాటం చేయవలసి వచ్చిందో ,అంతే పోరాటాన్ని మాట్లాడే భాష ,రాసే భాష ఒకే విధంగా ఉండడానికీ చేయాల్సి వచ్చింది .ఈనాడు వ్యవాహారిక భాషోద్యమం గురించి ప్రస్తావిస్తే నేటి తరానికి హాస్యాస్పదంగానే ఉంటుంది . కాలమిచ్చిన తీర్పు వల్ల నేడు కొన్ని వందల పేజీలు మనం మాట్లాడే భాషలోనే అచ్చవుతు ప్రజల మధ్యకు వస్తున్నాయి .

కాని పూర్వం మాట్లాడే భాష వేరుగా , రాసే భాష వేరుగా చెలామణి అవుతూ వచ్చింది.అయితే ఈ భేదం పట్ల పూర్వం మనకంత నిరసన భావం కూడా లేదు .భారతదేశం లో సార్వత్రిక విద్యా విధానం అమలు లోకి వచ్చిన తర్వాత పరిస్థితుల్లో మార్పులొచ్చాయి .1852సంII లో మద్రాసు ,బొంబాయి, కలకత్తాల్లో విశ్వ విద్యాలయాలు ఏర్పాటు చేశారు.వాటిలో చదువుకొన్నవారు దేశంలో విద్యావ్యాప్తికి కృషి చేస్తారని తలచారు. అయితే ఆంగ్లం లో చదువుకోవడం వల్ల దేసభాషల అభివృద్ధికి వీరు తగిననత కృషి చేయలేదనే చెప్పవచ్చు.1901లోగవర్నర్ జనరల్ గా ఉన్న లార్డ్ కర్జన్ సిమ్లాలో ఒక సమావేశం ఏర్పాటు చేసి ప్రాథమిక స్థాయి నుంచి విశ్వవిద్యాలయ స్థాయి వరకు పరిష్కరించవలసిన సమస్యల గురించి చర్చించి 150 తీర్మానాలను చేశారు. దానిలో భాగంగా మాతృభాషలో వ్యాసరచనలను నిర్బంధపాఠ్యాంశంగా ప్రవేశపెట్టాలని అలాగే ఇంగ్లీషు లోని పుస్తకాలను ప్రాంతీయ భాషల్లోకి అనువదించేటప్పుడు వారికి శిక్షణ కల్పించాలనినిర్ణయించారు ఇలాంటి తరుణంలో1906 సంవత్సరంలో J.A ఏట్స్ గంజాం ,విశాఖ ,గోదావరి జిల్లాలకు పరీక్షా అధికారిగా నియమించబడ్డాడు ఇతనికి తెలుగు బాగా ఒంట బట్టింది .ఆయన మన పుస్తకాల్లో ఉన్న తెలుగుకి, ఆ పుస్తకాలను బోధించే అధ్యాపకులు మాట్లాడే తెలుగు మధ్య భేదాన్ని గుర్తించి ఆయన ఆశ్చర్యపోయారు.ఈ విషయం గురించి కళాశాల అధ్యక్షులైన టి. శ్రీనివాస అయ్యంగారు ని ఈ విషయమై ప్రస్తావించగా విజయనగరం లో ఉన్న గురజాడ పల్లాకిమిడి లోని గిడుగు రామ్మూర్తి పంతులు తనకంటే బాగా చెప్పగలరని సూచించాడు. ఏట్స్ వాళ్ళిద్దరిని సంప్రదించి చర్చించి ఈ వ్యవహారిక,గ్రాంధిక భాషా బేధాల వ్యత్యాసాన్ని తగ్గించడానికి ఉపాధ్యాయ వార్షిక సమావేశాలు ఏర్పాటు చేసి గిడుగు చేత ఉపన్యాసాలిప్పించాడు. ఇది పండితులందరికీ కంట్లో కారం అయింది. ఈ సమయంలోనే స్కూల్ ఫైనల్ పరీక్ష F.A స్థానంలో ఇంటర్మీడియట్ వచ్చింది. అప్పుడు విద్యార్థులు ఎంచుకోవలసిన అనువాద అంశాలు,

వ్యాసాలకు సంబంధించి రగడ మొదలైంది. ఆ సమయంలో P.T శ్రీనివాసయ్యంగారు Language Life and Deathఅనే పుస్తకాన్ని ప్రచురించారు. ఈ విధమైన పరిస్థితులు నెలకొని ఉండడంతో వ్యవహారిక భాషకు నిరసనగా ఒక ఉద్యమాన్ని లేవదీశారు.

ఈ గడబిడను గమనించి మద్రాసువిశ్వవిద్యాలయం 1911లో సెప్టంబరు 8న ఒక సంఘాన్నిఏర్పాటు చేసింది.ఇందులో 9 మందిసభ్యులు ఉంటారు. ఉంటారు ఇందులో లో నలుగురు గ్రాంథిక వాదులు, నలుగురు వ్యవహారిక భాష వాదులు ,ఒకరు తటస్థులు. వీరు అనేక సభలు సమావేశాలు జరిపిన తరువాత గిడుగు రామ్మూర్తి పంతులుఏ Memorandum of Modern Telugu;గురజాడ Decent పత్రం పుణ్యాన శిష్ట వ్యవహారిక భాషలోనే రచనలు సాగించాలనే నిర్ణయానికి వచ్చారు. కానీ గ్రాంథిక వాదులు వ్యవహారిక వాదాన్ని ఎదుర్కోడానికి ఆంధ్ర సాహిత్య పరిషత్తు ఏర్పాటు చేశారు. శిష్ట వ్యవహారికాన్ని గ్రామ్యంమని ఊరూరాసభలు జరిపి సంతకాలు సేకరిస్తూ వచ్చారు. మొట్టమొదట బోధనారంగంలో గ్రాంథికం ఏలుబడి చెల్లుతూ వచ్చింది. క్రమంగా ఉత్తరోత్తరా వచన రచనల్లో వ్యవహారిక భాషా ప్రాచుర్యం పెరుగుతూ వచ్చింది .క్రమక్రమంగా కాల ప్రవాహంలోఅన్ని రంగాల్లోనూ వ్యవహారిక భాష వేళ్ళూనుకుంది దీనికి ప్రధాన కారకులు గిడుగు, గురజాడలు. గిడుగు సిద్ధాంతవాది అయితే గురజాడ ఆచరణ వాది. గిడుగు భాషా సంస్కరణకు, కందుకూరి సంఘ సంస్కరణకు తన సాహిత్యం లో ప్రతిఫలింప చేసి ఆధునిక వైతాళికుడు అయ్యాడు. గురజాడ సహాయంతో సహాయంతో గిడుగురామ్మూర్తి పంతులు భాషా సంస్కరణకు తన జీవితాన్ని ధారపోసాడు.పూర్వరచనలన్నీ శిష్టవ్యవహారికం లోనేసాగినాయని, మధ్యలోనే భాష కృతకంగా మారిపోయిందని భావించిన గిడుగు రామ్మూర్తి పంతులు ఆ విషయాన్ని నిరూపించడానికి వ్యవహారిక భాషను పునఃప్రతిష్ట చేయడానికి కినాలుగు మార్గాలను అనుసరించారు.

1. భాషా తత్త్వాన్నివివరిస్తూ ప్రపంచంలోని ఇతర భాషావాఙ్మయమంతాలౌకిక భాషలోనే సాగిందని అలాగే తెలుగు భాషలో కూడా ఆయాకవులు ఆనాటి శిష్టవ్యవహారికాన్ని కావ్యాల్లో ప్రయోగిస్తూ వచ్చారని కాల పరిణామంలో మధ్యలో తెలుగు పరిస్థితి మారిందని ఇతని అభిప్రాయం. ఆ విషయాన్ని ఉదాహరణ పూర్వకంగా నిరూపించారు

2. తాళపత్ర గ్రంథాల్లోనూ, గ్రంధ పరిష్కారాల్లోనూ లౌకికభాష స్థానంలో గ్రాంథిక భాషను చేర్చారని భావించి లక్ష్య సహితంగా నిరూపించారు.

3. గ్రాంథిక భాషను నిర్వచించడం, స్వరూపాన్ని నిరూపించడం కష్టమని తేల్చి చెప్పారు. భాషా స్వరూపాన్ని వర్ణించే వ్యాకరణ గ్రంథాలే పరస్పర విరుద్ధ భావాల్ని వ్యక్తం చేస్తున్నాయి. ఒక వ్యాకరణం ఒక పదాన్ని గ్రామ్యంగా పేర్కొంటే మరొక వ్యాకర్త దాన్ని గ్రామ్యం కాదంటారు. వారికి వారే ఏది తప్పో ఏది ఒప్పో సమగ్రంగా చెప్పలేకపోతున్నారు. గ్రాంథిక భాషలో మాత్రమే రాసిన గ్రంథం మచ్చుకి ఒక్కటి కూడాఉండదని గిడుగు అభిప్రాయం ఇది ఇతని మూడో మార్గం.

4. ప్రాచీన కవులు అన్నీకావ్యాల్ని సమగ్రంగా పరిశీలించక పోవడం వల్ల వ్యాకరణ కర్తలు,నిఘంటు కారులు ,పండితులు తప్పుగా భావించి లక్షణ విరుద్ధమని,గ్రామ్యాలని నిందించిన రూపాలు వందలకొద్దీ కావ్యాల్లో కలవని నిరూపించారు . వ్యాకరణం ప్రయోగ మూలం కావడంవల్ల కవి ప్రయోగం లక్షణం కంటే బలవత్తర మైనది. కవులు ప్రయోగించిన రూపాలు ఆ లక్షణంతో సమన్వయం కాకపోతే ఆ లక్షణమే అసమగ్రమవుతుంది ,అంతే కాని ఆ కవి ప్రయోగాలు నింద్యాలు, గ్రామ్యాలు కావని అలాంటి ప్రయోగాలు వందల కొద్ది కావ్యాల్లో కలవని చూపించడం నాలుగోమార్గం. అందుకే "ఆర్యవ్యవహారంబుల దృష్టంబు గ్రాహ్యంబు" (బా.వ్యా-సం.ప 23) అంటారు బాలవ్యాకరణం లో చినయసూరి.

ఈనాలుగు మార్గాలను ఉదాహరణ సహితంగా నిరూపించడానికి గిడుగు రామ్మూర్తిపంతులుగారు 4 గ్రంథాలు రాశారు.

1.వ్యాసావళి

2.గద్యచింతామణి

3.ఆంధ్రపండిత భిషక్కుల భాషాభేషజం

4.బాలకవిశరణ్యం

ప్రస్తుత వ్యాసం నాలుగో మార్గాన్ని నిరూపించే బాలకవిశరణ్యాన్నిచర్చించడం ప్రధాన లక్ష్యం వ్యాకరణాల్లో ఇలాంటి పరిస్థితి నెలకొనడానికి ప్రధాన కారణం ఆ మూలాగ్రం వాఙ్మయాన్ని చదవక పోవడమే కారణం అంటాడు. ప్రధానంగా ఈ గ్రంథంలోబాల వ్యాకరణ సూత్రాలు చెప్పిన రూపాలను తీసుకొని వాటిని ని సాధు నిరూపణ చేయడానికి పూనుకున్నాడు .సాహిత్యంలో ఉపయోగించిన శబ్దాలను అసాధువులని చెప్పడం తప్పని ఇతని అభిప్రాయం. జనవ్యవహారంలో లేని దానిని కవి ప్రయోగించడు కొన్ని గ్రంథాలను ప్రమాణాలుగా తీసుకుని ఇవి సాధువులు , అసాధువులని, నిందాలని పేర్కొనడం తగదని ఇతని అభిప్రాయం.

వాఙ్మయమంటెల్లజూచినవారలెవరు?
బాస యెల్లను బండితల్పాపుకొనిరి?
సాహసముగాది పెద్దల సభ్యభాష
తప్పుతప్పనిదూరుట?తగనికవులు
పల్కులును దప్పులంటయు వాసిగనుక--

అని నిరసనవ్యక్తంచేశాడు.అలాగే .....

లోకయాత్ర కొరకు లౌకికభాషలు
పుట్టి ప్రజలనోట నొందియుండు
జీవలోకమందు జీవింపుభాషలు

జనుల తలపుదెలుపు సాధనములు

లోక వ్యవహారంలో ప్రజల భావాల్ని తెలిపేది భాషని ,కాళ్లు చేతులు అవి ఎలా తమ పనులు చేస్తాయో అలాగే భాష ఉచ్వాస ,నిశ్వాస కరణ ప్రయత్నాల ద్వారా తన విధిని నిర్వర్తిస్తుందని ,ఈ శబ్ద సిద్ధిని తెలపడానికి శాస్త్రాలు సరిపోవని అభిప్రాయపడుతూ ,పరిమితమైన శబ్ద జాలానికి కాక లోక భాషకు ప్రక్రియను ఏర్పరచినవారే గొప్పవారని వివరించారు.

లోకమందుభాషలలోన నున్న
సిద్ధి శబ్దాల పరిపాటి చిత్తగించి
మేరమీరక ప్రక్రియలేరుపరచి
వ్యాకృతికి ద్రోవచూపినవారి గనుడు

దీన్నిబట్టి చూస్తే అసలు భాషకు వ్యాకరణం ఏర్పరచడం కష్టమనే అభిప్రాయం మనకు కలుగుతుంది. వ్యాకరణ వేత్తలు చెప్పిందే వేదం కాదనేది గిడుగు అభిప్రాయం .ఇక్కడ ఒక ఉదాహరణను పరిశీలిద్దాం.
"కూతు శబ్దముప్రాథమైక వచనంబునకు రువర్ణంబగు"(బా.వ్యా-ఆ.ప 8) "కూతురు-కూతులు- కూతురులు – కూతుళ్ళు-కూతురిని ఇత్యాది రూపంబులు గ్రామ్యంబులని యేరుంగునది " అనే సూత్రం ప్రకారం కూతురు మాత్రమే సరి అయిన రూపమని,గ్రాహ్యమని అర్థం . మరి శిష్టవ్యవహారంలో ఉన్న కూతురిని- కూతురికి - కూతుళ్ళూ మొదలైన రూపాలన్నీ గ్రామ్యాలైయిపోయాయని, అవి రాయడానికి తగినవి కాదని పండితులు వాటిని బహిష్కరించారు. అందువల్ల పూర్వపు గ్రంథాలను అచ్చు వేసేటప్పుడు, పరిష్కరించేటప్పుడు ఆ వ్యవహారిక భాషా పదాల స్థానంలోఈ రూపాన్ని చేర్చారు. వ్యాఖ్యానాల్లో, టీకల్లో కూతురు ,కూతురిని అని ఉన్న చోట్ల అంతా ఆ కవులకు అపఖ్యాతి కలుగుతుందని లేక గ్రామ్యాలనో వాటిని దిద్ది వేశారు. అయితే జీవాద్భాష ఒకరు దిద్దితే అక్కడే ఆగేది కాదు. సాక్షాత్తు చిన్నయ్యసూరే తాను రాసిన హిందూ ధర్మ శాస్త్ర గ్రంథం లో కూతుండ్రు అని రాశాడు. ఇది తప్పని గాని ఒప్పని గాని తన లక్షణగ్రంథంలో చెప్పలేదు. తను రాసినశబ్దాన్నే తాను గ్రహించలేదు కాబట్టి ఏది తప్పు, ఏది ఒప్పని మనంనిర్ణయించలేమంటాడు.

ఇక్కడ మనం చెప్పదలచేదేమిటంటే ఏవ్యాకరణమూ ప్రమాణమూకాదు అలాగనీ నిరాదరణీయమూ కాదు. పాణిని అష్టాధ్యాయిలోనే కాత్యాయనుడు 10 వేలకుపైగా తప్పులుదిద్దాడు. అలాగే బహుజనపల్లి సీతారామాచార్యులు మొ. వారు బాలవ్యాకరణం లో వదిలిన అనేక విషయాల్ని ప్రస్తావించారు. ఇక్కడ మనం చిన్నయ సూరిని తప్పుపట్టలేము, ఆయన గ్రందమే వేడమని చెప్పలేదు. శిస్తుల ప్రయోగాల నుండి శేషమును తెలుసుకోవాలని చెప్పాడు. అంతేగాక లక్షణ విరుద్ధమైన దానిని పెద్దలు వాడితే దానిని యదా ప్రకారంగానే గ్రహించాలన్నాడు. ఇది తెలియని మనము ఇవి మాత్రమే ప్రయోగార్హాలని , ఇవి గ్రామ్యాలని, నింద్యాలని చెప్పడం , అవి ప్రయోగానికి అనర్హాలని చెప్పుకోవడం మన పండితుల తప్పని నిరూపించాడు. ఈ

అంతరం వల్లనే శిష్ట వ్యవహారిక భాషని, గ్రాంధికభాషని రెండు విభాగాలైంది. ఒకప్పటి శిష్టవ్యవహారికమే నేడు గ్రాంధికమని మన గిడుగు వారల అభిప్రాయం.

నన్నయ్య 'ప్రవాహినీ దేశ్య' అన్నారు.భాష నిరంతరం మారుతూ ఉంటుంది. ప్రాచీనులు వాడిన ఆనాటి వ్యవహారిక భాషను ఆ ప్రక్రియలతో సహా అనుసరించడం సరికాదంటాడు.

ఏరు పారునట్లు పారుచునుండును
దేశ భాష తెరుగు తెలియుటరది
మారుచుండు గాని మారుపు గనరాదు
లోటు చూచి కనుడు లోని గుట్టు
మనమే కానలేము మనము మారెడుచొప్పు
భాసయొక్కటే కాదు బ్రహ్మండ
మెల్ల మారుచుండు తెరున్గా లొక్కో
ఎప్పుదేద్ది కలదో యప్పతికడే నిత్య
మదియ మనకు సేవ్యమగుట యొప్పు.

భాషకేకాదు బ్రహ్మాండానికీ మార్పు సహజమనీ ఎప్పుడు దేనిని వ్యవహరిస్తామో అదే నిత్యమని దానినే మనం అనుసరించాలని చెప్పి వ్యవహారిక భాషోద్యమాన్ని నడిపిన కారణాన ఈనాడు మనం ఆ ఫలాలను అనుభవిస్తున్నాము. ప్రతీ రంగంలోనూ వ్యవహారిక భాష మాత్రమే ప్రయోగించ బడుతుంది. ఇంకా సాహిత్యమైతే ప్రాంతీయతనూ ఆదరిస్తుంది. మాండలిక సాహిత్య సృష్టికి ఊపిరి వ్యవహారిక భాషోద్యమమని చెప్పవచ్చు. ఈనాడు వ్యవహారక భాష ప్రయోగం కోసం కూడా ఇంత ఉద్యమం జరిగిందా అన్న స్థాయిలో వ్యవహారిక భాష వేయిచెరుగులా తెలుగు నేల నలుమూలలా విస్తరించింది. దీనికి కారణమైన గిడుగు రామ్మూర్తి పంతులు గారికి , గురజాడ గారికి ఆంధ్రజాతి ఋణపడ్డది. ఈ ఘనులను ఇలా స్మరించుకోవడం చంద్రునికో నూలుపోగులాంటిది.

ఆధార గ్రంథాలు :

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5. గిడుగు రామమూర్తిసాహిత్యవ్యాసాలు - సంకలనం అక్కిరాజు రమాపతిరావు.

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# AGRAHARAS AND BRAMHAPURIS IN INSCRIPTIONS OF CHALUKYA' JAYASIMHA II

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## Introduction:

Education has been considered as a prime part of human life for growing intellectual and physical since ancient age, which guides person going in noble way. In ancient times, children were admitted to Gurukula in childhood and grammar, Sanskrit, Veda, vedanga, logic, Upanishads, Poetics, etc were being taught to children in Gurukula by teacher. Hiuen Tsang who had come to the court of Pulikeshi II, famous king of Baadami Chalukya dynasty quoted regarding Childhood and education in Si.yu.ki. of his literary work that Boys were admitted to Gurukula in their age of 5 years old ,which was also refered by Dr. M.Chidanadamurthy(1). Education would be started after Upanayana, Education was a prime part of Social growth in ancient days. Ghatikasthanas, Bramhapuris, Mathas, Agraharas were centers of education, which were being run in form of institutions. The above four institutions were supporting and together conducting educational activities. Kings, Queens, Mahamandaleshwaras, Mahasamanthas, Mahamathyas, Mahapradanas, Mahajanas and rich merchants had converted common villages as Agraharas', in which Tempels, Mathas were built, regarding this Testimonies of charity were found. Aim of this present Article is to study the Bramapuris and Agraharas in inscriptions during the reign of Chalukya Jayasimha II.

## Objectives of Study:

1. To study the Bramapuris and Agraharas in inscriptions during the reign of Chalukya Jayasimha II.
2. To analyze the education system during the period of Chalukya Jayasimha II.

## Research Methodology:

Research methodology is descriptive and analytical data is based on Primary and secondary. For this study data and information has been collected

with the help of Fieldwork, Volumes of inscriptions, Books, Magazines, Newspapers, Research Journals.

**Agraharas:**

The Name Agrahara is refered in many inscriptions of Jayasimha II of Chalukya. Dr.M.Chindanandamurthy defines that AGRA means best; AHARA means country or place (2). Agraharas were the places or villages which were assigned to Scholar Brahmins to hold their Educational and Religious function as gift. In this village, not only Brahmins were staying and other caste People were also there, but All Revenue of the village was going to Brahmins (3), means that Brahmins were enjoying revenue of treasury against service provided by them. So Establishing of Agraharas were considered as work of religious and sacred (4). Agraharas had grown as part of village or city or separately. Dr.Shantha Kumari Quoted that since Gurukulas were part of Agraharas, Scholars who were studying in Gurukulas would be Mahajanas, because of this Agraharas had developed well (5).

Concept of Agrahara were there during reign of Kadamba in Karnataka, when Mayuravarma visited the Kanchi for Ashwamedhayaga, Kanchi was a Agrahara and Ghatikasthana. Mayuravarma had gifted 12 Agraharas including Thalagunda and Possession of land to Brahamins who were welcomed from Ahhichathra of Uttar Pradesh (6). Dr. D.M. Nagaraju quoted the reference of Dr.Shantha Kumari that Thagarathe, Shivamoga District, Karnataka is an most ancient Agrahara (7). Thus developing Agraharas had developed as Prime centers during Badami Chalukya reign.

Inscription of ladakhan temple at Ihole quotes that there were 500 Mahajans headed by Binnama Somayaji.

Agraharas were not only a religious centers and also social workshop centers and had independent political administration. Mahapradhanadandanayaka or Samanthadipathi of the state had control over this village and were imposing and collecting tax, the collected tax was being spent for charity and development of Agraharas, Usually Mahajanas were rulers of these Agraharas.

Agraharas were cultured wealth centers. Agrharas were categorized as Agrahara, Piriya Agrahara, Kiriya Agrahara, Maha Agrahara, Anadi Agrahara, Parameshwara Datti Agrahara, Uttama Agrahara, Sri rama Datti Agrahara and etc on the basis of their importance (8).

Inscription of Guddada bevina halli Haverri District, Ranibennur taluk, (Period was destroyed) During reign of Chalukya Jayasimha II shows that Kundaraja, Mahamandaleshwara of Chalukya Jayasimha II had control over Banavasi 12000, 18 Agraharas, Santhalige1000 and was nightmare and

Sathigana Chatta to Cholas and as per this inscription, Kundaraja had control over 18 Agraharas, but more information has not been found in this inscription regarding them.

Salur inscription which is in ShikaripuraTaluk, ,Shivamoga Dist and belongs to A.D. 1017 refers that Saliur was a prominent Agrahara (10) and Manevergade Kethamalla Karanikapramukas gifted kannasoge to found tank for Salur people for charity of Banavasi Puravadishvara Srimath Kudmarasa who was son of Srimad Irivabedanga .

Inscription of Belur of Bijapur district, Badami taluk dated to A.D.1021, Dec 24 refers that During reign of Jayasimha II, Perur was an Agrahara, Akkadevi sister of Jayasimha II was ruling Kisukadu70 and converted Perur as Agrahara in the memory of elder brother Tribuvana Malla Vikramaditya (11) and started Thri Purusha School and gifted 500 Mathras land, 50 houses, flower garden for food and accomodation for 500 hundred students at Perur. Manneyachatta gifted this charity.

Rona inscription of reign jayasimha II of Dharwad District, Rona Taluk and AD 1022, December 25 refers that Rona was a prominent Agrahara. In the inception of this inscription, Description of Rona was found. Sri Sankimayya son of Aythaverma who was Scholar of Maha Agrahara of Rona made moolasthana at Rona and his elder brother founded 12 Brahmins choultary and gifted land, garden and oil mills for these. Maniyara of Rona dug wells in Arave and Aythavarma, Rudramaya, Dachimaya sons of Machimaya handed over gifted land by their father to 104 Brahmins (12).

Telgi inscription which belongs to AD.1032 at Kodalura Shankara Narayana Sannidi quotes about telagi agrahara inside the Bikkiga 70 (13). In this inscription, refered that Kannamaya who was head of Telgi Agrahara gifted a Matharu paddy field to Karigoda of bikkagana Kere. Mahasampadhipathi, Puravareshwara, Bramha Kshatriya, Madura Vamshodbhava Srimadalayya was ruling Banavasi 12000, Santhalige 1000 During reign of Jayasimahadeva II in the era of 959 on Saturday, Summer Solstice.

Kuppaguddee was open battle field to Mandalika Kunkunda. He killed many warrior and became an angel and his son, Mahasamathadhipathi Jayasimha Deva built Aleshwara Temple in the memory of his father at Agrahara, Kuppagudde and gifted Paddy field, garden for deity, worship, light of God. It has been refered in the inscription of AD.1033, Shivamoga, Sorabataluk (14).

Inscription of A.D.1042 Which is in Achapura, Sagarataluk, Shivamoga District, quotes regarding an Agrahara (15). Gonarasa who was younger brother of Bijjarasa who was Mahamandaleshwara of Jayasimha II was ruling Santhalige 1000 division as mahasamantha. Andasura founded an Agrahara, where also built temple and erected god idols of Shouryamarthanda and

Goneshwara and worshiped foot of Kriyashakthi Pandit who was disciple of Kalamukha Thapodhanagranya Vadirudra Panditha in the era of 964 on chitrabanusumvtsara, Vaishakashudha Akshayathrithiya on Sunday, Solitiece and assigned Goneshwar math and Shouryamarthanda temple, for which he gifted garden ,land for education and saints.

The above Inscriptions conclude that Agaharas were developed well during the reign of Jayasimha II. These Agraharas had local governments. Mahajanas who were head of these Agraharas were giving Charity and were striving for over all development of Agraharas over crossing their limit of power, because of Agraharas were wealthy.

During this time, Agriculture activities, building tanks and business were going under the Mahajanas of Agrahara (16), hence Agraharas had developed as centers of Education, religious, economic and cultuaral activities.

**Bramhapuris:**

Bramhapuris were the places where Brahmins were living. these may be called as Bramhapuri or Bramhanapura. Bramhapuris were part of Agraharas as street of Agraharasand were adjacent to temples. Numbers of Bramhapuris were very less compared to Agraharas, most probably Brahmins were not wishing to live separately, because Mahajans of Agraharas were brahmins. Brahmins were research scholar and had got skill in veda, vedanga, logic, poetics and many more things,which concludes from above discussion, but Brahmins who were living in Bramhapuris were common community and were living as part in the Agrahara and village .They also engaged in studying of veda, vedanga and other studies and were executing as Mahajanas. Establishment of Bramhapuri was as important as Agraharas at that time, hence it was known equal to that of building a temple, Supportably formation Bramhapuris were sacred, in which Accommodations were being provided for eligible Brahmins.

Pura Inscription which belongs to the reign of Jagadekamalla, Jayasimha II in A.D.1018. October 27, Koppala District, Kustagi, taluk quotes of Bramhapuri and during reign of Jagadekamalla, his mahasamanthadhipathi (17). In this inscription during reign of Jagadekamalla, Mahaprachandadandanayaka (name was destroyed ) was ruling Kelawadi 300. In the light of Monday eclipse, gifted 5 mathras paddy field to Kondayavari Ayyanayya head of Belvanage Agraahara in front of the village at temple of God Pampastanavirupaksha , it is also refered as gift for Jannayyabhatta, Chamundayya shanangi and Brahmins, Mulastana devaru, bramhadevaru, Kalidevaru. clearly mentioned in this inscription that how much gift had been given for each one. As per inscription, 5mathras paddy field to Jannayya Bhatta, 150 mathras to chamundayya shanangi including 12 Brahamins and bramhapuri, 3 mathras for mulastana god, 48 mathras to Kalideva, 12 mathras to

Bramhadeva, this inscription refers that charity was gifted for alivate to problems.

Brmhapuris had developed support of religious activities within the environment of tempels (18). Bramhapuris were part of Agraharas or street of Agraharas or village. Brahmapuri was the street, where Brahmins were living. Brahmins of bramhapuri were highly educated and were also scholar as Maha Brahmins of Agrahara, in matter of education, bramhapuris had not shown any speciality, formation of Bramhapuris was not only Brahminsstaying there, there lived common people and also were engaged in religious and educational activities at that time. Hence Brahmins of Bramhapuris were part of education, preaching education and daily meditation. When observing these particulars, Bramhapuris were alternative for Agraharas and had developed as part of these and were centers of cultural, religious activities.

**Conclusion:**

The above discussion concludes that During the reign of Jayasimha II, Agraharas and Bramhapuris were religious and educational activitiy centers and most number of Agraharas had developed ,but number of Bramhapuris were very less. Because urban towns and cities were very less in the medieval and ancient age. Bramhapuris were part of Agrahara, village or urban areas. The People believed that establishment of agraharas and Bramhapuris and giving charity was sacred. Kings and queens, Mahamandaleshwaras, Mahasamanthas, rich merchants, were assisting to manage fiancé to Agraharas and Bramhapuris, intention of this assistance was to advertise education and brahamins also were given charity to bramhapuris and Agraharas. During this time, Agriculture activities, building tanks, business were going under the Mahajanas, hence Agraharas had devolped as centers of Education, religious, economic and cultuaral. Bramhapuris were alternative for Agraharas and had developed as part of these and were centers of cultural, religious activities.

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# INTERLINKAGE BETWEEN GEOGRAPHY EDUCATION WITH ECO AND SUSTAINABLE TOURISM

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## Abstract

Geography as a discipline evolved to understand the complex inter-relationship between man and environment. While passing through its various phases of development, various branches as per the transformations originated and expanded the horizon of Geographical inquiry. One amongst them is the tourism Geography which is providing information about the ways, mode and repercussions of expanding tourism at the world level. Due to technological advancement, urbanization, globalization and preference for materialistic life are causing the population at the world level to explore the areas as tourists per their convenience. This exploration has not only given the tourism as recognition of Industry, but also caused its proliferations in different branches. Along with that this world wide surge of tourists all over the world has placed tremendous pressure on the available resources of the chosen destinations. The balance between the nature and man got disrupted due to overriding of commercial interests on the delicacies of natural component.

With the above mentioned background, this paper attempts to explore the role of geography education as a mediator to develop sensitivity about the prevailing issue at the school level,i.e how does including topics related with eco-tourism at the school level would cause the children to take a lead and further as an adult to use the tourist places not only as a leisure pursuit,but as an active participant in boosting the economy.

The methodology of this paper would be based on the reviewing of the second hand material available for the topic as well using them for the analytical purpose also.

**Key Words**: Geography Education, Eco tourism, Sustainable Tourism

## Introduction:

### 1.1 What is Geography?

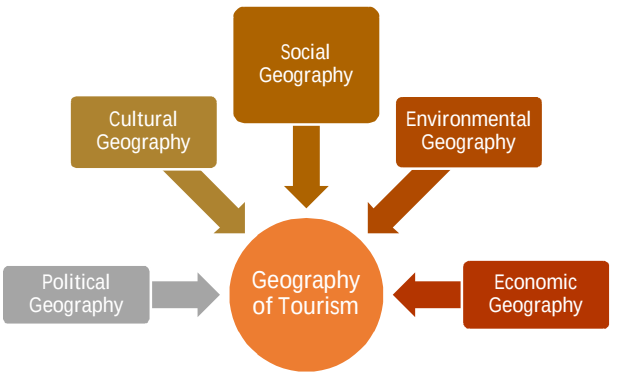
Man since evolution expressed keen desire to know about different places of the Earth. The transformation from hunter gatherer to regular production of crops, from cave dwellers to living in ultra modern equipped facilities lead homes, evolving different modes of transports on the basis of the distance and reaching to the extent of conceptualization of human being as a 'Global citizen' are benchmarks of human civilization, which probably would not have been possible if human beings confined to the native place only. After settling down the basic necessities of life, always interest has been shown to the places away from home, sometime to find peace, sometime for leisure and sometime simply to know unknown. All these mentioned conduct and attribute has been attempted formally by the discipline of Geography. Geography as the

word indicates is the 'description about Earth'. This description mainly focuses on studying the interaction of men with the nature i.e how does man through his interaction understood the available physical realities followed by informing about the kind of adjustments and changes one has made over the surface. It might be the reason that geographers starting using the word 'spatial' as an 'essential modifier in framing their questions and forming their concepts. The word spatial comes ,of course from 'space', ***and to geographers it always carries the idea of the way things are distributed, the way movements occur, and the way processes operate over the whole or a part of the surface of the earth*** .'( Gettis,et;el ,Human geography, p.6)[1]

Geography as a spatial science is replete with details of explorers who played very significant role in developing understanding about the places. Here the contribution of Ritter and Humboldt, etc. are noteworthy who travelled extensively and threw light on the flora, fauna and human features of those visited places. Humboldt visited Bavaria, Austria, Switzerland and Italy to observe the nature closely.[2] Later on during the age of discovery; the expeditions of Columbus, Vasco De Gama have broadened the horizon of human understanding about different places of the Earth.

**1.2 Geography of Tourism**

While keeping its major thrust on understanding the relation between man and nature in the spatial term, geography as a subject known for its two major bifurcations – physical and human. The former put its major thrust on understanding the physical aspects through geomorphology, climatology, oceanography etc. whereas the latter laid its emphasis on human behavior correspondence to all these physical phenomena through its numerous branches like Agriculture geography, economic geography, Social Geography, political geography, Urban geography, cultural geography etc. In the continuation of all these, an emergence of a new branch i.e of 'Geography of Tourism' was quite noteworthy. The geography of Tourism by itself is not a new idea. In fact, it might be taken as the applied part of all the major branches of human geography as given below-




The literature in this regard shows its origin around 1920 when intensively the impact of tourism on the economic activities was studied. The tourism Geography provides information about the ways, mode and repercussions of expanding tourism at the world

level. In this context, if one look at the nature of the geography of tourism, then it attempts to describe the whole journey of human movements in a precise form. For the spatial investigators, different terminologies are available like travelers, explorers in general and geographers in particular. Prior proceeding further, one may be curious to know that how does tourist different from the travelers, explorers and geographers? These differences have been very aptly described by Nelson Velvet in his book ' An Introduction to the Geography of Tourism as ' ***the explorers were recognized to be individuals who traveled to places that had not previously been extensively visited or documented by other from their society. Likewise, travelers were considered to be those who traveled for a specific purpose, such as business enterprises or official government functions.' [3](P.26).*** As far as the definition of geographer is concerned, he/she according to dictionary.com defined as ' ***a person who specializes in geographical research, delineation and study.*** (https://www.dictionary.com/browse/geographer)[4] On the other hand, the word 'tourist' ,based on the definition of United Nations World Tourism Organization (UNWTO) is '***a person who travels to and stays in a place outside of his or her usual environment for not more than one consecutive year for leisure, business, or other purposes***.' Or ' ***individuals who did not travel for any purpose other than the experience of travel itself and the pleasure they derived from that experience***. ( from Nelson,V ibid.)[3]

The tourism has been recognized as a fully fledged industry where countries are working hard to generate revenue by satisfying the need of the tourists across different regions. Geographers study the spatial expressions of tourism as a human activity, focusing on both tourist generating and tourist –receiving areas as well as the link between. The core components geography of tourism according to Boniface and Cooper are:[5]

First, **the countries of origin of tourists, or generating areas** – these areas represent the homes of the tourists, where the journeys begin and end. The key issues to examine in tourist generating areas are the features which stimulate demand for tourism and will include the geographical location of an area as well as its socio-economic and demographic characteristics. These areas represent the main tourist markets in the world and naturally enough, the major marketing functions of the tourist industry are found here

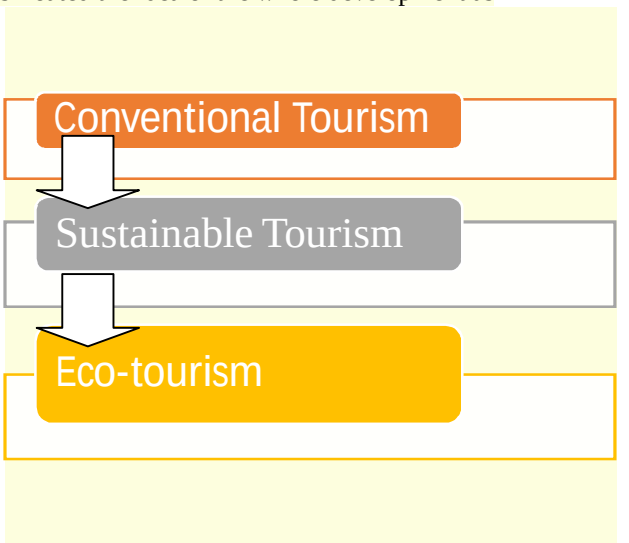
Second, **the tourist destinations themselves**- These areas attract tourist to stay temporarily and will have features which may not be found in the generating areas. The tourist industry located in this area will comprise the accommodation, retailing and service functions, entertainment and recreation. ( The Geography of Travel and Tourism, P.4)

Finally, **the routes travelled between these two sets of location** ( Leiper,1979). These two types of areas are a key element in the system as their efficiency and characteristics shape the size and direction of tourist flows. Such routes represent the location of the main transportation components of the tourist industry.

Proceeding further, while abiding the core definition of tourist given by Nelson V as 'individuals who did not travel for any purpose other than the experience of travel itself and the pleasure they derived from that experience' (ibid) it has been seen these individuals have grown exponentially due to technological advancement, urbanization,

globalization and preference for materialistic life. All these are causing the population at the world level to explore the areas as tourists as per their convenience. According to the estimate of United Nations World Tourism Organization, there were 25 million tourists estimated worldwide in 1950 which increased to 1.4 billion 68 years later. (https://ourworldindata.org/tourism)[6] . In India, according to tourism report '***Over 10 million foreign tourists arrived in India in 2017 compared to 8.89 million in 2016, representing a growth of 15.6%. Domestic tourist visits to all states and union territories numbered 1,036.35 million in 2012, an increase of 16.5% from 2011***.' (https://en.wikipedia.org/wiki/Tourism_in_India)[7] This surge at the national as well as at the international level if bringing economic benefits to the subjected countries ( generating employment, personal development, social development) , is creating serious environmental problems also. The excessive numbers of tourists' visits put tremendous pressure on the available resources. The superseding commercial interest normally creates resource crisis to the local people and degrade the quality of the environment. The article on 'Environmental impact on Tourism, summarizes the overall impact of tourism on environment as ' ***Negative impacts from tourism occur when the level of visitor use is greater than the environment's ability to cope with this use within the acceptable limits of change. Uncontrolled conventional tourism poses potential threats to many natural areas around the world. It can put enormous pressure on an area and lead to impacts such as soil erosion, increased pollution, discharges into the sea, natural habitat loss, increased pressure on endangered species and heightened vulnerability to forest fires. It often puts strain on water resources, and it can force local populations to compete for the use of critical resources***.' (https://www.gdrc.org/uem/eco-tour/envi/one.html )[8]

Overall influence is so much intensive, that as allied part of tourism ,the concept of eco-tourism and 'sustainable tourism' have evolved which mainly intends to sensitize the visitors as well as the host to treat this endeavor with responsibility and awareness. Bran (2000) has floated the idea of the whole development as



## 2. Methodology of the Paper

The methodology of this paper is largely based on deliberations emanating from reviewing the literature in this regard. The main books referred for this paper are related with human geography like sixth edition of 'Human Geography, Landscape of Human Activities by Getis,G,f,2001, 'An introduction to the Geography of Tourism' by Nelson,V(2013), 'The Geography of Travel and Tourism', second edition by Bonifice,G, B,Cooper,C,(1996). The online papers like 'Impact of tourism on Indian culture' presented fourth International conference on language, society and culture in Asian Context by S.,P.P (2016), 'Ecotourism in Developing Countries: A Critical Analysis of the Promise, the Reality and the Future' by O,Magio,K,V,V,M et al. 'EMERGING ENVIRONMENTAL ISSUES WITH THE DEVELOPMENT OF TOURISM INDUSTRY IN INDIA: A STUDY' by Rajamani,A and Rizal,P (2014), 'Ecotourism as a viable alternative for economic development of Romanian rural communities' Andre,R,D,Gogonea,M,R(2014) in 'Bulletin UASVAM (Agriculture), 'Geography of Tourism' by Hall,C.M, ' World Geography of Travel and Tourism' by Lew,A,Hall ,M et.el (2008), 'Relationship between Geography-Tourism and Tourism's Effects According to High School Students' by Koca,N (2018) etc. were referred. Along with all these geography textbooks at the secondary level ( from VI to XII) were also consulted to review the status of geography education and assessing the scope of inserting geography of tourism in such a manner so that children after receiving this exposure could incline towards ecotourism and sustainable tourism in the future.

**3. Edelson, Pitts** et.al in their project on 'Road Map for the Geography Education in the 21st century ' assert the need of Geography education as '***K–12 geography education is critical preparation for civic life and careers in the 21st century. It also is essential for postsecondary study in a wide range of fields, from marketing and environmental science, to international affairs and civil engineering.***

***Everyone in modern society faces personal decisions that require geographic reasoning. These decisions, such as where to live and how to travel from place to place, can have an enormous impact on one's life Education in Promoting Eco and Sustainable tourism[8]***

Now with due cognizance of geography education as a viable tool for preparing the people as tourist with dual sense of responsibility and personal satisfaction, there is a need to revamp the geography education as per the state of the art practices. t is quite paradoxical also that on the one hand geography has been recognized as a spatial science with taking cognizance of all spatial movements, on the other hand it has not been successful in transacting its core spirit amongst its readers. Geography of tourism by accommodating all the main branches of human geography is equipped to tourists to evolve themselves in an eco friendly manner. This preparedness needs to be percolate down to the school level so that children as a future citizen of the country as well of the globe could come out with best practices.

The reviewed literature in this regard clearly manifests the negligence of this important branch of geography in the education at different levels. In the geography textbooks, the bifurcation of physical and human aspects is accepted, but their implications on tourism have not been addressed properly. With the above mentioned

background, this paper attempts to explore the role of geography education as a mediator to develop sensitivity about the prevailing issue at the school level,i.e how does including topics related with eco-tourism at the school level would cause the children to take a lead and further as an adult to use the tourist places not only as a leisure pursuit, but as an active participant in boosting the economy.

In order to understand it, following are being given the textbook topics of geography textbooks, offered at the secondary level, means grades VI to XII prescribed by NCERT ( National Council of Educational Research and Training)

Source: http://ncert.nic.in/ebooks.html, downloaded on 14th September 2019[9]

The above mentioned syllabus of geography based on NCERT textbooks, framed on the basis of National Curriculum framework 2005. The review of the whole syllabus clearly shows that there is a lot of scope to insert the significance of different places of the earth from the tourist perspective along with developing awareness to emerge as eco-friendly tourist. Further, it also shows the apathetic behavior of the curriculum planners of geography to mould the subject as per the contemporary requirements of the society. Comparison of the content of these textbooks with the textbooks written two decades back reveals the shrinkage of spatial information lying about the other places of the world. Earlier, there used to be topics like 'our neighboring countries',' Europe', 'Australia' etc. in the textbooks which were helpful in developing understanding about the places other than the native ones, The topics like 'Resources', 'Our Environment', 'Life in Tropical Region','Life in the Temperate Region', 'Lifeline of Indian Economy', 'Occupation' ,'Ocean' etc. keep a vast scope to be moulded from the tourist perspective. This may not only revive the status of geography, but also train the children to develop sensitivity about the tourist places. In order to develop sustainable tourism along with eco-tourism, the geography education should try to revamp itself in the following manner.

1.The **basic notions of geography** should be cleared with varied examples of places.( The basic notions as given by Gettis,G.F in their sixth edition of the book ' Human Geography' are

1. Places have location, direction, and distance with respect to other places
2. A place may be large or small; scale is important.
3. A place has both physical structure and cultural content
4. The characteristics of places develop and change over time
5. The elements of places interrelate with other places
6. The content of places is rationally structured
7. Places may be generalized into regions of similarities and differences' (P.7) ibid[1])

2. Children should be sensitized about the usage of places through application of simulation, role play, stories and observation as core methods of teaching geography.

3. Children can be assigned tasks like to submit report after their visit to any place as a tourist with the Parents, focusing on mentioning the eco-friendly activities they have done in the subjected place.
4. Workshops, panel discussions, poster making competitions related with spreading the message of eco-tourism can be held frequently in the school.
5. Children living in the popular tourist places with the help of the geography teachers can take initiatives in generating awareness amongst the community members and visiting tourists to have usage of resources in a responsible manner.
6. Through the basic skills of geography like mapping, visuals, tables and graphing, children can be prepared to evolve as eco-friendly tourist later on their life.

**Conclusion**

This paper mainly attempted to explore the role of geography education in spreading the sensitivity for the sustainable tourism and eco tourism due to its emphasis on spatial movement and study of places as the key features. The paper by citing the offered topics in the geography textbooks at the secondary level tried to draw the attention about the potential of those topics to be converted hugely to promote eco-tourism. The paper concludes by giving the recommendations to the curriculum planners to revamp the geography curriculum by inserting some concerns of the geography of tourism also.

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# IMPORTANCE OF WOMEN EMPOWERMENT IN THE PRESENT INDIAN SOCIETY: A STUDY

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**Abstract:**

In the present era, Women's are playing the leading role for improving Indian society. The growth of women education in rural areas is quiet slow due to large number of women's in our country are illiterate, they are very weak, backward, exploited and many more. Yet in India, 7.5% women are educated of the world's total population. So it is observed that if their quality of life along with education is improving, the maternal mortality rate is declining and literacy rate increasing gradually. In this time education is the most important factor for women empowerment, welfare and prosperity. So, education is a key to unlock the golden moment of women empowerment in India. It brings to retrenchment in inequalities and enhances to participate everywhere i.e. doctor, pilot, teacher, lawyer, political leader etc. Government has facilitated for women in every sector and many constitutional laws are providing for equalization and equal right for women. Therefore, this research paper discusses the importance of Women Empowerment in the present Indian society as well as some suggestions to improve the changes that need to be considered for women empowerment and economic development.

**Keywords**: Women education, Women empowerment.

**Introduction**:

"Educate one man, you educate one person, but educate a woman you educate a whole civilization." Mahatma Gandhi.
Education is the most important factors in our society and it is the basic requirement for every citizen. It helps the individual to reduce inequality and play a central role in human development that impacts the overall social and economic development. Higher level of literacy and education leads to better attainment of health, nutritional status, economic growth, population control, empowerment of the weaker sections and community as a whole. There has always been gender discrimination toward the development of women. They do not have their rights and neither is considered independent to take any decision. In order to provide equal status in the society, women need to be empowered. Educating women uplifts their life as well as the quality and entire family also[23]. The term "empowerment" has been used widely by the government, NGOs, academics, donor agencies and women activists since in the early 1980s. In

India empowerment is not limited to any organization but it is an expansion of education, health care, training, social area, political area, sports, IIT, IT sector etc. However, the concept of empowerment has broadened to include the growing concerns of the women's movement for gender equality and social justice. It develops the capability and strength to influence the direction of social change. Recently women empowerment has been recognized as a central issue and it is determine the women status in our society. Abolition of gender discrimination in society and participation of women in decision making process at all levels is the mark of women empowerment. On this realization, a number of policies, programs, project and action research has been taken to ensure empowerment of women in India. Empowerment of women leads to benefit not only to the individual woman but also to the families and community.

**Concept of women empowerment:** The idea of 'empowerment' comes from the theory of social change. Empowerment differs on predominantly aggregative and integrative theory of democracy. Women empowerment also enrich social enhancement of all women in our society. So it may be stated that women's empowerment is defined as the process in which their spiritual, political, social and economic status is raised. The empowerment of women is about dealing with the legacy of apartheid and the transformation of society, particularly of power relations between women, men, institutions and laws[17]. The National Policy on Education (1986) has emphasized the promotion of women's education in all areas of learning and thus eliminates any sex based stereo typing with the guarantee of equality before the law.

**Objective of the Study:** The objective of the present study is to find out the importance of education towards women empowerment in modern Indian society.

**Methodology:** The present study is based on the review of information collected from secondary sources and some information has also collected through online media.

**Review of Literature**: Sen, Gita and Grown, Caren (1987) illustrated that, women's empowerment prove the transformation of the society, help to enhance the civil order, property and inheritance rights, and control over women's bodies and labour. Women empowerment also helps in skill training, leadership on the side and democratic process, dailogue, participation in policy and decision-making, and techniques for conflict resolution. It enriches to develop the leadership qualities, entrepreneurship, and exposure to the outside world[22]. Sushama (1998) described, women empowerment help to participate social, political and economic spheres of in life[36]. Rajput Pam and Tiwari (2001) described the psychological empowerment is the most important aspect of every women life. It is a process, which make increase their motivation, self-interest and morale[26]. Srivstavand Mira Shivaa (2001) mentioned that women empowerment is significant in every sector and social empowerment also the part of empowerment[34]. Kapur, Promilla (2001) discussed women's empowerment could be considered as a process to gain power [20]. Chauhan & Bansal (2002) mentioned the various dimensions of 'women empowerment'. According to them, empowerment means giving legal and moral power to an individual in all spheres of life[8]. Dutta (2002) mentioned that women's are still considered as the 'woe of society' and this is the reason why various policies and programmes fail to achieve the best results in the present day scenario[11]. K. Murugaiah (2002) observed about women's work and empowerment enhances women's income that helps to build the power of women in the society[24]. Parvathy & Kartikeyan

(2002) explained the importance of education in the modern age. Proper training and guidance also helps to achieve the empowerment[25]. Shrivastava (2002) discussed about the various policies and plans for the development of women in India. Women's status and conditions have changed to a great extent in the post-independence period[31]. Suguna (2002) mentioned women empowerment is a phenomenon of the nineties[35]. Bose (2004) discussed how far women empowering go in actually[7]. Bhowmik (2005) said that the tribal women's participation has seen in almost all the fields. But there are limited positions and authorities in the society. So they overcome the unbalanced and incomprehensive situation by empowerment [6]. Ahmad (2008) said that women empowerment means not only greater external control but also growing inner capability as greater self-confidence and inner transformation of one's consciousness [1]. Akhtar (2008) described the empowerment of women is an important issue in India as well as in the world [2]. Azad (2008) mentioned that women have been dominated by males. They have been marginalized in both, the socio-economic sphere and the political mainstream. The role of self-help groups (SHGs) is very important for empowerment of women, because it involves equality participation, decision making process and access to opportunity. [3]. Elliot (2008) described the economic empowerment also enhance the women power in our society and it uplifts social mobility and socialization. This empower also generate to improve of income and it fight against poverty[12]. Jha, Nishikant (2008) described the women empowerment is a worldwide problem in the present day scenario. Government provides many schemes for empowering the women's [18]. Sanyal Tapati (2008) illustrated the inequalities among the rural-urban females[28]. Singh Prasad Thakur (2008) observed that development processes have increased the male dominance over women and increased their deprivation [37]. Vinay (2008) discussed in his paper women empowerment and development in Global Scenario in India. He has suggested the socio-economic and political empowerment also anxious to every woman, but still a large section of women in the developing countries are far away from the developmental process [32]. Chiranjeevulu and Krishna Murty (2011) described education is most important to women. It provided with better health care facilities so on [9]. Duflo (2011) discussed women's empowerment and economic development is the collaborative part in society [10].Ranganathan and Rao (2011) described that women's empowerment is the method of enabling an individual to think, behave; take action and control work in an autonomous way. Empowerment can create social transformation by providing a social environment in which one can take decisions and make choices either individually or collectively[27]. Bhattacharjee (2015) said that education is an important aspect of women and it is one of the most powerful tools to change the position of women in the society as well as uplift the family[4]. Singh, Khushboo (2016) concluded that the impact of literacy and education on empowerment of women as well as the suggestion to improve the changes that need to be considered for women empowerment and economic development[33]. Khatri Rita (2016) described that the impact of literacy and education on empowerment of women as well as the suggestion to improve the changes that need to be considered for women empowerment and economic development [21].

**Historical Perspective of women empowerment in India:** The history of Indian women can be divided into three periods i.e. Ancient, Medieval and Modern. An

ancient India had free access to education. They were expected to participate in Vedic sacrifices and utter mantras. We got some references of such learned ladies i.e. Visvavara, Lopamudra, Apala, Urvasi, Ghosa, Sulabha, Lilabati, Maitreyi, Saswati, Kshana, Gargi and others. Maitreyi, the celebrated wife of the most learned philosopher of ancient India, Yajnavalka, used to hold discussion on abstruse philosophical questions with her husband. In the Vedic period, women had access to education in India and gradually lost this right.

However, in the British period there was revival of interest in women's education in India. During this period, various socio religious movements led by eminent persons like Raja Ram Mohan Roy, Ishwar Chandra Vidyasagar emphasized on women's education in India. Jyotiba Phule, Periyar and Baba Saheb Ambedkar were those leaders of the lower castes in India who took various initiatives to make education available to the women in India. Later, the country got independence in 1947 and the government has taken various initiatives to provide education to all Indian women. Durgabai Deshmukh committee (1959) plays the vital role in women education. Hansa Mehta Committee (1962), M. Bhaktvatsalam Committee to look into the causes of public support particularly in rural area for girls' education and public Corporation. Kothari commission (1964-66) has provided three forms of education for women empowering and also in 1986, the policy has been recommended "operation black board". On the other hand, to develop the primary education and to achieve the aim of universalization of primary education up to age level 6-14 years, some schemes of programs has been operated i.e. District Primary Education Programme (DPEP), Sarva Shiksha Abhiyan (SSA), National Literacy Mission (NLM), Right to Education Act(REA) 2009, Knowledge Commission(KC) etc. In present day Central Govt. and State Govt. has also introduced Integrated Child Development Services (ICDS) project. These projects are maintenances by women teacher. Women's education in India plays a very important role in the overall development of the country. It not only helps in the development of half of the human resources, but in improving the quality of life at home and outside [23].

**Right of Children to Free and Compulsory Education:** The Right of Children to Free and Compulsory Education Act or Right to Education Act (RTE) is an Act of the Parliament of India enacted on 4 August 2009, which describes the modalities of the importance of free and compulsory education for children between the age of 6 to 14 years in India under Article 21A of the Indian Constitution. It is enforced in 2010 by the Indian Government.

'Free education' means that no child, other than a child who has been admitted by his or her parents to a school which is not supported by the appropriate Government, shall be liable to pay any kind of fee or charges or expenses which may prevent him or her from pursuing and completing elementary education[15,42].

**Sukanya Samriddhi Yojana (SSY):** The SSY account is meant to provide a small deposit investment for the girl children under 10years or less as an initiative under "Beti Bachao Beti Padhao" campaign. The main focused on securing a bright future of the girl child in India by facilitating the parents of a girl child in building a found for the proper education and a carefree marriage expenses of their child. A Sukanya Samriddhi Account can be opened any time after the birth of a girl till she turns 10. A minimum

deposit of Rs 1,000 and maximum of Rs 1.5 lakh can be deposited in the scheme throughout the financial year. This account can be open any post office or authorized bank [49].

**Beti Bachao Beti Padhao:** Beti Bachao Beti Padhao (BBBP) scheme was started on January 22, 2015 as a joint initiative of the Ministry of Women and Child Development, Ministry of Health and Family Welfare and Ministry of Human Resource Development under coordinated and convergent efforts to empower the girl child. First, it was initiated in 100 districts with low girl child sex ratio. The main aim of Beti Bachao Beti Padhao (BBBP) scheme was to stope gender discrimination of children and abolish the practice of sex determination. To ensure the survival and protection of girl and also to ensure higher participation of girls in education and other areas. According to Prime Minister Narendra Modi said that, "our mantra should be: son and daughter are equal" [52, 53].

**Janani Shishu Suraksha Karyakram:** Government of India has introduced an awareness scheme of Janani Shishu Suraksha Karyakram (JSSK) on 1st June, 2011. The main aim of this scheme is to provide free maternal and neonatal services in all public health institutions in order to encourage institutional deliveries and thereby reduce infant and maternal mortality. The initiative stipulates free drugs, diagnostics, blood and diet, besides free transport from home to institution between facilities in case of referral and drop back home. These scheme is estimated to benefit more than 12 million pregnant women who access Government health facilities for their delivery. It is an initiative those who still choose to deliver at their homes to opt for institutional deliveries. All the States and UTs have implementation of this scheme [43].

**Mahila Shakti Kendra Scheme:** The Government of India has approved a new scheme namely, "Mahila Shakti Kendra Scheme" (MSKS) on 2017-18 to empower rural women through community participation and to create an environment in which they realize their full potential. The scheme would be operational at multiple levels. The national level and State level structures will offer technical assistance to the respective governments on matters concerning women, whereas the District and Block level centers will extended assistance to this scheme and provided a foothold to similar schemes. The main objective of the scheme is framed for the empowerment of women who belong to the rural community. These women will be proved with the essential impetus to establish smaller business unit. Over and above, the scheme is intended to create awareness of the roles to be played by these women [44].

**Kanyashree Prakalpa:** The Kanyashree Prakalpa has designed Department of Women Development and Social Welfare, Government of West Bengal. The United Nations has awarded the West Bengal Government the first place for Public Service for its 'Kanyashree' scheme. A conditional cash transfer scheme with the aim of improving the status and well-being of the girl child in West Bengal by incentivizing schooling of all teenage girl and delaying their marriages until the age of 18, the legal age of marriage. This scheme will be implemented henceforth in all the districts of the State. The main characteristic of these scheme are to preventing trafficking and exploitation of the girl child, Reducing the incidence the drop outs, especially amongst and consequently increasing the median age of first birth. Discouraging early marriage of

girls to ensure compliance with the legal provisions pertaining to the minimum age at marriage and eradicating undernutrition and mal-nutrition of the girl child [45].

**Sabooj Sathi Bicycle Distribution Scheme:** Sabooj Sathi Bicycle Distribution Scheme was initiated by the West Bengal Government. Hon'ble Finance Minister, announced in his Budget Speech of 2015-16, distribution of bi-cycles to estimated 40 lakh students of class ix to xii studying in Govt. aided School and Madrashas. The main objectives of the scheme are empower the students, especially the girls and reduce drop outs in higher education, to encourage students to take up higher studies and to increase attention in school and also to promote environmental-friendly[50,51].

**Rajiv Gandhi Scheme for empowerment of Adolescent Girls-Sabla (RGSEAG):** Rajiv Gandhi Scheme for empowerment of adolescent Girls-Sabla is an initiative launched on 1st April, 2011. The scheme was introduced Ministry of women and child Development in India. It is a pilot programme in 200 districts. The main aims of this scheme to facilitate self-development and empowerment of young girl, to improve their nutrition, nourishment and health status, to improve their home skills, life skills and vocational skills education[54,55].

**Indira Gandhi Matritva Sahyog Yojana (IGMSY):** Indira Gandhi Matritva Sahyog Yojana is a maternity benefit program run by the government of India. The scheme was launched in 2010 as Indira Gandhi Matritva Sahyog Yojana (IGMSY). It was renamed as Matritva Sahyog Yojana in 2014 and again as Pradhan Mantri Matru Vandana Yojana (PMMVY) in 2017. The scheme was implemented by the Ministry of women and child Development in India. The main aims of these scheme was to promoting appropriate practice, care and institutional service utilization during pregnancy, delivery and lactation. Encouraging the women to follow (optimal) nutrition and feeding practices, including early and exclusive breastfeeding for the first six months; and also the providing cash incentives for improved health and nutrition to pregnant, lactating mothers [44].

**Self-help group:** It is a financial mediates peer-controlled, informal association. This is usually composed of 10–20 local women or men. These groups are started by governmental organizations (GO) that generally have broad anti-poverty agendas. Self-help groups are seen as instruments for goals including empowering women, developing leadership abilities among poor and the needy people, increasing school enrolments and improving nutrition and the use of birth control.

Self-help group have been able to mobilize small savings either on weekly or monthly basis from persons who were not expected to have any savings. They have been able to effectively recycle the resources generated among the members for meeting the emergent credit needs of members of the group. And also groups member's financial security as primary focus and other common interest of members such as area development, awareness, motivation, leadership, training and associating in others social intermediation programmes for the benefit of the entire community. In the aforesaid scheme, the central focus was on the women empowerments[13, 46].

**Barriers of women empowerment:**

**Violence:** Violence is the prime factor which opposes women's empowerment. Physical, emotional, mental torture and agony were the deep rooted problems in the

society from ancient to till date which are responsible for decline in female sex ratio as well as a barrier for education.

**Gender inequality:** It is the vital problem in present time. For empowering women, gender equality is the most important entity.

**Family restrictions**: Illiterate guardians are not willing to send their female children to the educational institute. Because, they think women are only saved into their home.

**Early marriages:** Early marriages are another obstacle in society. It was common throughout history. Today, child marriage is still fairly widespread, particularly in developing countries, such as parts of Africa, South Asia, Southeast Asia, West Asia, Latin America and Oceania. The countries with the highest observed rates of early marriages below the age of 18 are Niger, Chad, Mali, Bangladesh, Guinea, etc. [56]

**Trafficking:** Women trafficking is another problem in our own society in present era. Women and girls are usually trafficked for the purpose of sexual an economically exploitation, particularly prostitution and pornography, forced labour including, commercial, agriculture and domestic work. Women trafficking are a criminal phenomenon that violates basic human right. In the recent decades it has emerged problem and requiring new solutions for its [57].

**Women empowerment in education:** It can be described the impact of education towards women empowerment in this era. Education helps women to known the society as well as world, come out from the darkness of illiteracy to the light of education. It helps a woman to know, responds to challenges in their life, raise their voice of exploitation, dowry, and early marriage etc.[30.] Recently, women education has upgraded from informal to formal by teaching them how to manage business organizations, school, college, hospital and every academic sector etc. Acquisition of formal education ensures effective and efficient contribution of these women to the management of different sectors of the society. The formal education is mainly to empower both male and female gender in order to contribute greatly and equally to the advancement of the society. Women education involves the systematic means of equipping women with skills, abilities and experiences through formal education for personal as well as professional growth and thus development of the society. Women empowerment is now becoming a global issue in India. Indian constitution has been recommended some important article for develop the women empowerment and growing the equality[38].

In 1986, The National Policy on Education (NPE) was formulated and in 1992 revised policy has provided a separate and protected space for women's empowerment through the Mahila Samakhya Programme. This educational programme aimed at promoting women's education for equality.

Education also brings a reduction in inequalities and improving their status within the family. To bring more girls, especially from marginalized families of SC, ST, OBC and minority are now involved in school, college, work place etc. Govt. is provided mainstream education for their uplift and essential things are also provided for them. Some examples are i.e. free book, uniform, boarding and lodging, clothing, mid-day meal, scholarships, free circles, kanyashree and so on[5].

In 2009, the Government of India (GOI) has passed the 'Right of Children to Free and Compulsory Education Act' (RTE), which guarantees every Indian child from 6 to 14 have the right to enrolled and to complete eight years of elementary schooling[15]. The

upward trend in the access of girls to education, at all levels is has reflected across the GOI's enrollment statistics between 2013-2014, the enrollment of girls as a percentage of total enrollment in primary education has increased from 43.8 percent to 48.2 percent, while the enrollment of girls as a percentage of total enrollment in upper primary education increased from 40.9 to 48.6 percent (ASER 2015). In India, 7.5% women are educated of the world's total population. India ranks 113 of 135 on the 'World Economic Forum's Gender Gap Index'.

A Census chart has given below to describe the literacy rate about last 7 years[39]. The age group of 5 and above has mentioned in Census 1951, 1961, 1971 and also the age group of 7 and above described 1981, 1991, 2001 and 2011 Census. In these years, the literacy rate has given below:

Table: 1-Literacy Rate in India about last 7 years.

| Year of Census | Males | Females | Male and Female gap in the literacy rate |
|---|---|---|---|
| 1951 | 27.16 | 8.86 | 18.30 |
| 1961 | 40.40 | 15.35 | 25.05 |
| 1971 | 45.96 | 21.97 | 23.98 |
| 1981 | 56.38 | 29.76 | 26.62 |
| 1991 | 64.13 | 39.29 | 24.84 |
| 2001 | 75.26 | 53.67 | 21.59 |
| 2011 | 82.14 | 65.46 | 16.68 |

Sources: Census of India[16].

Table: 2-Gender Gap Rate: Census 1991-2011.

| Year | 1991 | 2001 | 2011 |
|---|---|---|---|
| India | 24.85 | 21.59 | 16.68 |
| Non EAG states | 21.14 | 17.72 | 13.34 |
| EAG states | 30.32 | 26.89 | 20.97 |

Sources: Census of India [16].

This table is shown that how the Gender Gap Rate changed from 1991 to 2011.
Literacy rate among the total population of the last 2 Census report given below:
Table: 3-Literacy Rate in India of Total Populations: Census of 2001-2011.

| Literacy Rate | Total Populations | Males | Females |
|---|---|---|---|
| 2001 | 560753179 | 336571822 | 224181357 |
| 2011 | 778454120 | 444203762 | 334250358 |
| Increased in 2011in compare with 2001 | 21770094 | 107631940 | 110069001 |

Sources: "Figures at a Glance"[40]

Table: 4-Literacy Trends in India of EAG (Empowered Action Group) states:

| Year | 1991 | | | 2001 | | | 2011 | | |
|---|---|---|---|---|---|---|---|---|---|
| | P | M | F | P | M | F | P | M | F |
| India | 52.21 | 64.13 | 39.29 | 64.83 | 75.26 | 53.67 | 74.04 | 82.14 | 65.46 |
| Non EAG states | 60.09 | 70.34 | 49.20 | 70.64 | 79.25 | 61.53 | 78.24 | 84.76 | 71.42 |
| EAG states | 41.65 | 56.00 | 25.68 | 57.22 | 70.09 | 43.21 | 68.86 | 78.96 | 57.99 |

Sources: Census of India[16].

According to the 2011 Census of India, the literacy rate amongst the female age group of 7 years was 65.46 percent, as compared to 82.14 percent of the comparable male population. This shows a 16.68 percent gap in male to female literacy rates, down from the 21.59 percent gap recorded in the 2001 census. Later, an Empowered Action Group has developed the category of non EAG states and EAG states of female are improving. As a result, women literacy rate has increased 2437,061 in 2011 [21].

India has worked in a multipronged way through Sarva Shiksha Abhiyan (SSA), the Education for all campaign, to enhance the access and retention of girls in school. The programme ensuring that there is a school available at every kilometer of each inhabited area, by giving free textbooks to all girls up to class 8, separate toilets for girls, recruitment of 50 percent female teachers, gender-sensitive textbooks and so on.

India has been successful in acquired gender parity in school and college education. Even in technical and professional education such as law, medical, IT, engineering, management etc., the presentation of women is significantly increasing. Today every fourth worker in India is a women and one-third of all certified medical researchers, banking sector, IT workers and chartered accountants are women. So women are now empowering power both in private and public life firmly. In political area 46 percent women are panchayat members and 1.3 million women in positions of power in Indian society. According to UNICEF, maternal mortality rate reduced from 212 deaths per 100000 live births in 2007 to 167 deaths in 2013. Financial inclusion has also increased tremendously and last five year 53 percent of women have saving bank account.

In addition, two focused interventions especially for girls the National Programme for Education of Girls at elementary Level and the Kasturba Gandhi Balika Vidyalaya have been launched to reach out to girls from extremely marginalized social groups, girls from lower castes, and families living below the poverty line.

In addition, the following schemes and policies demonstrate the Indian Government's commitment to promoting education access, quality, and the necessity of targeting girl's education.

Government of India launched a scheme in 2008. This is Incentive to Girls for Secondary Education. It has the objective to reduce dropouts and promote the enrollment of the girl child belonging mainly to Scheduled Caste and Scheduled Tribes (SC/ST) communities.

**Conclusion:** There is a positive relationship between education and woman empowerment. In present day the issue of women empowerment has been facing certain serious challenges, which are outcome of some certain evil norms and attitude such as child labor, child marriage, illiteracy, superstition, partial attitude of the parents, female feticides, etc. and in such a situation women empowerment is an urgent necessity for every society. In order to promote women's empowerment, it is necessary to create an environment that will allow women to participate in educational programs and share the benefits. The educational and other policies for women empowerment should be implemented in reality for empowering women in the world. The evils of poverty, unemployment and inequality cannot be eradicated by man alone. Equal and active participation of women is obligatory. Unless women are educated, they will not be able to understand about their rights and their importance. So it is conclude that women empowerment through education is now an important facet in this era. It means education has not only educated a person but also helps to frame the society or civilization for further needs.

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# GLOBAL FINANCIAL CRISIS AND ITS IMPACT ON INDIAN COMMERCIAL BANKS

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**Abstract:**

Banking sector is the basic instrument for the economic growth of a country. A strong banking sector plays a vital role of the flourishing economy. Failure of the banking sector adversely impacts various other sectors. This study is an attempt to analyze the number of bank branches, Deposits, Investments and loans and advances of the scheduled commercial banks before and after the global financial crisis. Secondary data was collected for the period from 2000 – 2018 from RBI website. Regression using dummy variable is applied for analytical purpose. From the study it is concluded that the banks took the practice of 'ever greening', where fresh loans were given to some promoters to enable them to pay off their interest effectively pushed the recognition of these loans as non-performing to a later date, but did not address the root causes of their unprofitability which affect their regular banking business of deposits, loans and advances and investment in growth aspect.

**Key Words:** Global Financial Crisis, Commercial banks

## Introduction:

The Banking system of the country is the base of the economy and economic development of the country. It is the most leading part of the financial sector of the country as it is responsible for more than 70% of the funds flowing through the financial sector in the country. In India, banks are not doing terribly well. They have lent unwisely. As a result, many loans have "become overdue" and a number of borrowers are not in a position to pay back their debt. This has made many a loan a non-performing asset (NPA). When borrowers are in default or in arrears on scheduled payments of principal or interest for specified period, usually 90 days, the loan is classified as NPA. All banks around the world have some NPAs but, if they become too large, banks can collapse. If the banks are big enough, this can cause the meltdown of the entire financial system.

According to CARE Ratings, India had the fifth highest NPA ratio in the world, ranking only after Greece, Italy, Portugal and Ireland. India's NPA ratio stands at 9.85%, while major economies such as Britain, the US; Japan and Germany have ratios less than 2%. According to the latest Financial Stability Report of the Reserve Bank of

India (RBI), the NPA ratio is set to deteriorate to 12.2% by March 2019, which would put India in fourth position, overtaking Ireland. As per the RBI, 11 public sector banks are under the prompt corrective action category, which means that the poor quality of balance sheets has to be addressed immediately to avoid potential meltdown.

**Review of Literature**

**1. Mittal (2017)** tried to compare the performance of public sector banks with that of private sector banks in India for the period 2005 to 2016. The major objective of the study was to measure the health of the banking industry with respect to the size of non-performing assets. To analyze the growth of non-performing assets, different ratios were used. The study found that the extent of non-performing assets was comparatively more in public sector banks.
**2. Adwani (2018)** tried to compare the productivity of employees of top public and private sector banks for the year 2016-17. The study evaluated different ratios for these banks to analyze the efficiency of employees. It was observed that for Indian banks, public sector banks had higher business per employee but poor profit per employee as compared to private sector banks.
**3. Sharma and Sharma (2018)** analyzed the financial performance of three selected Indian commercial banks, namely, Punjab National Bank, Canara Bank and State Bank of India; for the period 2016-17. Using financial ratio analysis, the study concluded that State Bank of India dominates the banking scenario, and has outperformed Punjab National Bank and Canara Bank for majority of the indicators.

**Need and Objectives of the study:**

In the recent years, the entire banking sector has been plagued by issues of rising bad loans and bank failures. Non-performing assets is increasing in the banking industry and has become a serious threat to the banks' existence and survival. Rising debts, non-repayment issues, and loan defaulters have become an area of major concern; which is now the prime focus of the policy makers and the government.

There have been major transitions and transformations in the banking history. Banks have shifted from traditional methods of banking to new domains as technology based banking and digital banking. Large numbers of studies have been undertaken on the subject of bank performance in India. Still, continuous measurement and evaluation of bank performance is imperative. Against this background, the study attempts to review, measure and analyze the performance of Scheduled Commercial Bank Groups in India before and after global crisis. The objectives of the study are:

1. To compare the number of branches of scheduled commercial banks before and after global financial crisis
2. To compare the Deposits of the scheduled commercial banks before and after global financial crisis.
3. To compare the Investments of the scheduled commercial banks before and after global financial crisis.

4. To compare the Loans and Advances of the scheduled commercial banks before and global financial crisis.

**Hypothesis formulated:**

H1: The number of branches of scheduled commercial banks differs significantly before and after global financial crisis.
H2: The Deposits of the scheduled commercial banks differs significantly before and after global financial crisis.
H3: The investment of the scheduled commercial banks differs significantly before and after global financial crisis.
H4: The loans and advance of the scheduled commercial banks differs significantly before and after global financial crisis.

**Research Methodology:**

The present study adopts an analytical and descriptive research design. The data was collected from RBI website and its various series of publications. The data was collected from the year 2000 to 2018.

**Tools used for the study:**

The financial tools used for the study are the number of branches of the scheduled commercial banks, Deposits of the scheduled commercial banks, Investments of the scheduled commercial banks and Loans and Advances of the scheduled commercial banks. Multiple Regression with dummy variables in excel is used to analyze before and after global financial crisis.

**Analysis and Interpretation:**

**a) Hypothesis Testing:**

$H_0$: The number of branches of the scheduled commercial banks does not differ significantly before and after global financial crisis.
$H_1$: The number of branches of the scheduled commercial banks differs significantly before and after global financial crisis.

| Year | Rural | Semi-urban | Urban | Metropolitan | Total | Dummy variables |
|---|---|---|---|---|---|---|
| 2000 | 32734 | 14407 | 10052 | 8219 | 65412 | 0 |
| 2001 | 32562 | 14597 | 10293 | 8467 | 65919 | 0 |
| 2002 | 32380 | 14747 | 10477 | 8586 | 66190 | 0 |
| 2003 | 32303 | 14859 | 10693 | 8680 | 66535 | 0 |
| 2004 | 32121 | 15091 | 11000 | 8976 | 67188 | 0 |
| 2005 | 32082 | 15403 | 11500 | 9370 | 68355 | 0 |
| 2006 | 29649 | 15943 | 12258 | 11728 | 69578 | 0 |
| 2007 | 29771 | 16716 | 13103 | 12349 | 71939 | 0 |
| 2008 | 30293 | 17960 | 14343 | 13325 | 75921 | 1 |
| 2009 | 30943 | 19282 | 15356 | 14288 | 79869 | 1 |
| 2010 | 31971 | 21013 | 16748 | 15432 | 85164 | 1 |
| 2011 | 33460 | 23318 | 17681 | 16447 | 90906 | 1 |
| 2012 | 36093 | 26068 | 18920 | 17493 | 98574 | 1 |
| 2013 | 39368 | 28798 | 19971 | 18342 | 106479 | 1 |
| 2014 | 44843 | 31835 | 21584 | 19554 | 117816 | 1 |
| 2015 | 48247 | 34113 | 23115 | 20824 | 126299 | 1 |
| 2016 | 50554 | 35959 | 24363 | 21958 | 132834 | 1 |
| 2017 | 49844 | 39073 | 25050 | 26697 | **140664** | 1 |
| 2018 | 50824 | 39652 | 25351 | 26641 | **142468** | 1 |

**Model Summary**

| Model | R | $R^2$ | Adjusted $R^2$ | Std. Error of the Estimate | Change Statistics | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | $R^2$ Change | F Change | df1 | df2 | Sig. |
| 1 | .751[a] | .565 | .539 | 18872.68347 | .565 | 22.049 | 1 | 17 | .000 |

a. Predictors: (Constant), Dummy Variables

**Coefficients[a]**

| Model | Unstandardized Coefficients | | Standardized Coefficients | t | Sig. |
|---|---|---|---|---|---|
| | B | Std. Error | Beta | | |
| 1 (Constant) | 67639.500 | 6672.501 | | 10.137 | .000 |
| Dummy variables | 41178.136 | 8769.385 | .751 | 4.696 | .000 |

a. Dependent Variable: No. of Branches

A multiple linear regression was calculated to predict number of branches of the scheduled commercial banks before and after global financial crisis. A significant regression equation was found ($F(2, 18) = 22.049$, $p > 0.000$), with an $R^2$ of 0.565.

At 5% level of significance t test shows the probabilistic significance as 0.001 which is greater than 0.05 (prescribed). Hence the hypothesis is accepted and it may be concluded that there is a significant difference because of the effort taken by government for financial inclusion programme to reach the people.

**b) Hypothesis Testing:**

H0: The deposits of the scheduled commercial bank do not differ significantly before and after global financial crisis.

H1: The deposits of the scheduled commercial banks differ significantly before and after global financial crisis.

| Year | Deposits | Dummy Variables | Year | Deposits | Dummy Variables |
|---|---|---|---|---|---|
| 1999-00 | 9003.07 | 0 | 2010-11 | 56158.74 | 1 |
| 2001-01 | 10552.33 | 0 | 2011-12 | 64535.49 | 1 |
| 2001-02 | 12026.99 | 0 | 2012-13 | 74296.77 | 1 |
| 2002-03 | 13556.23 | 0 | 2013-14 | 85331.73 | 1 |
| 2003-04 | 15755.30 | 0 | 2014-15 | 94338.38 | 1 |
| 2004-05 | 18375.59 | 0 | 2015-16 | 100926.51 | 1 |
| 2005-06 | 21646.79 | 0 | 2015-17 | 111139.36 | 1 |
| 2006-07 | 26969.34 | 0 | 2017-18 | 117940 | 1 |
| 2007-08 | 33200.61 | 1 | | | |
| 2008-09 | 40632.01 | 1 | | | |
| 2009-10 | 47469.19 | 1 | | | |

**Model Summary**

| Model | R | $R^2$ | Adjusted $R^2$ | Std. Error of the Estimate | Change Statistics | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | $R^2$ Change | F Change | df1 | df2 | Sig. |
| 1 | .806[a] | .650 | .629 | 22638.20980 | .650 | 31.569 | 1 | 17 | .000 |

a. Predictors: (Constant), Dummy Variables 1

**Coefficients[a]**

| Model | | Unstandardized Coefficients | | Standardized Coefficients | t | Sig. |
|---|---|---|---|---|---|---|
| | | B | Std. Error | Beta | | |
| 1 | (Constant) | 15985.705 | 8003.816 | | 1.997 | .062 |
| | Dummy Variables 1 | 59102.367 | 10519.075 | .806 | 5.619 | .000 |

a. Dependent Variable: Deposits

A multiple linear regression was calculated to predict the deposits of the scheduled commercial banks before and after global financial crisis. A significant regression equation was found (F (2, 16) = 144.9868, p> 0.001), with an $R^2$ of 0.947708. At 5% level of significance t test shows the probabilistic significance as 0.482 which is greater than 0.05 (prescribed). Hence the hypothesis is accepted and it may be concluded that significance exist because of more deposit mobilization after crisis in order to protect their funds by investors.

**c) Hypothesis Testing:**

H0: The Investments of the scheduled commercial banks does not differ significantly before and after global financial crisis.

H1: The investments of the scheduled commercial banks differ significantly before and after global financial crisis.

| Year | Investments | Dummy variables | Year | Investments | Dummy Variables |
|---|---|---|---|---|---|
| 1999-00 | 4138.71 | 0 | 2010-11 | 19236.33 | 1 |
| 2001-01 | 4919.08 | 0 | 2011-12 | 22339.03 | 1 |
| 2001-02 | 5880.58 | 0 | 2012-13 | 26130.51 | 1 |
| 2002-03 | 6930.85 | 0 | 2013-14 | 28832.62 | 1 |
| 2003-04 | 8020.61 | 0 | 2014-15 | 29775.92 | 1 |
| 2004-05 | 8697.37 | 0 | 2015-16 | 33278.35 | 1 |
| 2005-06 | 8665.05 | 0 | 2016-17 | 36521.75 | 1 |
| 2006-07 | 9509.82 | 0 | 2017-18 | 41,263 | 1 |
| 2007-08 | 11773.29 | 1 | | | |
| 2008-09 | 14495.51 | 1 | | | |
| 2009-10 | 17250.06 | 1 | | | |

**Model Summary**

| Model | R | $R^2$ | Adjusted $R^2$ | Std. Error of the Estimate | Change Statistics | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | $R^2$ | F Change | df1 | df2 | Sig. |
| 1 | .796[a] | .633 | .611 | 7331.36672 | .633 | 29.303 | 1 | 17 | .000 |

a. Predictors: (Constant), Dummy variables 2

**Coefficients[a]**

| Model | | Unstandardized Coefficients | | Standardized Coefficients | t | Sig. |
|---|---|---|---|---|---|---|
| | | B | Std. Error | Beta | | |
| 1 | (Constant) | 7095.259 | 2592.030 | | 2.737 | .014 |
| | Dummy variables 2 | 18440.775 | 3406.594 | .796 | 5.413 | .000 |

a. Dependent Variable: Investments

A multiple linear regression was calculated to predict the Investments of the scheduled commercial banks before and after global financial crisis. A significant regression equation was found (F (2, 16) = 150.705, p > 0.000), with an $R^2$ of 0.949592.

At 5% level of significance t test shows the probabilistic significance as 0.001 which is greater than 0.05 (prescribed). Hence the hypothesis is accepted and it may be concluded that t significance exist because banks park their surplus funds in the investment.

**d) Hypothesis Testing:**

H0: The loans and advances of the scheduled commercial banks do not differ significantly before and after global financial crisis.

H1: The loans and advances of the scheduled commercial banks differ significantly before and after the global financial crisis.

| Year | Loans and Advances | Dummy Variables | Year | Loans and Advances | Dummy Variables |
|---|---|---|---|---|---|
| 1999-00 | 4434.69 | 0 | 2010-11 | 42974.88 | 1 |
| 2001-01 | 5356.83 | 0 | 2011-12 | 50735.59 | 1 |
| 2001-02 | 6457.43 | 0 | 2012-13 | 58797.73 | 1 |
| 2002-03 | 7392.33 | 0 | 2013-14 | 67352.13 | 1 |
| 2003-04 | 8641.41 | 0 | 2014-15 | 73881.60 | 1 |
| 2004-05 | 11508.36 | 0 | 2015-16 | 78964.67 | 1 |
| 2005-06 | 15168.10 | 0 | 2016-17 | 81161.97 | 1 |
| 2006-07 | 19812.35 | 0 | 2017-18 | 87460.00 | 1 |
| 2007-08 | 24769.36 | 1 | | | |
| 2008-09 | 29999.24 | 1 | | | |
| 2009-10 | 34967.20 | 1 | | | |

**Model Summary**

| Model | R | $R^2$ | Adjusted $R^2$ | Std. Error of the Estimate | Change Statistics | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | $R^2$ Change | F Change | df 1 | df2 | Sig. |
| 1 | .821[a] | .673 | .654 | 17279.69858 | .673 | 35.032 | 1 | 17 | .000 |

a. Predictors: (Constant), Dummy variables 3

**Coefficients[a]**

| Model | | Unstandardized Coefficients | | Standardized Coefficients | t | Sig. |
|---|---|---|---|---|---|---|
| | | B | Std. Error | Beta | | |
| 1 | (Constant) | 9846.438 | 6109.296 | | 1.612 | .125 |
| | Dummy variables 3 | 47523.051 | 8029.188 | .821 | 5.919 | .000 |

a. Dependent Variable: Loans and Advances

A multiple linear regression was calculated to find the Loans and Advances of the scheduled commercial banks before and after global financial crisis. A significant regression equation was found (F (2, 15)=176.83, p> 0.000), with an $R^2$ of 0.9567.

At 5% level of significance t test shows the probabilistic significance as 0.001 which is greater than 0.05 (prescribed). Hence the hypothesis is accepted and it may be concluded that significance exist because of lesser than the expected growth after crisis.

**Findings:**

1. At 5% level of significance t test shows the probabilistic significance as 0.532 which is greater than 0.05 (prescribed). Hence the hypothesis is accepted and it may be concluded that the number of branches of the scheduled commercial banks differ significantly before and after global financial crisis. The number of branches has increased up to the year 2016 and there was a gradual decline after 2017. This is due to initiatives taken by the Government to develop digital banking system. Another point is that banks expansion has attained saturation period in recent period.
2. At 5% level of significance t test shows the probabilistic significance as 0.482 which is greater than 0.05 (prescribed). Hence the hypothesis is accepted and it may be concluded that the Deposits of the scheduled commercial banks differ significantly before and after the global financial crisis. This is because of tightening financial conditions due to low deposit growth and the initiatives taken by the bank in accelerating the rate of economic growth and disposable income, holds the key to higher deposit mobilization.

3. At 5% level of significance t test shows the probabilistic significance as 0.482 which is greater than 0.05 (prescribed). Hence the hypothesis is accepted and it may be concluded that the Investments of the scheduled commercial banks differ significantly before and after the global financial crisis. The difference in interest rate for investments plays a major role for the investors. There was a decline in investments during 2003-2008 but due to reforms in interest rates the investment pattern gradually grows in recent years.
4. At 5% level of significance t test shows the probabilistic significance as 0.482 which is greater than 0.05 (prescribed). Hence the hypothesis is accepted and it may be concluded that the Loans and Advances of the scheduled commercial banks differ significantly before and after the global financial crisis. The loans and advances initially show a decline after the crisis and there was a gradual improvement due to the steps taken by RBI in improving the economy.

**Conclusion:**

The experience gained by banks across various countries post recent global financial crisis has given another opportunity to the banking sector to review and renew its approach towards factors decisive to its extant working and future sustenance. A lot of loans currently classified as NPAs originated in the mid 2000s at a time when the economy was booming and business outlook was very positive. Large corporations were granted loans for projects based on extrapolation of their recent growth and performance. With loans being available more easily than before, corporations grew highly leveraged, implying that most financing was through External Commercial

Borrowings rather than internal promoter equity. But as economic growth stagnated following the global financial crisis of 2008, they repayment capability of these corporations decreased. This contributed to what is known as India's Twin Balance sheet problem, where both the banking sector (that gives loans) and the corporate sector (that takes and has to repay these loans) have come under financial stress. When the project for which the loan was taken started underperforming, borrowers lost their capability of paying back the bank. The banks at this time took the practice of 'ever greening', where fresh loans were given to some promoters to enable them to pay off their interest effectively pushed the recognition of these loans as non-performing to a later date, but did not address the root causes of their unprofitability which affect their regular banking business of deposits, loans and advances and investment in growth aspect.

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# योगदर्शने अष्टाङ्गयोगकला

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(**विषयसारांशः** – योगशास्त्रस्य विषयो भवति मुक्तिः। कैवल्यं वा समाधिः। योगशास्त्रे उक्तम् - 'योगश्चित्तवृत्तिनिरोधः' योगः समाधिः अर्थात् समाधिलाभायास्माकं किमपि कर्तव्यम्। तत्तु भवति अष्टाङ्ग(अष्ट+अङ्ग)योगस्य क्रियाणां पालनम्।)

प्रकृतधर्मः साधनसापेक्षः। धर्मस्य मूलं साधना, अतः धर्मः न तु केवलं वितर्कः, विचारः, आलोचना, मतभेदा इति। अपि तु यत्र शास्त्राणां युक्तिविचारस्य समाप्तिः, ततः धर्मस्य सूचना भवति। निरपेक्षः, परमसत्यस्य साक्षादुपलब्धिश्च एवं जीवनस्य प्रात्यहिककर्मणामन्तरे ईश्वरीयभावस्य प्रकाशनमेव धर्मः। मानवात्मनः ब्रह्मस्वरूपस्योपलब्धिः, आध्यात्मिकचरित्रसंघटनम्, आध्यात्मिकसत्ये प्रतिष्ठापनञ्च जीवनधर्मस्योद्देश्यम्।

**योगः –** संस्कृतभाषा अत्र धर्मानुष्ठानिककार्ये परिलक्ष्यते। शारीरिकस्य नैतिककार्यप्रणालीनाञ्च प्रतिपालनं योगशास्त्रस्य सर्वप्रथमा शिक्षा। हिरण्यगर्भः योगस्य प्रथम उपदेष्टा इति। तद्योगमाश्रित्यैव महर्षिपतञ्जलिना प्रणीतं पातञ्जलयोगदर्शनम् अथवा योगसूत्रम्। महर्षिपतञ्जलिः शेषनागस्य अवतारो वर्तते। युजिर् योगे इत्यस्माद्धातोः घञ् प्रत्यये योगशब्दो निष्पन्नः। चिन्तनं मानवानां धर्मः। यदा मानवः विविधचिन्तनेभ्यो विमुक्तो भवति तदा विमुक्तचिन्तनस्य मानवस्य मनो लयावस्थां प्राप्नोति, सैवावस्था योगनाम्ना प्रत्याख्याता। योगशास्त्रं मुख्यतः दैहिकं, मानसिकं, आध्यात्मिकविज्ञानप्रबोधकञ्च भवति।

योगशास्त्रस्य विषयः शास्त्रभेदेन सम्प्रदायभेदेन च बहुप्रकारकः भवति। तन्त्रे उक्तम् – शिवशक्त्योः मेलनमेव योग इति। इतोऽपि योगस्य सप्तदश स्वरूपाणि दृश्यन्ते। योगस्य अष्टौ अङ्गानि सन्ति। यथा - 'यमनियमासनप्राणायामप्रत्याहारधारणाध्यानसमाधयोऽष्टावङ्गानि' –योगसूत्रम् 2.29

पुनः अष्टावङ्गानि द्विविधानि। यथा - 1) बहिरङ्गम् – यमः, नियमः, आसनम्, प्राणायामः, प्रत्याहारः।

2) अन्तरङ्गम् – धारणा, ध्यानम्, समाधिः।

**यमः –** 'अहिंसासत्यास्तेयब्रह्मचर्यापरिग्रहा यमाः' योगसूत्रम् 2.30

अर्थात् अहिंसा, सत्यम्, अस्तेयम्, ब्रह्मचर्यम्, अपरिग्रहः इत्यादयः पञ्च यमाः। यो 'महाव्रतः' इति नाम्ना अभिधीयते।

अहिंसा – अहिंसा शब्दस्य अर्थः प्रेम इति। जीवहत्या न करणीया, अपरस्य हानिः न करणीया, अपरस्मै कष्टं न दातव्यम्। अहिंसा शब्दो भवति कायिकः वाचिकः मानसिकश्च।

मानसिकाहिंसा – आत्मवत्सर्वभूतेषु अर्थात् सर्वभूते(प्राणिसमूहः) एक एव आत्मा इति चिन्तनीयम्। कस्मै अपि कदापि मानसिककष्टं न देयम्।

वाचिकाहिंसा – कदापि कठोरवचनं न वक्तव्यम्। अर्थात् कटुवचनद्वारा यस्य कस्यापि हृदयोपरि कष्टं न देयम्। सर्वदा मधुरं, प्रियं, हितकारि, आनन्ददायकं, उत्साहवर्धकञ्च वचनं वक्तव्यम्।

कायिकाहिंसा – शस्त्रेण कोऽपि कदापि न पीडितव्यः। शारीरिकनिर्यातनं न करणीयम्। सुखभोगलाभार्थं जीवहत्या न करणीया। जीवहत्या महापापम् इति चिन्तनीयम्। "अहिंसा-प्रतिष्ठायां तत् सन्निधौ वैरत्यागः"

सत्यम् – सत्यवचनम् इत्युक्ते सिद्धवाणी। सत्यपालनेन साधकस्य अन्तः एकः आध्यात्मिकशक्तिः जागरिता भवति। साधकस्य मनः दर्पण इव भवति अतः लोभः, क्रोधः, मोहः, रागः, दोषः, भयम्, मिथ्याभाषणम्, मिथ्याचरणं सर्वं वर्जनीयम्। शास्त्रे उक्तम् –

सत्यं ब्रूयात् प्रियं ब्रूयात् मा ब्रूयात् सत्यमप्रियम्।

प्रियञ्च नानृतं ब्रूयात् एष धर्मः सनातनः।।

अर्थात् सत्यं वाक्यं वक्तव्यं परन्तु शब्दः प्रियः मधुरश्च भवेत्, परन्तु प्रियम् असत्यभाषणं न वक्तव्यम्। यथा नेत्रहीनं जनं कदापि अन्धं न वदेत्। तत्तु सत्यम् इति सर्वे जानन्ति परन्तु तत् अप्रियम्। इति हेतोः अन्धजनः सुरदासः इति नाम्ना आह्वातव्यः। महर्षिवाल्मीकिः रामस्य आचरणविषये उवाच – 'रामो द्विर्न भाषते' अर्थात् श्रीरामचन्द्रः कदापि असत्यभाषणं न कृतवान्। शास्त्रे उक्तम्- 'सत्यमेव जयते नानृतम्'। सत्यकर्मणार्थं साधकजनः मानवाय एकं राजपथं कृतवान् – 'महाजनो येन गतः स पन्थाः' अर्थात् महत्पुरुषस्य पन्थाः तस्य आचरणं च सर्वश्रेष्ठं तथा योग्यम्। अतः मनुष्यस्य अपि तथैव करणीयम्। तत्तु कर्तव्यं तथा धर्मः।

अस्तेयः – स्तेयशब्दस्य अर्थो भवति चौरकार्यम् अर्थात् अस्तेयः नाम अचौर्यकार्यम्। अतः अपरस्य वस्तुनि लोभः मोहः क्रोधश्च न करणीयः। अपरस्य किमपि वस्तु अनत्तवा न हरणीयम्।

ब्रह्मचर्यम् – सनातनधर्मस्य श्रेष्ठः शिष्टाचारः ब्रह्मचर्याश्रमः। (ब्रह्म+चर्य) ब्रह्मचर्य इत्युक्तौ निवासः। अर्थात् ब्रह्मचर्यशब्दस्य अर्थः विचरणं, नारीस्मरणं, नारीचर्चा, सौन्दर्याकर्षणं, भोगविलासः, ऐकान्तिकमेलनं, मैथुनादिब्रह्मचर्यस्य वैशिष्ट्यं नास्ति। एतद् भवति बौद्धिकब्रह्मचर्यम्। अश्लीलगीतश्रवणं गायनञ्च, अश्लील-उपहासः सौन्दर्यस्य स्तुतिः निन्दायाश्च वर्जनं भवति वाचिकब्रह्मचर्यम्। अनन्तरं नारीस्पर्शः आलिङ्गनं, चुम्बनं, रोगावस्थादि शारीरिकब्रह्मचर्ये न भवति।

अपरिग्रहः – शब्दस्पर्शरूपरसगन्धादिसम्बद्धं किमपि भोगवस्तु न स्वीकरणीयम् इति अपरिग्रहः तथा स्वल्पे तुष्टिः इति।

**नियमः** – 'शौचसन्तोषतपःस्वाध्यायेश्वरप्रणिधानानि नियमाः' (योगसूत्रम्.2.32) अर्थात् शौचम्, सन्तोषः, तपः, स्वाध्यायः, ईश्वरप्रणिधानम् एते पञ्च नियमा भवन्ति।

1. शौचम् – शौचं द्विविधं यथा – बाह्यम् आभ्यन्तरञ्च। गोमुत्रं, त्रिफला, रीठा, सुगन्धिवस्तु स्वीकृत्य स्नानादिकार्यं भवति बाह्यशौचता। अनन्तरं मनसि अहंता, ममता, रागः, द्वेषः, ईर्ष्या, भयम्, कामः, क्रोधादि भवति आभ्यन्तरशौचता।
2. सन्तोषः – सुख-दुःखम्, लाभ-क्षतिः, यश-अपयशः, सिद्धि-असिद्धिः, अनुकुलता-प्रतिकुलता सदा-सर्वदा सन्तुष्टः प्रसन्नचित्तो वा भवति चेत् सन्तोषो भवति। येन केनचित् सह दुर्व्यवहारः परित्यक्तव्यः।
3. तपः – मन-इन्द्रियादि-संयमेन धर्मपालनार्थं कष्टसहनेन व्रताद्यनुष्ठानकरणं भवति तपः। बुभुक्षातृष्णाशीतोष्णादीनां सहनं तथा एकादशी-अमावस्या-पूर्णिमासु व्रतादिपालनं भवति तपः।

4. स्वाध्यायः – कल्याणप्रदशास्त्राणाम् अध्ययनं इष्टदेवमुद्दिश्य मन्त्रजपादिकरणम् ओङ्कारगायत्रीमन्त्रादिपठनं वेदोपनिषद्गीतापुराणादीनामध्ययनं भवति स्वाध्यायः।

5. ईश्वरप्रणिधानम् – अस्माकं जीवने सर्वकर्म(बुद्धि-वाणी-शरीरद्वारा सृष्टम्) ईश्वरस्योपरि समर्पणीयम्। प्रणिधानशब्दः भक्तिविशेषः, तस्य अर्थो भवति अर्पणम्। अर्थात् कर्म-कर्मफलं सर्वम् ईश्वरस्य चरणकमले अर्पितं भवति ईश्वरप्रणिधानम्।

**आसनम् –** पातञ्जलयोगसूत्रे उक्तम् - 'स्थिरसुखमासनम्' (योगसूत्रम्.2.46) अर्थात् सुखपूर्वकं स्थिररूपेण बहुकालपर्यन्तम् उपवेशनं भवति आसनम्। 84 लक्षम् आसनानि सन्ति। किन्तु केवलं 33 आसनसमूहः मुख्यरूपेण चिन्तितः योगिभिः। योगासनं हठयोगस्य एकं महत्त्वपूर्णम् अङ्गम्। योगासनं मानवानां कृते अधुना बहु उपयोगि भवति। शारीरिकमानसिकाध्यात्मिकस्वास्थ्यलाभाय योगासनं सरलं साधनम्। नियतरूपेण प्रतिदिनं योगासनस्य अभ्यासेन अस्माकं मनः एकाग्रं भवति। शरीरं सम्यक् भवति धैर्यता स्फूर्तिः साहसश्च आगच्छति। यथा – सूर्यनमस्कारः, पद्मासनं, सिद्धासनं, भेकासनं, वज्रासनं, नटराजासनं, हलासनं, धनुरासनं, नौकासनं, सर्वाङ्गासनं, शीर्षासनम् इत्यादयः।

**प्राणायामः –** 'तस्मिन् सति श्वासप्रश्वासगतिविच्छेदः प्राणायामः' (योगसूत्रम्.2.49) अर्थात् आसनान्तरं श्वासवायोः अन्तः प्रेषणम् एवं अन्तस्थवायोः बहिःप्रदेशे निष्कासनं भवति 'श्वासप्रश्वासः' तथैव प्राणशब्दः भवति वायुः, आयामः इत्युक्तौ नियन्त्रणम्। अर्थात् श्वासवायोः नियन्त्रणं भवति प्राणायामः। प्राणायामः त्रिविधः यथा – पूरकः, रेचकः कुम्भकश्च। पूरको भवति श्वासवायोः बहिः प्रदेशात् अन्तः प्रेषणम्। रेचको भवति अन्तस्थश्वासवायोः बहिः प्रदेशे निष्कासनम्। कुम्भको भवति पूरके गृहीतम् अन्तःस्थितवायोः उदरभागे स्थापनम्।

प्राणायामद्वारा मस्तिष्कं जागरितं भवति। तस्य विकारः दूरीभूतो भवति। इतोऽपि पिट्टुइटारि ग्रन्थिः विकसितो भवति। योगसाधकजनानां कृते प्राणायामः प्रयोजनीयः। प्राणायामद्वारा तेषां व्यक्तित्वं निर्मितं भवति।

**प्रत्याहारः -** 'स्वविषयासंप्रयोगे चित्तस्वरूपानुकार इवेन्द्रियाणां प्रत्याहारः' (योगसूत्रम्.2.54) प्रति+आहारः = प्रत्याहारः(भोजनस्य अन्ते) शब्दस्पर्शरूपरसगन्धाः एते इन्द्रियाणां भोजनानि सन्ति। यदा इन्द्रियेण साकं मनसः मेलनं भवति तदा विषयेण सह एकीभूतानन्तरं विषयज्ञानं न भवति।

**धारणा –** 'देशबन्धश्चित्तस्य धारणा' (योगसूत्रम्.3.1) अर्थात् धारणा भवति धारणम्। यदा मनसि किमपि वस्तु धारयितुं योग्यता भवति एवञ्च किञ्चित् समयपर्यन्तं तत् स्थिररूपेण स्थापनं क्रियते तदा धारणा भवति। धारणा भवति मनसः विकसितः शक्तिः। धारणाशक्तिं विना योगशक्तिः न भवति। धारणाशब्दस्यार्थो भवति संयमः। संयमशब्दस्यार्थो भवति वस्तुविशेषज्ञानम्। अतः धारणा या मनसः विचरणस्थानं सीमितं निश्चितञ्च करोति।

पञ्चतत्त्वधारणा – पञ्चतत्त्वधारणा भवति पृथिव्यप्तेजोवाय्वाकाशाः। पञ्चतत्त्वात् प्राणिजगतः सृष्टिर्भवति। अस्माकं शरीरे पञ्चतत्त्वस्य साम्यावस्था भवति तस्य फलस्वरूपं भवति अस्माकं सुस्वास्थ्यजीवनम्।

**ध्यानम् –** पातञ्जलयोगसूत्रे उक्तं यत् – 'तत्र प्रत्ययैकतानता ध्यानम्' (योगसूत्रम्.3.2) धारणात्परं यदि धारणीयपदार्थे चित्तवृत्तेरेकतानता भवति तर्हि तद् 'ध्यानमि' त्युच्यते। धारणाद्वरा स्मरणशक्तिः मेधाशक्तिश्च वर्धते। सर्वविधविषयमवगन्तुमर्हता भवति। इतोऽपि मानसिकैकाग्रता वर्धते।

मन्त्रजपः – मन्त्रविज्ञानमतिप्राचीनम्। मन्त्रस्योल्लेख्यविषयो वेदशास्त्रे वर्तते। मन्त्रशब्दस्य अर्थो भवति 'प्रकटध्वनिः' योगिनो ध्यानावस्थायां मनसा मन्त्रजपं करोति। परन्तु तस्य ध्वनिस्तरङ्गसदृशः न तु मन्त्रः। मन्त्रेण शक्तेस्तथा नवजीवनस्य प्राप्तिर्भवति। यथा – शिवमन्त्रो वैराग्यभावनां वर्धयति। केषाञ्चिन्मते जपो विविधो भवति। यथा – 1) वाचिकजपः 2) उपांशुजपः 3) नित्यजपः 4) चलजपः 5) अखण्डजपः 6) अजपाजपः इत्यादि।

**समाधिः –** 'तदेवार्थमात्रनिर्भासं स्वरूपशून्यमिव समाधिः' (योगसूत्रम्.3.3) मानवजीवनस्यैकमात्रं लक्ष्यं भवति समाधिः। परन्तु समाधिशब्दस्यार्थः केनापि सम्यग्रूपेण ज्ञायते। समाधिशब्दस्यार्थो भवति चित्तस्य समाधानम्। समाधेर्लक्षणं भवति ज्ञानम्। पूर्णज्ञाने सति समाधिर्भवति। सर्वे समाधिं प्राप्तुमिच्छति। कोऽपि समाधिं प्राप्नोति चेत् तस्य चरित्रं ज्ञानं चैतन्यञ्च परिवर्तितं भवति। कस्मिन्नपि विषये धारणा, ध्यानादनन्तरं विषयसम्बन्धिपूर्णज्ञानं भवति चेत् समाधिर्लभ्यते।

**उपसंहारः** – सर्वश्रेष्टजन्म मनुष्यजन्म। अतः मिथ्याजगतं प्रति आसक्तित्यागः प्रयोजनम्।अस्माकं जीवनस्य लक्ष्यं भवति कैवल्यम्। तर्हि योगस्य अष्टाङ्गकलायाः आचरणेन ईश्वरस्य साक्षात्कारः परमतत्त्वज्ञानप्राप्तिश्च भवति।

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# SABARIMALA TEMPLE CASE : A THOUGHTFUL INTROSPECTION

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Given below are some thoughtful insights which may be analysed in the present Sabarimala Temple Case

## MAINTAINABILITY OF THE PETITION –

Article 32 of the Constitution of Vindhu lays down that ;
*32. Remedies for enforcement of rights conferred by this Part*
*(1) The right to move the Supreme Court by appropriate proceedings for the enforcement of the rights conferred by this Part is guaranteed*
*(2) The Supreme Court shall have power to issue directions or orders or writs, including writs in the nature of habeas corpus, mandamus, prohibition, quo warranto and certiorari, whichever may be appropriate, for the enforcement of any of the rights conferred by this Part*
*(3) Without prejudice to the powers conferred on the Supreme Court by clause ( 1 ) and ( 2 ), Parliament may by law empower any other court to exercise within the local limits of its jurisdiction all or any of the powers exercisable by the Supreme Court under clause ( 2 )*
*(4) The right guaranteed by this article shall not be suspended except as otherwise provided for by this Constitution*

A Public Interest Litigation can be filed, called PIL for the enforcement of fundamental rights that have been denied or breached. This is indeed the greatest weapon of judicial activism and a direct means of enforcing social equality as well, however it has its own limitations at the same time. It is imperative that the petitioner has suffered any particular damage, in order to file a PIL. Article 25 of the Constitution guarantees to all persons the freedom of conscience, and the right freely to profess, practise and propagate religion. This is however subject to public order, morality and health, and to the other provisions of Part III of the Constitution. In this case, the PIL can only be filed under Article 32 as violation of fundamental rights, if the petitioner's own rights have been violated in the temple. The filing of petition is flawed as it urges upon the Court to decide a matter that can be decided and managed by the religious sect or denomination exclusively. By interfering with the religious rights of a community the Court cannot judge a case where the petitioner does not ascribe to the faith being dealt with and questioned. This is a question of faith more than an issue of Equality, because if women claim equality to enter the temple, the temple and the sect thereof will also claim the protection given to them under Article 25. The issue cannot be adjudicated on the basis of Article 14 because it cannot be applied ;
Two conditions are required to apply Article 14;
• The classification must be founded on an intelligible differentia; and

• It must have a rational nexus with the object sought to be achieved by the impugned law.

In this case the differentia needs to be analysed from the point of view of the class of people following the rituals at Sabarimala temple and women who seek equality. Since the right of women to enter the temple is in dissonance with the religious freedom of the sect , the court needs to review the religious practice, which would be a breach of the fundamental religious right of the sect. A judicial review of the practices at the Sabarimala temple is not possible by the Court as the Constitution has already granted that degree of freedom to the sects. Second of all, the question of equality of women in entering and worshipping in the Sabarimala temple cannot be considered. This is because the demand placed in front of the Honourable Court can be fulfilled only at the cost of the nature of the deity. In order to enter the temple to worship, the faith and respect in the decorum of the temple and the respective nature of the deity needs to be preserved. Ironically that would be desecrated the moment they deny the nature of the deity and enter. Hence this petition is not only ambiguous but also attempts to strike at the group autonomy and collective conscience o0f a group involved in practising their respective religious freedom. Secondly , the petition has been filed by non believers and non followers of the sect being put to question. In this case Article 14 cannot be applied, and the PIL cannot be considered. As religion as a fundamental right is protected by the Constitution itself, Courts normally do not delve into the intricacies of religious affairs, as that would be unconstitutional. It can only act if an aggrieved person from that sect petitions or brings a complain.

Another matter which assumes importance is that whether the petitioners can at all file this petition or not ? A famous case in this regard needs to be taken into consideration:

*Hans Muller of Nurenburg v. Superintendent, Presidency Jail, Calcutta & Ors*[1]

In this case, Court held that a person can impugn a particular law under Article 32 only if he is aggrieved by it.

Hence it becomes imperative that petitioners have suffered, which is clearly not the case here. Secondly as the petitioners are non believers of the faith, hence the Court cannot adjudge a case at the cost of harming the faith of any sect, and if women want to worship and they claim faith in the deity or the temple, then that needs to be followed strictly according to the prescribed rules of worship, not by altering the modus operandi of worship completely.

In a pluralistic society if religious freedom and unique religious practices are brought under the lens of scrutiny of rationality or judicial review, a serious harm would be inflicted upon the faith and the constitutional right to defend it. Where diversities need to be respected by giving them respective freedom, such a step would harm communal harmony. By encouraging such PILs, minority communities and their freedom to profess religion would be seriously hampered, at the same time the degree of autonomy with which the religious affairs of a sect is managed will be compromised, all leading to a socio cultural dissent. In this way the incorporative state would soon give

[1] (1955) 1 SCR 1284 : AIR 1955 SC 367.

way to rigid rational judgements obliterating age old traditions. Not every religious aspect can be perfected by rational thinking of this century, certain things are best left to faith, and certain observances are simply the product of faith and should not be challenged for grater harmony.

**THE QUESTION OF DISCRIMINATION -**

Article 26 of the Constitution of India states that:

Freedom to manage religious affairs Subject to public order, morality and health, every religious denomination or any section thereof shall have the right
(a) to establish and maintain institutions for religious and charitable purposes;
(b) to manage its own affairs in matters of religion;
(c) to own and acquire movable and immovable property; and
(d) to administer such property in accordance with law

In the present case, Sabarimala temple and its devotees can defend their own customary practice by the power bestowed upon them by the Constitution itself. Followers and the worshippers of Sabarimala temple constitute a distinct sect by virtue of belonging to a common deity, a common name for their sect, a common place for worship and hence it is in their best interest to determine, practice and propagate their distict faith. Before debating on the practice being discriminatory or not, the Constitutional protection that the devotees at Sabarimala get, needs to be taken into consideration.

In the famous case of
*S.P. Mittal Etc*. **v.** *Union of India And Others*[2],
*The Honourable Supreme Court held in this case that in case of a religious denomination, there are two prerequisites for such a qualification, one being a set of rituals and the other being common organisation as designated by a common name in this regard. Sabarimala devotees do conform to these necessary preconditions and hence need to be recognised as a denomination. In this regard the exclusionary practice has to be understood as an essential condition or a discipline pertaining to the deity presiding over the temple of Sabarimala- LORD AYAPPA. The deity in this temple is in the form of a Naishtik Brahmachari- which means a state of being a perennial celibate. Celibacy is a vow to abstain from marital relationships and remaining in one's own penance to achieve spiritual upliftment and emancipation. Yajnavalkya Smriti* explains this form;
**a naishtika brahmachari is one who undertakes a vow to remain a celibate till his death**.
In addition to this, there is a requirement of the person being seated in position and an extreme degree of control over the senses, called – ""*vijitendriya*". It also involves sense control over, eyes, ears, mouth (and tongue), nose, skin, hands, legs, reproductive organ

[2] **(1982) 1983 AIR, 1 1983 SCR (1) 729**

and excretory organ and mind. Hence it is expected that such a person would completely abstain from coming into contact with women of the reproductive age.It is a regulation to keep the person away from any source conducive to procreation.

The second aspect to be taken into consideration is the deity bestowed with human like qualities, the combination of mundane characteristics with a sense of divinity being involved. Agama Shastras elucidate on the importance of temples and the associated deities in them. Deities are and possess a distinct character of their own, and when a temple they are subjected to conditions as are human beings subjected to. In the case of *Sri Adi Visheshwara of Kashi Vishwanath Temple, Varanasi, vs State of UP*[3], it was held that :

Deities can own property with their interests vested in them, and priests would simply have the role of managing the estates owned. The rulings in Court indicate the intention of Courts to recognise deities as persons or rather "legal persons "as stated under Article 21 of the Indian Constitution. There have been circumstances where deities have been involved into legal battles thereby affirming their existence as persons. In this sense the deity has the right under Article 14 to have its fundamental rights properly preserved. Being a Naishtik Brahmacharya, it is his fundamental requirement to abstain from women of the prescribed age group, hence the regulation prohibiting the entry of women of a certain age is not discriminatory but rather an exercise of a right by the deity.

The situation must be viewed keeping in mind not just some fabricated feminist issues but the considerations of a pluralist society that keeps different religions together in a framework of society. It is a question of faith and the perspective matters the most in this case, while at the same time issues of social importance need to be adjudged at the same time. In this particular instance, the question of discrimination is void ab initio as it is a matter of personal right of the devotee and of the section therein devoted at the same time. While not allowing women of a particular age group might seem discriminating, but it needs to be judged from the circumstantial point of view. Indian Constitution has awarded each section propagating their religion, the freedom to do that. Indian state is incorporative of distinct individualities; it respects religious sects and practices maintaining a non interfering secular ground.

Speaking of discrimination, Article 15 provides;

*Prohibition of discrimination on grounds of religion, race, caste, sex or place of birth*

*(1) The State shall not discriminate against any citizen on grounds only of religion, race, caste, sex, and place of birth or any of them*

*(2) No citizen shall, on grounds only of religion, race, caste, sex, place of birth or any of them, be subject to any disability, liability, restriction or condition with regard to*

*(a) Access to shops, public restaurants, hotels and palaces of public entertainment; or*

*(b) The use of wells, tanks, bathing Ghats, roads and places of public resort maintained wholly or partly out of State funds or dedicated to the use of the general public*

*(3) Nothing in this article shall prevent the State from making any special provision for women and children*

[3] [1997 (4) SCC 606

*(4) Nothing in this article or in clause (2) of Article 29 shall prevent the State from making any special provision for the advancement of any socially and educationally backward classes of citizens or for the Scheduled Castes and the Scheduled Tribes*

In the sub clause (1), the grounds are explicitly specified. And the case of Sabarimala does not fit in with any of these grounds mentioned. The selective prohibition is hence not amounting to discrimination, rather conformity with a custom of antiquity and a mark of reverence to the presiding deity at the temple. If women as a class were prohibited from participation, it would amount to social discrimination. However, this is not so in the present case. Girls below 10 years, and women after 50 years can freely enter this Temple, and offer worship. The classification of women between the ages of 10 to 50 years, and men of the same age group, has a reasonable nexus with the object sought to be achieved, which is to preserve the identity and manifestation of the Lord as a 'Naishtik Brahmachari'. This prohibition can in no stretch of imagination be considered to be derogatory to women, as it is but for the sake of the deity to be worshipped. A deity is the sole essence in a temple . IT needs to be understood that the concept of GOD is a western influence, while Hinduism specifies 33 types of Gods and at the same time allows for devotion at an individual level in any condition. People can practice and meditate in at their own liberty but a temple is a place of practising spiritual advancement. A temple seeks to fulfil a spiritual purpose and hence the entire *Agama Shastras* delineate on the modus operandi of worship and the subsequent construction of temples. When viewing a temple, the focus is on the deity, towards whom a devotee's prayers are addressed to. The deity is a manifestation of the spiritual enigma that a devotee seeks op obtain as a result of his systematic prayers, a deity is a guide or a revelation that simplifies the object of devotion. It is a way in which a person can focus the objective of his meditation. In situations where a devotee observes penance, hardships, it is again the deity that will show him the purpose he is striving towards. It is a simplification of a complexity beyond discretion, an idol serves as a symbol, a motif or an image representing the abstract conception of the omnipresent god. The idol worship focussing on the deity of a temple constitutes an essential element of religion of Hinduism.

In this sense,

*" With the growth of anthropomorphism came the increased use of images and the construction of temples for daily services. Icons were known to the ancient people of the lower Indus Valley, and stray allusions to images have been traced in some Vedic texts. But the first undoubted historical reference to image worship by an Aryan tribe occurs in a passage of Curtius, who states that an image of Heracles was carried in front of the Paurava army as it advanced against Alexander. Patanjali refers to the exhibition and sale of images of Siva, Skanda, and Visakha by the Mauryas who rose to power at the end our period. Temples of a primitive kind are mentioned already in the Satapatha Brahmana, but these were not meant for iconic worship. In the epic, however, we have clear references to temples sacred to deities."*[4]

[4] R.C Majumdar, An Advanced History of India,3rd edition

Hence history bears sufficient testimony to the fact of a residing deity and connected idolatry. Apart from this , there is a significant case confirming the importance of deity ;

*Tilkayat Shri Govindlalji Maharaj etc. v. State of Rajasthan & Ors.*[5],
A cutting emphasis was laid on the types of rituals to be performed when Lord Krishna was worshipped in the form of a child. This shows that religion does not merely lay down a code of ethical rules for its followers to accept, but also includes rituals and observances, ceremonies and modes of worship which are regarded as integral parts of the religion. Worship and devotion cannot emanate out of nowhere, they need a material manifestation and that is precisely provided by the associatyed rites and rituals. These rituals are organised on the basis of the deity to be worshipped and therein lies the importance of the nature of a deity. In this case, Sabarimala temple's associated rituals are centred on the nature of the presiding deity, who is a celibate. At the same time it is his nature that needs a complete abstinence from women. The perspective is protection and preservation of the deity and his rights as embodied by Article 21 and Article 14 of the Constitution, not the women and their entrance in the temple.

Worship is comprised of two cardinal aspects, one being the worshipper and the other being the worshipped. In this case both of them have the right to protect their interests and which they are doing by exercising the selective prohibition. Hence the said practice does not amount to discrimination.

## RIGHT OF THE TEMPLE AUTHORITY

The Government of India is considered a parliamentary democracy. The country consists of 29 states and accommodates various religious, racial, traditional and linguistic groups and their values and customs. As such the culture is a melting pot of diversities in which each individual wants to conform to one's own belief system. Sharing such a belief system by a group of people gives rise to a collective conscience. It is again implied that there are more than one such group with their own interests. Being a democracy , the Government is elected by the people and it caters to the needs of the people as well.In this situation , the fundamental objective of the Constitution would be to secure individual rights of the people. Since people are different, hence matters concerning them need to be judged from their respective point of views.Article 26 states that ;

*Freedom of conscience and free profession, practice and propagation of religion*
*(1) Subject to public order, morality and health and to the other provisions of this Part, all persons are equally entitled to freedom of conscience and the right freely to profess, practise and propagate religion*
*(2) Nothing in this article shall affect the operation of any existing law or prevent the State from making any law*

[5] (1964) 1 SCR 561 at 582 : AIR 1963 SC 1638

*(a) regulating or restricting any economic, financial, political or other secular activity which may be associated with religious practice;*
*(b) providing for social welfare and reform or the throwing open of Hindu religious institutions of a public character to all classes and sections of Hindus Explanation I The wearing and carrying of kirpans shall be deemed to be included in the profession of the Sikh religion Explanation II In sub clause (b) of clause reference to Hindus shall be construed as including a reference to persons professing the Sikh, Jaina or Buddhist religion, and the reference to Hindu religious institutions shall be construed accordingly*

The practice of restricting women of a particular age group from the temple of Sabarimala, serves to protect the dignity of the deity . Religion is deeply connected with beliefs and is intricately woven with the character of a deity who is being worshipped. In the case of the deity, his being a Naishtik Brahmacharya restricts him from the presence of women. That he does not or will not come in contact with women is a matter of faith that many believe in . As people worship the deity , the sacrosanct force is the nature of the deity and that cannot be breached. Allowing women to enter would be desecrating the divinity and the nature of deity, subsequently a sacrilege meted out to the worshippers at Sabarimala temple, as it needs to be analysed how important it is to maintain this selective ban for the collective conscience of the group following the religion and the deity's nature thereof. In this sense , the non allowance of women forms an essential practice because the deity being a celibate abstains from women of the procreative age. It is not because of some biological phenomenon of menstruation that makes them impure, it is rather a requirement of the deity for the sake of preserving its nature and celibacy. The practice forms a part of the religious rights of the sect of people worshipping inside Sabarimala and a continuation of this ban would be important in the light of the faith that they keep in the shrine, thereby directly relating it with Articles 25 and 26 of the Constitution. In order to prove that the exclusion is indeed a part of religious affairs, certain case laws need to be considered.

In subsequent rulings , Indian judiciary has upheld religious rights of the people of the country in accordance with Article 25 and Article 26 of the Indian Constitution. In the case of *John Vallamattom v. Union of India*[6]*;*
It was held that any religious practice integral to any religion would be protected, as considered sacred by belief. In the case of *Dara Singh v. Union of India*[7] *;*
The State would not unnecessarily interfere in the religious matters of any particular religion. In the case of Sabarimala, interference of a State is not only unnecessary but also unconstitutional as it seeks to alter an age old practice integral to the belief system of devotees and it implies State interfering and attempting to alter such customs as may be disrespectful to not only the deity and the sect worshipping at Sabarimala temple but

[6] AIR 200 SC 2902
[7] (2011) 2 SCC 490

at the same time to the sect who believe in the deity . This interference would mean a breach of Article 25 and 26 of the devotees and that would be unconstitutional.

With respect to customs, these are practices which have been followed since antiquity and often they become an integral part of a religious practice. These customs define ways of rituals and other practices surrounding worship. In the case of
*Krishna Singh v. Mathura Ahir*[8]*;*
The Court refused to interfere with a particular custom and refused to alter it in its judgement.
Thus case serves as an essential precedent for our present case. The custom of women of a particular age not entering the Harimala temple is not simply old but it is integral to the nature of the Deity and the faith in celibacy of the devotees. In the famous case of
Acharya Jagdhishwaranand Avdhut v. Commissioner of Police, Calcutta[9] :
The court refused to alter or prevent the practice of a special kind of dance that was an integral customary practice of the religion and formed a part of the faith as well.

One important aspect that needs to be brought under the lens is that of the Constitutional morality. The Constitution serves to protect all the communities by granting them basic freedoms in their respective ambits of religious activities. A community is protected to ensure its continuance; hence the belief systems of a community are subsequently protected as well. In the case of ;
*Ratilal Panachand Gandhi v. The State of Bombay & Ors ;*
It was held that all essential practices in the pursuance of the religion would also amount to be a part of the religion itself.
The practise of celibacy and austerity is the unique characteristic of the deity in the Sabarimala Temple. Hindu deities have both physical and philosophical form. The same deity is capable of having different physical and spiritual forms or manifestations. Worship of each of these forms is unique. In this case the form of deity is celibate, requiring complete abstinence from women and hence it is essential to regulate the entry of women as an important practice followed in the religion and course of worship. The main idea to be considered here in this case is that of the “Essentiality Test”. By means of this test , any practice or ritual or custom needs to be weighed as whether it is essential for the furtherance of the religion or continuation of worship or is it fundamental to its tenets. The Constitution has its own principle of morality in religious matters. It cannot apply rationality or morality to adjudge any ritual. On the other hand it needs to preserve such rituals as part of the religious rights of communities following it. The court is not the competent authority to determine the cardinality of a custom towards the religious sect, but it can only consider opinions centring around it. The thing will speak for itself just the way a custom of antiquity will speak the fact that it has been followed over a long period of time. The command and authority of a custom will help the Court determine its essentiality and need to remain unchanged. In this way it is evident that there are certain customs that need to b followed as being essential. In

[8] AIR 1980 SC707
[9] AIR 1984 SC 512

the same way the exclusion of women falls under such a religious practice as it will preserve the nature of the deity and thereby sustain the faith of the sect.

Since it is an important practice , hence it becomes a right of the sect to practice it as well. In this sense the aspect of Constitution needs to be judged as well. Equality and non-discrimination are certainly one aspect of Constitutional Morality. However, the concept of equality and non-discrimination in matters of religion cannot be viewed in isolation. Holding a concept of Equality alone for consideration would be an injustice to all those religious specifications that would get obliterated by morality from a non believer and non follower's point of view. At this juncture of argument it needs to be clarified that, Article 15 does not apply in this case, as the category of temples have been explicitly avoided in it, thereby hinting at the increased autonomy of religious affairs and their management. Further the article provides for the ground of 'sex' but in the case of Sabarimala temple , women as a sex are not banned from the temple, rather only a selective age group is , in conformity with the nature of the deity. In this case , to safeguard the religious customs, temple authorities can exercise this ban. It would definitely be included in the scope of power bestowed upon by the Article 25 and Article 26 of Constitution of India. In the case of *Bira Kishore Devi v.* State *of Orissa*[10]*;*
Administration of a temple is solely the responsibility of the temple authorities .
This brings us to the matter of administration of Sabarimala Temple; in this case the prohibition of women is in consonance with the customary traditions of the place,and since it is essential and important , it needs to be sustained at the same time. This impliedly becomes the sole responsibility of the temple authorities to perform.Hence the temple authorities can practice this prohibition, as it is an essential practice being followed. With the faith of a large group coalescing on the nature of the devotee, when the sect believes in Lord Ayappa as being a Naishtik Brahmachari, and they perform penances towards attaining spiritual emancipation from the enigmatic manifestation of Lord in his temple abode, it seems quite important for the authority to take all steps to maintain the decorum of the worship, and in this case the entry of women of the said age group directly clashes with the interests of the material form of the deity, and it becomes all the more a duty for the authorities to practice the regulation of prohibition.

## DENOMINATIONAL CHARACTER OF THE TEMPLE

The temple of Sabarimala has a denominational character as its followers have a common deity to be worshipped; they have common ritualistic observances and practices as well. The temple derives its denominational character by virtue of its organisation, and unique style of worship specific to this particular place. There are clear attributes that there exists identifiable features. These are in conformity with the accepted features and are as follows;
• Ceremonial law relating to the construction of Temples;
• Installation of Idols therein;

[10] AIR 1964 SC 1501

• Place of consecration of the principle deity;
• Where the other Devatas are to be installed;
• Conduct of worship of the deities;
• Where the worshippers are to stand for worship;
• Purificatory ceremonies and their mode and manner of performance;
• Who are entitled to enter for worship; where they are entitled to stand and worship; and, how the worship is to be conducted.

Keeping the accepted features of a denomination in mind, the devotees at Sabarimala do constitute a religious denomination, and are entitled to mange their own affairs as guaranteed by Article 26 of the Constitution. The devotees are expected to follow a 41-day austerity period called as 'Vritham' prior to the pilgrimage. This Vritham period unifies devotees into one common sect, persuing the penances to appease Lord Ayappa.They are expected to bath twice in a day and visit the local temples regularly only wearing plain black coloured traditional clothing. It is also believed that in order to achieve the purpose of the pilgrimage one has to take a hike through the traditional mountainous forest path which runs up to 61 kilometers. This journey is undertaken by the devotees together. They become unified as a sect . This sect is that of Lord Ayappa – with unique rites and rituals common to them.

In the following cases, it has been observed that the courts have defined religious denominations in a unified way , *Sardar Syedna Taher Saifuddin Saheb v. State of Bombay*[11], *Raja Bira Kishore Deb v. State of Orissa*[12], *Shastri Yagnapurushadiji and others v. Muldas Bhundardas Vaishya and another*[13]

The presence of a multiplicity of religions and religious practices makes it a Herculean task to determine the essential tenets of a religion and those parts of a religious practice which would be indispensable. Hence Judiciary has in he course of subsequent rulings established how the significance of certain religious practices need to be determined in the ligh of the religion being taken under consideration. In the famous case of ;

*Commissioner., Hindu Religious Endowments, Madras v. Sri Lakshmindra Thirtha Swamiar of Sri Shirur Mutt*[14],

The Supreme Court formulated the 'essentiality test' when defining religion. Certain aspects of a religion were to be identified as being central or cardinal to the practice and accordingly given importance. Hence the Courts need to take into account the perspectives and the people involved in a particular practice .Another case ;

*Sri Venkataramana Devaruand Others v.The State of Mysore and Ors*[15],held that ;

[11] [1962] Suppl. 2 SCR 496
[12] (1964) 7 SCR 32
[13] (1966) 3 SCR 242 : AIR 1966 SC 1119
[14] 1954 AIR 282, 1954 SCR 1005
[15] 1958 AIR 255, 1958 SCR 895

Although the restriction on a particular caste as a whole had been relaxed, but they were still prohibited to enter during certain special ceremonies as directed by the board thet manages the temple. In this case it has to be noted down that the Court had placed special emphasis on the Board managing the affairs of the temple and had recognised the customs of the temple to get an important consideration. In yet another case , *Durgah Committee, Ajmer v. Syed Hussain Ali*[16]*;*
It was held that no new religious right can be bestowed and given the protection of Article 25 . Only those rights which are present and covered under Article 25 can be given protection. Administration of one's religious affairs comes well under the ambit of Article 25 and the devotees at Sabarimala temple enjoy that right. Allowing women of the prescribed age group to enter the premises of the temple would amount to a breach of the right bestowed upon by the constititution.

The Constitution is not a fountainhead of morality that screens every possible aspect under the modern liberal lenses and reject anything that creates a dissonance with it. On the contrary Courts need to preside over an entire subcontinent divided by unique traditions, customs, belief and faiths, united by the Constitution. As the guardian of the Constitution, it acts as the legal protector of the people, a guarantee that each individual would be protected along with his interests.

Courts are expected to judiciously determine fundamental questions on the basis of the Constitution. Framed as a constitutional question, not allowing menstruating women to enter Sabarimala temple presents a conflict and a clash between the scope and extent of an individual's right to pray and a community's right to manage its own affairs of religion. It is a clash of competing autonomous aspects where judges must balance the claims made on the basis of what the Constitution demands. Treating a regulation of prohibition simply as unconstitutional and discriminatory may appear prima facie but myopic and constricted in judgement at the same time.

With regards to the unconstitutionality of the exclusion of Women, certain issues are to be considered, this is not an argument against the Courts interfering in religious practices on the touchstone of equality and non-discrimination. Quite the opposite: when marginalised groups within cultures or religions challenge oppressive norms or practices, more often than not, they will *need* an external authority, a protector who will guarantee the continuation of their religious practices and this role has to be taken up by the courts. In the case of *Riju Prasad v State of Assam,*it was held that ;
The provisions of protection of customs under Articles 25 and 26, are immune from challenges meted out by the part III of the Constitution.This ruling is significant in the sense that it seeks to uphold the group consensus that is created in a collective mass of people bound by their own common religious practices. Secondly this shows the true role of Judiciary as guaranteeing every individuality a chance to preserve itself in the fabric of the pluralistic society.

This establishes an important case law in this case. The custom of women not being allowed to enter cannot be seen as unconstitutional , rather it has to

[16] 1961 AIR 1402, 1962 SCR (1) 383

be conceived as a right granted to the deity under the Constitution. The Temple is a place of practising the rituals that are associated with devotion and the deity. In this sense a temple is definitely bound by certain rules and codes that need to be followed. The prohibition on the entry is such a kind of rule, that needs to be followed. Its the right perspective by which the situation is to be analysed. The question that has importance in this case is of guarding the nature of Sabarimala temple from an outer intervention that essentially questions faith from the eyes of a non believer.

Article 26 of the Indian Constitution secures the right of a religious institution to manage its own affairs, and the exclusion of women entails an essential practice.

Further, according to Article 25(1) ;
*Subject to public order, morality and health and to the other provisions of this Part, all persons are equally entitled to freedom of conscience and the right freely to profess, practise and propagate religion*

So in order to respect the nature of the presiding deity, a particular rule has been brought into practice. The aspect of discrimination is nullified by the fact that women in this case are not barred as a class or as a basis of their gender. Women below 10 and above 50 are gladly accepted into the temple. The distinction is quite pin pointed at a particular age group of women . So this does not amount to any unconstitutional discrimination. It was held in the case *Sri Venkatramana Devaru v. State of Mysore and others*[17]*;*
The temple cannot completely restrict a particular class of people,but can restrict entry of a section in certain rituals.

Article 25 is subject to Part III of the Constitution but Article 26 is subjected to only three conditions –public order , morality and health.As a result of which , the fundamental rights of the religious denomination are not subjected to Articles 14 or 15 of the Constitution. Furher , the practice of not allowing women into the premises of the temple is a managerial step by the temple committiees, as it is for the sake of preservation of the nature of the deity. Faith is deeply connected with reverence and this reverence is invoked by the nature of the deity inside the temple.Now the nature of the deity calls for abstenance from women. If in this case women are allowed to enter, it will not simply breach the freedom of religion enjoyed by the sect but at the same time amount to desecrating Varnappan deity and the decorum of the Harimala Temple at the same time. If the faith is insulted, it would hit at the entire community and duisrupt the group autonomy at the same time. It would therein be unconstitutional to breach the basic religious rights of a community. The freedom to profess their religion is covered under Article 26 and this is a constitutional safeguard to preserve the faith. In the land of diversities, the constitution has a greater duty to protect minority faiths not just from majority but also from floodgates of modern thought process. Any liberal ideology or modern thought cannot breach the pillars of faith which binds devotees by the threads of devotion , With religion being a right, faith and the belief that people bestow upon faith is also a right that they are entitled to enjoy, and if

[17] (1958) SCR 895 : 1958 AIR 55

thus faith of the minority section is humiliated then it would be the duty of the court to reinstate it .

Article 25.2(b) cannot be interpreted to mean that customs and practices sacred of a place can be easily overridden. Furthermore the claim of preventing the said section of people do not amount to discrimination, nor does Article 25.2(b) apply as women as a caste or sex have not been banned. It's just the women of reproductive age, symbolic of procreation who are banned and that too because the nature of the deity calls for to do so, and that it forms a part of the custom and belief that has been followed since time immemorial and command respect and allegiance as a matter of antiquity.

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# A CRITIQUE OF VICTORIAN MORALITY: A STUDY WITH REFERENCE TO GEORGE ELIOT'S LIFE AND WORKS

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**Abstract**

This paper is a critique of Victorian morality with reference to the life and works of George Eliot. George Eliot's primary interest in analysing a character from its moral perspective has provided her art of characterisation with a new height. She firmly believes that a human character is not cut in marble but it evolves as time passes. A chronological study of her novels reveals that almost all her major characters have not only evolved from egoism and moral blindness to strict morality and vision but they have questioned the double standards and hypocrisy of Puritan Morality of Victorian era.. In other words, the characters who are receptive to this positive growth have emerged as the leading figures in her novels.. Unlike her Victorian predecessors like Dickens and Thackeray, George Eliot's interest in analysing a character from moral and psychological perspectives has provided her art of characterisation with depth and endurance. The following chapters are devoted to discuss the literary craftsmanship and ingenuity of this great Victorian novelist.

**Key Words**:Character, Hypocrisy, Moral, Positive, Growth

## Introduction :

Born and brought up in an orthodox Christian family and influenced by her evangelist aunt Mrs. Elizabeth Evans, George Eliot used to attend churches in her youth . However, in her later years she became an intellectual lady and in course of time she lost faith in orthodox Christianity. It was only under her elite father's influence that she began to attend the church again. But eventually, she questioned the Christian concept of God, heaven and hell, and in the immortality of human soul. It was because George Eliot was a rationalist, she did not want to adhere herself to the irrational Christian concept. Instead she kept herself in touch with the development of the latest scientific, religious and philosophical thought of the age. Basil Willey, a celebrated critic, observes that there was no novelist like George Eliot who has epitomised the entire century in her novels beginning from the standpoint of `evangelical Christianity ' and ending to " religion of Humanity"

George Eliot, true to the consciousness of the century, had the instinct to tolerate the ordinary while admiring the ideal, to cling to the old while accepting the new and

retaining the core of tradition while criticising their forms. Sober conservative zeal and reforming impulse a"e the leading motive of her life; her lifelong quest was to achieve a synthesis between these two opposites, to harmonise the static and dynamic principles, tradition and enlightenment, the head and the heart. It is this tension which forms the basis of all her novels. George Eliot, before taking up novels as an expression of her creativity, immersed herself deeply in philosophical reflections; and the works which influenced her most were Charles Bray's *Philosophy of Necessity*, Spinoza's *Ethics*, and *Tractatus Theologico-politicus*, David Strauss's *Leben Jesu* and Feuerbach's *Das Wesen Des Christenthums (The Essence of Christianity).* Eventually she translated the books of David Strauss and Feue[r]bach into English for the common people. Though the works, referred to here, helped in shaping her *life* and thought, paradoxically enough, she never fully followed any of the ideas emanated from these works.

So, before Marian Evans adopted the pseudonym 'George Eliot' in 1857, she was already an experienced, and exceptionally well-read writer. She had made a modest living as an editor of the 'Westminster Review' and she was established as the companion of a married man, one of the most gifted intellectuals of the day, George Henry Lewes. After the acclaim accorded to *Adam Bede* in 1859, George Eliot, the intensely moral novelist, steadily eclipsed the immoral and Godless Miss Evans. In a sense that eclipse sprang from the very nature of her fiction.

Quite interestingly though an unconventional woman, she upheld conventions in her works. Her liaison with a married man seems scarcely to have touched the treatment of sexuality and marriage in her fiction. G.H. Lewes, the thinker, the immediate inspirer and first critic of her novels, may have been of cardinal importance to her development as a writer, but the nature of their relationship is never reflected in the norms of conduct accepted by the characters.

Even Maggie Tulliver, the heroine who springs most directly from the novelist's own roots, when steps beyond narrow moral conventions, her freedom is not celebrated, it becomes tragically awkward. This is not to argue that George Eliot rejoiced conventions in her books because she allowed fiction to represent her own unease with unconventionality, but to suggest that in seeking to establish a new basis for moral action she was first determined not to offend her readers by touching raw nerves. She became a major naturalistic novelist because she was able to present so impressive and observant a picture of ordinary, and often conventional, man and woman. She is a great moral novelist because she ought to explain and give substance to a personal morality which can function without a supernatural fiat.

Her single-minded devotion was to explore a view of life that would give modern man a sense of purpose, dignity and ethical direction. She wrote to Clifford Allbutt:

The inspiring principle which alone gives me courage to write is that of so presenting our human life as to help my readers in getting a clearer conception and a more active

admiration of those vital elements which bind men together and give a higher worthiness to their existence. (*George Eliot's Letters*, ed. by Gordon Haight,OUP,1976.Bk.IV p.472)

The 'vital elements' of which Eliot speaks here are natural and humane rather than divine. This is made perfectly clear by a letter to Mrs. Posonby in which Eliot asserts that her novels have the conclusion that " fellowship between man and man, which has been the principle of development — social and moral — is not dependent on the conception of what is not man; and that the idea of God, so far as it has been a highly spiritual influence, is the idea of a goodness entirely humane". *(George Eliot's Letters*, ed. by Gordon Haight,OUP,1976.Bk.IV p.198.)

As to George Eliot's mode of writing Leslie Stephen is of the opinion that the novelist tries to permeate her works with an ethical impulse. Two general ideas are pervasive in her view; first, stress on sympathy and secondly, an emphasis on intuition as the method of making moral judgements. She believes in the fact that men's deeds determine them as much as men determine their deeds. If we yield to temptation and sin, suffering and nemesis are sure to follow us. We have to reap the consequences of our own actions. Her characters suffer because they violate some moral codes and yield to temptation sometimes consciously and often unconsciously. Hetty Sorrel in *Adam Bede,* Maggie Tulliver in *The Mill on the Floss,* Romola in *Romola,* Lydgate and Dorothea in *Middlemarch, and* Gwendolen in *Daniel Deronda* suffer for this reason. However, it is difficult to point out George Eliot's moral views within the categories of any standard philosophical notion. She insists on the fact that there cannot be any particular law to ascertain morality. Any moral judgement must be made in the light of the complex context of any event. Mora! behaviour needs, as George Eliot thinks, a kind of impartiality, an ability to observe nobility and goodness in man and woman and to ignore their selfish desires . George Eliot does not like the dominance of self to the exclusion of the moral fibre of life. Her passionate conviction is that man's sense of immorality lies in the mode of his self-love. Unless there is a concomitant ability to excel in compassion for others, there can be no escape from the fetters of the self, however powerful the mind is.

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Eliot's plots rely heavily on the moral struggle between altruism and egoism. *Middlemarch* plays out this ethical debate clearly. "We are all of us born in moral stupidity, taking the world as an udder to feed our supreme selves,''(Eliot, *Middlemarch* 208) says the narrator, but she also says "Dorothea had early begun to emerge from that stupidity" (Eliot, *Middlemarch* 208). Rosamond, on the other hand, "had been little used to imagining other people's states of mind except as material cut into shape by her own wishes" (Eliot, *Middlemarch* 208). She is, George Eliot writes, "Entirely occupied not exactly with Tertius Lydgate as he was in himself but with his relation to her" (Eliot, *Middlemarch* 208). But it is a struggle for even Dorothea to enter fully into Casaubon's point of view, to "conceive that he had and equivalent center of self, whence the lights and shadows must always fall with a difference" (Eliot, *Middlemarch* 208), and much of the novel depicts her progress in the capacity of sympathy and altruism.

Because ethical judgments require sympathy and compassion, in George Eliot's view only real-life situations (such as novels can depict) can teach us about ethics. Neither general rules nor rational arguments are sufficient. A letter of July 5, 1859, often-quoted, makes, the argument clear:

If art does not enlarge men's sympathies, it does nothing morally. I have had heart cutting experience that opinions are a poor cement between human souls, and only effected ardently long to produce by my writings is that those who read them should better able to imagine and to fill the pains and joys of those who differ from themselves in everything but the broad fact of being struggling erring, human creatures. (*George Eliot's Letters,* ed. by Gordon Haight,OUP,1976.Bk.IV p. 72)

"Self-interested desires'* (Eliot, *Middlemarch* 175) are something to be fought against and conquered in Eliot's novel. "I know nobody as troublesome as self' (.*Middlemarch* 502), the narrator declares in *Middlemarch.* Her novels present some characters who are unable to move out of self-absorption and others who learn painful lessons as a result of trying to struggle towards a less egocentric world view. Barbra Hardy sees the characters as part of a complex pattern within the novels. This patterning highlights themes for the reader and gives shape to the novels. "Two formal features which are most conspicuous are antithesis, or contrast, on the one hand, and correspondence, or resemblance, on the other" (Hardy, Barbara. *The Novels of George Eliot: A Study in Form*, Pg.108) As readers we are invited to see this pattern in many ways, and whereas in earlier novels the correspondence between characters may be fairly obvious and straight forward (Hetty versus Dinah in *Adam Bede),* this becomes more complex and sophisticated later. Thus in *Middlemarch* there are fruitful parallels between Dorothea and Lydgate and between Dorothea and Rosamond.

In the section of *The Mill on the Floss* entitled 'The Great Temptation', Eliot presents us with a very difficult moral dilemma. Maggie must choose between her love for Stephen Guest and her sense of duty to her cousin Lucy Deane and to her admirer Philip Wakem. Eliot creates here a compelling sense of the powerful almost overwhelming mutual

attraction between Maggie and Stephen. We are told that it is like opium and their feeling has the solemnity belonging to all deep human passion. Stephen tries to persuade Maggie that their mutual love is natural and by the discovery of it they have been saved from a mistake. He points out that a mere out-ward faithfulness to their previous lovers would be nothing but a sham. Moreover, the reader is acutely aware, that these tender scenes provide an opportunity for Maggie to taste real joy in an otherwise bleak life.

However, Maggie's own judgment is unflinchingly on the side of renunciation. Maggie tells Stephen: "Many things are difficult and dark to me; but one thing I see quite clearly-that I must not and cannot seek my own happiness by sacrificing others" (Eliot, *The Mill* 472). Once Maggie has temporarily abandoned her principled position by allowing herself to drift off with Stephen in the boat, she is severe in judgment on herself:" the irrevocable wrong that must blot her life had been committed: she had brought sorrow into the lives that were knit up with hers by trust and love" (Eliot, *The Mill* 473). She is absolutely right but she suffers acutely for her mistake afterwards.

*Daniel Deronda* provides us with the fascinating Gwendolyn Harleth. In chapter 4, the narrator, with delicately judged irony informs us: "Always she was the princess in exile, who in the time of famine was to have her breakfast-rollmade of the finest-bolted flour from the seven thin ears of wheat" (Eliot, *Daniel* 102).Gwendolen's luxurious self-absorption allows herself to glide over early difficulties with more ease than most; even by the end of the novel she still has the implicit impression which had accompanied her from childhood that whatever surrounded her was somehow specially for her. This impression is so strong that she fails to understand until the last possible moment that Daniel Deronda, the man whom she idolizes, is in fact going to marry someone else. Up to this point, Gwendolen has not really considered the lives of others except in so far as they have affected her personally; the revelation of Daniel's quite separate agenda comes as something of a shock to her.

Blind egoism gives rise to self-deception in the characters and this is removed through self-discovery. Daniel Cottom points out: "It is the presumption of self-discovery through self- sacrifice that constitutes the running argument of all of Eliot's writing" (Cottom, Daniel. *Social Figures: George Eliot, Social History and Literary Representation.* Pg.162). *Adam Bede* provides good examples of people seeing why they want to see rather than reality. Hetty sees Arthur, and Adam sees Hetty exclusively as answer to their own yearning. Thus Adam persists in attributing imaginary virtues to Hetty, he created the mind he believed in out of his own, which was" large, unselfish, tender," (Eliot, Adam, 56). despite all evidence to the contrary. His determined ability to believe in his own subjective fantasy of Hetty is illustrated particularly well by the incident in which he realizes that Hetty is the owner of a rather expensive locket which contains two locks of hair - Hetty's and some hair of a much lighter colour. He correctly fears the worst: "there was something in Hetty's life unknown to him; that while he had been rocking himself in the hope that she would come to love him, she was already loving another" ( Eliot, Adam, 173). However, Adam's mind goes on to weave for

himself an ingenious web of probabilities in this situation. He decides that because she is so found of finery she has bought it herself. He has problem with her obvious discomfort at his seeing the locket but explains this away to his complete satisfaction by her acceptance that it was wrong for her to spend her money on it, and she knew that Adam disapproved finery. This, moreover, is a proof she cared about what be liked and disliked. He decides that the locket must contain a bit of her father's or mother's hair, who had died when she was child, and she would naturally put a bit of her own along with it. He moves himself from anxious suspicion to complacent self- satisfaction in on time at all.

In her magnum opus, *Middlemarch* (1872) the novelist observes ' we are all of us born in moral stupidity, taking the World as an udder to feed our supreme selves'* (Eliot, *Middlemarch* 173) This novel, written on a vast panorama and having the scope of Tolstoy's *War and Peace,* mainly centres around the moral growth of two impractical visionaries.

Dorothea Brooke, unlike Maggie Tulliver, appears to be a bold and mature woman as she displays the ability to withstand the criticisms of her individual choice and decision. However, Dorothea's decision to accept happy conjugal life and motherhood has put a question mark on woman's intellectual abilities and her sphere of activities. Lydgate's predicament is the result of his being of man of a weak moral fibre. He decides to marry Rosamond only being attracted by her outer beauty who ultimately brings his downfall. A feminist scholar observes 'Dorothea represents a woman's desperate attempt to establish an identity for herself, to create a space for her self-expression. Her muted plea to make life good for anything is the cry of an entire generation of women seeking some form of identity. Eliot shows her entrapped in a male-dominated society desperately trying to seek opportunities to realize her latent qualities'. (Choudhury Sheila Lahiri, (2002), *The Reclining Ariadane ; A Gender Reading of George Eliot's Middlemarch, Pg 115)* Though George Eliot's last novel *Daniel Deronda* (1876), dwells on the 'Jews question', the central attraction of the novel lies in the moral upgradation of the heroine Gwendolen Harleth and the moral enlargement of the hero Daniel Deronda.

*Middlemarch* also provides many examples of self-deception and because of the way in which the narrator moves from a particular example to generalization; we are all invited to see ourselves as part of the fellowship of illusion. Eliot refers to the few imaginative weeks called courtship in this novel and this is a recurrent idea in her writing. Gwendolen, in *Daniel Deronda* is walking amid delusion on her wedding day and Maggie feels that she and Stephen are enveloped in an enchanted world whilst they are on the river in the *Mill on the Floss.* Despite the fact that her sister Celia points out to Dorothea her error with regard to Sir James Chettam and says: "you always see what nobody else sees; it is impossible to satisfy you; yet you never see what is quite plain" (Eliot, *Middlemarch* 208), Dorothea goes on to perceive Casaubon, too, in her own self-created image. Thus when she looks into his mind, she sees there a vague labyrinthine extension which she herself had created. Lydgate does exactly the same. Despite his experience with Laure, Lydgate repeats his previous error and constructs

Rosamond as he wants her to be rather than what she is. His suppositions are entirely rose-tinted; something which is betrayed by the language used when he saw Rosamond as a creature who would bring him the sweet furtherance of satisfaction and beautiful life. Lydgate extends his optimism to encompass the behavior of his future father-in-law, whom he imagines will provide useful sum in the form of a dowry, to make payment easy. Eliot tells us in this novel that we are all bom in moral stupidity. Both Dorothea and Lydgate emerge from that stupidity when they take responsibility for their partner, not as an idealized object, but as a being with their own center of self. This involves both in suffering and a voyage of self-discovery, which runs alongside the discoveries that they make about others.

However, it is difficult to point out George Eliot's moral views within the categories of any standard philosophical notion. She insists on the fact that there cannot be any particular law to as certain morality. Any moral judgment must be made in the light of the complex context of any event. Moral behavior needs, as George Eliot thinks, a kind of impartiality, an ability to observe goodness of others against selfish desires of some people. George Eliot does not like the dominance of self to the exclusion of the moral fiber of life. Her passionate conviction is that man's sense of immorality lies in the mode of his self-love. Unless there is a concomitant ability to excel in compassion for others, there can be no escape from the fetters of the self, however powerful the mind is. Unlike her Victorian predecessors like Dickens and Thackeray, George Eliot's interest in analyzing a character from moral perspectives has provided her art of characterization with depth and endurance.

Though the world has undergone a considerable progress and has become sensitive and liberal, true to admit, the puritan 'moral code' practised in Victorian era has not changed lock, stock and barrel. What was condemned in Eliot's time would be criticised in these days as well. The act of Maggie's elopment, Hetty's illicit sex, Rosamond's extra-marital affairs, Romola's unilateral decision to break the wedlock or Gwendolen's loyalty towards Deronda would be questioned in present society as well. So an act of morality or immorality has a universal dimension.Herein lies the relevance and acceptability of George Eliot's novels.

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# DETERRITORIALIZING MINORITIES: COW SLAUGHTER BAN AND MOB LYNCHING IN INDIA

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**Abstract**

Signs of 'deterritorialization' could be discerned from the Central government's notification, titled the Prevention of Cruelty to Animals Rules, 2017, stipulating that those who wish to sell cattle, may do so only after formally stating that the animals are not "brought to the market for sale, for slaughter," thus, effectively, prohibiting the sale of cow and buffaloes for slaughter. This move is perceived to be an indirect ban on consumption of beef as part of their diet, by a substantial segment of the society. Pertinently, this 'signifier' appears to be 'atmospherizing' the politico-religious ideology of 'Hindutva', that runs counter to the 'secular' fabric of the country. A series of violent incidents that spiralled out as an offshoot of the imposition of the cattle-ban in many states, signify the process of deterritorialization that seems to have been triggered through an attempt to control what one should consume as food. The absence of pluralism and polyvocality after the coming to power of the present ruling Government, since 2014 in India, and cow slaughter-ban, in particular, is deliberated upon.

**Introduction**

After the World War II, with the emergence of new ideas, theories, material practices and novel technologies facilitating the speed and intensity with which the ideas and practices permeated the national imaginary, across national boundaries promoting the sense of 'the global' undermining the deeply engrained notions of community tied to a sovereign and demarcated territory containing relatively homogenous populations (Appadurai, 2006; Albrow, 1997; Beck, 2005). The ideologies dominating the world today are no longer exclusively articulations of the national imaginary but reconfigured ideational systems that constitute early-stage translations of the dawning global imaginary (Steger, 2009). In the wake of globalisation in the 1990s, the world was expected to move towards the global imaginary surpassing the national imaginary. Deterritorialization, considered a central feature of globalization, implies the growing presence of social forms of contact and involvement which go beyond the limits of a specific territory (Giddens 1990), taking us closer to the external generating closeness in distance and a relative distancing from what is close (I Marti, 2006). "Deterritorialization, whether of Hindus, Sikhs, Palestinians or Ukranians, is now at the core of a variety of global fundamentalisms, including Islamic and Hindu fundamentalism. …the problems of cultural reproduction for Hindus abroad has become tied to the politics of Hindu fundamentalism at home". (Appadurai and Breckenridge, as cited in the book The Social Theory, continuity and confrontation, Garner, Hancock, 2014).

Talking about fundamentalism in India, there are a lot of incidents happening around, especially the ones that are affecting the day to day lives of people. Coercive behaviours, with the power of politics and dominant social ideology, people in a democratic country have been dictated to change their long-standing practices in an undemocratic way, in the name of morality. Religionists and humans more generally have the cognitive tendency of anthropomorphism, overgeneralization, essentialism … binary thinking, hierarchical thinking, linear-causal thinking, and tendency to divide the social or intellectual world into communities of good/right us and bad/wrong them. The most significant cognitive tendency being confirmation bias, where we notice and remember what confirms our established beliefs and to overlook or forget what contradicts them. (De Cruz & De Smedt 2007, Smith, 2010). One such sites of suppression that has been felt recently is the control over food culture. Food is an important aspect of culture and every food culture we have now, has a deep rooted history/reason for being the way it is. Our very existence is determined by 'what we eat and how we eat'.

The Central government's notification in 2017, titled the Prevention of Cruelty to Animals Rules, stipulates that those who wish to sell cattle like bulls, cows, buffaloes and camels, may do so only after formally stating that the animals are not "brought to the market for slaughter". This effectively, prohibits the sale of cow and buffaloes for slaughter. This move is perceived to be an indirect ban on consumption of beef as part of their diet by a substantial segment of the society. Pertinently, this 'signifier' appears to be 'atmospherizing' the politico-religious ideology of 'Hindutva', that runs counter to the 'secular' fabric of the country. A series of violent incidents that spiralled out as an offshoot of the imposition of the cattle-ban in many states, signify the process of deterritorialization that seems to have been triggered through an attempt to control what one should consume as food. There is an attempt to deterritorialize the beef consuming sections of the society, thus laying the foundation to an ultimate exclusion. The arbitrariness with which the notification was issued, has given power to many fundamentalists to take law into their own hands to enforce the ban, adding to the deleterious impact of the rule. A section of the society appears to have been emboldened by the legal backing given to what was, hitherto, a part of the non-justiciable Directive Principles of State Policy. As a result, there have been mob-violence, cow-vigilantism and murderous lynchings, all in the name of cow-protection. The line of flight, the resistance of the system, reterritorialization, in places like Hyderabad and Kerala, is assigned a negative value and condemned in the name of sacredness and prevention of cruelty to animals.

Beginning with a detailed preface to the historical information on beef consumption in Indian food culture, the study aims to throw light on communities consuming beef as their main source of protein, then and now, and the circumstances that led to the promotion of vegetarianism and 'sacredness' of the cow. It also examines the right of every community to enjoy freedom of choice of food under the Constitution of India, which may find negation in the implementation of beef-ban.

**History of Beef eating, Beef ban and right to food**

Hindu and sanskritic elements are emphasized as the contribution of India to the world History. And, the presence and role of other religious and linguistic cultures, such

as Buddhism, Jainism or even Islam, as it evolved in India, in the construction Indian civilization is generally not recognized. (Thapar, Romila, 2004). The eating of beef has always been in the civilization that emerged in this part of the world. And beef eating was reserved for specific occasions, such as rituals or when welcoming a guest or a person of high status. The economic value of the cow enhanced its veneration. This may have contributed to the later attitude of regarding the cow as sacred and inviolable. Eventually, it became a matter of status to refrain from eating beef and the prohibition was strengthened by various religious sanctions (Thapar, Romila, 2004).

In 1955, Congress had banned cow slaughter in 24 states across the country. By June 2017, 18 Indian states had banned the slaughter of cattle. "The main attempt to sanctify cow in the name of Hindutva is to disenfranchise Muslims. Other than the beef-eating Muslims and Christians, the lower caste Hindus are also the target of Hindutva's hate brigade. Attacks of this has been going on since Hindutva began in 1923. In 2002, five lower-caste Hindus were lynched in a north Indian town, for skinning a cow". (Doniger, wendy, 2017). According to the father of the Indian constitution, BR Ambedkar, the principle of untouchability initially emerged as a practice to ban the consumption of eating beef and the Brahmans found it convenient to say that those who ate beef were untouchables, rendering Islam and Christianity alien and communal by Hindu fundamentalists.

"The right to food", according to the UN special rapporteur (2001), "is the right to have regular, permanent and unobstructed access to quantitatively and qualitatively adequate and sufficient food corresponding to the cultural traditions of the people to which the consumer belongs, and which ensures a physical and mental, individual and collective, fulfilling and dignified life free from anxiety". Article 21 of the Indian Constitution states that Right to life is not mere existence like an animal, but the right to live with dignity. Adding to this, the preamble to the Indian constitution states that "we, the people of India, having solemnly resolved to constitute India into a sovereign socialist, *secular*, democratic republic and to secure to all its citizens.

Currently 72 communities in Kerala prefer beef to the expensive mutton. Not all of them come under the socio-cultural construct of 'untouchables'. And, it is a myth that Muslim rulers introduced beef eating in India. The number of Indians eating beef and buffalo meat went up from 7.51 crore in 1999-2000 to 8.35 crore in 2011-12, according to the National Sample Survey Office (NSSO).

**Hypothesis**

The Central government's notification in 2017, titled the Prevention of Cruelty to Animals Rules has triggered lynching of the beef eating sections of the society.

**Methodology**

A triangulation study of the incidents of violence in Haryana and Uttar Pradesh (UP), before and after the announcement of cow slaughter ban, has been attempted, through the analysis of media reports published from time to time.

A quantitative analysis of the number of news reports on mob lynching and violence in the most read English daily 'Hindustan Times' in UP, Lucknow edition and Dainik Jagran is done.

News reports of the most read English daily 'Hindustan Times' in Haryana, Chandigarh edition and Dainik Bhaskar were also surveyed for the study.

The Key words used for the search in the Newspaper archives are Beef ban, cow slaughter, cow slaughter ban, cow vigilante, Gau Rakshak, cattle thieves, cattle trader, cattle smuggler.

The nature of the titles of the news stories related to cow protection and mob lynching were also analysed.

**Area of Focus**

In 2015, Uttar Pradesh, a Muslim man Akhlaq was lynched, when suspected of storing "beef" at his home. This state has the highest number of Muslims eating buffalo meat, 1.73 crore, followed by West Bengal, 1.5 crore and Assam, 57 lakh. In terms of percentage, the Muslim beef/buffalo eating population is highest in Meghalaya (94 per cent) followed by Lakshadweep, 78 per cent and Sikkim, 72 per cent. U.P. and Maharashtra have this figure around 47 per cent.

Uttar Pradesh and Haryana are among the few states that has witnessed more number of mob lynching in the country. Therefore, the reported cases of mob lynching in the name of cow, in these two states are chosen for the study.

**Data Collection**

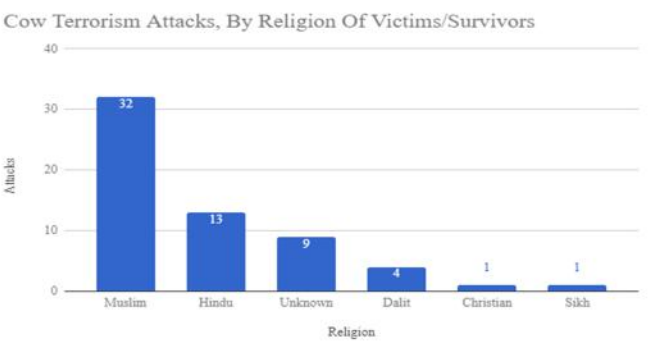
**Secondary Data**

The secondary data forms the basic understanding for the hypothesis formulation for this study. Between 2010 and December 2017, 3% of the total attacks related to cow vigilantism happened between 2010 and 2014.

| | 2010 to 2014 | Jun 2014 to Dec 2017 |
|---|---|---|
| Attack related to cow vigilantism | 3 % | 97% |
| Murders | -Nil- | 28 |

*Courtesy: (IndiaSpend, a data journalism initiative)*

In 24 attacks, as per media reports, the attackers were mobs or groups of people belonging to Hindu groups, such as the Vishwa Hindu Parishad, Bajrang Dal and local Gau Rakshak Samitis. Between 2010 and 2017, Muslims were the target in 51% of the violence.



There were 28 murders in 63 incidents, of which 86% of the people murdered were Muslims.

| | |
|---|---|
| No. of incidents | 19 |
| Total no. of people killed | 28 |
| Muslims murdered | 86% |
| Hindus murdered | 14% |

Cow Vigilante activities were reported from 19 Indian states. Uttar Pradesh and Haryana lead the list. One incident was reported from the North-East (Assam).

**Findings and Discussions**

Arrests, violence and murders reported in Hindustan Times, Chandigarh edition and Lucknow edition, UP.

| Year | Arrests | Violence | Murder | News Items |
|---|---|---|---|---|
| 2011 - 14 | 40 | 12 | 1 | 67 |
| 2014 – 17 | 92 | 92 | 9 | 127 |

**2011 – 14: Murders: 1**
Muslims – Nil-
Others - Nil-
Cow Vigilante - 1

**2014 – 17: Murders: 9**
Muslims murdered - 7
Others - 2
Cow Vigilante - Nil

**News Items include:**

- Banning of Beef and pork festival in JNU
- Muslim Men arrested for killing Cow Volunteer
- A senior judge said the "cow should be declared a national animal and people who slaughter cows should be sentenced to life in prison".
- "Condemn the brutal mob-attack on the woman, who exposed illegal cow slaughter. This violent attack today in Bengaluru is another proof law & order breakdown under @cmofkarnataka Sh. @Siddaramaiah," he tweeted.
- 'Will break hands and legs of those who disrespect, kill cows': BJP MLA
- Noose for cow killers, vows Chhattisgarh CM
- Stray cattle menace, ill maintained cow shelters and cattle on road leading to fatal accidents.
- Dadri lynching accused dies in jail, villagers drape coffin in tricolour, refuse to cremate body.

**Conclusion**

The number of news items and the violence related to Cow protection has increased many folds in the period between 2014 and 2017. The media reports show a clear difference in the kind of news that appeared on media, before and after attempts

made by the ruling parties of those states, to protect cows. The open remarks instigating violence in the name of cow, in communally sensitive areas has increased and could also have led to the communal imbalance in those states. The Muslims and Dalits were the most affected sections, in the cow vigilante acts. This situation definitely is an attempt to deterritorialize the population that consumes beef and is involved in businesses dealing with Cow.

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# EMPLOYEE ENABLEMENT AT SCALING ORGANIZATION

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## Abstract

The main idea of this is to give the proper description of Human Resource Enablement (HRE) inside of a organization's culture as a contemporary evolving trend in Human Resource Management. Employee enablement gives employees the ability to continue performing high-level job functions, while employee engagement ensures your team is dedicated to the company vision and overall goals. When Organization move beyond Employee Engagement to Employee Enablement, it empower employees with training, development and the skills & competencies to make smart decisions. This paper tries to conceptualize the employee enablement & recognize the strategies and benefits in scaling organization.

**Keywords:** Human Resource Enablement, Human Resource Management, Employee Enablement, Employee Engagement, training, development.

## Introduction

Employee Enablement refers to the process that involves taking the employees in an organization above the existing stage. They are hence empowered in advanced manner beyond the current engagement stage. During the empowered procedures, the employees are therefore provided with the right operation tools as well as appealing circumstances (Hewitt, 2012). The provision of this conducive environment translates to the delivery of quality output. In every business enterprise, it is critically ideal for every employee to enhance productivity. Therefore, the management is at the verge of higher expectations in terms of not only productivity but also good performance.

While executing their duties, the employees tend to be careful and considerate and work hard to avoid any form of inconvenience. Execution of duties and responsibilities becomes a very significant consideration in any company. The human resource department, therefor, needs to undoubtedly equip itself with the necessary etiquettes which tend to be passed to the employees. Nevertheless, several prerequisites are connected to employee enablement (Mazzei, 2014). Not only engagement but also

empowerment becomes vital aspects of strengthening employee enablement. Without the conjunction of these two factors, the employees in any organization tend to deliver very poor quality results. Employee survey ensures that managing body enables the employee to portray the required characteristics and qualities.

Proper survey over the behaviors of employees calls for a well-managed business enterprise. Under this dimension, Employee enablement relates to giving the right duties to employees to make them perform to their best. Creating and issuing them with a supportive working environment enhances the productivity. The right tools, equipment, funds, training as well as a unity from coworkers create a strong bond in the working environment. Some of the barriers that can hinder proper working should be eliminated. Red tape, as well as procedure restrictions can adversely affect the normal functioning of the business.

Skills are very important for every employee. It is very hard to compare the performance of an enterprise with skilled labor and without. A very significant variation exists between the two there by defining the importance of skills to employees. Skills are always acquired through careful training. For the effectiveness of any training, it is always good for the employees to be equipped with oncoming skills as the occupation demand. Some skills are outdated and they may be little help because of the advancing technology. The human resource department is also mandated to provide enough tools to enable continuous working conditions.

**Review of Literature**

This part of the research gives the relevant literature related to employee enablement. It, therefore, gives a discussion of the above mentioned objectives. Employee Enablement has got many issues concerned with it which are strongly supported by various literatures. Strategies that enhance employee enablement tend to be highly considered. Employee enablement also harbors numerous benefits as well as some connected ideas. This portion, therefor, discusses the relevant literature based on the study objectives.

According to several types of research, inferences have been reached at that many organizations have numerous workers with low results provided. This is because the firms lack the necessary tools and equipment which conform to the type of service. Proper information to the employees also ensures that they perform the intended tasks to the maximum. Good information enables the employees to have authority as well as the capability to make clear decisions (Vergara,2017). Employees enablement formulas enable the workers to give out a good performance. The first formula, therefore, calls for higher performance which accrues from enablement plus engagement (Enablement Engagement= High Performance).

Employee engagement, therefore, enables the employees to be committed so that they can effectively achieve the set objectives as well as the goals. On the other hand, enablement enables the employees to perform the duties of the company perfectly. This means that engagement is concerned with commitment while enablement deals with the ability to perform. The well-known mistake done by many organizations is that they tend to place more concern on engagement than enablement. This is very risky as the two aspects are equally important and they greatly influence the performance. The

results are always severe frustrations to the employees. These employees are always committed to deliver, but they are hindered due to lack of enablement.
When these challenges arise, most of the employees tend to seek for enablement as an effort to solve the challenge. In the case of enablement failure, they may equalize the level of engagement to the enablement level so tht they can work on an equal basis (Larso,2015).
Additionally, some of them may decide to abandon the organization and migrate to where they can be properly be enabled. The second formula of employee enablement tends to incorporate the aspect of empowerment whereby

**Empowerment** + **Engagement** + **Enablement** = **High Performance**

In this case, empowerment provides employees with the autonomy of decision making during the undertaking of their duties. This means that employees can come to decisions on lower level which helps in easier solving of problems as well as affecting their performances. Additionally, every employee can be accountable for anything which can accrue from the decisions made. The results of empowerment are higher productivity by the employees and inherent services to customers. The employees are also willing to change with time as technology and management changes.

**Objectives of the Study**

1. To study the conceptual framework of Employee Enablement
2. To determine the strategies that lead to successful employee enablement
3. To determine various benefits associated with employee enablement
4. To identify the ideas involved in employee enablement

**Methodology**

Generally, literature review summarizes research spread over a specific timeline about a particular topic and identifies main themes and issues. Moreover, it gives you new insights from the existing literature which has not been revealed earlier. Carrying this thought forward our review gives the developments and trends in the area of employee enablement which will help organizations to improve their employees' productivity and motivation. Finally, future research directions are given at the last for potential researchers.

**Data Collection**

Our study has taken only academic journal articles to review. Firstly, we searched the following databases with these keywords employee enablement, employee engagement, human resource management,training and development.

1. JSTOR
2. Management & Organization Studies: A SAGE Full Text Collection
3. PsycINFO
4. Science Direct
5. Scopus

We selected all the papers containing any of the above mentioned keywords in the

entire text. This gave us a total of 50 papers out of which we selected papers belonging to timeline and further filtered them by reading their titles, abstracts and keywords which reduced our number of papers to 27. For reassuring that papers are relevant for our review we read and analysed the introduction section of them and finally we get 18 papers.

## DISCUSSION

### Strategies for Successful Employee Enablement:

Not only Permana but also Larso (2015) stated that the Creation of a transparent culture in the organization is very important aspect. This strategy enables the business to manage and enhance employee enablement. Transparency is an ideal contributor to the decisions made by the employees. This means that the company is quite aware of the kind of employees they have. On the other hand, employees are clearly keen and aware of their roles. The employees also understand the reason as to why they perform various tasks. Therefore, transparency leads to provision of context which drives every employee to give out efficient outcomes. The context also makes them be more focussed as it gives a proper picture of the organization's motives.

Activities such as assisting employees to understand the business initiatives enhance transparency. Additionally, understanding the company goals and performance data enhances equality and employees become objective oriented (A kanno, 2015). They feel honored by the management, and they make sure they perform their tasks to the maximum. Respectable feedback mechanisms can also lead to a good performance by the employees. Efficient self-corrections aid in enhancing the transparency culture of the business organization. Therefore, transparency is a very critical strategy in the company.

According to Radda (2015), listening culture also defines a very important strategy that enhances employee enablement. Most of the companies geared towards effecting employee enablement tend to build a listening culture. The human resource department identifies whatever every employee needs so that they can improve and perform their tasks to their level best. This calls for every employee to have his or her ear rooted to the ground. They hence take note on every issue highlighted by the management and address it using the right actions. The company, therefore, creates forums where employees can comfortably voice their concerns and opinions regarding the company's desires. This boosts engagement and employees feel not only empowered but also trusted.

Providing immediate learning avenues is also another vital aspect. Currently, many fast paced working places calls for employee's enablement. The world is highly advancing in terms of technology. Therefore, flexibility in a workplace is becoming very important. This, therefore, demands the organizations to enhance business mobility for the betterment of not only the customers but also the company itself. Employees should, therefore, be equipped with the right information so that thay can give it to the customers as required by the management (Permana,2015). In case the companies need to affect employees enablement, immediate learning should be given consideration. Therefore, the firm will have to leverage mobility power.

Considering not only the learning but also development directives portrays an important aspect. Most of the forward thinking companies have advanced in this formality. Nevertheless, in case the management requires to assemble and have a good breed of employees, initiatives must be given the necessary target. They need to be hyper-personalized so that the right employees can be cultivated. The focus hence translates to continuous learning and curative adoptions. These two aspects are in line with the requirements of the employees. A quite comprehensive as well as streamlined dissemination of knowledge plays a significant role. Disbursement of training items leads to acceptable retention of knowledge.

Analysis of enablement measures is also an important strategy. According to recent studies, most of the firms tend to be updated to the current affairs. They, therefore, access their initiatives which are synched to development. Regardless of the location that the employees might be, the management ensures that information reaches them at the right time. Collaboration is also vital and shapes the knowledge economy. Currently, it is apparent to come across proactive learning platforms which are aimed at getting rid of performance barriers. This guarantees the organization of the better placement of people whi can have an ideal succession. This, therefore, calls for proper diagnostics which are in line with mind context.

Typically, several such activities always go beyond the existing subject that is meant for motivation. This, therefore, takes into account the overall achievement parameters as well as those factors which cause the influence. The creation of a conducive environment calls for assurance to the employees that the right skills will be passed to them. This will definitely translate into proper responsibilities (Vergara,2017). Not only training but also development initiatives cannot be seen as a single time event. It is hardly an event where most employees attend in the circumstances where they are onboarding or swiping duties. In the current era of employee enablement, it is very ideal to place training on the first bench. Training should, therefore, be a continuous process because companies goals are rapidly evolving.

It is therefore very important to ensure that employees' skills are up to the present. The skills should, therefore, be tuned with not only the advancement but also the changing working demands. Assisting every employee to obtain business clarity on the struggles present make them strong and bound. Additionally, some of the recognition programs aids in the creation of enabling employees who are bound to succeed.

**Benefits of Employee Enablement**

It is very critical for any business organization to uphold employee enablement. It is always the wish of every firm to make huge profits margins at every end of the financial year. For this to happen, it, therefore means that every aspect of the business must be looked at in a special way (Luan, 2014). It all starts with the machinery or rather the tools that enhance maximum production. For the employees to perform well, this calls for their enablement through decent working tools alongside the apprehend skills. The human resource department has to understand the importance of employee enablement in that company.

Employee Enablement, therefore, ensures that employees are always on the right track.

This enables the company to get maximum benefits and therefore competing fully with the outside market. In most circumstances, employees tend to contribute more to the business rather than their advantage. This means that they can act as real brand advocates for the firms as well as boosting the productivity (Taylor, 2014). Once the company engages its employees, it, therefore, calls for the management to find means of committing them to the tasks. The company, therefore, tends to understand the nature of every employee and creates a personal profile for each one of them.

Employee Enablement ensures that employees understand even the internal affairs of the business. It is not only about the goals and targets to be met. They are even involved in decision making forums where they can contribute not only in the running but also the management of the company. The guidance, as well as the empowerment, is given to them learn and develop additional skills that highly boosts the firm. In the end, what matters is the output generated and the picture portrayed to the outside world. The company hardly tends to lower the standards of employees. They train them on the basis that they can be managers of business in the years to come. Therefore, enablement transforms employees to be superior in every chapter of business.

The technology is evolving and advancing at a very high magnitude. Machines and modern working tools have become obvious in many organizations. This, therefore, enables the employees to interact with these tools which even advances their know how. It is not ideal for specific personnel to operate the new machines. It calls for the training of everyone which promotes job swiping. Revenue is the prime factor in any organization. Therefore, managers do not hesitate to equip their employee's with all kinds of skills. Employee enablement therefore largely contributes to the firm's revenue thereby making the company grow on a large scale basis.

The overall turnover is very vital in the business organization. Therefore, many companies need employees equipped with modern skills. Without enablement, you can be very certain that the company can face challenge in terms of final revenue (Thompson, 2002). Employee enablement, therefore, allows the companies to record an efficient number of costs synched to the overall turnover. It also allows the company to maintain a good system involved with the records of company expenditure. Performance by the employees always makes the company expenditure. Performance by the employees always makes the company be proud of its laborers. Their enablement makes them perform to their level best without necessarily being supervised.

**Ideas Involved in Employee Enablement**

According to Singh (2015), it is very ideal to provide more than occupation to the employees. In the present days, it is very easier to lose high skilled employees in the company. This accelerated by the fact that they know of similar companies with modern and better management. This, therefore, calls for the firms to have ideas on how to maintain their trusted employees. The leaders are always requested to treat their juniors with respect because the foundation of the company is founded on these employees. It becomes a challenge for the employees to work at their best if the job itself is not enabling. The management bodies need to get various ideas that make not only the skills but also the abilities of employee utilized.

Conducting surveys in all business aspects is very important. Most of the developed countries have comprehensive management of employees, and this can be passed on to other less developed nations. Borrowing ideas as well as creating exchange programs are some of the terminologies that can assist companies to learn from one another (Berger, 2014). A company can have some terminologies which are absent from another company. Through exchanges, they can adopt each other's strategies thereby establishing a permanent partnerhip. It is not always about competition but rather the ideas that can be gotten from various organizations.

It is also ideal for the human resource department to establish a vivid vision that is applicable in the future. This means that the management should aim at making the employee understand even the internal forces of the comapany. The more frequently any leader communicates the affairs of the firms to his juniors, the more trust he gains. This means that the employee will be ready to contribute to the vision of the company. The human resource managers, therefore, need to deploy some e-learning modules which can pass the ideas to the long waiting employees.

The management should also put acros more information on the output rather than the inputs incorporated. This means that the company should not always focus on the period worked. The success of every business should hence be measured on the basis of outcomes rather than the inputs. The employees can work for any hours as long as it is in line with the agreement made. They can agree on some conditions such as overtime charges and these standards always maintain their relationship with the management (Schepers,2016). However, the output measurement approach shifts all the roles to the employees. This is because they get empowered to work in a manner which fits their requirements.

Another idea that has been circulating in the business world is about the need to hire proactive employees. Employees who are lively and willing to perform always changes the appearances of the company. The proactive nature can be identified during job iterviews because the interviewer can grasp some unique personalities (Rai, 2012). Attitude is also vital, and it determines how an employee perceives the duties and roles assigned to him or her. Any impression be it negative or appealing determines the kind of employee that you higher in your company. Leaders should also watch and follow whatever they promise to the employees. Studies reveal that most actions by the senior staffs have an impact on the employees. Therefore, they should always be positive.

## CONCLUSION

Employment formalities have diversified due to various complex backgrounds in the world of business. Globalization has greatly fueled the fierce competitions existing in current markets. There has been an advancing industry structure that calls for advancement in the ways tht companies are undertaking their daily tasks. For them to compete in fierce market, they need to employ strategies that ensure their continuity. Adoption of more flexible business strategies can boost the productivity of each company. However, employee enablement is a vital aspect that will make every plan to be successful. It is therefore advisable for the firms to equip their employees with skills which are alligned to advancing technology. All of these considerations will see the company being able to withstand the competition in the market while getting higher

revenues.

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# THE ANALYSIS OF ROOT CAUSES BY MEANS OF THE "FISHBONE" DIAGRAM

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## ABSTRACT:

The risk has been and will remain one of the main problems of any pharmaceutical company during its activity, whether it is a financial activity, a production activity, a management activity or else. The risk is a matter which should not be neglected. Root cause analysis is a structured team process that assists in identifying underlying factors or causes of an adverse event. The Fishbone Diagram is a tool that helps identify, sort and display possible causes of a specific problem or quality characteristic. So this Cause and Effect Diagram referred to as the "Ishikawa diagram," and the "fishbone diagram," because the complete diagram resembles a fish skeleton. The diagram illustrates the main causes and sub causes leading to an effect. It is a more structured approach than some other tools available for brainstorming causes of a problem
(e.g., the Five Whys tool).

**Keywords:**Risk, Fishbone Diagram, Root Cause Analysis

## INTRODUCTION:

The Ishikawa diagram or Fishbone diagram is a graphic representation, which helps the processing and organization of ideas and conclusions to be formulated in case of problems and the identification of their causes, and it may be used in any type of activity.[1]This diagram also represents a tool that helps logical and systematic processing of the causes and sub causes of certain problems or of certain effects that related to a particular activity, regardless of its type.[2]Fishbone diagrams is also known as Ishikawa diagram, herringbone diagram, cause-and-effect diagram or Fishikawa. [3]

History of Fishbone diagram- Ishikawa diagrams were proposed by Kaoru Ishikawa in the 1960s,who pioneered quality management processes in the Kawasaki shipyards and in the process became one of the founding fathers of modern management. It was first used in the 1960s,and is considered one of the seven basic tools of quality management, along with the histogram, Paretochart, check sheet, control chart, flowchart and scatter diagram. It is known as a fishbone diagram because of its shape is similar to side view of a fish skeleton.[4]

Brassard and Ritter (1994, 23) assert that the CED "enables a team to focus on the content of the problem, not on the history of the problem or differing personal interests of team members." Andersen and Fagerhaug (2000, 14) write that the CED is "an easily applied tool used to analyze possible causes to a problem," while Wilson, Dell, and Anderson (1993, 195) call it a "highly visual technique which aids the process of defining the elements of a problem or event and determining how itprobably occurred."[5]

Causes are usually grouped into major categories to identify these sources of variation. The categories typically include:[6],[7]

Manpower/People: Anyone involved with the process
Methods/Processes: How the process is performed and the specific requirements for doing it, such as policies, procedures, rules, regulations and laws
Machines/Equipment: Any equipment, computers, tools, etc. required to accomplish the job
Materials: Raw materials, parts, pens, paper, etc. used to produce the final product
Measurements: Data generated from the process that are used to evaluate its quality
Mother Nature/Environment: The conditions, such as location, time, temperature, and culture in which the process operates[5]

**MATERIALS AND METHODS:**

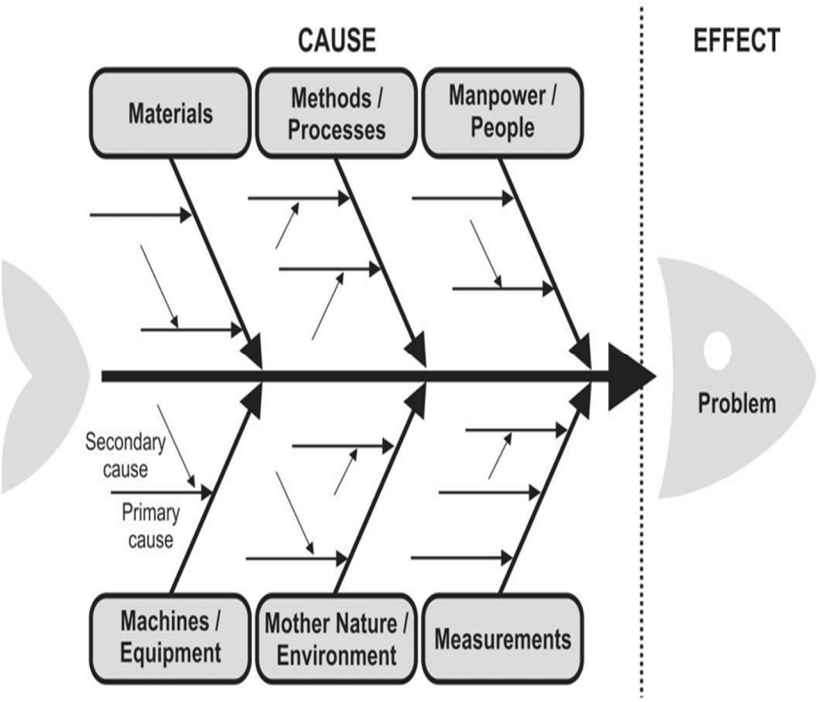
In justifying the theoretical basis of this article I started from the theoretical presentation of the fishbone diagram, a presentation that is meant to indicate its meaning and its role in the management of a company.[8] In economic theory and practice there is a wealth of possibilities to address and analyze this theme, so my approach and analysis module complements and develops current and past studies that have addressed this subject.[9]
The materials used consist of a set of specialized works published in different books, various articles and online sources.[10]The methodology used in this article demonstrates its own vision in terms of describing the scientific approach and it is based in particular on a qualitative research that will help understand the topic approached and highlight the main issues addressed.[10]The basis of this article is a fundamental research - the activity developed mainly in order to acquire new knowledge about phenomena and processes, in formulating and verifying hypotheses, conceptual models and theories.[11]

**DESCRIPTION:**

**Appearance**

A generic Ishikawa diagrams have a box at the right hand side, where the effect to be examined is written. [12]The main body of the diagram is a horizontal line from which stem the general causes, represented as "bones". These are drawn towards the left-hand side of the paper and are each labeled with the causes to be investigated often brainstormed beforehand.[13]
These can be found using the 5 Whys technique. When the most probable causes have been identified, they are written in the box along with the original effect.[14]The more populated bones generally outline more influential factors, with the opposite applying to bones with "fewer branches". Further analysis of the diagram can be achieved with a

paretochart. [15]The fishbone concept can also be documented and analyzed through depiction in a matrix format.[16]




**COMMON CATEGORIES IN FISHBONE DIAGRAM**[17]

| **The M's** (Manufacturing industry) | **The P's** (In Marketing industry) | **The S's** (In Service Industry) |
|---|---|---|
| Machine(Equipment) | Plant /Place | Surroundings |
| Method(Process) | Promotion | Supplies |
| Man Power(People) | People | Systems |
| Material | Positioning Skills | |
| Mother Nature(Environment) | Procedures Safety | |
| Management (Policies) | Price | |
| Measurement(Inspection) | Product | |
| Maintenance | | |
| Marketing(Promotion) | | |

**GENERAL PROCEDURE**

The cause-effect chart (the Fishbone Diagram) is a method for the analysis of complex problems that present several interrelated causes.

One of the key aspects of this technique is the use of cause-effect chart. Because of the way it looks, this diagram technique is also called Fishbone Diagram (or Ishikawa Diagram). [18]

The method uses a combination of visual representation (branches) and brainstorming techniques for obtaining the causes. For building a fishbone chart we use arrows or branches: [19]

- Primary branch: represents the effect;
- Major branch: corresponds to the major cause;
- Minor branch: corresponds to the causative and more detailed factors.

**STEPS:**

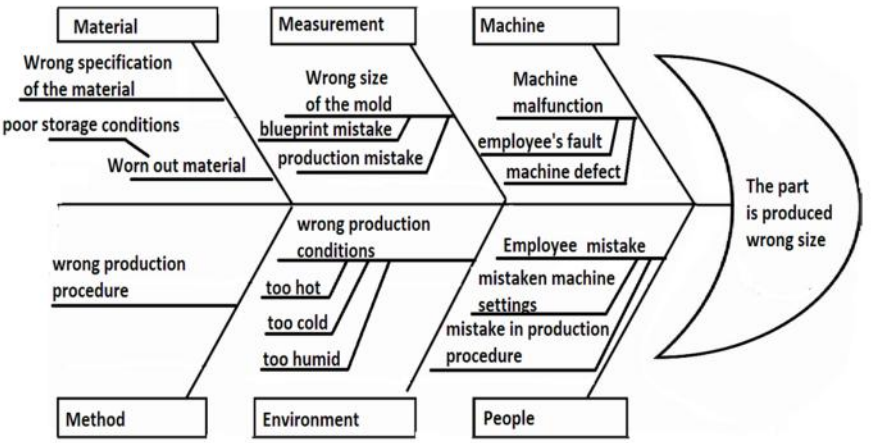
The steps in building a Fishbone diagram: [20]

I. The identification of the problem.
II. The description of the problem on the right side of the chart. This may be the problem itself or a symptom, but at this stage no one can know for sure.
III. We draw a horizontal line directed towards the box describing the problem. This arrow will serve as backbone. This is the starting point in identifying and grouping the major and minor causes.
IV. We identify potential causes are we group them into categories. The major categories are: people, processes, materials, equipment, environment, etc. The main categories are identified by means of the brainstorming technique, trying to list them all. During the graphic representation on the diagram we must take care to save enough space between categories in order to later add individual causes. Each of these major categories will be explored in detail.
V. We continue the brainstorming activity on the causes by means of the detailed analysis for each main category identified. We write the detailed cause on a slanting line connected to the main category.

- Basically, the Fishbone technique is a very successful technique in that it does not involve the use of statistical methods, the visual representation is simple, human-readable, it values a series of elements and causes that characterize a particular situation, it helps to identify some possible causes of variation and allows for the determination of the fundamental cause, it encourages the participation of the members of the group to problem solving, and last but not least it represents an easy and simple technique to find solutions for improvement.[21]
- Analyzing the stages of the Fishbone diagram we draw the conclusion that it can be easily applied to general issues that can arise in all branches of an organization. For example, it can be applied to solving problems such as the decrease of profit, the decrease of market shares, the loss of suppliers, the loss of contracts, etc.[22]
- The categories involved within a Fishbone diagram are: people involved in the process; methods of written policies, procedures, laws, rules applied throughout the

process; cars represented by equipment, computers; consumable materials; measuring data quality; the internal and external environment. [23]

**Example of Fishbone Diagram**[24]




**ADVANTAGES**[25]

I. Helps to determine root causes.
II. Uses an orderly, easy-to-format.
III. By using a fishbone diagram, you are able to focus the group on the big picture as to possible causes or factors influencing the problem or need.
IV. Even after the need has been addressed, the fishbone diagram shows areas of weakness that once exposed can be rectified before causing more sustained difficulties.
V. Encourages group participation.
VI. Indicates possible causes of variation.
VII. Increases process knowledge.
VIII. Identifies areas for collecting data.

**DISADVANTAGES**[26]

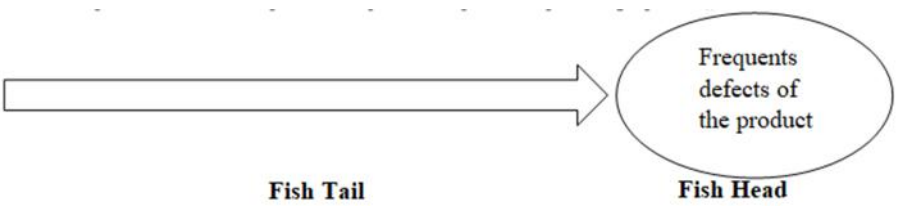
**I.** As a weakness, the simplicity of the fishbone diagram may make it difficult to represent the truly interrelated nature of problems and causes in some very complex situations.

**II.** Unless you have an extremely large space on which to draw and develop the fishbone diagram, you may find that you are not able to explore the cause and effect relationships in as much detail as you would like to.

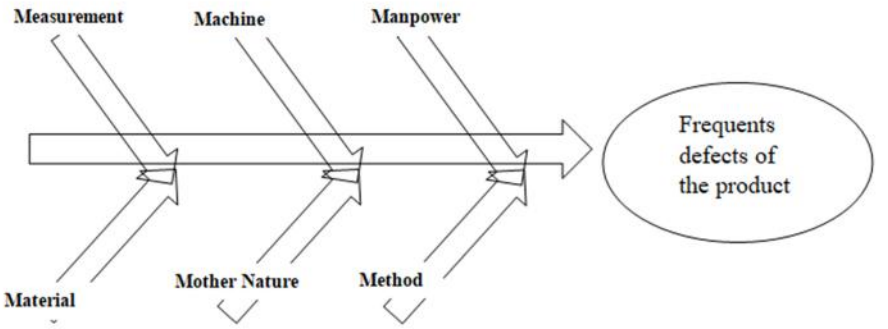
## IDENTIFY THE CAUSES OF A PROBLEM USING:THE FISHBONE DIAGRAM

As mentioned above, the Fishbone diagram or cause-effect diagram is an analytical tool that helps identify the causes of a problem, namely the modification of a process or phenomenon.[27] It aims at presenting and identifying schematically the primary and secondary causes that have led to the appearance of symptoms. Subsequently, these causes are analyzed and removed. [28]

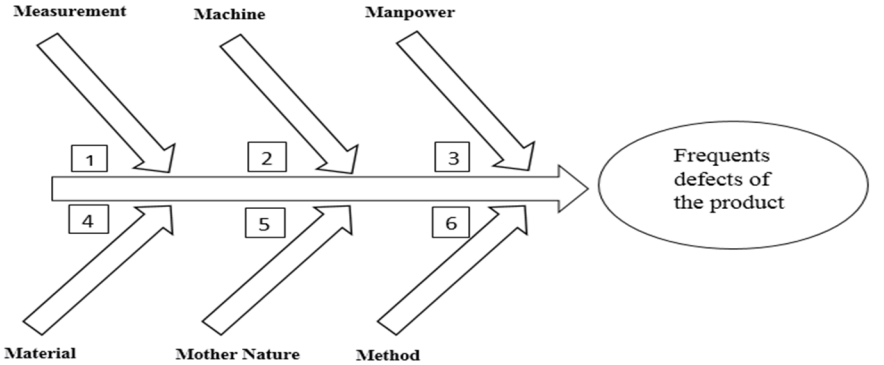
The starting point in drawing up this diagram is to identify the problem and the effect produced by this problem. [29]Thus, the problem will be the head of the fish, and the spine will be represented by the causes that have led to the problem.[30]
As an example, I took as a defect problem frequent in the process of producing a product.[31]




Once the problem has been identified, the main causes of the problem will be identified by discussing and analyzing the deficiencies of the work carried out. After identification, the identified causes will be inserted into the fish tail.[32]
Major cause category branches can be initially identified using the four Ms: material, methods, machines, and manpower, or more correctly, the four Ps: parts (raw materials), procedures, plant (equipment), and people. Categories can also be tailored depending on the problem.[33],[34]




After identifying the main causes that have led to a problem, we will identify the underlying causes of each major cause.[35] In this sense, brainstorming will be used. By using the brainstorming method during the process of identifying the causes of the problem, participants concentrate more easily and at the same time they are motivated, facilitating the assessment of possible causes according to their level of importance in the chart hierarchy. [36] , [37] , [38]




1. **Measurement :** Incorrect Parameters
   Not capable Measuring device
   Incorrect time interval of Measurements
2. **Machine:**Low Yield
   Maintenance
   Outdated
   Not Validated

3. **Manpower :**Low Number
   Unmotivated
   Poorly Trained
4. **Material :** Poor Quality
   Not Supply on Time
   Inappropriate
5. **Mother Nature :**Stress
   Toxicity
   Condition of work Unsuitable
6. **Methods :**Underperforming
   Inappropriate
   Complex

After the Fishbone diagram, we will analyze the main and secondary causes as well as the sub-cases, and in these analyzes we can use statistical, analytical methods, etc. [39] After discussions, opinions, suggestions, the company's management will make the decisions to resolve the problem they are confronted with.[40]

**DISCUSSION:**

- It indicates that the CED is an easy-to-use tool for developing and classifying root cause categories.[41], [42]
- It assumes the existence of enough knowledge to be able to isolate and identify probable root causes,but the identified causes may not be specific or reasonable.
- The CED has the potential to highlightinformation that is lacking or inadequate through thelack of identified causes in certain categories; however,it does not identify relationships between factors, hasno formal mechanism for selecting and evaluating rootcauses, and may be influenced by group bias.[43]
- The Fishbone diagram is used to identify, analyze, and classifypossible relationships among critical issues using a nonlinear structured method.[44]
- The Fishbone diagram does not have a mechanism for evaluating the integrity of the output, and may rely too heavily on subjective judgments of factor relationships.[45]
- If the selected root cause is trustworthy, it produces aclear managerial decision for an action. [46]Each analysistool has distinguishing characteristics that canpotentially affect group output. Therefore, reliabledecision making requires that managers have aworking knowledge of root cause analysis tools, theirProcesses, and their likely outcomes.[47]

**CONCLUSION:**

- The Fishbone technique is a simple technique by means of which the problem to be solved is written in the "fish head", and afterwards the causes are specified along the "fish bones" and they are divided into categories.[48]

- Alternatively, root cause analysis tools must also have the characteristics to promote collaboration,stimulate discussion, be readable or understandable, and have mechanisms for evaluating integrity.[49]
- The implications for management are that effectiveproblem solving requires the identification of specific and reasonable root causes. [50]
- Several methods exist for identifying root causes, but their effectiveness is dependent on the rigorous application of the group and the integrity of the selected root cause.[51]

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# RE-READING OF KABIR'S TEACHINGS TO KNOW THEIR ESSENCE

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Much have been made about Kaibr and his teachings. At the name of original text of Kabir, scholars from R.N. Tagore to Dr. Dharamveer tried to apropriate Kabir. Thus real Kabir was missing. What Winand M. Callewaert observed in the connection of Hundred poems of Kabir by Tagor will be proper to quote here. "The authenticity of these poems is very questionable; it appears that most of them were probably not composed by Kabir. This kabir is less caustic & more constantly ecstatic than the sharp eyed observer of socity who apears in older collections. This observation agrees with my theory of appropriation.[1] So many texts have been compiled on Kabir's Name that real Kabir & his teachings become very complicated task to reach final conclusion. So it is not easy to know exactly what actually Kabir wanted & what he was forced to want to say. He was antithesis to the Brahmnical order & their intelligencia . So he was not properly read & understood. Not only during Kabir's time even centuries after him, he was misinterpreted among scholars because intellectual means to be Dvij & their superiarity complexed mind. Some so called liberals among them overtly tried to esteblish Kabir but covertly they also damaged them.

As Winand M. callwaert observed: 'Kabir very soon was appropriated by imterseted parties (from the Gorakh panthis & Ramanandis in the 17th century to the Brahmans like Hazari P. Dvivedi or other social groups in 20th century) for their own ideological purpose or benifit.[2] Real Kabir & his teachings are to be searched and need scientific tempor & effort as Ambedkar did to know real Buddha & his teachings. Whatever Kabir said infavour of Bhakti, Sumiran, Jap of Nirgun Ram, Allah &against Maya, Jagat, Body, Mullah, Pandit, Outwardshows etc. could not be easily understood until unless one rises above the limitations of religious & Bhakti movement. Actualy it create contradictions in Kabir's teachings. It has wider socio economic & political prospects. So not so much easy his poetry as it outwardly looking simple & plain. Kabir points us to the idiomatic core of a language's history, where there is a ceaseless struggle between competing claims for nation in such terms as tradition, history and Community... The icon of Kabir in currency today has two dimensions. There is on the one hand the sceptic Kabir who negates everything, belongs to no one, and affirms no identity. On the other hand there is Kabir the dalit god who affirms everything by negating it.[3] Whatever such contradictions appeared & whatever such he said was forced by the medieval mind set of people. Nothing could be said or no body could interact with the medieval society without mixing religion, Atma, Parmatma, Ram, Govind, Allah, Swarg, Nark, Maya, Kaya in pure worldly subjects & problems. The contractors of religions misusing the faith, conscience of innocent people for their vested interests, material gains.

Had Kabir not born in the medieval society, he would have not used this genre , language to awaken the people. Actually he was humanist, rationist & revolationary thinker & activist. He tested the mythical, Puranic, blindfaith-ridden subjects on his

logic & reasoning.[4] Like Buddha he two taught to the people not to take things for granted. Unfortunately he was born in such age & society where it was fated to use old bottle for new wine & completely new bottle & new wine not acceptable to the people. So he used undesirably old symbols & imageries to express new & somewhat ultramodern revolutionary thought just to give message of humanity, dignity & brotherhood- the essence of social justice. That's why he insisted to remember Nirgun Rama[5] to recite Ramnam & Bhakti[6] & Sumiran[7], Like wise he remembered 'xkdy ukbd ohByk* & his soul-bride married with Raja Ramram, the groom etc & alerted people to short living world & body *;g llkj dkxn dh ifM;k* *foufl tk; dkxn dh ifM;k* *;g ru dkpk dEHk g] <cdk ykxk QfV x;k dN u vk;k gkFk* etc. This type poetry of Kabir confused or more proper to say critics of Kabir misused this poetry to confuse people with his teachings. Actually Kabir, if was not opposed to all this he was not happy also with these teachings. Whatever as such he said it had its specific context. Those who in depth worldly people & luxury loving oppressing classes exploited people for the entertainment of their these ambitions were targeted by these desperate teachings so that they may might awaken & proceed to leave bad habbits.

Otherwise Kabir believed in philosophy of work is worship & world where human being is born with *eu"k tUe nyHk vg *ghjk tue veky ;g*- He did not belive in outwardshows,[8] oral recitation of Rama & other world of swarg. He believed in diginity of labour & conduct. His Rama, Allah Khuda, kaya, kasi , Mathura, Dwarika etc. Lie in holy heart.[10] Unity of speech and deed unity in ¼dFkuh&dju½ & company of noble character people. His conduct should be reflected through his work, deed, speech & thinking.

He like a scientist believed in cause and effect relationship of a thing. That's why he argumentated with the pandits & Mullah Quzi & others. Where they failed to answer, Kabir alleged them & attacked vehemently[11]. He believed in unity of thought & action. He did what he taught. He believed in holy heart, noble conduct-the supreme deity decides one's fate here he used new wine in old bottle removing blindfaiths.

Real Kabir is not only in criticising pandey, Pandit, Mullah, Quzi, Yogi, Shaiva, Shakt etc. Actually he is yet to be known. He is true disciple of Satguru. He is hard working weaver. He is prodignity of labour. He believed & implemented in his life simple[12] living & heigh hinking.[13] He is very sweet natured fellow.[14] He is true socialist who believed in equalitarian distribution of means of livelihodd.[15] He is much worried about this world, family life & the poor people. Many 'Pads' of kabir depict the worst condition of peasants & their exploitation by the administration.[16] He is very much worried about education & hunger because old education & books are antihuman, against love & brotherhood, divide people on basis of caste, colour, creed, religion, gender etc. His comment on valueless reading & writing of his time, are more relevant even today.

^if<&2 d iRFkj Hk;k fyf[k&2 Hk;k tk bV@dg dchj l;kj dh yxh u ,dk NhVAA

That's why he attacked - ' iLrd nm ogk;*\ Those appropriated Kabir & his teachings according to their biased mentality & tried to prove Kabir to be pure Bhakt, individual saint isolated from real world, hundred percent Spiritual, every inch involved in affairs of Atma - Pramatame- maya, etc & who used only mystic lipstick- ^ykyh ej yky dh ftr n[kk frr yky@ykyh n[ku e x;h e Hkh gk x;h yky&are now exposed. They are unable to reach Kabir, We should go mto the processing making of the text (poetry), then we can reach to know the essence of his teachings.[17]

The essence of his teachings is problem of 'roti', poverty, misery Poverty breeds hatered, enmity & the contractors of society misused this weakness to misguide & divide the people. Kabir being sufferer of that misery- &^tn dk ekb tukfe;k dn u ik;k l[k*[18] So he reached to the conclusion that &^u dN n[kk Hkko Hk tu e] u dN n[kk ikFkh e@dg dchj luk Hkkb lrk tk n[kk lk jkVh eA[19] He dreamt a secular & democratic society & country providing social justice - right to equality, liberty, fraternity & pursuit of happiness for all without any discrimination . ^^ge okslh ok n'k d tgk tkfr oju dy ukfg** He was one of pioneers of social & religious freedom. He was extremely critical of gross inequalities and social injustices practised by both Hindus & Muslims. He was a great believer in the equality of mankind. For him like Mahatma Gandhi, Truth & God were synonymous.[20]

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eu eFkjk fny }kfjdk dk;k dkl h tkfuA
l[k lcjh ckfgjk] D;k gt dkc tkbA
tkdk fny lkfcr ugh] rkdk dgk [knkbAA
fny e [kkt fnyfg fny [kktk ;gh jghek jkekAA

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# TO ANALYSE THE DYEING PROPERTIES OF *Thespesia Populnea Flower* AND *Eichhornia Crassipes Flower* WITH THEIR SYNERGESIC EFFECTS

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**Abstract:**
Thespesia populnea, otherwise known as Portia Tree, Eden Apple, Pacific Rosewood, or Indian Tulip Tree, belongs to the Malvaceae family. It was found all over the world on the coasts. It's a small tree or shrub with arborescence. Methanol extract of Thespesiapopulnea flowers with high antibacterial activity of flavonoids,alkaloids, tannins and anthroquione glycosides, steroids phenolic antioxidants. Antifungal activity has been shown by methanol extracts of the flower buds. The flowers ethanol extracts showed antihepatotoxic activity. The flowers produce a yellowish color that is water-soluble. Eichhornia Crassipes is a freely floating perennial aquatic plant native to tropical south America, also known as water hyacinth. It is considered the worlds most troubling aquatic weed, introduced as an ornamental plant in India in 1896. The plant also has delicate lilac flowers that can be used to produce dye.An effect arising between two or more agents entities, Factors, or substances that produces an effect greater than the sum of their Indi dual effects. It is opposite of antagonism. It had a synergistic effect on the item and they all began playing harder and working together much more effectively. In this study the selected two flowers extraction were mixed to get effective properties. By Mixing of water hyacinth flower extraction with Portia flowers extraction we can get another new color and increased values of presented properties.

**Key words:** Thespesia Populnea flower, Eichhornia Crassipes flower, Extraction dyes, Synergistic Effects.

## I. INTRODUCTION

### 1.1.Thespesia Populnea Flower

Thespesiapopulnea, otherwise known as Portia Tree, Eden Apple, Pacific Rosewood, or Indian Tulip Tree, belongs to the Malvaceae family. It was found

all over the world on the coasts. It's a small tree or shrub with arborescence. Methanol extract of Thespesiapopulnea flowers with high antibacterial activity of flavonoids,alkaloids, tannins and anthroquione glycosides, steroids phenolic antioxidants. Antifungal activity has been shown by methanol extracts of the flower buds. The flowers ethanol extracts showed antihepatotoxic activity. The flowers produce a yellowish color that is water-soluble.It is a small tree or shrub that at maturity reaches a height of about 10 m and a trunk diameter of up to 60 cm. It grows fast and its bole is short and often crooked. The leaves are thin, green bluish, and heart-shaped broadly. The flowers are bell-shaped, yellow, and occur alone. Fruits are capsules that are rounded.

The root is poisonous. Plants that are fully established are highly tolerant of drought, strong winds, and saline conditions. Such characteristics make it suitable for the control of coastal erosion. It is possible to eat raw or cook young leaves, flowers and buds of flowers. The fruits are consumed and stored. Unripe fruits are eaten as a vegetable, raw or fried.Anti-fungal activity has been shown by methanol extracts of the flower buds. The flower's ethanol extracts showed antihepatotoxic activity. The flowers produce a water-soluble yellowish color. The bark is a tannin source. It also yields a good cordage, fishing lines, coffee bags, and caulking ships thread. It is possible to use seed oil in lamps. Wood, berries, seeds, and all producing coloring leaves. Often producing gums are fruits, seeds and bark. The leaves are used as wrappers for food. For light building, flooring moulds, musical instruments, utensils, vessel bodies, boat construction, oil, etc., wood is highly valued.

### 1.1.1. Medicinal Use of Thespesia Populnea Flower

Portia tree is often used in traditional medicine, where a range of ailments are handled with bark, root, leaves, flowers and fruits. Plant parts of Portia tree, particularly bark, root, leaves, flowers, and fruits, are all used in traditional medicine against a wide variety of conditions such as pleurisy, cholera, colic, fevers, herpes, urinary tract problems, abdominal swelling, hair lice, swollen testicles, rheumatism, coughs, asthma, inflammation.The tree's leaves were made into a paste and applied to inflammation as a bandage. The oil produced by the leaves and castor oil is applied to the areas of pain and inflammation. The fruit's milky secretion is linked to skin diseases. The bark paste is applied to leucoderma and other skin infections externally. The bark prepared decoction is administered internally for toxic conditions, ascites and inflammations. The roots ' decoction is a good tonic for the body.

### 1.2. Eichhorni a Crassipes Flower

Eichhorniacrassipes, also known as water hyacinth, is a free floating perennial aquatic plant native to tropical South America. It is regarded as the most troublesome aquatic weed of the world ,which was introduced in India as an ornamental plant in 1896. It has complex root structure and rapid growth rate which result in dense interlocking mats of the weed on water surface. The weed grows best in warm water rich in macronutrients and most of our water bodies are in this condition. Thus it affects water transportation, fish production, hydroelectric projects, irrigation, potability of water, etc.

Water hyacinths are called "tristylous" and have three flower morphs. Because of the length of their pistil the flower morphs are named: long, medium and short. However, tristylous populations are limited to the native lowland water hyacinth range of South America; the M-morph prevails in the introduced range, the L-morph occurs occasionally and the S-morph is completely absent. This geographic distribution of floral morphs shows that founding events played a prominent role in the worldwide spread of the species. In order to use these weeds, extensive research is now being carried out. Phytoremediation is used to remove heavy metals from water. The farm was used as animal feed, fertilizer, manufacturing of handicrafts, paper boards, mushroom substrates, and solid condition. There are applications for all parts of the weed. The plant also has delicate lilac flowers that can be used to produce dye.

#### 1.2.1.Medicinal Use of Eichhornia Crassipes Flower

This plant has beautiful lilac flowers that can be used for extraction of dye. Anthocyanin isolated from the flower. The water hyacinth's pale purple flower contains just one delphinidin glycoside. Anthocyacin (water soluble vacuolar pigmets) may appear red, violet, blue or black depending on their PH. The antioxidant activity found in anthocyanin, the anti-inflammatory, anti-viralandanti-cancer effects. A number of conditions (including high blood pressure, colds and urinary tract injections) have long been treated with anthocyanin-rich substances in herbal medicine. Recent research suggests that anthocyanins can also help to identify major health issues, including disease and cancer. Although Hyacinth is not known for its hair care benefits, it provides that amazing fragrance of a fresh flower to the shampoos and conditioners.

### 1.3.Synergistic Effects

An effect arising between two or more agents entities, Factors, or substances that produces an effect greater than the sum of their Indi dual effects.

It is opposite of antagonism. It had a synergistic effect on the item and they all began playing harder and working together much more effectively.Synergistic effects are nonlinear cumulative effects of two active ingredients with similar or related outcomes of their different activities, or active ingredients with sequential or supplemental activities. For example, vitamin E is an antioxidant and vitamin C may help to recycle oxidized vitamin E into active vitamin E, thus, a synergisticeffect may be possible between the two.

The history of drug combinations can be traced back 1900 years to HuangdiNeijing. Nowadays, drug combinations have been widely used in biomedical research and clinical practice to treat disease. Traditional Chinese Medicines (TCM) and well-established treatments for AIDS, cancer, and infectious diseases are vivid examples. TCM combines different compounds to increase therapeutic effectiveness, while minimizing toxicity and side effects. A combination of at least three active antiretroviral medications known as the AIDS cocktail not only delays the progression of AIDS, helps rebuild and maintain the immune system, and reduces complications, but also helps prevent drug resistance. Current cancer treatment also relies heavily on such drug combinations as anthracyclines, platinum drugs, and taxanes.These impressive successful examples fully illustrate the benefits of drug combinations.

With increasing mortality rates of immune compromised patients affected by invasive fungal infections and emergent drug resistance, new therapeutic strategies and effective antifungal drugs with new mechanisms of action are urgently needed. Thus, in-depth analyses of known successful and unsuccessful drug combinations would yield a greater understanding of the patterns of synergistic drug combinations and, at the same time, accelerate the development of new drug combinations. Synergistic drug combinations are a promising strategy and tend to improve therapeutically relevant selectivity

## III.METHODOLOGY

### 3.1.Extraction of dyes from Thespesia Populnea and Eichhornia Crassipes

The flowers Thespesia Populnea and Eichhornia Crassipes were collected and washed with distilled water. They were shadow dried for 3 weeks and grinded into fine powders. The fine powders were collected and stored in sterile containers. The bioactive compounds were extracts using soxhlet apparatus. About 100ml of solvent (Water/ Methanol/ Ethanol) was used for 20gm of powder. Soxhlet extraction was carried out for 30mins. The extracts were collected and stored.



FLOWER POWDER SOXHLET EXTRACTION EXTRACTED DYE

### 3.2. Materials Required

Fabric – 100%Cotton
Extracted solution – 100ml
M:L:R – 1:5
Drying Temp.- 60ºC -70ºC
Time – 30 minutes
Curing Temp. .- 60ºC -70ºC

### 3.3. Finishing of extracts on fabrics

The fabric samples were treated separately using citric acid as cross linking agent separately. The fabric specimens are treated separately with the pigments collected using citric acid as cross linking agent tool. The extracts are added to the fabricbydipand dry-method.
The finished fabricsweretakenanddriedat100-120oCfor5minandcuredat180oCfor3min

## IV.RESULT

In this study the selected two flowers ThespesiaPopulnea and Eichhornia Crassipesextraction were mixed to get effective properties(Synergistic Effect) By Mixing flowers ThespesiaPopulnea and Eichhornia Crassipesextraction we can get another new color and increased values of presented properties.




THESPESIA POPULNEA DYED FABRIC




EICHHORNIA CRASSIPES DYED FABRIC




THESPESIA POPULNEA AND EICHHORNIA CRASSIPES DYED FABRIC (SYNEGISTIC EFFECT)

## V.CONCLUSION

The extracted color from above two flowers gives very good colour on fabrics. The main benefits is there very few amount of extracted dyes gives more color. This color finished fabric shows special properties like antibacterial, antifungal and also antioxidant. Dyeing properties were analyzed. The color fastness test shows good to average further studies can be done by changing the mordents to give different shades and colors. The main advantage in this synergistic effect is the properties were more effective then usual.

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# A STUDY ON CUSTOMER RELATIONSHIP MANAGEMENT IN STANSON RUBBERS

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## ABSTRACT

This project is study about the "Customer Relationship Management in Stanson rubbers" was done under the auspicious company Stanson rubber products. The objective of the study was to find out the companies relation with the customers. The secondary objective includes the factors that induce the customers to purchase, their preference and the satisfaction level. Descriptive research design was adopted; Primary data is the data which is collected for the first for the sake of research study. Primary data used here is the questionnaire which is filled in by the customers and secondary data is the data which is collected already from the existing information and data. Sources of secondary data are the books, journals, existing reports and websites. The questionnaire was designed and the data was collected from 140 respondents. Statistical tools such as Chart, Percentage, ANOVA and Correlation analysis used. Major findings and suitable suggestion were also made. It is hoped that by a close study of the project will enable the company to understand the customer's preference, satisfaction level and the problems can also be resolved.

**Keywords:** CRM, Stanson rubber products, Satisfaction

## INTRODUCTION

CRM stands for Customer Relationship Management. (CRM) is perhaps the most important concept of modern marketing. Until recently, CRM has been defined narrowly as a customer data management activity. In its broader sense, CRM is the overall process of building and maintaining profitable customer relationship by delivering superior customer value and satisfaction. It deals with all aspects of acquiring, keeping and growing customers. The key to building lasting customer relationship is to create superior customer value and satisfaction. Organization can build customer relationships at many levels, depending on the nature of the target market. To build customer relationships, companies can add structural ties as well as financial and social benefits.

Successful CRM focuses on the profiling and understanding the needs and desires of the customers and is achieved by placing these needs at the heart of the

business by integrating them with the organizations strategy, people, and technology and business processes. CRM requires a synergistic integration of the strategy, people and technology of an organization. This integration leads to the creation of the service process that seek to develop an ongoing relationship with customers and results in creation of an exchange relationship that is mutually beneficial for both the organization and the customer. CRM must come from the top. It is an all-encompassing strategy, and no one department or call centre or Information Technology manager can drive the cross-functional process changes required. Thus, CRM is a Holistic approach. It is ideal from any organization's part of view that customers are the only assets.

## REVIEW OF LITERATURE:

According to **Peppers and Rogers (2011),** there is global tendency in customer relationship management that relates to the shift from transactional model towards the relationship model. In other words, Peppers and Rogers (2011) argue that satisfying customer needs as a result of on-time transaction is not sufficient today in order to ensure the long-term growth of the businesses.

**Ogunnaike Olaleke Oluseye (2014**) in his article "Customer Relationship Management Approach and Student Satisfaction in Higher Education Marketing" he found that the student's willingness to recommend to others increases when the student lifecycle in the university is well managed. It was also discovered that strong parent relationship management at the University enhances the student's willingness to recommend their Universities to others. He suggested that the recommended that Universities should adopt effective customer relationship management strategies to achieve student satisfaction.

## OBJECTIVES OF THE STUDY

- A study on customer relationship management in Stanson rubbers.
- To know about the socio- economic background of the respondents.
- To find out the satisfaction level of customers.

## HYPOTHESIS OF THE STUDY

- There is no significant difference between the satisfaction level of Stanson Rubber products.
- There is no significant difference between the satisfaction level of price and service in Stanson rubber products.

## NEED OF THE STUDY

- To understand the customers' expectations.
- To improve the overall customers satisfaction towards the products delivered.
- To understand the customers intention towards availing stanson products in future.

## RESEARCH METHODOLOGY

### RESEARCH DESIGN

This study employs both analytical and descriptive type of methodology. The study is conducted in two stages format, with a preliminary pilot study followed by the main study. The secondary data are collected from journals, magazines, publications, reports, books, dailies, periodicals, articles, research paper, websites, company publications, manuals and booklets. It is a plan of organizing framework for doing the study and collecting the data on the basis, the research design chosen for this study is descriptive.

### SAMPLING DESIGN

The primary data was collected among 140 respondents from Stanson Rubbers by random sampling method. The questionnaire was distributed to get the required data.

### SOURCES OF DATA

The study is based on the primary as well as secondary data. The study depends mainly on the primary data collected through a well framed and structured questionnaire to elicit the well-considers opinions of the respondents. The data collection for this study is both primary and secondary data.

### FRAMEWORK OF ANALYSIS

The selection of statistical tools was based upon the nature of data used and research objectives. The applied statistical analysis are percentage analysis, Karl Pearsons' Correlation and Analysis Of Variance.

## RESULTS AND DISCUSSIONS:

This section shows the analysis and interpretation of data used for the study.

**Table 1: Demographic profile of the respondents**

| Demographic profile | No. of respondents | Percentage |
|---|---|---|
| **Gender** | | |
| Male | 128 | 91 |
| Female | 12 | 9 |
| **Total** | **140** | **100** |
| **Age group** | | |
| 20-30 yrs | 4 | 3 |
| 31-40 yrs | 27 | 19 |
| 41-50 yrs | 71 | 51 |
| 51-60 yrs | 31 | 22 |
| Above 60 yrs | 7 | 5 |
| **Total** | **140** | **100** |

| **Educational qualification** | | |
|---|---|---|
| School | 8 | 6 |
| Graduate | 45 | 32 |
| Professional | 82 | 58 |
| Others | 5 | 4 |
| **Total** | **140** | **100** |

*Source Primary data

It is inferred that majority of the respondents (i.e) 91% are male and most of the respondents (i.e) 51% belong to the age group between 41-50 years and it is also inferred that most of the respondents ( i.e) 58% are professionals.

**Table 2: Opinion towards price**

| **Opinion** | **No. of respondents** | **Percentage** |
|---|---|---|
| Highly satisfied | 64 | 46 |
| Satisfied | 56 | 40 |
| Neither satisfied nor dissatisfied | 13 | 9 |
| Dissatisfied | 5 | 4 |
| Highly dissatisfied | 2 | 1 |
| **Total** | **140** | **100** |

The above table 2 portrays that 46% of the respondents are highly satisfied towards the price offered, 40% are satisfied, 9% are neither satisfied nor dissatisfied, 4% are dissatisfied and 1% are highly dissatisfied.It is inferred that majority of the respondents (i.e.) 46% are highly satisfied towards the price offered by the company.

**Table 3: Opinion towards service**

| **Opinion** | **No. of respondents** | **Percentage** |
|---|---|---|
| Highly satisfied | 42 | 30 |
| Satisfied | 58 | 42 |
| Neither satisfied nor dissatisfied | 34 | 24 |
| Dissatisfied | 4 | 3 |
| Highly dissatisfied | 2 | 1 |
| **Total** | **140** | **100** |

From the above table it is found that 30% of the respondents are highly satisfied with the service offered, 42% are satisfied, 24% are neither satisfied nor dissatisfied, 3% are dissatisfied, 1% are highly dissatisfied.It is inferred that majority of the respondents (i.e.) 42% are satisfied with the service offered by the company.

**Table 4: Satisfaction level of price and service- correlation**

| S.NO | Satisfaction level of price (X) | Satisfaction level of service (Y) | $X^2$ | $Y^2$ | XY |
|---|---|---|---|---|---|
| 1 | 64 | 42 | 4096 | 1764 | 2688 |
| 2 | 56 | 58 | 3136 | 3364 | 3248 |
| 3 | 13 | 34 | 169 | 1156 | 442 |
| 4 | 5 | 4 | 25 | 16 | 20 |
| 5 | 2 | 2 | 4 | 4 | 4 |
| **TOTAL** | **140** | **140** | **7430** | **6304** | **6402** |

Karl Pearsons formula:

$$r = \frac{n\sum xy - \sum x \sum y}{\sqrt{[n\sum x^2 - (\sum x)^2][\, n\sum y^2 - (\sum y)^2]}}$$

$$r = \frac{5(6402) - 140(140)}{\sqrt{[5(7430) - (140)^2][5(6304) - (140)^2]}}$$

$$r = \frac{12410}{14461.74}$$

$$r = 0.8581$$

$$r < 1$$

It is found that there is a perfect positive correlation. It is implied that satisfaction level of price and service are related.

**Table 5: Satisfaction level of stanson rubber products- One way Anova**

H0: There is no significance difference between the satisfaction level.

H1: There is significance difference between the satisfaction level.

| Particulars | Highly satisfied | Satisfied | Neutral | Dissatisfied | Highly dissatisfied | Total |
|---|---|---|---|---|---|---|
| Quality | 92 | 24 | 11 | 7 | 6 | **140** |
| Product rate | 18 | 32 | 40 | 32 | 18 | **140** |
| On-time delivery | 70 | 30 | 16 | 10 | 14 | **140** |
| Eco friendly produ | 8 | 16 | 34 | 60 | 22 | **140** |

| ct | | | | | | |
|---|---|---|---|---|---|---|
| Design | 26 | 37 | 31 | 29 | 17 | **140** |
| Ci | 214 | 139 | 132 | 138 | 77 | **G=700** |
| $Ci^2$ | 45796 | 19321 | 17424 | 19044 | 5929 | |
| Ni | 5 | 5 | 5 | 5 | 5 | **N =25** |
| $\sum Ci^2/ni$ | 9159.2 | 3864.2 | 3484.8 | 3808.8 | 1185.8 | **$\sum Ci^2$ /ni=215 02.8** |

N = 25
G=700
Correction factor (c.f) = $G^2/N = 700^2/25$
Correction factor (c.f) =19600
Find $\sum\sum xij^2 = 92^2+24^2+11^2 \ldots\ldots 29^2+17^2=29590$
Total sum of square (TSS) =$\sum\sum xij$ – cf= 29590-19600
TSS = 9990
Column sum of square (CSS) =$\sum ci^2/Ni$ – cf= 21502.8-19600
CSS = 1902.8
Error sum of square (ESS) = TSS-CSS= 9990-1902.8
ESS = 8087.2

| **SOURCE OF VARIATION** | **SUM OF SQUARE** | **D.F** | **MEAN SUM OF SQUARES** | **CALCALATE F = greater/smaller** |
|---|---|---|---|---|
| Between columns | CSS= 1902.8 | C-1 =5-1 = 4 | M1 = CSS/C-1 = 475.7 | F = M1/E = 475.7/404.36 C.V= 1.17 |
| Residuals | ESS= 8087.2 | N-C=25 -5 =20 | E = ESS/N-C = 404.36 | |

Degree of freedom = ( r1 , r2)
= ( Nr. df , dr. df)
= 4,20
Table value of 5% = 5.80
Calculated value < Table value
1.17 < 5.80.
$H_0$ is accepted
There is no significant difference between satisfaction level.

**SUGGESTIONS**

- Company should take necessary action towards the complaints of the customers.
- Company can improve the advertisement.

- Company can improve the customer awareness program.

## CONCLUSION

From this study it can be concluded that the customer relationship management in Company is satisfactory. The company is using various CRM practices like customization of the product, maintaining interaction with the customers regularly and providing good quality product etc. Customer relationship management has a certain impact on the profitability of the company. The study about the customer relationship will really have an impact on identifying the areas in which the management should be concentrated. From the overall study on the level of customers relationship with respect of Stanson rubbers, it is understood that majority of the customers are expecting customer awareness program to be conducted by the company. Most of the customers are satisfied with quality of the products produced. To improve the sales and services and effective advertising should be used and also the existing technology should be upgraded.

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# INCLUSION OF VISUALLY IMPAIRED STUDENTS IN EXTRA-CURRICULAR ACTIVITIES & FUNCTIONAL SKILLS ACHIEVEMENT IN IED-SS

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## Abstract

Inclusive Education (IE) is a new approach towards educating the children with disability and learning difficulties with that of normal ones within the same roof . It brings all students together in one classroom and community, regardless of their strengths or weaknesses in any area, and seeks to maximize the potential of all students. It is one of the most effective ways in which to promote an inclusive and tolerant society. The overall objective of the study is to find out the Involvement of visually impaired students in Extra-Curricular activities and the Functional skills of visually impaired students in Inclusive set up in Coimbatore district and differences among them due to age, gender and nature. The present study revealed that there is no significant differences in Involvement of Extra-Curricular activities due to different age groups, gender and nature. The present study also reported that the totally blind children showed independency in achieving Functional skills.

## INTRODUCTION

Inclusive education has grown from the belief that education is a basic human right and that it provides the foundation for a more just society. All learners have a right to education, regardless of their individual characteristics or difficulties. Inclusive education initiatives often have a particular focus on those groups, which, in the past, have been excluded from educational opportunities. It is known that 73 million children of primary school age were out of school in 2010, down from a high of over 110 million out-of-school children in the mid-1990s, according to new estimates by the UNESCO Institute for Statistics (UIS). About Eighty percent of Indian population lives in rural areas without provision for special schools. It means, there are an estimated 8 million children out of school in India (MHRD 2009 statistics), many of whom are marginalised by dimensions such as poverty, gender, disability, and caste.

**Inclusive education** is when all students, regardless of any challenges they may have, are placed in age-appropriate general education classes that are in their own neighborhood schools to receive high-quality instruction, interventions, and supports that enable them to meet success in the core curriculum (Bui, Quirk, Almazan, & Valenti, 2010; Alquraini & Gut, 2012) Inclusive schools have a collaborative and respectful school culture where students with disabilities are presumed to be competent,

develop positive social relationships with peers, and are full participating members of the school community (Jelas & Ali, 2014; Lamichhane, 2017).

An **Extracurricular activity (ECA)** or **Extra academic activity** (**EAA**) is an activity, performed by students, that falls outside the realm of the normal curriculum of school, college or university education. Such activities are generally voluntary (as opposed to mandatory), social, philanthropic, and often involve others of the same age. Co-Curricular activities complement the curricular activities and groom the students in the art of living and working together. It also professes co-ordination, adjustment and speech fluency, extempore and debating skills among students. Students with visual impairments will need particular assistance to acquire co-curricular skills primarily through vision. **Functional skills** refer to the skills that students learn that provide them with the opportunity to work, play, socialize, and take care of personal needs to the highest level possible. Students with visual impairments will need particular assistance with those skills acquired primarily through vision.

**SIGNIFICANCE OF THE STUDY**

Extra-Curricular activities and Functional skills have been given important consideration keeping in mind their significance towards the performance in day to day tasks. Comparatively significant research has been conducted on involvement of Visually Impaired students in Extra-Curricular activities in relation to age, gender and nature and on achievement of Functional skills in relation to age, gender and nature of visually impaired students.

**OBJECTIVES**

1. To study the involvement of visually impaired students in Extra-Curricular activities in relation to their age in inclusive set up.
2. To study the involvement of visually impaired students in Extra-Curricular activities in relation to the gender in inclusive classroom.
3. To study the involvement of visually impaired students in Extra-Curricular activities in relation to nature in inclusive education.
4. To study the achievement of Functional skills by visually impaired students in relation to their age in inclusive set up.
5. To study the achievement of Functional skills by visually impaired students in relation to the gender in inclusive classroom.
6. To study the achievement of Functional skills by visually impaired students in relation to nature in inclusive education.

**SCOPE AND LIMITATIONS**

This research study the involvement of visually impaired students in Extra-Curricular activities and achievement of Functional Skills in Coimbatore district school students in relation to a few selected variables like age, gender and nature. The involvement in Extra-Curricular activities is measured by using checklist and questionnaire. The main purpose of the study is to find out whether there is differences in age, gender and nature. Based on the analysis and discussion of results implications are drawn. Due to practical constraints the sample size was limited to 40 students in Coimbatore district in Inclusive schools. However, it is felt that inspite of the above mentioned limitations the findings of the study can be generalized to a great extent , since care was taken to make every step in the procedure of the study as objective as possible.

## REVIEW OF THE RELATED LITERATURE

Rahaman, Muhammed Mahbubur (2011) viewed a phenomenological study to understand and describe the inclusive education practices for students with disabilities in secondary schools in Bangladesh. This study intends to answer the main research question: How do teachers in secondary schools in Bangladesh understand inclusion? The research used a phenomenological research design consisting of participant interviews and observations. An additional questionnaire was used to measure teacher attitudes and understanding of teaching strategies. A total of 12 interviews (two for each participant classroom teacher) and 12 observations (two of each participant) were conducted. Participants found that student-centric evidence-based teaching and learning strategies are more effective than their traditional lecture-based teaching and learning.

Mumthas, N. S.; Shamina, E. (2011) conducted a study involving teachers in USA it was found that only 29 percent of general educators felt that they had enough expertise or training in inclusion (Hobbs and Westling 2002). The present study is an attempt to find out whether the prospective teachers have adequate awareness on the concept of inclusive education through an Awareness Test on Inclusive Education (Mumthas & Shamina, 2010). A sample of 300 prospective teachers at secondary level from various teacher-training institutions of Malappuram and Calicut districts were selected for the study. It is found that prospective teachers do not have adequate Awareness on Inclusive Education and it does not differ significantly irrespective of their gender, locale of Institution and type of management of institution.The study suggests that adequate training programs on Inclusive Education should be given to prospective teachers for successful implementation of Inclusive Education.

A 2000 quantitative study found 58% of time spent in a self-contained classroom was classified as “non-instructional,” compared to 35% of the time in a general education classroom. The students with severe disabilities in general education classroom were also 13 times more likely than their typical peers to receive direct instruction during whole-class time, and 23 times more likely to receive one-on-one support. This challenges the common argument that students with disabilities cannot receive individualized instruction in a general education setting.

A study looking at the outcome of 11,000 students with all types of disabilities found that more time in a general education classroom correlated to less absences from school, fewer referrals for misbehavior, and more post-secondary education and employment options.

Erten,et al ( 2012 ) conducted a study on conceptual and methodological challenges of doing research in the field of inclusive education and revisit school effectiveness research literature to inform future research. First, we present the rationale for inclusive education and briefly review the evolution of special needs education. Then, we discuss limitations of current research on inclusive

education. Next, we present school- and classroom-level findings of school effectiveness research to highlight how it can influence the inclusive education research agenda. We conclude by presenting future directions for research.

## METHODOLOGY

" The survey is in briefly a method of analysis in scientific and orderly form for defined purpose of given social situation of problem or population" Herman,(2005).The method adopted in the study is survey method. " Survey research is an organized attempt to analyze interpret and report the present status of social institution group or area Whitney, F. L (2005)

## SELECTION OF TOOL

Tool is an important instrument to collect data. For collecting new, unknown data required for the study of any problem one may use various devices. For every type of research we need certain instrument to gather new facts or to explore new fields. In the present study the investigator selected "Checklist" and "Questionnaire" as the most important tool for collecting data.

## CONSTRUCTION OF TOOL

**Checklist:**

The checklist was prepared to find out the functional and social skills of visually impaired students. The checklist consists of 30 questions including social skills, emotional management skills, communication skills, verbal behaviour and response skills and personal care skills. The response from the students for the above skills will be evaluated and marked by the researcher for every student selected for the research study.

**Questionnaire :**

The Questionnaire was prepared by the investigator .It consists of 10 questions to test their involvement in Extra-Curricular activities . The response from the students will be evaluated and marked by the researcher for every student selected for the research study.

## PILOT STUDY:

A pilot study is a' small scale replica 'of the main study. It is the rehearsal of the main study. It covers the entire process of research preparation of a broad plan of the study, construction of tools, collection of data, processing and analysis of data and report writing. The selected tool was first used with Avinashilingam Girls higher Secondary school and C.S.I Girls Higher secondary school with 14 Visually impaired children to find the reliability of the tool. After the tool was found to be reliable, it was used to collect data from other students in the other school for final study.

## SELECTION OF THE AREA

The area selected for the purpose of the study was limited to Coimbatore district only. The example selected for the present study consists of 40 students in 5 schools implementing IED –SS programme in and around Coimbatore district.

**Distribution of sample for the present study:**

**TABLE- 1**

| S.NO | SCHOOLS | BOYS | GIRLS | TOTAL |
|---|---|---|---|---|
| 1 | Avinashilingam Girls Hr.Sec.School, Coimbatore | | 8 | 8 |
| 2 | Government Hr.Sec.School,Karamadai | 4 | 1 | 5 |
| 3 | CSI Boys Hr.Sec.School,Coimbatore | 16 | | 16 |
| 4 | CSI Girls Hr.Sec.School,Coimbatore | | 6 | 6 |
| 5 | St.Michael Hr.Sec.School,Coimbatore | 5 | 5 | |
| | TOTAL | 20 | 20 | 40 |

The above table reveals that there are 40 visually impaired students in IED-SS programme in Coimbatore district. Out of 40 students 20 are boys and 20 are girls.

## ANALYSIS AND INTERPRETATION OF THE DATA

The data after collection has to be processed and analyzed in accordance with the outline laid down for the purpose at the time of developing research plan.The term processing implies editing, coding, classification and tabulation of collected data so that they are manageable for analysis. The term analysis refers to the computation of certain measures along with searching for patterns relationships that existing among data groups ( Kothari, 1990 ).

Interpretation refers to the task of drawing inferences from the collected facts after an analytical or experimental study. Interpretation leads to the establishment of explanatory concepts that can serve as guide for future research studies; it opens new avenues of intellectual adventure and stimulates the quest for more knowledge - Kothari ( 2006 )

The percentage analysis of functional skills and social skill among visually impaired students was done by the investigator and corroborated under the following headings.

**AGE OF SELECTED STUDENTS**

The percentage analysis of selected students with regard to their age groups was calculated in the following table.

**TABLE - 2**

**AGE OF SELECTED STUDENTS**

| AGE | No. | Percent |
|---|---|---|
| 14-16 Years | 20 | 50.0 |
| 17-19 Years | 20 | 50.0 |
| Total | 40 | 100.0 |

From the above table it can be said that visually impaired children in the age groups of 14 – 16 yrs and 17 – 19 yrs are 50 %.

**GENDER OF SELECTED STUDENTS**

The percentage analysis of selected students with regard to their gender was calculated and presented in the following table.

**TABLE - 3**

**GENDER OF SELECTED STUDENTS**

| GENDER | No. | Percent |
|---|---|---|
| Boys | 26 | 65.0 |
| Girls | 14 | 35.0 |
| Total | 40 | 100.0 |

It can be said from the above table that majority of them (65 percentage) were visually impaired boys and 35 percentage were visually impaired girls.

**NATURE OF SELECTED STUDENTS**

The percentage analysis of selected students with regard to their nature was calculated and presented in the following table.

**TABLE- 4**

**NATURE OF SELECTED STUDENTS**

| NATURE | No. | Percent |
|---|---|---|
| Total blind | 13 | 32.5 |
| Low vision | 27 | 67.5 |
| Total | 40 | 100.0 |

From the above table it can be discussed that 67.5 percentages were low vision and 32.5 percentages of students were totally blind. Majority of the sample were low vision students.

**COMPARISON OF INVOLVEMENT OF VISUALLY IMPAIRED CHILDREN IN EXTRA-CURRICULAR ACTIVITIES BASED ON THEIR AGE**

The T-test was applied to find out whether there is significant difference among the group in the average extra curricular activities skill scores.

**TABLE-5**

**COMPARISON OF INVOLVEMENT OF VISUALLY IMPAIRED CHILDREN IN EXTRA-CURRICULAR ACTIVITIES BASED ON THEIR AGE**

| | | EXTRA-CURRICULAR ACTIVITIES | | | T | df | Sig | |
|---|---|---|---|---|---|---|---|---|
| | | Mean | S.D | No. | | | | |
| AGE | 14-16 Years | 7.80 | 1.79 | 20 | 0.000 | 38 | NS | |
| | 17-19 Years | 7.80 | 1.51 | 20 | | | | |
| TOTAL | | 7.80 | 1.64 | 40 | | | | |

NS- Not Significant

The above table shows that the calculated T - value 0.000 which is lesser than the table value of 2.024 at 5 % level of significance. Since the calculated value is lesser than the table value it is inferred that there is no significant difference among the age groups in the average scores. Hence the hypothesis is accepted.

**COMPARISON OF INVOLVEMENT OF VISUALLY IMPAIRED CHILDREN IN EXTRA-CURRICULAR ACTIVITIES BASED ON THEIR GENDER**

The T-test was applied to find out whether there is significant difference among the group in the average extra curricular activities skill scores.

**TABLE-6**

**COMPARISON OF INVOLVEMENT OF VISUALLY IMPAIRED CHILDREN IN EXTRA-CURRICULAR ACTIVITIES BASED ON THEIR GENDER**

| | | EXTRA-CURRICULAR ACTIVITIES | | | T | df | Sig |
|---|---|---|---|---|---|---|---|
| | | Mean | S.D | No. | | | |
| GENDER | Boys | 7.85 | 1.67 | 26 | 0 .240 | 38 | NS |
| | Girls | 7.71 | 1.64 | 14 | | | |
| TOTAL | | 7.80 | 1.64 | 40 | | | |

NS- Not Significant

The above table shows that the calculated T - value 0.240 which is lesser than the table value of 2.024 at 5 % level of significance. Since the calculated value is lesser than the table value it is inferred that there is no significant difference between boys and girls in the average scores.
Hence the hypothesis is accepted.

**COMPARISON OF INVOLVEMENT OF STUDENTS IN EXTRA-CURRICULAR ACTIVITIES BASED ON THEIR NATURE**

The T-test was applied to find out whether there is significant difference among the group in the average extra curricular activities skill scores.

**COMPARISON OF INVOLVEMENT OF STUDENTS IN EXTRA-CURRICULAR ACTIVITIES BASED ON THEIR NATURE**

**TABLE-7**

| | | EXTRA-CURRICULAR ACTIVITIES | | | T | df | Sig |
|---|---|---|---|---|---|---|---|
| | | Mean | S.D | No. | | | |
| NATURE | Total blind | 8.23 | 1.83 | 13 | 1.161 | 38 | NS |
| | Low vision | 7.59 | 1.53 | 27 | | | |
| TOTAL | | 7.80 | 1.64 | 40 | | | |

NS- Not Significant
The above table shows that the calculated T - value 1.161 which is lesser than the table value of 2.024 at 5 % level of significance. Since the calculated value is lesser than the table value it is inferred that there is no significant difference between totally blind and low vision children in the average scores. Hence the hypothesis is accepted.

**C0MPARISON OF FUNCTIONAL SKILLS OF VISUALLY IMPAIRED CHILDREN BASED ON THEIR AGE**

The T-test was applied to find out whether there is significant difference among the group in the average Functional skill scores.

**C0MPARISON OF FUNCTIONAL SKILLS OF VISUALLY IMPAIRED CHILDREN BASED ON THEIR AGE**

**TABLE- 8**

| | | FUNCTIONAL SKILLS | | | T | df | Sig |
|---|---|---|---|---|---|---|---|
| | | Mean | S.D | No. | | | |
| AGE | 14-16 Years | 16.40 | 1.73 | 20 | 0.000 | 38 | NS |
| | 17-19 Years | 16.40 | 2.62 | 20 | | | |
| TOTAL | | 16.40 | 2.19 | 40 | | | |

NS- Not Significant

The above table shows that the calculated T - value 0.000 which is lesser than the table value of 2.024 at 5 % level of significance. Since the calculated value is lesser than the table value it is inferred that there is no significant difference among the age groups in the average scores. Hence the hypothesis is accepted.

**COMPARISON OF FUNCTIONAL SKILLS OF VISUALLY IMPAIRED CHILDREN BASED ON THEIR GENDER**

The T-test was applied to find out whether there is significant difference among the group in the average Functional skill scores.

**COMPARISON OF FUNCTIONAL SKILLS OF VISUALLY IMPAIRED CHILDREN BASED ON THEIR GENDER**

**TABLE- 9**

| | | FUNCTIONAL SKILLS | | | T | df | Sig |
|---|---|---|---|---|---|---|---|
| | | Mean | S.D | No. | | | |
| GENDER | Boys | 16.50 | 2.40 | 26 | .389 | 38 | NS |
| | Girls | 16.21 | 1.81 | 14 | | | |
| TOTAL | | 16.40 | 2.19 | 40 | | | |

NS- Not Significant

The above table shows that the calculated T - value 0.389 which is lesser than the table value of 2.024 at 5 % level of significance. Since the calculated value is lesser than the

table value it is inferred that there is no significant difference between boys and girls in the average scores.
Hence the hypothesis is accepted.

## COMPARISON OF FUNCTIONAL SKILLS OF STUDENTS BASED ON THEIR NATURE

The T-test was applied to find out whether there is significant difference among the group in the average Functional skill scores tabulated and represented graphically in fig.7.

## COMPARISON OF FUNCTIONAL SKILLS OF STUDENTS BASED ON THEIR NATURE

**TABLE- 10**

| | | FUNCTIONAL SKILLS | | | T | df | Sig |
|---|---|---|---|---|---|---|---|
| | | Mean | S.D | No. | | | |
| NATURE | Total blind | 17.38 | 2.63 | 13 | 2.049 | 38 | * |
| | Low vision | 15.93 | 1.82 | 27 | | | |
| TOTAL | | 16.40 | 2.19 | 40 | | | |

* - Significant at 5% level
The above table shows that the calculated T - value 2.049 which is higher than the table value of 2.024 at 5 % level of significance. Since the calculated value is higher than the table value it is inferred that there is significant difference between totally blind and low vision children in the average scores. Hence the hypothesis is rejected. From the table it is inferred that totally blind showed independency in achieving Functional skills.

## SUMMARY AND CONCLUSIONS

The findings of the study are as follows

1. By viewing the background information of students, it was found that both visually impaired boys and visually impaired girls were in equal percentage. (20 %).
2. It was found that majority of them 65 % were visually impaired boys and 35 % were visually impaired girls.
3. Regarding the nature, 67.5 % students were low vision and 32.5 % of students were totally blind. Majority of the sample were low vision students.

4. The T-test was applied to find out whether there is significant difference among the group in the average Extra curricular activities skill scores. The calculated T - value 0.000 which is lesser than the table value of 2.024 at22.5 % level of significance. Since the calculated value is lesser than the table value it is inferred that there is no significant difference among the age groups in the average scores.
5. The T-test was applied to find out whether there is significant difference among the group in the average Extra curricular activities skill scores.The calculated T - value 0.240 which is lesser than the table value of 2.024 at 24.5 % level of significance. Since the calculated value is lesser than the table value it is inferred that there is no significant difference between boys and girls in the average scores.
6. The T-test was applied to find out whether there is significant difference among the group in the average Extra -curricular activities skill scores. The the calculated T - value 1.161 which is lesser than the table value of 2.024 at 5 % level of significance. Since the calculated value is lesser than the table value it is inferred that there is no significant difference between totally blind and low vision children in the average scores
7. The T-test was applied to find out whether there is significant difference among the group in the average Functional skill scores.The calculated T - value 0.000 which is lesser than the table value of 2.024 at 5 % level of significance. Since the calculated value is lesser than the table value it is inferred that there is no significant difference among the age groups in the average scores.
8. The T-test was applied to find out whether there is significant difference among the group in the average Functional skill scores. The calculated
9. T - value 0.389 which is lesser than the table value of 2.024 at 5 % level of significance. Since the calculated value is lesser than the table value it is inferred that there is no significant difference between boys and girls in the average scores.
10. The T-test was applied to find out whether there is significant difference among the group in the average Functional skill scores. The calculated T - value 2.049 which is higher than the table value of 2.024 at 5 % level of significance. Since the calculated value is higher than the table value it is inferred that there is significant difference between totally blind and low vision children in the average scores. From the table it is inferred that totally blind showed independency in achieving Functional skills

## RECOMMENDATIONS

The research report's recommendations are outlined below, and presented thematically.

1. Efforts are necessary to provide the optimal learning experience for the visually impaired children in co curricular activities.
2. Provide in-service training to all mainstream teachers and primary education advisors on inclusive education.
3. To develop flexible curricula in accordance with individual needs of children, which will allow using different forms and methods of education.
4. The teaching should aim at the provision of sufficient experience for visually impaired children for optimum utilisation of their potentialities.

5. Provide right kind of learning materials and books for children with disabilities in Government schools
6. The teachers and parents should give more attention to tackle the problems faced by the visually impaired children in developing functional skills.

## CONCLUSION

Inclusive education has potential to benefit all students, their families and the whole community. Despite many barriers, inclusive education is gaining momentum everywhere. . The visually impaired children feel better in inclusive set up than in special school. A group with parent, teacher, society and student can bring anonymous change in inclusive education through co-operation. Parents and pupils have important contributions to make to shape the implementation of inclusion ( Lindsay , 2007 ). Inclusion is focused on presence, participation, and achievement. If everyone focus on this , the barriers in inclusive education will be eradicated which facilitate the visually impaired to excel academically and face challenges in all walks of life.

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# PARENTAL INVOLVEMENT TOWARDS CHILD'S EDUCATION AT JUNIOR HIGH SCHOOL/ELEMENTARY EDUCATION IN IMPHAL EAST DISTRICT, MANIPUR

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**Abstract**

Parental role in child's education is pivotal. Without which the child's education will be incomplete in this modern world as child will remain more hours at home than at school. Most of supports for the children are coming from family mainly. But, many parents do not know, what will be actual care to be taken up for their children. The way of systematic parental care is also discussed minutely in the study. The same study tries to find out and compare the quality of parental care for their children between the parents of Government and private schools. The study also tries to find out the suggestive measures to improve the quality of parental care towards their children, which will make their children perfect citizens in future.

## INTRODUCTION:

Parental involvement is often seen as a cornerstone in a child's education. It can make a considerable difference to child's school life, both in academics success and in general enjoyment at school. Parental involvement is known to be linked with improved behaviour, regular attendance and positive attitudes. It provides a support network for children which is particularly important when they face academics hurdles or other challenges in life. As a results children whose parents stay involved are more likely to have more self esteem, be disciplined have more self-motivation and tend to achieve better grades and also creates ties and strengthens bonds with children.

It also leads to the building of stronger relationships within the school, leading to clearer communication between teachers and participate in school activities. They gain a clearer understanding of what is expected of their children at school and they learn from teachers how to work at home to enhance their children's education.

**REVIEW OF RELATED LITERATURES OF STUDY: (1) Ballen and Moles (1994**) in "school-family partnerships. Strong families, strong school's as a type of parental involvement in children's education. it is not necessary for parents to know all the answers, however, it is important to demonstrate their interest by providing a quiet, well-lit place for doing homework, encouraging children's effort, being available for questions and being willing to discuss material the child is learning. (2) **Carter and Wojtkiewicz (2000)** studied differences in parental involvement between sons and daughters. They discovered that when it pertains to discussions about school, parents were more involved with their daughters however, when it come to being involved with their schooling directly, parents were more involved in the education of their son. (3) **Grolnick and slawiaczek (1994)** conduct a study on "parents" involvement in children's schooling: A multidimensional conceptualization and motivational model" it viewed PI as parents dedication of resources to a child. Their model incorporates both developmental and educational aspects of PI and differentiates parents overall involvement with their child from their involvement in the child's education. (4) **Epstein (1995)** proposed types of involvement which include parents establishing a home environment that supports child as students, school-to-home and home-to-school communications about school programs and children's progress parents and guardians volunteering at school, taking part in decision making at school and school collaborating with communities to identify and integrate resources. Parents should take advantage of opportunities to become involved with school administration and policy development for example, attend school board meetings and joint the PTA (parents teachers association). (5) **Catsambis (2001)** explored the impact of parental involvement on the success of high school seniors. She found the parental involvement during the senior year does impact student's success but not as much as it did in earlier years. She also found that educational expectations and parental encouragement were the most effective type of parental involvement in affecting academic success.(6) **Powell et al, (2010)** conducted a study on parents – school relationships and children's academic and social outcomes in public school pre-kindergarten. They examined the correlation between parent-school relationship and the academic outcome in public school prekindergarten "They examined the correlation between parent-school relationship and the academic outcome s of 140 students attending a state funded preschool program. School readiness was assessed at the beginning and end of the school year via eleven items derived from a parent interview. (7) **Arnold et al., (2008)** Later conducted a study to further examine the relationship between PI and pre-literacy development. PI assessed through teachers' responses to ten items of the Parent-Teacher Involvement Questionnaire (Reid, Webster-Straton & Beauchaine, 2001). The result of the study revealed small to medium sizes. Higher PI was related to pre literacy skills. Moreover, a significant positive correlation was found between SES and PI. (8) **Khajehpour (2011)** conducted a study on "Relationship between emotional intelligence, parental involvement and academic performance of high school students." This study investigated the relationship between emotional intelligence , parental involvement and academic performance of 300 high school students in Tehran, Iran. The participation ranged in age between 15 and 18 years. Researcher in this study used an adapted questionnaire. Results showed that both emotional intelligence and parental involvement could predict academic achievement in

high school students. (9) **Chaudhary and Muni (1995)** in "role of parental support in child's need satisfaction and academic achievement", observed that parental support had positive effect on their children's academic performance. They study on the role of parental support in children's need for satisfaction and academics achievement. The sample consisted of fifty children from 7th grade to 9th grade of equal number of boys and girls. Family effectiveness and need satisfaction, inventory and academics marks were used as measures in this study. (10) **Kaur (1999)** conducted a research on " Problem of Primary education as perceived by parents in relation to their attitude towards primary education". The researcher found as to what the levels of income and education of the parents affect on the perceptions about the primary education. It was found that parents respond differently on their perceptions to the problems in primary education on public and government schools, attitude of different genders with the difference on income and educational levels of the parents. (11) **Suresh kumar N Vellymalay (2012)** conducted a study on, "Bridging school and parents, parental involvement in their child's education. The parents also show higher involvement when the school is cooperative in discussing their child. In addition, findings also indicate that parents are more involved in their child's education when the parents are kept informed about the meetings, activities and events that they have to attend. (12) **Sarkar A.K. (1986)** conducted a study on, "Correlates of children attitude towards their parents". the important finding were that attitudes scores were normally distributed, boys and girls with favourable and unfavourable attitude did not differ with respect to their personality and the third born children attitude towards their parents differed significantly. (13) **Devi and Mayuri (2003)** studied " the effects of family and school on the Academic Achievement of residential school". The study was conducted on residential school children studying in IX and X classes. The result indicated that girls were superior to boys. Family factors like parental aspirations and socio economic status significantly contributed to academic achievement. (14) **Pati and Acharya (2005) i**n their study "Out of School Learning and its Impact on the Achievement of the Pupils" analyzed that the pupils who learn from parents or guardians after the normal school instruction had done much better achievement in the exam than those learned in group coaching or tuition learned by them. The authors recommend the need of parents or guardians to teach their children if uneducated parents than coaching or tuition instead of self learning to give the required instruction lacking from the school instructions.

**CONCLUSION**:

It can be concluded that the topic of the present study was not conducted by anybody before as the proofs and evidences are given above. So, the work of the investigator is the new area study for the improvement of elementary education in connection with parental roles in terms of child's education.

**JUSTIFICATION OF THE STUDY:** Parent's involvement in their children's improve children's academic outcomes and create and also create a connection between the home and school. And those who participate along with their children are well informed to the many aspects of their child's day to day life. Parental involvement in education of their children's has been significantly linked with the quality of education and academic achievement of children. Parents involvement not only make them understand their needs to work to increase the competency and confidence of the children but also able to influence decision made in the school and develop closer ties to their communities and neighbours. The information obtained by completing this study will be beneficial to parents, students and educators. The findings of this research may also be beneficial to educational institutions. The results can be utilized to develop school programs associated with parental involvement in school activities and decision. These can be implemented to bridge the gap between home and school while improving student's academic achievement.

**DEFINITION OF KEY WORDS USED:**

a. **Parents**: One who gives birth to or nurture and raised a child.
b. **Jr high school:** Junior high school also known as intermediate school or middle high school is an educational stage which exists in some countries, providing education between primary school and secondary school. The concept regulation and classification of middle schools as well as the ages covered vary between and sometimes within countries.
c. **Elementary Education:** Elementary education also called primary education following preschool but before high school. It usually encompasses grades 1-8 and students learn basic skills in areas such as reading, writing and maths.
d. **Kshetrigao A/C:** Kshetrigao is a town in Imphal east district of Manipur. It is located 6km towards south from district head quarter Porompat, 7km from state capital Imphal
e. **Parental involvement**: participation by a child's father or mother in a child's learning processed both in and out of school.

**OBJETIVES OF THE STUDY:**

1. To find out overall awareness level of the parental involvement in their child's education.
2. To compare the awareness level of parental involvement between the higher and lower qualification of parents within Kshetrigao Assembly Constituency.
3. To compare the awareness level of between employed and unemployed parents within Kshetrigao Assembly Constituency.
4. To compare the awareness level of parental involvement between the parents of Govt. and private schools in Kshetrigao Assembly Constituency.
5. To find out suggestive measures for the improvement of parental education and child care.

**HYPOTHESIS OF THE STUDY:**

1. There is no significant level of overall awareness on parental involvement in their child's education.
2. There is no significant difference between the awareness level of parental involvement between the higher and lower qualification of parents within Kshetrigao Assembly Constituency.
3. There is no significant difference between employed and unemployed parents within Kshetrigao Assembly Constituency
4. There is no significant difference between the awareness level of parental involvement between the parents of Govt. and private schools in Kshetrigao Assembly Constituency.

**DELIMITATION:**

1. The study was confined to the parents residing within Kshetrigaon Assembly Constituency, Imphal East Manipur.
2. The study was confined to 80 parents whose children were studying in class I to VIII at Govt. and Private Schools within Kshetrigaon Assembly Constituency, Imphal East Manipur.
3. The study was confined only within the academic calendar-2019-2020.

**METHODOLOGY:** The Descriptive Survey Method was employed for the proposed study. The population was consisted of parents residing in Kshetrigao Assembly Constituency, Imphal east, Manipur, the children are reading in class I to VIII at Government and Private Schools in Kshetrigao Assembly Constituency.
The investigator selected 56 numbers of parents randomly, residing within Kshetrigao Assembly Constituency, Imphal East, Manipur, the children are reading in class I to VIII in government and private schools on the basis of purposive sampling.

The sample is shown in the following ways :

| Government School-28 | | | | Private School -28 | | | |
|---|---|---|---|---|---|---|---|
| Matriculate-14 | | Under Matriculate-14 | | Matriculate-14 | | Under Matriculate-14 | |
| Unemployed 07 | Employed 07 | Unemployed 07 | Employed 07 | Unemployed 07 | Employed 07 | Unemployed 07 | Employed 07 |

**TOOL USED:** Self developed questionnaire was used to collect the relevant data of the study. This consisted of 25 questions relating to different areas of parental involvement among the parents. The questionnaire composed the statement covering various aspects of parental involvement. The questionnaire contained 25 items under the six areas of parental involvement namely:

1. 5 (five) questions on parenting.
2. 5 (five) questions on communication: school to home, home to school.
3. 5 (five) questions on learning at home.
4. 5 (five) questions on decision making.
5. 5 (five) questions on collaboration with community.

**SCORING TECHNIQUES**: The scoring key of the questionnaire provided to the parents of four schools was in the form of 2 points scale (yes/no) under Thurnstone scale. Scale in which 1 mark was given for right responses, whereas the wrong answer will be awarded 0 mark.

**STATISTICAL TECHNIQUES:** For analyzing and interpreting the result of the study form the collected data, following statistical techniques were used:

1. Percentage
2. Graphical representation and
3. T-test

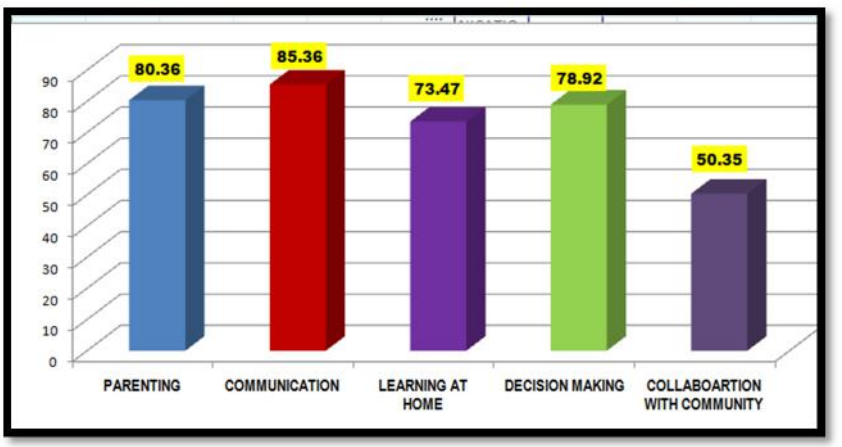
**ANALYSIS AND INTERPRETATION OF THE PRESENT STUDY:**

**OBJECTIVE-1: TO FIND OUT OVERALL AWARENESS LEVEL OF THE PARENTAL INVOLVEMENT IN THEIR CHILD'S EDUCATION:**

TABLE 1: Overall Awareness Level of the Parental Involvement in Their Child's Education.

| SL.NO. | Q.NO. | RIGHT RESPONSE | % | WRONG RE SPONSE | % |
|---|---|---|---|---|---|
| 1. | 01 | 56 | 100 | 00 | 00.00% |
| 2. | 02 | 36 | 64.28 | 20 | 35.72% |
| 3. | 03 | 54 | 96.43 | 02 | 03.57% |
| 4. | 04 | 25 | 44.64 | 31 | 55.36% |
| 5. | 05 | 54 | 96.43 | 02 | 03.57% |
| 6. | 06 | 54 | 96.43 | 02 | 03.57% |
| 7. | 07 | 53 | 94.64 | 03 | 05.36% |
| 8. | 08 | 41 | 73.21 | 15 | 26.79% |
| 9. | 09 | 44 | 78.57 | 12 | 21.43% |

| | | | | | |
|---|---|---|---|---|---|
| 10. | 10 | 47 | 83.93 | 09 | 16.07% |
| 11. | 11 | 46 | 82.14 | 10 | 17.86% |
| 12. | 12 | 34 | 60.71 | 22 | 39.29% |
| 13. | 13 | 30 | 53.57 | 26 | 46.43% |
| 14. | 14 | 44 | 78.57 | 12 | 21.43% |
| 15. | 15 | 52 | 92.86 | 04 | 07.14% |
| 16. | 16 | 54 | 96.43 | 02 | 03.57% |
| 17. | 17 | 45 | 80.36 | 11 | 19.64% |
| 18. | 18 | 48 | 85.71 | 08 | 14.29% |
| 19. | 19 | 35 | 62.50 | 21 | 37.50% |
| 20. | 20 | 39 | 69.64 | 17 | 30.36% |
| 21. | 21 | 29 | 51.79 | 27 | 48.21% |
| 22. | 22 | 40 | 71.43 | 16 | 28.57% |
| 23. | 23 | 19 | 33.93 | 37 | 66.07% |
| 24. | 24 | 18 | 32.14 | 38 | 67.86% |
| 25. | 25 | 35 | 62.50 | 21 | 37.40% |
| **OVERALL** | | **41.28** | **68.40%** | **31.60** | **14.72%** |



**CONCLUSION** : The overall awareness level of parental involvement in child's education of the parents within Kshetrigao assembly constituency comes out at the percentage of 68.40%. It is therefore, the first hypothesis that was constructed for testing that " There is no significant level of overall awareness on parental involvement in their child's education" is rejected as the level of awareness is very high at the level of 68.40%. However, improvement is required to be improved. And the highest parameter found in communication at the percentage of 85.36%. And lowest found in collaboration with community at 50.35%.

**OBJECTIVE-2: TO COMPARE THE AWARENESS LEVEL OF PARENTAL INVOLVEMENT BETWEEN THE HIGHER AND LOWER QUALIFICATION OF PARENTS WITHIN KSHETRIGAO ASSEMBLY CONSTITUENCY.**

TABLE 2: To compare the awareness level of parental involvement between the higher and lower level of parents within Kshetrigao assembly constituency.

| Sl. No | N | Qualification | Mean | SD | SED | t-test | Df |
|---|---|---|---|---|---|---|---|
| 1 | 28 | Higher | 19.86 | 2.53 | 0.58 | 2.50 | 54 |
| 2 | 28 | Lower | 16.28 | 2.22 | | | |

@ Remark - Significant

**INTERPRETATION:** From the above table no 2 it can be observe that the level of parental involvement in connection with the parents who have higher and lower qualification of junior high school /elementary education within Kshetrigao assembly constituency have the mean score 19.86 and 16.28 with standard deviation of 2.53 and 2.22 respectively .

The t-ratio of the two mean scores comes out to be 2.50 with a standard error of 0.58 which is greater than the level of significance at 0.01 therefore the second hypothesis of the study: "There is no significant difference between the awareness level of parental involvement between the parents, who are higher and lower qualification of schools in Kshetrigao Assembly Constituency" is rejected as there is significant difference between the level of parental involvement towards child's education among the higher and lower qualification within the Kshetrigao assembly constituency. It can be concluded that higher qualification parents of the children who are going at elementary schools are more involved than the lower qualification parents in terms of child's education.

**OBJECTIVE-3: TO COMPARE THE AWARENESS LEVEL OF PARENTAL INVOLVEMENT BETWEEN THE EMPLOYED AND UNEMPLOYED PARENTS OF GOVT. AND PRIVATE SCHOOLS IN KSHETRIGAO ASSEMBLY CONSTITUENCY.**

Table 3: To compare the awareness level between employed and unemployed parents within Kshetrigao Assembly Constituency.

| SL. NO. | N | JOB | MEAN | SD | SED | T-test | df |
|---|---|---|---|---|---|---|---|
| 1 | 28 | Employed | 18.36 | 2.48 | 0.78 | 2.65 | 54 |
| 2 | 28 | Unemployed | 17.78 | 3.41 | | | |

@ Remark- Significant

**INTERPRETATION:** From the above table no.3 it can be observed that of parental involvement in connection with the parents who are employed and unemployed of elementary education within Kshetrigao Assembly Constituency are found to have mean score of 18.36 and 17.78 with standard deviation of 2.48 and 3.41 respectively
The t-ratio of the two mean scores come out to be 2.65 with standard error of 0.78 which is greater than the level of significance at 0.01, Therefore the third hypothesis of the study that "there is no significant difference between employed and unemployed parents between Kshetrigao Assembly Constituency." is rejected as there is significant difference between the level of parental involvement towards child's education among the employed and unemployed parents within Kshetrigao Assembly Constituency.

It can be concluded that employed parents of elementary education are more involved than unemployed parents in terms of child's education.

**OBJECTIVE-4: TO COMPARE THE AWARENESS LEVEL OF BETWEEN THE PARENTS OF PRIVATE AND GOVT SCHOOLS WITHIN KSHETRIGAO ASSEMBLY CONSTITUENCY**

Table 4 : To compare the awareness level between the parents of Private and Govt. Schools in Kshetrigao Assembly Constituency .

| SL. NO. | N | Parents | Mean | SD | SED | t-test | df |
|---|---|---|---|---|---|---|---|
| 1 | 28 | Private | 18.36 | 2.48 | 0.65 | 1.80 | 54 |
| 2 | 28 | Govt. | 15.78 | 3.41 | | | |

@ Remark- Significant

**INTERPRETATION**: From the above table No.4 it can be observed that the level of parental involvement between the parents of private schools and Govt. schools of elementary education in Kshetrigao Assembly constituency are found to have mean score of 18.36 and 15.78 with standard deviation of 2.48 and 3.41 respectively.

The t-ratio of the two mean scores come out to be 1.80 with standard error of 0.65 which is greater than the level of significance at 0.01 therefore the fourth hypothesis of the study that "there is no significant difference between the awareness level of parental involvement between the parents of Govt. and private schools in Kshetrigao Assembly constituency "is rejected as there is significant difference between the level of parental involvement towards child's education among the parents of Govt. and private school within Kshetrigao Assembly Constituency.

It can be concluded that private school parents are more involved than Govt. school parents in terms of child's education.

**MAIN FINDING OF THE STUDY:**

1. The overall awareness level of parental involvement in child's education of the parents within Kshetrigao assembly constituency comes out at the percentage of 68.40%. It is therefore, the **first hypothesis** that was constructed for testing that "There is no significant level of overall awareness on parental involvement in their child's education" is rejected as the level of awareness is very high at the level of 68.40%.

2. Therefore the **second hypothesis** of the study: "There is no significant difference between the awareness level of parental involvement between the parents, who are higher and lower qualification of schools in Kshetrigao Assembly Constituency" is rejected as there is significant difference between the level of parental involvement towards child's education among the higher and lower qualification within the Kshetrigao assembly constituency.
   It can be concluded that higher qualification parents of the children who are going at elementary schools are more involved than the lower qualification parents in terms of child's education.

3. The **third hypothesis** of the study that "there is no significant difference between employed and unemployed parents between Kshetrigao Assembly Constituency." is rejected as there is significant difference between the level of parental involvement towards child's education among the employed and unemployed parents within Kshetrigao Assembly Constituency. It can be concluded that employed parents of elementary education are more involved than unemployed parents in terms of child's education.

4. The **fourth hypothesis** of the study that "there is no significant difference between the awareness level of parental involvement between the parents of Govt. and private schools in Kshetrigao Assembly constituency "is rejected as there is significant difference between the level of parental involvement towards child's education among the parents of Govt. and private school within Kshetrigao Assembly Constituency. It can be concluded that private school parents are more involved than Govt. school parents in terms of child's education.

**REMEDIAL MEASURES SUBJECT TO THE HYPOTHESIS OF THE STUDY:**

1. As far as the **first hypothesis** of the study, The overall awareness level of parental involvement in child's education of the parents within Kshetrigao assembly constituency comes out at the percentage of 68.40%., which is not high. Further improvement is required in the area of (1) Learning at Home (2) Collaborations with community.
2. As far as the **2nd hypothesis** of the study, it can be suggested that parents needs higher qualification, which is very useful in terms of child care and parenting in the modern age of technology. If parents are illiterate, they need the support from home tutor or tuition or coaching, so that their children will get benefit same like that of higher qualification.
3. As far as the **3rd hypothesis** of the study, it can be suggested that earning capacity is must to fulfil the needs of the children. From this we learnt that employed parents are more evolved than unemployed in connection with financial matter and knowledge. It is therefore, unemployed parents needs to improve their earning capacity.
4. As far as The **4th hypothesis** of the study concerned that Private schools are built around open communication between parents and administration, and they make it a priority to involve parents in the community. One of the accepted benefits of private schools is that they provide exceptional and challenging educational experience through extracurricular activities in the schools and also find dedication teachers in private school, while government school has less opportunity for the parents. Govt. schools need improvements upto the level of the private schools.

**OVERALL REMEDIAL MEASURES FOR FURTHER IMPROVEMENT:**

Parents play a vital role in the lives of their children. They are the ones who first teach their children on how to write and read. Parents are considered as role models to every child that, why they should have the potential to model positive attitudes and behaviours. All parents want their children to become successful, caring adults. Many parents involve in the process of imparting education to their children. The more the parents involve in the process of imparting education, the more the children excel in their academic career and to become productive and responsible members of society. The academic achievement of students may not only depend on the quality of schools and the teacher, rather on the extent of parent's involvement has a vital role to play in it. The parent has vital roles to play in the life of a child. Parental involvement is a catch-all term for many different activities including home, good parenting, helping homework, talking to teachers, attending school function through taking part in school governance. When schools, work together when families to support learning children tend to success not just in schools but throughout their lives, as the most accurate prediction of a students, achievement in school is not the income nor the social status but extent to which the student's parents is able to create a home environment that encourages learning and to express high expectations for their children's achievement and future careers.

Parental involvement in school has been linked with academic achievement as parental involvement has a powerful impact on the children's attainment. The impact of parental involvement arises from parental values and educational aspirations and that these are exhibited continuously through parental enthusiasm positive parenting style.

It has been concluded that parental involvement helps children to exhibit more positive attitudes, behaviour and a reduction in negative students behaviours such using drugs, violence and anti-social behaviours as parents involvement increase.

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# PHENOMENOLOGICAL ASPECTS OF NOEMA & NOESIS: AN ANALYSIS

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**Abstract:**
'Noema- noesis' concept is one of the most prime concepts of Husserl's phenomenology. In *Ideas,* Husserl introduces the terms to understand the structure of consciousness. Intentional act always has an act of thinking and an object of thinking. So, noesis refers to act of thinking and noema refers to object of thinking. Every intentional act has a noetis content. This noetic content corresponds to noema. Noema is an act of meaning which directs towards intentional object. According to Lyotard, every intentional act has an 'I- pole' and an 'object- pole'. Here, 'I- pole' means 'noesis' and 'object- pole' means 'noema'. Husserl also refers to the noema as the sense or meaning of the act. This paper attempts to show how 'noema- noesis' plays an important character in determining the desired goal in phenomenology.

**Key words:** Noema, Noesis, Phenomenological, Consciousness, Intentional act.

German philosopher Edmund Husserl is known for his revolutionary phenomenological method. He wanted to establish philosophy as a certain science like any other sciences by means of his phenomenological method. There were many concepts in phenomenology that were proposed by Husserl. One of the most important concepts in Husserl's phenomenology is the concept of intentionality. In this concept, his purpose was to search the structure of consciousness first. Because, he thought consciousness was the essential element of the concept of intentionality. Brentano initially introduced the idea of intentionality in the history of philosophy. In his concept, he mainly focused on to analyse

and describe the essential characteristics of consciousness. In Husserl's concept, his attempt was to explore the nature of consciousness. According to this theory, a consciousness is always directed towards an object. It means a consciousness is a consciousness of something. In other words, we may be say that, without anything a consciousness is nothing. There are mainly two parts present in every conscious act, one is act of consciousness and another one is object of the conscious act. These two things make an act as intentional act. For Husserl, consciousness is intentional, that means 'openness to' or 'relation to'. Here the term 'relation' is establish between the 'the act' and the meaning of the act. Husserl introduced the concept of noesis to understand the structure of consciousness in his *Ideas*. Both the term 'noema' and 'noesis' came from the Greek words. He used the term 'noema' in relation to the term 'noesis' to determine the intentional nature of an object. For him, the act of thinking is noesis and object of thinking is noema. Noesis is the thought of an object which was real, but noema was not the real object. It was become 'content' after bracketing. It was because he maintained that if we wanted to reach transcendental subjectivity of pure ego then we had to bracket out the actual existence of the worldly object. So, we are not able to say anything about the content, whether it is real or unreal. It is not necessary to conceive about the existence of perceiving (or judging and so on) an object. The object becomes content here. Content is something that may be real or unreal. This can be compared in context of thinking about golden mountains. The example of golden temple is contextual here because as a phenomenologist our goal is to find out certain knowledge and here in the concept of intentionality, we try to uncover the characteristics of consciousness as well as the process of gaining complete or certain knowledge. Through this concept we do not justify the fact whether the object is real or unreal. Therefore the significance of intentionality concept is an analysis process by which we can acquire knowledge about something which appears in our consciousness. So, as a phenomenologist our research will be concentrated towards in content or noema. According to Lyotard, every intentional act has an 'I-pole' and an 'object-pole'. Here, 'I-pole' means 'noesis' and 'object-pole' means 'noema'.[1] Husserl also refers to the

[1] Lyotard, Jean. Franscois, *Phenomenology*, trans. Brian Beakley, SUNY Press, 1991, p55

noema as the sense or meaning of the act. Sometimes it appears that Husserl uses the terms interchangeably. When we bracket out the real object (noesis) via process of reduction, it converts into content (noema). This often may appear that Husserl's motive is to know about the content or noema rather than knowing the real object. But in reality, use of method of reduction utilizes to gather new knowledge seizing the old. Unlike Kant, Husserl never emphasizes that it is not possible to know the noesis or the real object completely; only thing we are able to know is appearance or phenomena of the object because they are immanent and exist in transcendental state. Husserl applied the term noesis in a broader sense than noema.

Husserl uses the term 'noesis' in broader sense rather than 'noema'. But, there is some controversy regarding the nature of the perceptual noema. According to Smith and McIntyre, the noema is an abstract object, where Sokolowski and Drummond maintain that, the noema is the object we perceive after experience. Husserl describes noesis as the process of cogitation, while noemata as cogitate. Cogitation means the act of consciousness, whereas noemata refers to cogitate or content or object after process of bracketing. According to Husserl, every intentional experience has two phases. These two are- noetic or real phase and noematic or non-real phase. Every noetic phase of consciousness always corresponds to a noematic phase of consciousness. Noesis is a process of reasoning ormeaning that refers to intentional object. According to him, noetic meaning of transcendent object is discoverable by reason, while the noematic meaning of immanent objects is discoverable by pure intuition. Noetic meaning is immanent. Thus, noesis and noema correspond respectively to experience and essence.In the *Investigations* and the *Ideas,* Husserl begins to use the term 'noesis' as 'intentional acts' or 'act- quality' and 'noema' as 'act- matter'.[2]

Husserl's analysis of noema and noesis has given rise to a controversial discussion concerning the nature of the phenomenological theory of meaning and the nature of the intentional object. Noesis is called as concretely complete intentive mental process. Husserl's interest in the noema comes through a consideration of the relation between individual experiential act and its acts of grasping a meaning and referring to an object. After the bracketing of existence of object, Husserl again thinks

[2] Internet Encyclopedia

about the nature of the intentional object. Then, in a meditating stage, he finds a relation between sense and reference which Frege has proposed in his famous article 'sense- reference' in 1891. But, Frege's interest is not in the actual reference but only in the act of referring and intending reference of the act. Husserl posits noema as a single complex entity which takes care both of what Frege includes under the term sense and referential function of the act. In this sense, Husserl does not simply restate Fregean conception in his own terms, but essentially rethinking the relation between the act of meaning and object intends. But, there is a lack of clarity regarding the nature of noema. Is an immanent entity of consciousness a part of an occurrent thought? Or whether it refers to an object beyond the thought? Or whether it is an abstract ideal meaning through which an object is given?[3]

As a matter of fact, when a common person intends to know about any object, he always tries to focus just on the object. When he tries to comprehend a known object again, he applies all the previous knowledge onto that which may cause error in that knowledge. But, after bracketing the object what we should focus is the noema. He acknowledges this kind of reflection is 'unnatural'. This reflection is different from our ordinary act of reflection. If these two reflections are same then no difference exists between phenomenological and semantic or conceptual analysis at all. For this, we have to apply the reduction to create a new kind of reflection, which is self- consciously 'unnatural'. As we know, our consciousness always directs towards an object. When, I think of a box, it is the real object (box), it is the real box that my thought is directed to. Similarly, when I think about a golden mountain, then I focus on an object which is not existent in reality. The noema is not the object towards which the act directs, rather it provides to connect my occurrent thought to the intend object. Through the act of noema we grasp the object; it is the route to the object. So, we may say that our perceptual act has a noetic- noematic constitutions, because our act has a noema.[4]

Husserl's concept of noema and noesis somehow seems like, it leads into Berkeley's idealism and Kant's realism, but the explanation what Husserl gave was quite different. Though, he followed Kant's transcendental idealism. But, there is difference between Kant's phenomena- noumena

[3] Dermot, Moran, *Introduction to Phenomenology,* Routledge. USA, 2000, pp 155-56
[4] Dermot, Moran, *Introduction to Phenomenology,* Routledge. USA, 2000, p157

and Hussserl's noema- noesis. For kant, we can attain the knowledge of phenomena (apperence), but knowledge of noumena (originality of an object) is beyond our thinking. We can only know the phenomena. On the other hand, Husserl said that, we recognize the relation between noema and noesis by the method of reduction. The process of reduction helps us to analyse and understand the nature of both these concept of phenomenology.

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# UTILIZATION OF EXOTIC TREE AS TRADITIONAL MEDICINE

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## Abstract

In the present work, total 48 species of trees belonging to 21 families of angiosperms have been reported from college campus. Present work is the result of intensive ethnobotanical explorations of herbaceous plants of New Arts commerce college campus Ahemednagar district made during the period from 2019 to 2020. In Ahemednagar district few workers have done ethnobotanical work on some selected and small parts of the district. Pradhan and Singh (1999) have worked out flora of the district. In the present study, ethnobotanical information is collected on 48 trees species belonging to 21 families of angiosperms have been reported from college campus. Out of the 48 trees species collected, Polypetalae have12 families and 30 species, Gamopetalae have04 families and 07 species. Apetalae have 01 families and 03 species, included Monocotyledone have 03 families and 08 species have been collected.

## INTRODUCTION

Tree is a perennial woody plant. It most often has many secondary branches supported clear of the ground on a single main stem or trunk with clear apical dominance. Compared with most other plants, trees are long-lived, some reaching several thousand years old and growing to up to 115 m.

Trees are an important component of the natural landscape because of their prevention of erosion and the provision of a weather-sheltered ecosystem in and under their foliage. They also play an important role in producing oxygen and reducing carbon dioxide in the atmosphere, as well as moderating ground temperatures. They are also elements in landscaping and agriculture, both for their aesthetic appeal and their orchard crops. Wood from trees is a building material, as well as a primary energy source in many developing countries. Trees also play a role in shade, food like fruits, wood, to control the air pollutions etc.

India has two biodiversity hotspots the Western Ghats and the Himalayas, having-vast variety of flora and fauna and ranks $10^{th}$ in the global biodiversity of flowering plants. It is a home for threatened and endemic species that have immense ecological and commercial value. A thorough investigation of our flora has become an urgent necessity not only because of the economic and ecological importance of biodiversity but also of accelerated genetic erosion occurring as consequence of destruction of the forest and other habitat Inventory is a continuous process of searching and re-examining the earlier Findings. Therefore the present research works to generate the detailed floristic data of exotic trees of Ahmednagar. The study was undertaken with the following aims-

Survey, collection and documentation of the trees of Ahemadnagar ,Identification and inventorisation of the trees, Utility aspect of trees of college campus,List of exotic trees.

These floristic data will be useful for students, researchers, forest officers and policy makers etc.

## MATERIAL AND METHODS

The Ahmednagar- city of (Maharashtra state) area was preliminary surveyed for its floristic diversity during the period of 2019-2020 During work regular field visits were made to collect and documentation all the angiosperms. The field data such as habit, habitat, flower colour and odour was recorded. All the collected specimens were identified carefully and were processed as per the conventional methods of drying, poisoning, mounting and labeling (Jain and Rao. 1977; Rao and Sharma. 1990]. The collected specimens were identified by referring to various floras, monographs and revisions. The list of plants and families are arranged primarily as per the classification given by Bcntham and Hooker. The nomenclature of plant has been adapted and updated applying ICON and referring to latest taxonomic literature. For each species, correct botanical name followed by basionym and important synonyms, if any. Wherever necessary to connect the name with T. Cooke's 'The *Flora of the Presidency of Bombay',* Pradhan S. G. & N. P. Singh. *'Flora of Ahmednagar District (Maharashtra/, V.* N. Naik. *'Flora of Maratlrwada,. E.* D. Sharma *A! 'Flora oj Maharashtra Stale'* etc. have been given.

Online nomenclatural database such as 'The International Plant Names Index (1PNI) (http:// www.ipni.org) and $W^3$ Tropicos' (http://wvvw. tropicos.org) published on the internet also used. The citation is followed by short diagnostic description. The information on the phenology, illustrations and a field note on its habitat, identity and any peculiarity are provided.

**Study Area :** . Ahmednagar city .

The present work is done during 2019-2020 in different parts of Ahemadnagar. Old experienced men and women were interviewed to know about the utility of plants growing in their localities. Herbarium specimens of the exotic plants prepared and identification was done following standard literature Cooke, (1967) Singh et al., (2000 and 2001), Cooke, (1958), Pradhan and Singh, (1999). Herbarium specimens are deposited in the New Arts Commerce and Science College in Botany Department herbarium Ahemadnagar ,

### ANNONACEAE

**Annona reticulata** L. Sp. 537.1753; Hook, f & Thorns, in Hook. f. Fl. Brit. India 1: 78. 1872.
**Nativity**- Caribbean & Central America
*Common Name:* Ramphal
Trees. Leaves oblong-lanceolate, minutely pellucid beneath, apex acute, Flowers greenish Yellow, Fruits syncarpous, yellowish-red, Seeds smooth, black.
***Fls. & Frts***. July-November
***Distrib:*** Cultivated for its fruits.
***Uses:*** ***Medicinal***
*Acidity and stomach disorders: One tea cup of leaf extract taken orally twice a day for 7 days.
***Edible:*** Ripe fruits are eaten.
***Annona squamosa* L**. Sp. PI. 537. 1753; Hook. F. & Thorns. In Hook f. Fl. Brit. India 1:78 1872.
**Nativity**- Tropical America & West Indies
***Common Name :*** Sitaphal
Trees, Leaves oblong -lanceolate, glaucous beneath, and pellucid- punctuate. Flowers green.
Fruits yellowish-green. Seeds brownish-black, polished, oblong, c 2.0 x 0.5 cm.
***Fls:*** March-August
**Frts:** April-December
***Uses:*** ***Medicinal***

1. *Skin disease: Leaf paste applied for treating ringworm & itch.
2. Tooth ache: Crushed leaves kept on tooth.
3. To expel lice: Leaves crushed in water and applied on hair.
4. Cuts and wounds: Leaf paste applied for treating cuts, injuries & for healing wounds.
5. Head ache: warm leaves kepts on fore head to treat headache.
6. Boils: Leaf paste with salt applied externally until cure.

*Edible:* Ripe fruits are eaten.
*Vet:* Swelling and Wounds. Leaf paste applied externally.

**BIXACEAE**

*Bixa orellana* L. Sp. PI. 512. 1753.
**Common Name:** Shendri
**Nativity**-Tropical America
Small, evergreen trees, Leaves ovate, acute or acuminate at apex, truncate or subcordate at base. Flowers white or pink, in terminal panicles. Capsules ovoid orsubglobose. clothed with long soft prickles. Seeds trigonous rounded a grooved on the back, pulp red.

**FIs & Frts:** July-Novenber
**Distrib.:** Planted as a avenue tree
**Uses:** Dystenlry: 20-40 ml decocation of leaves taken twice a day for two days.

**TILIACEAE**

***Muntingia calabura*** *L. Sp. PI. 509. 1753; Murthy in Sharma et al. Fl. India 3: 570. 1993; Kothari in Singh et al. Fl. Maharashtra St. Dicot. 1: 411. 2000.*
**Nativity**- Southern Mexico, Central America & Bolivia
***Common Name:*** *Singapore Cherry.*
*Small trees, branches spreading; densely villous, glandular-pubscent. Leaves distichous. Inflorescence sessile, supra-axillary.Petals 5, white, rarely pink. Berries red or yellow, pulp juicy, sweet.*
***FIs & Frts:*** *Throughout year.*
***Distrib:*** *Cultivated in gardens for its fruits.*
***Uses:***
1. *In Mexico the fruits are eaten and sold in markets.*
2. *Leaves are used for making tea.*
3. *Fruits are used in the preparations of jams & jelly.*
4. **In traditional medicine, its flowers can be used as antiseptic and to treat abdominal cramps.**

**RHAMNACEAE**

***Ziziphus mauritiana*** **Lam. Encycl. 3:319. 1789.**
**Common Name: Bor**
**Nativity**-Afghanistan
**Small trees or large shrubs, armed. Leaves ovate-elliptic with rounded ends, slightly oblique at base, glabrous above and white-tomentose beneath. Flowers greenish- yellow. Drupes globose, fleshy, yellow or orange when ripe.**
**FIs. & frts: September-October**
**Distrb.: Common in villages, road side.**
**Uses: Medicinal**
1. **Tonic: leaf paste made in to 1 gm pills taken one are two pills twice a day for 6 days.**
2. **Urinary disorder or blood in urine: One tea cup juice of its stem bark with one tea spoon** *Cuminum cyminum* **seeds and sugars taken orally twice a day for 7 days.**
3. **Painful menstruation : One tea cup juice of its fresh stem bark with 1 tea spoon chilli powder and 7** *Piper nigrum* **seeds powder taken orally once a day for three days at the time of means period.**

**Edible: Ripe fruits are eaten. Fruits are also used to made chutney.**

**Misc:** **Wood is used to making agricultural implements, furniture and house construction.**

**FABACEAE**

***Gliricidia sejrium*** *(Jacq.) Kunth. Ex Steud. Norn. Bot. (ed. 2) Walp. Repert. Syst. 1: 679. 1842; Sanjappa, Legums of India 182. 1991; Kothari in Singh at al. Fl Maharashtra St. Dicot. 1: 770. 2000.* ***Ribinia sepium*** *Jacq. Enum. PI. Carib. 28. 1760.* ***Gliricidia maculate*** *H. B. & K. Nov. Gen. et Sp. 6: 393. 1823.*

**Common Name:** *Giripushpa, Undirmari*

**Nativity**- Mexico

**Fls. & Frts.:** *February - June*

**Distrib:** *It planted also on barren lands as a pioneer plant.*

**Uses:** **Medicinal**

1. ***G. sepium*** *leaves are rich in protein and highly diesible, and low in fiber and tannins. There is evidence of improved animal production (both milk and meat) in large and small ruminants when* ***G.sepium*** *is used as supplement.*
2. *Crude extracts have been shown to have antifungal activity. Reported to be expectorant, sedative and supportive.*

Misc: *1. The* ***Gliricidia*** *has light brown sapwood and dark brown heart wood turning reddish brown on exposure to air. It is hard, coarse textured with an irregular grain, very durable and termite resistant. Wood is utilized for railway sleepers, farm implements, furniture, and house construction.*

***Caesulpinia pulcherrima*** L. S\v\, Obs. 166.1791; Baker in Hook. f. Fl. Brit. India 2: 255. 1878; Cooke, Fl. Pres. Bombay 1: 440. 1958 (Repr); Sanjappa, Legumes of India 13. 1991; Moorthy in Singh et al. Fl. Maharashtra St. Dicot. 1: 796. 2000. ***Poinciana pulcheirima*** L., Sp, PI. 380. 1750. Erect shrubs; branches often unarmed or with few weak prickles. Leaves bipinnate; pinnae 6-8 pairs, leaflets 8-12 pairs, oblong or obovale-oblong. Flowers in terminal racemes. Corolla yellow or red; petals orbicular. Stamens long exerted, Pods flat. thin. Seeds 8-10, smooth.

**Common Name:** Shankasur

**Nativity**-West Indies & Tropical America

**FIs. & Frts.**: Almost throughout year.

**Distrib:** Cultivated throughout in gardens and backyards and near temples.

**Uses:** **Medicinal**

1. Maroon medicine men in Suriname have long known some of the medicinal uses for *Caesalpinia* ***pulcherrima,*** which is known as ayoowiri.
2. 4 gms from the roots is also said to induce abortion in the first trimester of pregnancy.

***Cassia fistula*** L. Sp PI. 377.
1753.

**Common Name:** Bahava

**Nativity** -Tropical South America

*Trees 10 m tall. Leaflets 4-8 pairs, ovate, Flowers yellow, lax, drooping receraes. Pods indehiscent. Seeds numerous, embedded in dark coloured pulp.*

***Fls. & Frts.***: *April-October.*

***Distrib:*** *Occasional in forest edges & road sides.*

***Uses:*** ***Medicinal***

1. *Tonsils: Decoction of fruits for gargling twice a day for 3 days.*
2. *Abortifacienl : Fruit pulp with* Butea monosperma *flower,* Zingiber officinale *rhizome powder and jaggery taken in equal proportion to make it 50 gms, taken orally once a day for 3 days.*

3. *Hair fall. Paste of seeds with* terminalia chebula *fruit pulp and* Cassia tora *seeds taken in equal proportion applied externally once a day for 15-20 days.*

***Edible:*** *Curry is made by flowers.*
***Vet:*** *Removal of Placenta: Handful crushed stem bark powder given orally with warm water.*
*Misc.:* *Wood is used for making agricultural implements and house construction.*

***Cassia siamea*** *Lam Encycl. 1: 648. 1785.*
***Common Name:*** *Kasud.*
**Nativity** -Sri Lanka
*Trees bark grey Leaves abruptly pinnate: leaflets 8-12 pairs, ovate-elliptic or elliptic-oblong coriaceous. Flowers yellow. Pods brown, beaked, compressed, and broadly oblong.*
***Fls.& Frts.:*** *August-June.*
***Distrib:*** *Planted as an avenue tree.*
***Uses:*** ***Misc.***
*1. The wood used for house construction and agricultural implements.*

**Delonix regia** *(Hook.) Raf. Fl. Tell. 2: 92. 1836; Sanjappa, Legumes of India 27. 1991; Moorthy in Singh et al. Fl. Maharashtra St. Dicot. 1: 803. 2000.* Poinciana regia *Bojer ex Hook. f. in Curtis, Bot. Mag. 56: 5. t. 2884. 1829; Hook. f. Fl. Brit. India 2: 260. 1878; Cooke, Fl. Pres. Bombay 1: 442. 1958 (Repr).*
***Common Name-*** *Gulmohor*
**Nativity** -Tropical Africa
**Deciduous trees, Leaves bipinnale; pinnae 10-20 pairs; leaflets narrowly oblong, 6-35 pairs. Flowers 6-12 in axillary racemes. Petals redthe upper white blotches, clawed with crisped orbicular limbs. Stamens 10. filaments long, red in the upper half. Pods woody, dark brown.Seeds 10-50, dark brown; mottled.**
**Fls. & Frts.: February - November**
**Distrib: Cultivated for its ornamental value.**
**Uses: It is fast growing & develops an umbrella-shaped crown, making it a valuable shade.**
**Misc.: The wood is of little value, although it is durable and resistant to water, and has been used for making fences posts.**

***Peltophorum pterocarpum*** **(DC.) Baker ex Heyne, Nutt. PI. Ned. Ind. 2: 755. 1927; Sanjappa, legumes of India 33. 1991; Moorthy in Singh et al. Fl. Maharashtra St. Dicot. 1: 804. 2000.** *Ingapterocartai* **DC. Prodr. 2: 441. 1825.** *Teltophorum ferrugenium* **Benth. Fl. Austr. 2: 279. 1864; Bekerin Hook. f. Fl. Brit. India 2: 257. 1878.**
**Common Name: Sonmohor**
**Nativity** -Australia
**Evergreen trees ; young branches brown tomentose. Pinnae 9-15 pairs; leaflets 10-20 pairs. Flowers in rather dense terminal panicles shorter than the leaves. Petals bright yellow. Pots flat, red-brown, narrowly winged in both surfaces. Seeds 3-6 compressed brown.**
**Fls. & Frts.: September - March**
**Uses:**
1. **fodder: It is suitable for use as a fodder.**
2. **Fuel: The tree is used as fuel wood.**
3. ***Tannin & Dyesruff*: The bark of P. *pterocarpum* has been an important component of the bark or black 'Sogo' dye in Java, used for batik work.**
4. **Medicine ; In traditional, medicine it is used as an astringent to cure or relieve intestinal disorders after pain at childbirth, sprains, bruises and swelling or as a lotion for eye trouble, muscular pains and scores. It is also used for gargles and tooth powders**

**Misc.: 1. The wood has wide variety of uses, including cabinet-making.**

***Saraca asoca*** (Roxb.) Wild. In Bluema 15: 393. 1968; Sanjappa, Legumes of India 35. 1991; Moorthy in Singh et al. Fl. Maharashtra St. Dicot. 1: 793. 2000. ***Jonesia asoca*** *Roxb.* In Asiat. Res. 4: 365. 1795; Wight, Ic. t 206. 1839. ***Saraca indica*** *auct.* Non L. (1753); Baker in Hookf. Fl. Brit. India 2: 271. 1878; Cooke, Fl. Pres. Bombay 1:456. 1958 (Repr).

**Common Name:** Sithecha Ashok

**Nativity** -Tropical South America

Trees. Leaflets oblong-elliptic, 4-6 pairs. Flowers fragrant, numerous in dense axillary racemes, bracteoles 2, amplexicaule, coloured. Calyx segments 4. Stamens 7 or 8, much exerted; anthers purple. Pods black, tapering at both ends. Seeds 4-8, slightly compressed.

**FIs. & Frts.:** December - May

**Uses:** **Medicinal**

1. It is use in treatment of excessive uterine bleeding extensive in India.
2. The plant is used also in dysmenorrheal and for depression in women.
3. It is useful in menorrhagia (scant menses), dysmenorrheal (painful menses, menstrual cramps), depression, bleeding hemorrhoids, uterine fibroids.

**MIMOSACEAE**

*Acacia nilotica* (L.) Willd. Ex Del. ssp, Indica (Bth.) Brenan in Kew Bull. 12: 84. 1957*;* ***Mimosa nilotica*** L. Sp. PI. 521.

**Common Name:** Babhul.

**Nativity** -North Africa

Trees bark longitudinally cracked. Pinnate 4-7 Pairs; leaflets 10-25 Pairs, linear-oblong. Flowers yellow in globode heads. Pods green, flat, beaked, shortly stalked. Seeds 2-12 per pod.

**FIs. & Frts.**: More or less through out the year.

**Distrib:** Common in west lands and road sides.

**Uses:** **Medicinal**

1. Burned wounds: Stem bark burnt to ash and applied with coconut oil for healing wounds.
2. Spermatogenesis: Leaves bark and fruit taken in equal amount and extract prepare with cow milk and sugar taken 100 ml twice a day for 21 days.
3. Menorrhagia: 20-25 ml extract of the bark with 250 ml of cow milk taken once a day for 5 days.
4. Cooling agent: 20 ml of root extract taken with one glass of butter milk once a day for 7 days.

**Vet:** Stomach ache: 100 ml decoction made by 50 gm fresh stem bark and given orally twice a day to cattle.

**Misc:**

1. Wood is used to making agricultural implements, furniture and house construction also used as fuel

***Acacia longifolia*** *Willd. Sp. PI. 4: 1052. 1806; sanjappa, legumes of India 49. 1991; Londhe in Singh et al. Fl. Maharashtra St. Dicot. 1: 825. 2000.*

**Common Name:** *Australian babhul.*

**Nativity** -Australia

*Trees; phyllodes narrowly lanceolate, falcate; conspicuously 3-5 nerved. Flowers in axillary spikes shorter than phyilodes. Corolla bright yellow, twice as long as calyx. Pods twisted. Seeds black, polished, and covered by silvery funicle.*

**FIs. & Frts.:** *August - November*

**Distrib:** *Planted by social forestry department and also as avenue trees.*

**Uses:**

1. *Fooder.*

2. *Flowers rich in pollen, they are often used in fritters.*
3. **Acacia** *seeds are highly nutritious and contain approximately 26% protein, 26% available carbohydrate, 32% fiber and 9% fats. The fat content is higher than the most legumes.*

**Misc:** *Yellow dye prepared from flowers and green dye is obtained from seed pots. The extensive root system of this plant helps to prevent soil erosion.*

***Albizia lebbeck*** *(L.) Bnth. In Hook. London J. Bot. 3:87. 1844 p p.('lebbek') & in Trans. Linn. Soc. 30: 562. 1875 p.p; Mimosa lebbeck L. Sp. PI. 516. 1753.*

**Common Name:** *Shirish.*

**Nativity** - Tropical America

*Trees. Leaves abruptly pinnate; leaflets 4-9 pairs, lateral, elliptic-oblong, terminal ovate-oblong. Flowers white, fragrant. Pods, pale yellow. Seeds 4-12.*

**FIs. & Frts.:** *March-December.*

**Distrib:** *Common along roadside.*

**Uses:** **Medicinal**

1. *Snake bite: One tea cup extract prepared by handful stem bark. Three doses to be given after the interval of 30 minutes as an antidote to snake bite.*
2. *Cooling effect: Powder of tender leaves with rhizome powder of Curcuma longa taken in equal proportion and made in to pills. One or two pills taken twice for 15 days.*
3. Dog bite: 10-12 seeds soaked for half an hour in human milk and dried (this is done repeatedly for 10 times) then seeds are crushed small pills are prepared. 3 pills are taken once to treat dog bite.
4. "Cough: Root bark crushed & soaked in goat urine. 5 gm eaten with ***Piper belle*** leaf.
5. Jaundice: 50-60 ml of leaf juice with 250 ml rice flour 'roti' prepared & eaten once a day until cure. Or seeds paste applied over eye once a day for 15 days.

***Vet:***

1. *Joint pain & swelling in legs: One Liter extracts 100 gm stem bark given orally once a day until cure to cattle.
2. *Stomach ache: Leaves along with ***cassia auriculata*** leaves in equal proportion crushed together & given orally thrice a day for 3-4 days to cattle.

***Misc:*** Wood is used house construction & packing cages.

***Calliandra haematocephala Hasskacl,*** Retzia 1: 216. 1855; Naluurk Tijdschr. Ned.- Indie 10: 216. 1856.

***Common Name****:* Powder puff tree

**Nativity-** Tropical America

A shrub with brown bark. Leaves alternate, bipinnate, up to 14 cm long, pinnae paired. 10-11 cm long, leaflets opposite, more or less sessile, 4-8 pairs, 1.5-3 cm long, lanceolate, apex acute slightly curved on one side near the apex, coriaceous. Flowers in axillary heads, scarlet. Calyx campanulate toothed. Corolla funnel-shaped, deeply 5 cleft. Stamens indefinite, monadelphous at the base, filaments filiform, much exserted. Ovary stalked, many ovuled; style filiform, stigma minute, capitate. Pods strap shaped, slightly falcate, flat.

***Fls. & Frts.:*** November - April

***Distrib:*** Ornamental cultivation: grown in gardens and parks.

*Uses:* ***Medicinal***

1. Antibacterial study evaluated ethanolic extractable constituents of bark ***calliandra haematocephala*** against selected bacteria. Results showed varied antibacterial activity.
2. Gastro protective study of butanolic extract for gastro protective effect in acute gastric lesion induced by acidified alcohol showed a gastro protective effect with moderate control gastric lesion and inhibition of hemorrhage and necrotic aspects of tissue injury.

*Leucaenu leucocephala*
**Common Name :**
Subabhul
**Nativity**- Colombia
Tree, forked when shrubby and branching strongly after coppicing, with greyish bark and prominent lenticels Leaves bipinnate with 4-9pairs of pinnae, variable in length up to 35 cm, with a large gland at the base of the petiole; leaflets 11-22 pairs/pinna, acute. Flowers numerous, in globose heads with a diameter of 2-5cm, stamens (l0 per flower) and pistil 10 mm long, anthers pilose, dehiscing at dawn. Pod 14-26cm x 1.5-2 cm, pendant, brown at maturity. Seeds 18-22 per pod , 6-10 mm long, brown.

**FIs. & Frts.:** Throughout the year.
**Distrib:** Suitable as an ornamental and roadside landscaping species.
**Other Uses:**
1. Unripe pods and seeds of all subspecies have been used by the native inhabitants of Mexico and Central America as a food or medicine since ancient times. Very young shoots used as a food by villagers in Thailand. Highly valued as ruminant forage and as a fuel wood by subsistence and semi-commercial farmers throughout Southeast Asia and parts of central Asia and Africa.
2. Timber: *L. leucocephala* has hard wood, with pale yellow sapwood and light reddish-brown heartwood the wood is known to be medium density and dry without splitting or checking. It is strong, medium textured, close grained and easily workable for a wide variety of carpentry purposes.
3. Gums and resins: Gum arises from Leucaena stems under ill-defined conditions of injury and disease or from sterile hybrids, especially *leucocephala* x *L. esculenta.* The gum has been analyzed and found similar to gum arabic and of potential commercial value.
4. Tannin or dyestuff Red. brown and black dyes are extracted from the pods, leaves and bark.

***Pithecellobium dulce*** ***(Roxb.) Benth. In Hook London J. Bot 3: 199. 1844*** *(Pithecolobium);* ***Baker in Hook. f. Fl. Brit. India 2: 302. 1878; Cooke, Fl. Pres. Bombay 1: 485. 1958 (Repr); Sanjappa, Legumes of India 71. 1991; Londhe in Singh et al. Fl. Maharashtra St. Dicot. 1: 828. 2000.*** Mimosa dulce ***Roxb. Pl. Corom. 1: 67. t. 99. 1798.***
**Common Name:** ***Wilayati Chinch***
**Nativity**- Mexico
**FIs. & Frts.:** ***January - June***
**Distrib:** ***Planted in garden and also naturalized.***
**Uses:**
1. ***The seed pods contain a sweet pulp that can be eaten raw or prepared as a smoothie.***
2. ***Wood is hard and lasting but because of irregular shape of bole and branches its use for rough carpentry works.***

***Prosopis julifera*** ***(Sw.) DC. Prodr. 2: 447. 1825; Sanjappa Legumes of India 72. 1991; Londhe in Singh et al. Fl. Maharashtra St. Dicot. 1: 824. 2000.*** Mimosa julifera ***Sw., Prodr. 85. 1788.***
***Common Name:*** ***Vilayati babhul***
**Nativity**- Mexico
***Scandent shrubs or small trees; branches zigzag. Leaves bipinnate; pinnae 2-4 pairs; leaflets 20 pairs. Flowers in dense axillary, peduncled spikes. Corolla pale yellowish, twice as long as calyx. Stamens exerted, anthers crested with deciduous gland. Seeds 10-20.***
**FIs. & Frts.:** ***August - June***
**Distrib:** ***Planted in garden and also naturalized.***
**Uses:**

1. *Mesquite pods are among the earliest known foods of prehistoric man in the new world. Today flour products made from the pods are still popular, although only sporadically prepared, mostly by Amerindians.*
2. *Pods are made into gruels, sometimes fermented to make a mesquite wine. The leaves can be used for forage.*

**Misc:** *The wood is used for parquet floors, furniture, and turnery- items, fencepost pilings, as a substrate for producing single-cell protein, but most of all for fuel.*

***Samanea saman*** *(Jacq.)* **Merr.** *in J. Wash. Acad. Sci. 6:46. 1916;Sanjappa, legumes of India 72.1991; Londhe in Singh et al. Fl. Maharashtra St. Dicot. 1:828. 2000.*
**Common Name:** *Parjanya Vriksha*
**Nativity-** Tropical America
*Unarmed trees. Leaves bipinnate; pinnae 4-6 pairs; leaflets 2-8 pairs. Flowers in long peduncled. globose heads.Corolla pale pink. Stamens long exerted filaments purple.*
*Seeds 6-10. embeded in brownish black, sweet pulp.*
**FIs. & Frts.:** *March-July.*
***Distrib:*** *Planted as avenue trees.*
**Uses:** **Medicinal**
*The root decoction is used in hot baths for stomach cancer in Venezuela Rain Tree is a traditional remedy for colds, diarrhea, headache, intestinal ailments and stomachache.*

**COMBRETACEAE**

***Temimtia catappa*** **L. Syst. Nat. ed. 2 : 674. 1767.**
***Common Name :*** **Deshi Badam**
**Nativity-** Tropical Asia

**Trees; branches in horizontal whorls. Leaves crowded at ends of branches obovate. Flowers sessile, in axillary spikes, white or yellowish-green. Fruits, ovoid or ellipsoid, usually reddish-green**

***Fls. & Frts.:*** **April-October.**
***Distrib.:*** **Avenue tree & cultivated for their fruits**
***Uses:*** ***Medicinal***
1. **Headache. Leaves dipped in edible oil heated over fire & applied externally.**

***Edible Use:*** **Fruits & seeds are edible**

***Terniinalia chebula*** **Retz. Obs. Bot. 5:31. 1788.**
***Common Name:*** **Hirda**
**Nativity-** Tropical Asia
**Trees, Leaves elliptic-ovate or elliptic-oblong. Flowers yellow, in simple or sparsely branched spikes, Drupes, elliptic or ovoid, 5-ribbed when dry.**
***Fls. & Frts.:*** **February-May.**
***Distrib:*** **Occasional in forests**
***Uses:*** ***Medicinal***
1. **Cough & asthma: One table spoon paste of fruits or stem bark taken with water twice a day until cure.**
2. ***Piles: Powder of its fruits with jaggery in equal proportion made in to 1 gm Pills taken one or 2 pills twice a day for 7 days.**
3. **Tooth ache: Fruit powder with *Emblica officinalis* fruit powder, 'crystal salt' and catechu, each in equal proportion prepared mixture used like tooth powder.**

4. ***Eye infection: Paste of fruit pulp with black salt one type of salt and butter milk applied externally daily night 7 days for eye infection.**
5. ***Hiccough: 40-60 ml decoction of fruit pulp with** *Ricinus communis* **roots.** Plumbago zeylanica **whole plant in equal proportion taken orally to check hiccough.**

**Edible Use:** **Seed cotyledons are eaten by children.**

**Vet:**

1. ***Tongue sores: 100 gm powder of fruits crushed given orally with water & powder of applied on tongue of cows.**
2. ***Expel foetus. Fruits or stem powder applied externally and put the fetus in.**

***Terminalla arjuna***

**Common Name :**

**Arjuna**

**Nativity-** Tropical Asia

**Tree up to 25 meter height; bark grey, smooth; leaves sub-opposite, 5-14 * 2-4.5 cm, oblong or elliptic oblong, glabrous, often in equilateral, margin often crenulate, apex obtuse or sub-acute, base rounded or sometimes cordate; petioles 0.5-1.2cm; glands usually two. Flowers small, white. Fruit 2.3-3.5 cm long, fibrous woody, glabrous with 5 hard wings, striated with numerous curved veins.**

**FIs. & Frts.:** **April - July**

**Distrib:** **Grows well along bank of streams, rivers, ravines, dry water courses.**

**Uses:** **Medicinal**

1. **The Arjuna was introduced into Ayurveda as a treatment for heart disease.**
2. **It is traditionally prepared as a milk decoction, arjuna in the treatment of wounds, hemorrhages and ulcers, applied topically as a powder.**

**MYRTACEAE**

***Callistemon citrinus*** **(Curits) Skeels in US Depl of Agric Bur PI. Ind. Bull. 282: 49. 1930; Kulkami in Singh et al. Fl. Maharashtra. St. Dicol. 2: 16. 2001.**

**Common Name: Bottle Brush**

**Nativity-**Australia

**Small trees. Leaves sessile, linear, sharp pointed, margins often revolute. Flowers sessile in axils of deciduous bract.Petals pink or red, deciduous. Stamens numerous; filaments red Capsules globose. Seeds numerous, minute, black.**

**Fls. & Frts.:** **September - February**

**Distrib:** **Planted in gardens.**

**Uses:** **The herbicide Mesotrione was developed as a synthetic analogue of leptospermone, a natural herbicide produced by the roots of** Callistemon cilrinus.

***Eucalyptus globules*** *LwiU.* **Rel. Voy. Rech. Perouse 1: 153, t. 13. 1799; Kulkarni in Singh et al. Fl. Maharashtra. St. Dicot. 2: 18. 2001.**

**Common Name: Nilgiri**

**Nativity-**Australia

**Trees, bark, flake off into long stripe. Leaves lanceolate. Flowers large 1-3 together on short peduncle.Calyx tube hard, bluish white, lid of calyx and corolla conical.**

**Fls. & Frts.:** **February - May**

**Distrib:** **Planted in gardens and avenue tree.**

**Uses:** **Medicinal**

1. **The oil is used as a flavoring agent in cold and cough medicines.**
2. **It is used in disinfectants, antiseptic liniments, ointments, toothpastes, and mouthwashes.**
3. **It is used by veterinarians for treating influenza in horses, distemper in dogs, and septicaemia in all animals**

***Psidiuni guajava*** **L. Sp. PL 470. 1753.**

**Common Name: Peru**

**Nativity-**Tropical America

**Shrubs, barks smooth peeling off. Leaves oblong-elliptic, pubescent on both sides. Flowers white, axillary, solitary. Berries oboid. pulpy.**

**Fls. & Frts.: November-June.**

**Distrib.: Planted for edible use.**

**Uses: Medicinal**

1. ***Diabetes: 40-60 ml decoction of handful leaves taken orally daily-early in the morning once to control the diabetes. (Or) 4-5 leaves soaked in water for overnight & water taken early in morning.**

**Edible use : Fruits are eaten**

**Misc : Wood is used for house construction.**

***Syzygium aimini (L) Skeels in U.S. dept. Agric. Bur PI Industr. Bull. 248:25. 1912*** *Myrtums cumini* ***L. Sp. PI. 471 1753***

**Common Name:** ***Jambhul***

**Nativity-**South East Asia

***Trees, bark thick, rough. Leaves elliptic-oblong or elliptic or ovate, subcoriaceous, close veined. Flower white, sessile or shortly pedicelled, crowded in heads on ends of laxly punicled-cymes. Berries, oblong or ovoid, purple, fleshy.***

***Fls. & Frts.: March-June.***

**Distrib.:** ***Common in villages & occasional in forests.***

**Uses: Medicinal**

1. ****Kidney Stone. Fruits directly eaten for dissolving kidney stones, (or) Fruit powder taken 1 spoon with water twice a day for 15 days to dissolve kidney stone.***
2. ***Stomach ache: One tea spoon powder of stem bark with pinch of salt taken orally for stomach ache.***
3. ***Toothache: Leaf juice is used for gargling and for teeth ache bleeding gums.***
4. ****Body ache and Rheumatism: One tea cup juice of handful stem bark with goat milk taken orally twice a day for 15 days.***
5. ***Tonic and Blood purifier: 40-60 ml extract of stem bark with goat milk in equal proportion taken orally twice a day for 15 days.***
6. ****Bone fracture: One table spoon powder of stem bark with 7*** *Piper nigrum* ***seeds powder taken twice a day for 30 days.***
7. ****Piles: One small glass decoction daily morning for 10 days.***

**Edible use : Ripe Fruits are eaten**

**Vet : Loose motions : One liter extract of 50gm fresh stem bark given orally a day thrice until cure.**

**Misc : Wood is used for making agriculture implements and house construction.**

**LECYTHIDACEAE**

***Conroupitu guianensis*** **Abul. PI. gui. 2: 708, t. 282. 1775; Pradhan in Singh el al. Fl. Maharashtra. St. Dicot. 2: 23. 2001.**

Common Name: **Kailashpati**

**Nativity** -Tropical America
**Large trees, usually unbranched straight trunk bark thick rough . Leaves crowded at the ends of branches, elliptic, serrate. Flowers in pendent racemes. Fruits large**
**FIs. & Frts.:** **Throughout the year.**
**Distrib:** **Cultivated in gardens.**
**Edible Uses:** **Fruits are edible**
**Misc:** **The flowers used to scent perfumes and cosmetics. The hard shells of the fruit are sometimes used as containers.**

**LYTHRACEAE**

***Lawsonia incrmis* L. Sp PI. 349.1753.**
**Common Name**: **Mehendi**
**Nativity** - Middle East
**Shrubs, spiny. Leaves sessile, lanceolate. Flowers white, in terminal & axillary cymes. Capsules globose.**
**FIs. & Frts.:** **June-December.**
**Distrib:** **Common in hedges & villages.**
**Uses:** **Medicinal**
1. **Tuberculosis: Paste of handful of tender leaves with seven *Piper nigrum* seeds taken early in the morning once a day for two weeks to treat tuberculosis.**
2. ***Clod & Fever: 10ml juice of leaves with equal amount of milk taken orally once a day for 3 days.**
3. ***Loose motion: Leaves with *Cuminum cyminum* seeds, sugar & "karjura' *Phonenix dactylifera* dried fruit taken equal proportion boiled in butter taken orally daily thrice for 2 days.**

**Misc:** **Coloring material from used to dye hands & nails**

**PUNICACEAE**

***Punica granatum* L. Sp PI. 472. 1753.**
**Common Name:** **Dalimbs**
**Nativity** -Asia
**Shrubs or small trees. Leaves oblong-lanceolate. Flowers red. Fruit a berry with numerous seeds surrounded by juicy pulp.**
**Fls. & Frts.:** **August-November.**
**Distrib.:** **Planted for its fruits.**
**Uses:** **Medicinal**
1. **Cooling effect: 'Sharbat' prepared by barks & root which is used as cooling.**
2. **Loose motion. Flowers paste with rice washed with water made 10 gm pills taken 1 pill twice a day for three days.**
3. ***Jaundice: 50-60 ml juice of fruits taken orally twice a day for 10-15 days.**

**Edible Use:** **Fruits are eaten.**

**SAPOTACEAE**

***Manilkara zapota* (L.) van Royen in Blumea 7:410. 1953; *Achrus sapota* L. Sp. PI. 2:470 1762.**
**Common Name**: **Chiku**
**Nativity** -Asia
**Evergreen trees. Leaves alternate, elliptic to elliptic-lanceolate. Flowers white. Berries globose. Seeds ellipsoid, black.**
**Fls. & Frts.:** **More or less throughout the year.**
**Distrib:** **Cultivated for its fruit.**
**Edible Use:** **Ripe fruit is edible.**
***Mimusops elengi* L. Sp. PI. 349. 1753**

**Common Name**: **Bakul**

**Trees evergreen. Leaves elliptic. Flowers white, fragrant, solitary or in clusters of 2-6. Berries ovoid, yellow when ripe, Seeds solitary, compressed, ovoid, shining, brown.**

**Fls. & Frts.:** **January-March.**

**Distrib.:** **Planted as a avenue tree.**

**Uses:** **Medicinal**

**Tooth decay and tooth ache: Decoction of stem bark used for gargling daily thrice a day for tooth decay.**

**Edible Use:** **Ripe fruit is edible.**

**APOCYNACEAE**

***Alstonia scholaris* (L.) R. Br. Mem. Wem. Nat. Hist. Soc. 1: 76.1811;** *Echites scholahs* **L. Mant. PI. 53. 1767. Common Name: Saptaparni**

**Nativity** - MalAsia

**Trees. Leaves whorled, obovate or oblong-oblanceolate. Flowers greenish-white, in umbellately branched, capitates cymes. Follicles cylindric. Seeds compressed, rounded with hairy fringe at both ends**

**Fls. & Frts.:** **December-March.**

**Distrib:** **Cultivated along the road sides & house gardens.**

**Uses:** **Medicinal**

**"Intestinal worms: 10-20 ml leaf extract or 1 teaspoon powder of inner stem bark**
**taken orally once a day for 3 days.**

**BIGNONIACEAE**

***Spathodea campanulataV*. eauv. Fl. Oware Benin 1: 47, t. 27. 1805; Cooke, Fl. Pres. Bombay 2: 410. 1958 (Repr.); Londhe in Singh et al. Fl. Maharashtra St. Dicot 2: 584. 2001.**

**Common Name**: **Pichakari, Akash Shevga**

**Nativity** - Colombia

**Evergreen or semideciduous trees. Leaves opposite or in whorls of 3, 1-pinate; leaflets 3-19. Flowers in erect, many flowered dense racemes. Calyx leathery, boat-shaped, dark brown tomentose. Corolla campanulate; lobes undulate margined, acute.**

**Fls. & Frts.:** **January - May.**

**Distrib.:** **Grown in parks, gardens and roadsides.**

**Uses:**

1. **Stem bark is used as a paste for wound healing.**
2. Flowers are applied to ulcers.
3. Timber is used for paper making.
4. Hunters reported to extract poison arrow poison from seeds.

***Jacaranda acutifoliu*** Humb. And Nonpl. **PI.** Acquin. 1: 59. t. 17. 1806; Londhe in Singh et al. Fl. Maharashtra St. Dicot. 2: 581. 2001.

**Common Name:** Nilmohar

**Nativity-** Brazil & NW Argentina

Deciduous trees.Leaves opposite, 2-pinnate, pinnate 14-24 pairs with as odd terminal which is longer and acuminate; leaflets elliptic-oblong.Flowers in loose, terminal, panicles.Corolla dark blue or pink.Capsules suborbicular. hard, dark brown or black.Seeds many, winged.

**Fls. & Frts.:** March - October.

**Distrib.:** Grown as avenue tree and in gardens

**Uses:**

1. The flower extract was screened for its use as an acid base indicator in various acid titrations.
2. *Jacaranda acutifolia* flower extract alone can serve the indicator in weak acid and weak base titration, where generally mixed indicators are employed.

***Tabebuia argentea*** (Bur. and Schum.) Britt. In Sc.Surv. Porto Rico & Virgin Isl. 6: 197.1925; Londhe in Singh et al. Fl. Maharashtra St. Dicot 2: 584. 2001. *Tecoma argenteaBur.* and Schym. in Mart. Fl. Bras. 8 (2): 332. 1845.

**Common Name:** Silver trumpet

**Nativity**-Paraguay

Deciduous trees. Leaves opposite, digitate; leaflets 5. Flowers in terminal, captitate racemes. Corolla rubular-funnel sharped; limb irregularly spreading; lobes obtuse.

**Fls. & Frts.:** March - April.

**Distrib:** Grown in gardens.

**Uses:** Ornamental

**VERBENACEAIE**

***Tectona grandis*** L. f. Suppl. 151.1781.

**Common Name:** Sag

**Nativity** -Indonesia

Trees, Leaves elliptic or obovate, upper surface glabrous & rough, lower surface stellate grey or pawny tomentose inflorescences of erect, terminal panicles. Flowerswhite. Drubs subglobose.

**FIs. & Frts.:** August-December.

**Distrib.:** Abundant in dry deciduous forests.

**Uses:** **Medicinal**

1. *Cramps & Rheumatism: 20-30 ml decoction of stem & wood powder taken orally once a day for 1 week.
2. Stomach ache: 1 tea cup extract of stem bark twice only.
3. For promoting fertility: 1 tea cup extract of root bark with 7 *Piper nigrum* seeds powder & 7 oil drops given orally.

**Misc:**

1. Wood is good quality timber, used to making agriculture implements, furniture, house construction, walking sticks & musical instruments.
2. Leaves are used to making plates.
3. Flowers used in religious ceremonies (Ganesh Chaturthy)

**MORACEAE**

***Artocarpus heterophyllus*** **Lam. Ency. 3: 210. 1789; Laxmi and Venkanna in Singh et al. Fl. Maharashtra St. Dicot. 2: 930. 2001 . A** *mtegrifolia* **auct. Non L. f. 1781; Grah. Cat. 192. 1839; Hook.f. Fl. Brit. India 5: 541.1886; Cooke, Fl. Pres Bombay 3: 158. (Repr.)**

**Common Name**: **Phanas**

**Nativity** -South East Asia

**Large, deciduous trees. Inflorescence from main branches, enclosed by glabrous, deciduous, leafy scales.Male flowers in heads. Perianth 2-lobed. Female protruding. Syncarps oblong-globose, perianth, thick, fleshy. Seeds elliptic-oblong.**

**FIs. & Frts.:** **January - March.**

**Distrib:** **Cultivated in gardens for their fruits.**

**Uses:** **Medicinal**

1. **The leaves of** *Artocarpus heterophyllus* **tree are useful for curing fever, boils and skin diseases. When heated, they prove useful in curing wounds.**

2. **To heal ulcers, the ash of** *Artocarpus heterophyllus* **leaves is burnt with corn and coconuts hell and used either alone or mixed with coconut oil.**
3. **The roots** of *Artocarpus heterophyllus* **tree forms the remedy for skin diseases, fever and diarrhea.**
4. **The latex of fruits is can be mixed with vinegar to heal abscesses, snakebites and glandular swellings.**

**Edible:** **Ripe fruits are eaten.**

**Misc:**

**The wood of** *Artocarpus heterophyllus* **tree is widely used in manufacturing musical instruments, furniture, doors, windows and roof constructions.**

***Ficus benghalensis* L. Sp. PI. 1059. 1753.**
**Common Name: Wad**
**Nativity-**Asia
**Trees, with numerous aerial roots from spreding branches; twigs. Leaves ovate. Figs sessile, axillary, paired, ripening, orange-red, dipressed-globose. Tepals free, 2-3 in male, 3-4 galls & female flowers: anthers shortly mucronate.**
**FIs. & Frts.:** **April-June.**
**Distrib:** **Common along road sides in villages & towns.**
**Uses:** **Medicinal**

1. **Stomach ache: 5 drops of latex mixed with small amount turmeric powder, made into small pills taken orally twice a day for 2 days.**
2. *** Spermatogenesis:** *Phonix dactylifera* **seeds are taken out from fruits & plants latex is filled in it & kept overnight & 2 fruits eaten for about 15 days to promote spermatogenesis & reduce sterility. Same is also considered as tonic.**
3. **Tonic: Tender prop roots extract are given as tonic to children.**
4. ***Colic: 10 gm tender leaves crushed with rice & taken in equal proportion, add milk, crushed & taken orally once a day until cure.**
5. ***For promoting fertility: Tender prop roots with** *Azadirachta indica* **seeds taken in 2:1 proportion crushed with human milk, made in to 2gm pills 1 pill taken twice a day on third day to 4th day during menses period.**
6. **Foots cracks: Latex applied externally until cure**
7. **Eye infection & good vision: Latex with sugar applied on layer twice a day for 15 days.**
8. **Boils on head: Ash of matured leaves with** *Lawsonia inermis* **leaves and catechu taken equal proportion applied externally with coconut twice a day for 3 days.**
9. **Blood dysentery: 1 tablespoon of latex with jaggery taken orally with milk twice a day until cure.**

**Vet:** **Bone fracture inner bark wrapped over fracture arm and tied from outside & extract of propped given orally** *Vi* **liter twice a day until cure.**

**Misc:**

1. **Timber for house construction & used as fuel**
2. **Leaves are used for making plates.**
3. **Leaves used in religious ceremonies.**

**CASUARINACEAE**

**Casuarina equisetifolia** ***L. Amoen. Acade. 4: 143. 1759.***
**Common Name:** ***Sum***
**Nativity-**Madagascar

*Tall tree, braches modified into clododes. Leaves reduce to scales. Flowers small. unisexual monoecious. Carpophores pubescent, cone like.*

**FIs. & Frts.:** *February-March*
**Distrib.:** *Cultivated on field edges.*
**Uses:** *Wood is used for house construction*

**STRELITZIACEAE**

***Ravenala imidagascariensis*** *J. F. Gmel. Syst. 567. 1791; Baker in Hook.f. Fl. Brit. India 6: 198. 1890; Cooke, Fl. Pres. Bombay 3: 250. 1958 (Repr); Lakshmi in Sharma et al Fl. Maharashtra St. Monocot. 90. 1996, Naik, Fl. Marathwada 2: 837. 1978.*

**Common Name:** *Traveler's palm*
**Nativity-** Madagascar

*Robust, tall arborescent herbs. Leaves distichous, closely setting, ovate-oblong, spreading, Flowers sessile, subzygomorphic, in compact monochasial cymes, each flower enclosed in bract. Stamens 6. Capsules linear-oblong.*

**FIs. & Frts.:** *October - January*
**Distrib:** *Commonly cultivated in gardens.*
**Uses:** **Medicinal**

1. *It is widely used in folklore medicine in the treatment of diabetes and kidney stone problems.*
2. *Seeds were reported to be antiseptic*

**ARECACEAE**

***Caryota urens*** *L. Sp. PI. 1189. 1753; Beck. & Hook f. in Hook f. FI. Brit. India 6: 422. 1892; Cooke, Fl. Pres. Bombay 3: 315. 1958 (Repr.); Lakshmi in Sharma et al. FI. Maharashtra St. Monocot. 1: 189. 1996.*

**Common Name :** *Bherli mad*
**Nativity-** Tropical Asia

*Large trees, covered with corky edges. Leaflets fasciculate or alternate, serrate-toothed on margins, margin irregularly lobed.Flowers numerous, in pendulous, many spadices. Dupes, reddish. Seeds 2, hemispheric, black, striated.*

**Fls. & Frts.:** *Throughout the year.*
**Distrib.:** *Frequent on walls of forts, in the forests.*
**Uses:** *Food, beverage, fiber, timber, ornamental.*

***Cocos nucifera*** *L Sp. PI. 1188. 1753*

**Common Name** : *Naral*
**Nativity-** Malaysia

*Trunk, annulate, thickened at the base. Leaves, leaflets equidistant, linear-lanceolate, spadix, stout, androgynous, simply panicled; branches bearing scattered female flowers towards their bases & numerous males above. Fruits-3 gonously obovoid or sub globose, green or yellowish.*

**Fls. & Frts.:** *Throughout the year.*
**Distrib.:** *Cultivated on field edges.*
**Uses:** **Medicinal**

1. *Wounds: Ash of external fibers of dried fruits applied with coconut oil.*
2. **Mouth ulcer: gargling by flower juice twice a day until cure.*
3. **Psoriasis: fruit fiber ash with snake fat "Kubusam" applied externally twice a day until cure of psoriasis.*
4. **Wounds due to burning: coconut oil with lime water taken in equal proportion boiled & applied externally until cure.*
5. **Sores on tongue : Fruits ash with few* ***Piper longum*** *seeds powder applied with honey until cure.*

***Edible Use :*** *Fruit endosperm eaten raw & also used various food preparation.*

***Vet :*** **Wounds: ash of fruits fiber applied externally until cure*

***Misc :***

1. *Leaves used in preparation roof of marriage mandapas & huts.*
2. *Dry husk used for making ropes.*
3. *Fruits offered to god & goddesses.*
4. *Leaves used for decoration during socio-religious ceremonies.*
5. *Leaves used for making brooms, mats & basket, etc.*

***Roystoneu regia*** *(H.B. & K.) Cook in Bull. Torreu Bot CI. 531. 1901; Naik. Fl. Maharashtra 2: 888. 1998.* **Oreodoxa regia H.** *B. &K. Nov. Gen. and Sp. 1: 305. 1815; Cooke, Fl. Pres. Bombay 3: 321. 1958 (Repr.); Blatt. Palms Brit. Ind. Ceyl. 396, t. 73. 1978; Lakshmi. In Sharma et al. Fl. Maharashtra St. Monicot. 204. 1996.*

**Common Name:** *Bottle palm*

**Nativity-**Mexico & Central America

*Large trees. Stems annulate, bottle* shaped. *Leaves large crowded at the neds top,* petioles enclosing *stem; leaflets linear-ensiform. Flowers* gTeenish-*white, numerous in spathes. Spadices 3-4 simultaneously. Drupes small, elliptic ovate, stiated.*

**Fls. & Frts.:** *September - March*

**Distrib.:** *Commonly cultivated in gardens as avenue trees.*

**Uses:** **Medicinal**

*1 .They are also used as a treatment for diabetes.*

**Misc:**

1. *The seed is used as a source of oil and for livestock feed.*
2. *Leaves are used for thatching and the wood for construction.*
3. *The roots are used as a diuretic and for that reason they are added to* **lifey,** *a Haitian drink, by Cubans of Haitian origin.*

**Thrinax barbadensis** *Lodd. In Mart. Hist. Nat. Palm. 257. 1838; Blatt. Plams Brit. Ir Ceyl. 68. 1978 (Repr); Lakshmi. in Sharma et al. Fl. Maharashtra St. Monocot. 205. 1996.*

**Common Name:** *Fan shaped palm*

**Nativity-**North America

**Medium sized hermaphrodiate palm. Leaves fan-shaped, broadly orbicular. Flowers numerous, greenish-white in spadix. Spadices usually longer than leaves and pendent in fruiting. Seeds globose.**

***FIs. & Frts.:*** **September - December**

***Distrib.:*** **Commonly cultivated in gardens.**

***Uses:*** **Ornamental.**

***POACEAE***

***Bambusaarundinacea*** **(Retz.) Wild. Sp.Pl. 2:245. 1799;Hook.f. Fl.Brit. Ind.7:395. 1896;Blatt. And McC, Bombay Grass. 283. 1935; Cooke, Fl. Pres..Bombay 3:569. 1958(Repr.) Laksmi. In Sharmaet al.Fl. Maharashtra St. Monocot. 412.1996. Bambusa arundinacea Retz. Obs. Bot. 5:24. 1788.**

***Common Name :*** **Kalak.**

**Nativity-** Myanmar

**Perennials. Culms tufted, 24-25 m high, erect, branched, armed; nodes prominent. Culms-sheaths coriaceous, variable in shape Leaves linear-lanceolate, with stiff apex. Penicles compound, with loose clusters of spikelets on spicate branch lets. Spike lets oblong, 3-6 flowered Grains oblong**

***FIs. & Frts.:*** **December-January.**

***Distrib:*** **Wild or cultivated forming dense strand.**

***Uses:*** **The interior stalks or stems (bamboo hol!ows)of female plant containing silicious concretions(deposit) called tabasbir (bamboo**

**Manna) in the interior of stem of B.arundinaceae; young shoots, leaves, articulations, seeds and roots.**

***Bambusa vulgaris*** **Schrad.in Wendl. Collect. PI. 2:26,147,1810; Hook. f.,Fl. Brit. Ind., 7:391.1896:BlattandMcC, Bombay Grass. 3:282.1935; Cooke, Fl. Pres. Bombay 3:570. 1958 (Repr); Lakshmi. in Sharma et al. Fl. Maharashtra St. Monocot 413. 1996.**

***Common Name :*** **Bamboo.**

**Nativity-**South East Asia

**Perennials, Culms tufted. Terete, 6-15 mhigh, erect: nodes hardly raised with usually a ring of brown hairs. Leaves linear-lanceolate, apex twisted. Penicle large, with clusters of spikelets.**

***FIs. & Frts.:*** **Rare, once in every 20 years.**

***Distrib :*** *Cultivated in region.*

***Uses :***

**Medicinal**

1. *Bombusa vulgaris has historically been used to treat coughs and excess mucous and help alleviate fever.*
2. *The prebiolic xylloligosaccharides found in Bombusa vulgaris may contribute to in improved intestinal health and reduced risk of digestive disorder.*

**Other**

1. *Bamboos used for building houses and bridges.*

**RESULTS**

**In Ihe present work, total 48 species of trees belonging to 21 families of angiosperms have been reported from college campus. Present work is the result of intensive ethnobotanical explorations of herbaceous plants of New Arts commerce college campus Ahemednagar district made during the period from 2019 to 2020. In Ahemednagar district few workers have done ethnobotanical work on some selected and small parts of the district. Pradhan and Singh (1999) have worked out flora of the district. In the present study, ethnobotanical information is collected on 48 trees species belonging to 21 families of angiosperms have been reported from college campus. Out of the 48 trees species collected, Polypetalae have12 families and 30 species, Gamopetalae have04 families and 07 species. Apetalae have 01 families and 03 species, included Monocotyledone have 03 families and 08 species have been collected.**

**Table 6.1 - Differentiation of Dicotyledons and Monocotyledons in the area of study**

| Sr. No. | Class | Subclass | Family | Species |
|---|---|---|---|---|
| 1 | Dicots (d) | Polypetalae(p) | 12 | 30 |
| | | Gamopetalae (g) | 04 | 7 |
| | | Apetalae (a) | 02 | 03 |
| | | Total (p + g + a) | 18 | 40 |
| 2 | Monocots (m) | | 03 | 08 |
| | Total (d+m) | | 21 | 48 |

**Table 6.2 - Number of dicot and monocot Species, Genera and Family**

| Number | Species | Genera | Families |
|---|---|---|---|
| **Monocots** | **08** | **07** | **03** |
| **Dicots** | **40** | **16** | **18** |
| **Total** | **48** | **23** | **21** |

| TABLE-LIST OF EXOTIC TREE WITH NATIVITY | | | |
|---|---|---|---|
| Sr.No. | Name of plants | Family | Nativity |
| | Polypetalac | | |
| 1 | *Annona reticulata* L. | Annonaceae | Caribbean & Central America |
| 2 | *Annona squamosa* L. | Annonaceae | Tropical America & West Indies |
| 3 | *Polyalthia longifotia* (Sonn.) Thwaitcs, | Annonaceae | Sri Lanka & India |
| 4 | *Bixa orellana* L. | Bixaceae | Tropical America |
| 5 | *Muntingia calabura* L. | Tiliaceae | Southern Mexico, Central America & Bolivia |
| 6 | *Zizyphus mauritiana* Lamk | Rhamnaceae | Afghanistan |
| 7 | *Gliricidia sepium* Qacq.) Kunth. Ex Sleud. | Fabaceae | Mexico |
| 8 | *Caesalpinia pulcherima* (L.) Swartz | Cacsalpiniaceae | West Indies & Tropical America |
| 9 | *Cassia fistula L.* | Caesalpiniaceae | Tropical South America |
| 10 | *Cassia saimea* L. | Cacsalpiniaceae | Sri Lanka |
| 11 | *Delonix regia* (Boj ex Hook.) Raf. | Caesalpiniaceae | Tropical Africa |
| 12 | *Pellophorum plerocarpum (DC.) Baker & Heyne* | Caesalpiniaceae | Australia |
| 13 | *Saraca asoka (Roxb.) de Wilde* | Caesalpiniaceae | Tropical South America |
| 14 | *Tamarmdus indicus L.* | Caesalpiniaceae | Tropical Africa & Sudan |
| 15 | *Acacia nilotica (L.) Willd. ssp. indica* | Mimosaceac | North Africa |
| 16 | *Acacia lungifolia Willd.,* | Mimosaceae | Australia |
| 17 | *Albizia lebbeck (L.) Willd. var. lebbeck* | Mimosaceae | Tropical America |
| 18 | *Calliandra haematocephala Hassk* | Mimosaceae | Tropical America |
| 19 | *Leucaena leucocephala (Lamk.) de Wit.* | Mimosaceae | Colombia |
| 20 | *Pithecolobium duke (Roxb.) Benth.* | Mimosaceac | Mexico |
| 21 | *Prosopis juliflora (Sw.) DC.* | Mimosaceac | Mexico |
| 22 | *Samanea saman (Jacq.) Merr.* | Mimosaceae | Tropical America |
| 23 | *Terminalia calappa L.* | Combretaccae | Tropical Asia |
| 24 | *Terminalia chebula Retz.* | Combretaceae | Tropical Asia |
| 25 | *Terminalia arjuna (Roxb.ex dc)* | Combretaccae | Tropical Asia |
| 26 | *Callistemon citrinus (Curtis) Skeels* | Myrtaceae | Australia |
| 27 | *Eucalyptus globulus Labill.* | Myrtaceae | Australia |
| 28 | *Psidium guajava L.* | Myrtaceae | Tropical America |
| 29 | *Syzygium cumin/ (L.) Skeels* | Myrtaceae | South East Asia |
| 30 | *Couroupita guianensis AuBl.* | Lecythidaceae | Tropical America |
| 31 | *Lawsonia inermis L.* | Lythraceae | Middle East |
| 32 | *Punica granatum L.* | Pimicaceae | Asia |
| | Gamopetalae | | |
| 33 | *Manilkara zapola* (L.) Van Royen | Sapotaceae | Asia |
| 34 | *Mimusops elengi* L. | Sapotaccae | Asia |
| 35 | *Alstonia scholaris* (L.) R. Br. | Apocynaceae | Malasia |
| 36 | *Spathodea campanulata* Beauv | Bignoniaccae | Colombia |
| 37 | Jacaranda acutifolia Humb. & Bonpl. | Bignoniaccae | Brazil & NW Argentina |
| 38 | Tabebuia argentea (Bur. & Schum.) Britt | Bignoniaceae | Paraguay |
| 39 | Tectona grandis L. | Verbenaceae | Indonesia |
| | Apetalac | | |
| 40 | Casuanna equisetifolia L. Amoen. | Casuarinaccae | Australia |
| | Monocotyledons | | |
| 41 | Ravenala madagascanensis J.f. Gmelin | Strelitziaceae | Madagascar |
| 42 | Dypsis decaiyi (Jum.) Beentje and J. Dransf. | Arecaccae | Malaysia |
| 43 | Caryota wens L. | Arecaccae | Tropical Asia |
| 44 | Cocos nucifera L. | Arecaceae | Malaysia |
| 45 | Roystonea regia (H.B. & K.) Cook | Arecaceae | Mexico & Central America |
| 46 | Thrinax sp. | Arecaceae | North America |
| 47 | Bantbusa amndinacea Willd. | Poaceae | Myanmar |
| 48 | Bambusa vulgaris Schrad. | Poaceac | South East Asia |

## CONCLUSION

Ahemednagar district is rich from ethnobotanical point of view. Indigenous people use several plants for medicine, food, house construction and other purposes. Their life is clearly related to the plants growing in nearby areas. Although, medicinal uses of plants reported in the present work is less known or new and infact are much less than what still remains with indigenous people.

Ethnobotanical explorations during the period from 2019 to 2020 in the present study area lead to the following conclusions.

A medicinal use in major literature adds significance to present work and indicates the need of thorough scrutiny or investigations for the active principles of these plants.

Such studies may provide information to the workers in the field of pharmacology and phytochemistry in screening of individual species, for particular disease. Further investigations on utilitarian plants to check their efficacy and safety are necessary, so that those can be further utilized for medicinal purposes in proper way.

The formulation herbal drugs either with single plant or a mixture of more than one plant, with appropriate mode of use and dosage should be encouraged. As the plants are being used successfully by the tribal.

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# ROLE OF WOMEN EDUCATIONA IN MADRAS STATE- A STUDY

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The spread of education brought about changes that were more fundamental in the case of women than men, "To men it brought a new conception of the world of its material resources,[1] ethical standards and political possibilities but to women it brought slowly but potently a new conception of themselves. If men reassessed themselves as citizens in a new India, women revalued themselves as human beings in a social order."[2] The influx of Western education into the country had its impact on women's emancipation.[3] This system of education introduced a new spirit of understanding, a better appreciation of life in the community and gave an impetus to rethinking of values. The individuals educated under this system openly criticised social evils such as early marriages, polygamy, dowry, infanticide, sati and temple dancing. They severely criticised the seclusion of women and their colossal illiteracy.[4]

Srinivasa Pillai, a great social reformer and his likeminded colleagues founded the 'Hindu Progressive Improvement Society' in November 1852 in Madras. Srinivasa Pillai, had a long record of service in various charity organisations including Monegar choultry, the Pachaiyappa's charities and the Madras Literary Society. The major aims of the society were the promotion of widow remarriage, the encouragement of female education and the upliftment of depressed classes. In 1864, 'Veda Samaj' was established in Madras, along the lines of Keshab Chandra Sen's *Brahmo Samaj of Bengal. The members of the Veda Samaj pledged their support to women's emancipation by providing female education; propagating widow remarriage, restraining child marriage etc. The Veda Samaj was reorganised and renamed as the Brahmo Samaj of South India *i n 1871. Theosophy started spreading in South India after 1881. The first branch of the Society in the South was founded in Tirunelveli. Later the Madras branch of the Theosophical society was formed with Ragunatha Rao as President and T.Subha Rao as Secretary.

In the midst of religious and communal fanaticism, some liberal minded Brahmins in the Madras Presidency advocated for widow remarriage. In 1874 the 'Madras Hindu Widow Marriage Association' was formed, to encourage the marriage of Hindu widows. Highly educated people like Rama Iyengar and Muthusamy Iyer became active members. A South Indian Conference, was convened by the Hindu Women's Marriage Association on 31st December 1884 at Madras, but the participation was restricted only to the graduates, presumably with a view, to enlist the support of the educated young men in the cause of social reforms. Some of the important resolutions passed in the conference were, that every graduate should promote female education and widow remarriage and discourage infant marriage.[5] Both the press and public platforms were literally used for spreading these ideas among the people. To some extent the role played by the journal Indian Social Reformer was remarkable. The journal was not satisfied with mere passing of resolutions advocating the education of women or condemning infant marriages. On the other hand the journal considered it as a "Sad waste", for it felt that the "urgent need was the reconstruction of the society" on the national basis of equality of sexes.

Veerasalingam (1848-1919) was a great pioneer in widow remarriage movement in the South. He started 'Widow Remarriage Association' in Andhra in 1880. He gave public lectures and wrote articles in many Telugu periodicals. Veerasalingam, performed the first widow remarriage in Rajamundry in 1881. He opened a 'widow's Home at Madras in 1900, another at Rajamundry in Q 1905 for the benefit of widows.[6] Widow remarriages were celebrated in different parts of the state under the leadership of various social reformers. In Madras Chentsal Rao and Raghunatha Rao were responsible for the spread of widow remarriage movement.

The persons who married the widows were mostly educated. Some of them came forward with the spirit of reform, some others for publicity and few for the sake of financial assistance which was offered by the Widow Remarriage Association. In Madras G. Subramania Iyer, a learned Brahmin and the founder of the news paper The Hindu in English and Swadesmitran in Tamil challenged the practice of perpetual widowhood and fought against it by conducting the marriage of his widowed daughter. His daughter Sivapriyammal lost her husband at her 13th age. From that time onwards he began to propagate for widow

remarriages. As a challenge to the society, he took his widowed daughter and a boy of his choice to Bombay in 1889, and conducted their marriage in Bombay. The marriage created some sort of antagonism into the minds of orthodox Brahmins against G. Subramania Iyer. But, the Brahmin community could not excommunicate him due to his hold on government and the public." But the work of social reformers and the government did not bear fruit owing to the deep-rooted religious faith and superstitious beliefs and social customs.

Poet Subramania Bharathi championed the cause of women in Madras Presidency. Periyar E.V. Ramaswamy broke with the Congress in 1925 on the issue of Brahmin-Non Brahmin problem and started Self Respect Movement with a view to bringing about an all-round change in the Tamil Society. He opposed the purdha system, and held that Purdha system would pave the way for the decline of the society. He encouraged widow remarriage, education of women and the careers of women.

The Western education had made the girls less particular about tradition, religious beliefs, caste rules and rituals. It has produced a situation in which young girls did not have the time to learn rituals from their mothers and grandmothers. The educated wife has less of traditional culture to pass on
to her children. For girls, the attainment of puberty is no longer manned by the elaborate ritual that characterised it a few decades ago. The shaving of a Brahmin widow's head, as part of the funeral rite for her dead husband has also largely disappeared. Widow Remarriage is no longer strongly disapproved. The native associations, voluntary organisations added impetus to this awakening. The beginning of the twentieth century witnessed the rise of a large number of women's organisations. Women themselves became conscious of their right to receive education and became more self reliant. A number of enlightened women then started establishing women's associations in different parts of the country with a view to carry out the social, political and cultural advancement of Indian women. Women's Indian Association, Madras, founded in May 1917 was the first organisation "whose aim was to be All-India in scope, to include as members all types of Women, who were residents in India and to birfd them together for mutual service and the good of the country. The Indian Ladies Samaj was organised in Madras during 1923-24. Its aim was to protect minor girls from undesirable associations and guardianship, and to educate and train them for an

independent and honourable profession. All these created some sort of awareness for the emancipation of women.

In 1929, the Subbarayan's ministry abolished the system of separate hostels for the Brahmins, Non-Brahmins and the Christian girls studying in Madras city and introduced the common hostel system where caste and religion were no criteria. Likewise hostels for widows were thrown open to all communities. Women's Indian Association, Madras, 1917 The Women's Indian Association, was started by Mrs.Dorothy Jinarjadasa at Adyar, Madras on 8th May 1917. She was sincerely assisted by an Irish lady Mrs.Margaret Cousins. Its first president was Annie Besant, and for eight years Dorothy Jinarjadasa remained its honorary secretary. The aims and objects of the association were the following:

1. To present to women their responsibilities as daughters of India.
2. To help them to realise that the future of India lied largely in their hands, for as wives and mothers they had the task of training, guiding and forming the character of the future rulers of India.
3. To bind women into groups for the purpose of self development and education, and for the definite service of others.
4. To secure for every girl and boy the right of education through schemes of compulsory primary education, including the teaching of religion.
5. To secure the abolition of child marriage and to raise the age of consent for married girls to sixteen.
6. To secure for women the vote for municipal and legislative councils as it was or might be granted to men.
7. To secure for women the right to be elected as members on all municipal and legislative councils.
8. To establish equality of rights and opportunities between men and women.[7]

The Association which had a central, organisation at Adyar, Madras, had grown steadily ever since. Within the first year of its conception thirty three branches were formed in many towns. Branches were formed wherever possible with a local secretary to arrange the work suitable to local conditions. Local branches were self governing and made their own arrangements and managed their own finance. Through correspondence with the head quarters secretary and through the official

magazine of the association Stri Dharma, the different branches and members were united with a sense of strength, courage and inspiration.

The association had a committee, consisting of a President, a Vice President, a General Secretary, a Treasurer and an Advisory Council of the Secretaries of all the branches. Branches of Women's Indian Association Tamil
Coimbatore, Enangudi, George Town, Madras, Kuttalum, Kumbakonam, Madurai, Mayavaram, Namakkal, Pollachi, Salem, Tanjore, Thirumiyachur, Trichinopoly, Vellore, Vettaikaranpudur and Viralimalai.[8]

The modern women are no longer bound by false standards of modesty and reserve. Owing to the growth of Female Education, she no longer considers feminine etiquette to be one of total subordination and helpless dependence on man. She has the confidence, born of ability, to compete with others on an equal footing. To accelerate the process of the emancipation of women, the educated elite among women were engaged in a variety of public activities. Annie Besant, Muthulakshmi Reddi and Kamala were the pioneers in this regard. The Movement was geared to securing equal rights in inheritance, marriage, requirement of the consent of both parties for marriage and the right to share equal responsibilities along with men in offices as well as in domestic affairs.

The Dawn of the Twentieth Century marked the beginning of a new era in
the annals of the History of Education of Women in the Tamil Country. During
the British Period, the diffusion of Western and Non-Hindu Ideas created a stir in the Tamil Country. The British Administrative System was based on the 'Rule of Law' and the reforms of Bentinck and Dalhousie and no wonder the Missionaries questioned the unequal treatment of the various sections in Hinduism. Further, the reformist zeal encouraged Mrs. Annie Besant to organise the Theosophical Society at Adayar near Madras. The Society stood for the Emancipation of Women in the Tamil Country. This was followed by the establishment of 'The Women's Indian Association,' and 'The South Indian Women's Association' which stood for the abolition of social evils and thereby helped the elevation of the status of women in the Tamil Country. Besides, the birth of a prose literature in the Tamil Country in the Nineteenth and Twentieth Century's served as a powerful weapon of thought and expression. The writings of Bharathiyar

and Bharathidasan gave new impetus to fight for their rights.[42] The emergence of Social Reformers like Periyar E. V. Ramasamy Naicker and Thiru V.Kalyana Sundaram created an atmosphere, conducive to Social Reforms in the Tamil Country. [43] While these measures paved the way for social reforms in general and the Emancipation of Women in particular, it was the introduction of Western System of Education that had created the climate for these reforms.[44]

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# INDUSTRIAL PSYCHOLOGY

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## Introduction

It is a branch of psychology came in the existence in 1901. It's the 3/4$^{th}$ of all the branches of psychology, to understand the human problem in job area. It's the result of tremendous expansion of industries. It deals with the process of the people to adapt survive and flourish. It is a broad field to understand mental processes and behaviours. It's useful in selection of workers, development and management to take safety measures, are the scope of this branch. Resist the changes is the human tendency. Not to accept and maintain 'Status – quo' and change is hurdle to them. Learning has some characteristics:

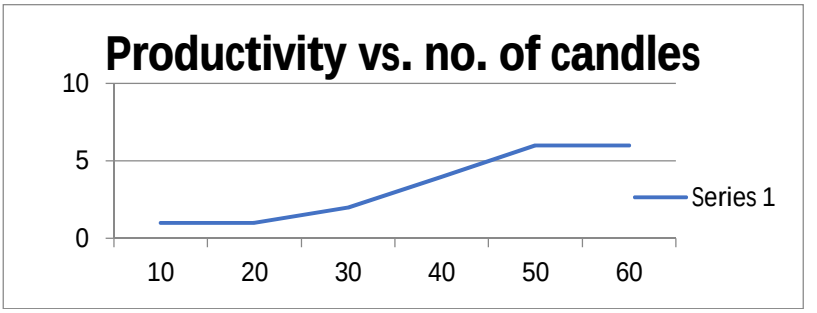
i. It changes behaviour if there is no change, there is no learning.
ii. Learning comes through experience.
iii. Change may last for some time.
iv. Thinking for other person, is also very important because it depends on how we are different from others.

## Hawthorne Experiments

These are the series of experiments to investigate many of the dependent variables amongst the workers. The most significant result of this is, the fact that workers get affected with these factors outside the job to the greater extent those who are in job itself and organise into informal social groups.

Hawthorne Studies can be divided into five parts.

i. **Experiments on illumination:** In this experiment, workers in certain groups were tested for the productivity on the bases of light produces by different number of candles and finally the result was that the numbers of candles were changed to high production.




ii. **Relay assembly test room:** The initial purpose of this experiment was to exercise more direct control over the workers that could have influenced the performance by dividing people in small groups in separate room away from regular working force. It's simple and high repetitive. It requires an accurate rate of production. It has two parts.

a) Second relay assembly test room
b) Mica Splitting test room

In which the bases of wage payment remain at the same individual pace rate but changes in working condition are similar to test room experiments.

iii. **Mass interviewing programme:**
It's an interview process that is done for the improvement in supervision to improve moral. It's helpful for securing the information provided by employees.

iv. **Bank wiring observation room:**
This part of Hawthorne experiment is done to get more exact information about social groups within the company. It was obtained to get information from large number of employees.

v. **Personal counselling:**
All the four studies indicate lack of accomplishment, relationships of employees and importance of this work fifth study is an effort to bring this important area into focus. There were two objectives, first was non-authoritative and impartial to diagnose the problem of employees and teach them to work in supervision. The second was to improve the method of communication within the company.

## Work Place

Environment and features of this affects it. The problem of high production and making to work more pleasant has been approached through the introduction of change in milieu.

There is a fundamental difference in this approach which in high in efficiency is attained as a result of time motion studies. Generally it's related with the size of work area other approaches are refine selection tech to high efficiency. There are many more factors responsible that can affect efficiency which are as follows:

i. **Music in industry:** Music during repetitive factory work results in a slight increase in production. There is a need amongst office workers. Employee may affects to get influence by the music to receive drastic positive, effects to success. Music broadcast by radio requires minimum investment but it has a disadvantage also. FM stations generally have less numbers for the industrial use.

ii. **Noise:** It is a distracter and interfering with efficiency in an experiment to determine the effects of noise for example, a typist become used to the clatter of the machine because it's a necessary part of its work where is a person sitting next to him gets irritated. Reports about noise tells us whatever is irritating is harmful. It may not be taken emotionally otherwise it may curtail the production and bring deafness in some situations.

iii. **Colour:**
Colours give a very important sensation in the mind of workers to work. It's an article which can remove your tiredness and increase production. We can receive greater scientific results with safety measures thorough colours in the factory. The evidence on the relation between colour in industry and increase the production is based upon data. It is most important factor.

iv. **Miscellaneous:**
Cafeteria, snack bar, library, soda fountain, sand witch and ice cream such things always create problem to management but it's for psychological relaxation for people.

v. **Light (Illumination):**
Artificial lighting can't match up with the day light because important parts of lighting which is considered is intensity, glare, location and combo of artificial and natural light.

**Leadership**

It is seen in all organisations. This is an essential group. Every employees or employer need a leader. Elective selection is totally dependent on management to assess and evaluate workers. Top management means big boss, middle management is boss, front management are supervisors. These three work on different level of duties.

**Leadership Criteria:**

Are you respected by everyone?
Are your rules are followed?
Do you look out for employees?

Do workers like you?

There are two approaches to study leadership:

i. **Trait approach:** In this we study about simple people having Quite Simple logics for success good leaders correspond good people only.
ii. **Behavioural approach:** This leadership has
We see enthusiasm among people they must have super intelligence, initiative power aggressiveness.

**Types of Leadership**

➔ **Imperial:** In this we talk of experience of individual. Generally they have:
i. Wide variety of examined group behaviour.
ii. Principles of leader behaviour.
iii. Tested theory of their investigation.

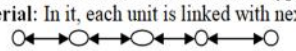
➔ **Humanistic:**
It's the II group in leadership theory. It talks about employees who have developed their modals in more inductive fashion. This theory is lacking infactual support, its difficult to evaluate workers on these theories.

**Organisation Culture**

Organisational psychology occupies itself with the study of organisational processes. It talks about development theories and its behaviour to improve any organisation. It is closed on one of its boundaries to human relation psychology. It's touched with experimentation psychology.
Organisation is group of worker who meet twice or thrice in a day. They have different mentality, taste, and working ability and so on.

**Organisational Structure:**
Any organisation is linked in three different types of linkage system:

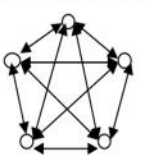
i. **Serial:** In it, each unit is linked with next unite with each side.



ii. **Radial:** In this, each unite is connected to central unit.



i. **Circular:** Each unit is linked to each other for betterment of productivity.



**Exchange Theory**

The essential element of this theory is to see the operation of organisation as the establishment of balance between workers and management.

**Group Theory**

Group theories are those which take the pts of you about human relation, co-operation, and friendliness in primary group it's critical to a successful organisation because management had to made aware of the importance of social aspects of work and its influence upon the success.

**Value Theories**

The conflict of value systems, because many theories tell us value theories are totally different from each every individual in any organisation, to determine the effectiveness and Stability of the organisation system.

**Structural Theories**

An organisation is not a machine and it is inappropriate to imply mechanistic theories on it.. Organisation should be taken as living organisms as they are dynamic, adaptive to change and highly responsive to the world around them.

**Situational Theory**

Many theories of organizational behaviour have taken the situation as the focal point for solving the conflict between individual at organizational goals. It may be some attempts to shape the tasks to fit the organization.

## Conclusion

Industrial Psychology demands change in attitudes and outlooks of the employees. One importance of IP is to govern the employee's behaviour in workplace, school and colleges. Learning is very important in Psychology

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# BUILDING AWE THROUGH THE SACRED MENSTRUATION: BUSTING THE MYTH OF MENSTRUATION BY UNRAVELLING THE MYTH OF CHENGANNUR MAHADEVA TEMPLE WHERE NATURE MEETS THE DIVINE

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**Abstract**

The unique aspect of the temples of India lies in the stories that they have to tell. Every temple can be called a storehouse of multitudes of myths and legends that are distinctive. These myths and legends not only evoke wonder but also compel the people to think. Chengannur Mahadeva Temple, located in the Alappuzha district of Kerala is a home to many exciting legends that break the existing stereotypes in the Hindu tradition. This temple also has a *Bhagavathi* temple that celebrates the menstruation of the Goddess Parvathy. Nature, myth and divinity combine together in this ritual where the idol is believed to menstruate and blood stains are spotted in the *udayada* of the Goddess. Instead of believing it a taboo, from the ancient times people celebrate this as a sacred event that is a symbol of fertility, marriage and birth. This festival is known by the name *thriputharattu.* Other than this, the temple houses several other interesting myths that amaze the listeners. The temple is a perfect example of worshipping the Female power of nature. This paper analyses the menstruation myth and festival that surrounds the Chengannur Mahadeva Temple. This paper also explains the other myths associated with this temple and the importance of nature that is brought out by the eco-narrative of the myths and legends that live through this temple

**Key Words:** Eco Narrative, Menstruation Festival, Sacred, Mythology, Landscape,Ecofeminism

## Introduction

"Myth basically serves four functions. The first is the mystical function,... realizing what a wonder the universe is, and what a wonder you are, and experiencing awe before this mystery....The second is a cosmological dimension, the dimension with which science is concerned – showing you what shape the universe is, but showing it in such a way that the mystery again comes through.... The third function is the sociological one – supporting and validating a certain social order.... It is the sociological function of myth that has taken over in our world – and it is out of date.... But there is a fourth function of myth, and this is the one that I think everyone must try today to relate to – and that is the pedagogical function, of how to live a human lifetime under any circumstances" (Campbell,1 988). The different enchanting phenomena in nature that couldn't be explained at a time when science was non-existing and mythology and legends served this purpose. Oral tradition has paved way for the transfer of mythical stories in the form of folktales and legends that give prominence to human attributes (through gods and goddesses) and explores the relationship between man and nature through the technique of legend mapping. The primitive and indigenous

people have worshipped nature and its beings and considered them as divine or sacred. This results in the merging of nature and myths thus creating a plethora of sublime rituals and ceremonies that become the background of many cultures and traditions. India is one such country that houses multitudes of exotic rituals and ceremonies that evoke wonder and excitement to the whole world. This paper tries to unravel the so called taboo of menstruation in India by bringing into light the legends and ceremonies surrounding the Chengannur Temple that is known for its rare 'menstruation festival' of Goddess Parvathy. A lot of myths surround this temple out of which this paper focusses on the *Thripputhu* festival of Goddess Parvathy. This unique festival not only celebrates the menstruation of goddess Parvathy, but also unearths the menstruation wisdom by breaking the existing taboos and stereotypes surrounding menstruation. It also gives human attributes to the goddess by believing the goddess to be menstruating which is a natural phenomenon in the female body.

**Unravelling the Myths and Legends of Chengannur Mahadeva Temple**

Chengannur Sree Mahadevar and Sree Parvathy temple is located in Chengannur, Alappuzha district of Kerala, in the southern bank of river Pamba. It is believed that this temple was built by the great architect Perunthachan, the son of Rishi Vararuchi. According to the legend or *ithihasa*, all *devas*, *asuras*, sages etc assembled in Kailash for witnessing the sacred event of the marriage between Lord Shiva and Goddess Parvathy. This made all the weight of the world get accumulated in one side and this besca a matter of worry to the *Thrimurthi's* (Brahma, Vishnu and Shiva). And to bring balance to the world, they asked sage Agasthya to go to Shonadri (present day Chengannur) and meditate. Agasthya was reluctant to do so as he would miss the auspicious marriage but agreed to do so when Shiva promised to visit him in Shonadri along with Parvathy after the marriage.

After the marriage Lord Shiva and Parvathy came to Chengannur to meet Agasthya but during this time the Goddess came of age and her first menstruation started. Everyone was ecstatic as a woman's first menses was celebrated like her first wedding. The Goddess' thripputhu (menses) was celebrated like a festival with all the festivities and rituals. The temple was constructed after this as a reverence to this incident as the place was declared as an auspicious place. The idol of Lord Shiva was installed facing the east and Goddess Parvathy facing the west. On one occasion the head priest noticed a red stain in the udayada (inner skirt) of the Goddess and he took the cloth to his wife and the women of the house. The ladies inspected the cloth and confirmed that it was menstrual blood. The idol of the Goddess was shifted to another room where she was given all the needed devotion and care by the village women. On the fourth day, the idol will be taken to the Pamba river accompanied by aarattu (a sacred procession) by placing the idol on the back of an elephant and given a ritualistic bath in the river. Idol is bathed in oil, milk etc. After the bath, the Goddess is taken to the main temple and installed there again. It is believed that conducting the pooja with natural products and bathing the Goddess in the river water will wash away all the tiredness caused during the menstrual flow and thus refreshes the idol. Nature and beings of nature play an important role in all the rituals surrounding the thripputhu aarattu. Earlier blood stains were seen every month but now-a-days the Goddess bleeds only once in three or four months and it gives rise to the thripputhu aarattu.

At a time when menstruation is believed to be a taboo, this ritual and the people of this area believe that this is a very powerful event and praying to the Goddess during this time can cure diseases like infertility, irregular periods and can also solve marital discourses. They believe menstruation to be a life giving process and thus celebrate it. The udayada of the Goddess with the blood stain is considered as a very auspicious possession to own and thus people from far away places visit this place to buy this clothe. Once, a British resident named Mr Munro laughed at this ritual and stopped all grants for the ritual, as a result his wife started bleeding heavily and no doctors could make her alright. At last the village people advised him to pray to the Goddess and apologize. After offering the prayers, his wife was cured just like a miracle.

According to another myth, there was a small rock in the place of the temple and once a tribal women was sharpening her knife in that rock and suddenly she saw blood blowing from that rock. She was shocked and informed the people. The residents decided to construct a temple and treat the rock as sacred. Some believe that the place got it's name Shonadri from this incident. The next myth is centered around Lord Shiva and Sathi devi. Sathi once attended an Yajna conducted by her father Daksha. But her father insulted Shiva and this broke her. She immolated herself because of the sorrow and thus burnt herself. Shiva was heartbroken and started to do the thaandava (which had the power to destroy the world) carrying the body of his wife. Mahavishnu cut the body of Sathi into 108 pieces with his Sudarshana Chakra in order to stop the wrath of Lord Shiva and thus save the world from destruction. It is believed that the different parts of her body fell on different regions and the 108 regions came to be known as Shakthi Peeths. Shonadri was the place where the womb of the Goddess fell. The idol was first made in stone and then was remade in panchaloha (5 kinds of metals) to save the idol from a predicted fire.

Chengannur temple is not the only the temple in India with a menstruating Goddess idol. Kamakhya Temple in Guwahati is also known for the Kamakhya Devi who is believed to menstruate every year in the month of Ashaad (June). She is also called as the 'Bleeding Goddess' as the idol turns red every year. There is also another speciality with this temple as the sanctum sanctorum of this temple consists of the Female reproductive organ which is called the 'mythical womb' with the vagina of the Goddess. This is one of the Shakthi Peeths in the myth of Shiva and Sathi as it is believed that it is at this place that Sathi Devi's womb and vagina fell. The people of this place also celebrate the menstruation festival of the Goddess in all colour and splendor. They even celebrate it as the time for women and young girls to celebrate, wear new clothes etc.

Shonadri was selected for the Sacred meditation by rishi Agasthya to balance the world due to its natural landscape and due to its location in the banks of river Pampa. Shonadri itself means 'red mountain'. Nammalvar, the great poet has sung about this temple. What gives more prominence to this temple is that all the myths associated with this temple connects the Female Goddess with the elements of nature, thus building a bridge between women and nature which gives forward the theory of Ecofeminism. Even the natural elements like rock, milk, mountains, animals like elephant that appear

in the myths related to Chengannur temple defines an eco narratives that defines the mythical truth.

**Conclusion**

At a time when modernity has conquered culture, skylines has conquered nature and greed has conquered humanity, people go behind taboos that can even be the base of existence. When the thoughts of people are blurred by stereotypes, these myths and legends of the ancient times function as eye openers through several cultures and ceremonies that worship the importance of processes like menstruation. Even the myths related with this temple are related with the five elements of nature i.e. the panchabhootas. Water, fire, earth, wind and sky work as purifying factors in the rituals and stories thus defining the sacredness of nature. This legends are myths are not only stories but also convey the truth that menstruation itself is a life giving process which regenerates life and sustains humanity. It also throws light on the aspect of how nature and women coexist as one embracing the state of motherhood which needs to be celebrated and worshipped rather than bullied and hided. So it is best said that "The female form lends itself best to represent matter because both create life within themselves. The male form lends itself best to represent soul because both create life outside themselves" (Pattanaik,2008). Menstruation should not be treating as an impurity rather it should be celebrated as an event of fertility and life. Instead of isolating menstruating women from the mainstream they should be taken care of with all reverence during this time as they are in a state of regeneration. This paper thus opens the scope of further study of the ironical fact of restriction of women from entering sacred places even when this state of being they are going through can even be called sacred.

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# A COMPARATIVE STUDY ON THE ATTITUDES OF B.Ed. STUDENT TEACHERS OF TWO B.Ed. COLLEGES IN IMPHAL WEST DISTRICT TOWARDS TEACHING PROFESSION

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**Abstract**
An attitude plays a great role in our life. The positive attitude is the prime factor for a successful life. So, the positive attitude of the teachers play a pivotal role in teaching-learning process, which will leads job satisfaction as well as effective teaching too. Teacher training being provided at teacher educational institutions will lead the fullest development of positive attitude among teacher Trainees of B.Ed. course. The trainees who are admitted to the course need positive attitude towards the course for maximum development of skills during the training. Thereby, those trained teachers will bring out the quality education as they are so serious of their profession. It is therefore, this study was conducted to find out the level of attitude among the admitted B.Ed. trainees whether all trainees are having positive attitude towards the course. The study also tried to compare the level of attitude among trainees to find out the college best college where trainees are more positive than other college. The study also tries to find out some of the suggestive measures to improve the level of attitude among the trainees for better quality education in the schools.

**Key terms used:** Attitudes, B.Ed. Student Teacher, Teaching Profession etc.

**INTRODUCTION:** Teaching is a complex activity. It is a process in which students are provided with a controlled environment for interaction with the purpose to promote a definite learning in them. Teaching involves a search for meaning in the world. It is a life project, a calling that is organizing Centre of all other activities. Teaching is past and future as well as present. It is background as well as foreground. It is depth as well as surface. Teaching is pain and humor, joy and anger and dreariness'. Teaching is world building. It is an architecture and design. It is purpose and moral enterprise. It is way of being in the world. Teaching breaks through the boundaries of the traditional job. And it is the process that define all life and teaching itself.

Teaching involves human nurturance, connectedness, warmth and love. (Hargreaves, 1994). The word "**Attitude''** is defined within the framework of social psychology as subjective or mental preparation for action. It is outward and visible postures and human beliefs. Attitudes determine what if individual will see, hear, think

and do. They rooted in experience and do not become automatic, routine conduct. As defined by Allport (1935), "Attitude is a mental or neural state of readiness, organized through experience, exerting a directive or dynamic influence upon the individuals response to all objects and situation with which it is related". An attitude towards teaching profession is an emotionalized tendency, organized through teaching experience to react positively towards teaching. It is a learned emotional response, set for or against teaching. Individuals will have a positive attitudes towards those objects which enable them to achieve the values held and form negative attitudes towards object which hinder the achievement of values.

**REVIEW OF RELATED LITERARTURES:**

**(1) ROY (1991)** studied the relationship between teacher attitude and teaching efficiency. **Objectives:** i) to know attitudes of teachers towards teaching profession teaching at different level. ii) To check the effect of teachers towards teaching profession. **Main finding: (**i) There was a positive relationship between them. (2) **Cornelious (2000)** conducted a study on a study of teacher effectiveness in relation to attitude towards teaching profession. **Findings:** i) There was a significant positive relationship between effectiveness and their attitudes towards teaching profession. ii) There was close correlation between male teacher effectiveness and their attitude towards teaching profession. (3) **Rao (2008)** studied the development and application of a scale for measuring attitudes towards the new pattern and education and empirical validation of its psychometric properties. **Main findings:** i) There was a significant gender difference in the attitude towards teaching science ii) female general, were significantly more positive than the males in their attitudes iii) there was a significant living area difference in the attitudes scores. (4) **Maurya (2011)** in a study of the relation between teachers' attitudes and teacher efficiency of **university** and pre-university lectures. **Objectives:** i) To study the attitudes and teaching efficiency ii) To see the sex differences in teaching efficiency. **Main findings of the study:** i) External surroundings contributed a great deal in formulating teaching attitude. ii) Frequent changes in the curriculum adversely affected teaching efficiency. iii) Attitude and academic achievement were not significantly related and (iv) sex difference existed both in teaching proficiency and adjusted. (5) **Marcus (2016)** ''The attitude of teachers towards creative learning and teaching" Objectives**:** to study the attitudes of teachers of higher secondary stages towards teaching. ii) to compare the attitudes of teacher, up to the age of 30yrs and other 30 yrs. of higher secondary stage towards teaching. **Findings:** I) there was no significant difference in the attitude of teachers of higher secondary stages towards teaching profession. (6) **Joan and Pilley (2000)** study on bureaucratism of college teachers and their attitude towards teaching profession. **Findings:** In this study, it was represented that, the age and experience of college teachers appear to have definite positive relationship with their attitudes towards the teaching profession; as age and experience increase, their attitudes towards teaching profession grew more favorable, the teachers who had developed sound attitudes towards the teaching profession were relatively more traditional and impersonal. (7) **Reddy (2005)** studied the attitudes of student teachers and success of student teachers, and reported that attitude of teachers do not significantly influence the success of

student teachers. (8) **Birendra Singh (1999)** a study of the attitudes of teachers of Assam university towards higher education. (9) **Kumar (1995)** in a study found that there is significant difference in the attitude of male and female teacher trainees towards teaching profession. (10) **Sucheta (2014)** Effect of teacher education programmed on the attitude of teachers towards teaching profession. (11) **Nirmala (2017)** studied attitude of married lady teachers of Mizoram University towards the teaching profession. (12) **Ramakrishna (1980)** revealed through his study, that women teachers have a significant and more favorable attitude towards teaching than men teachers . (13) **Bhandarkar (1980)** in a study on polytechnic teachers attitude towards teaching profession and its correlates, found that attitude towards teaching profession is not significantly related to the qualification of the teachers . (14) **Saraswat of Agra University in (2009)** studied on attitudes of trained high school teachers of Aligarh towards their professional training and the student perception of their teachers. (15) **Mishra (2015)** A study of the attitudes of teachers working in Government –Aided conventional Sanskrit vidyalayas of Varanasi towards teaching profession. (16) **Goyal (2000)** A study of the relationship among attitudes, job satisfaction, adjustment and professional interests of teacher education in India. **Findings:** There was no significant difference in the attitudes and professional interest of different categories based on sex, age, qualification, and experience. (17) **Singh Ajit (2008)** studied on "secondary school teacher's attitudes towards teaching in relation on their classroom behavior". **Finding:** i) coefficients of correlation range from 0.8 to 0.13. None of the correlation coefficient is significant. Thus shows that teachers' attitude towards teaching and their teaching behavior are not related. ii) There is no significant relationship between teachers' attitude towards teaching and the indirectness of their teaching verbal behavior. (18) **Maurya (2009)** "A study of the relation between teacher's attitude and teacher efficiency of university and pre- university lectures'' **Main findings of the study**: i) External surrounding contributed a great deal in formulating teaching attitude. ii) Frequent changes in the curriculum adversely affected teaching efficiency. iii) Attitudes and academic achievement were not significantly related and iv) sex differences existed both in teaching proficiency and adjustment.

**CONCLUSION**: It can be concluded that the topic of the study is the new area of the study as no one has conducted the same study before as the proofs are above.

**JUSTIFICATION OF THE STUDY:** With the enrolment of the right to education (RTE) act, 2009, from April 1, 2010, on the one hand and implementation of the Sarva Shiksha Abhiyan (SSA) on the other, enrolments in primary education have been increasing considerably, as a result, huge number of students will be looking for enrolment in the secondary education sector. To meet the challenge of "number, quality and equity'', large scales input in terms of teachers and other infrastructural facilities will be required. Considering this fact, the government of India launched the Rashtriya Madhyamik Shiksha Abhiyan (RMSA) in 2007 for universalization of access to an improvement of quality at the secondary and higher secondary stage.

To effectively implement the programmed for Universalization of secondary education, we need inter alia, competent teachers; we need to select the right type of teachers who have positive attitudes and desirable teacher like qualities. Teacher

training institutions have initiated "half – heartedly" some schemes for stirring and stimulating the student – teachers who enter their portals for receiving professional training. A teacher's attitude not only affects his behavior in the classroom but also influence the behavior of his students. Hence the availability for the right type of teachers having positive attitudes towards their profession is highly called for. This will make learning more effective and productive. In the present study, an attempt is being made to find out the extend of attitudes of student teacher towards teaching profession.

The findings of the study that would be emerging from this study will help us to understand the attitudes of teacher trainees thereby enabling us to inculcate favorable attitudes in the student teacher by changing the organizational climate of teacher training institution and also by enriching the social emotional climate of their classroom teaching.

**STATEMENT OF THE PROBLEM: "A Comparative Study On The Attitudes Of B.Ed. Student Teacher Of Two B.Ed. Colleges In Imphal West District Towards Teaching Profession".**

**DEFINITION OF KEY WORDS USED:**

a) **Attitudes:** In psychology, attitudes are a psychological construct, a mental and emotional entity that inheres in, or characterize a person. They are complex and an acquire state through experiences. It is an individual predisposed state of mind regarding a value and it is precipitated through a responsive expression towards a person, place, thing, or event (the attitude object) which in turn influences the individual thoughts and action.

b) **B.Ed.:** A bachelor of education (B.Ed.) is a graduate professional degree which prepares students for work as a teacher in the schools, through in some countries additional work much be done in order for the student to be fully qualified to teach.

c) **Student Teacher:** A student who is studying to be a teacher and who, as part of the training, observes classroom instruction or does closely supervised teaching in an elementary or secondary school.

d) **Teaching Profession:** The act of person who teaches the profession of a teacher.

**e) RKSDCE:** Raj Kumari Sanatombi Devi College Of Teachers' Education.

**f) DMCTE:** Dhanamanjuri College Of Teacher Education.

**Objectives of the study:**

1. To find out the overall level teaching attitudes of B.Ed. student teachers of DMCTE and RKSDCE towards teaching profession.
2. To compare the attitudes of male and female B.Ed. student teachers of DMCTE and RKSDCE towards teaching profession.
3. To compare the teaching attitudes of arts and science student teacher of DMCTE and RKSDCE towards teaching profession.
4. To compare the overall attitudes of DMCTE and RKSDCE towards teaching profession.

**Hypothesis of the study:**

1. There is no significant overall level of teaching attitudes of B.Ed. Student teachers of DMCTE and RKSDCE towards teaching profession.
2. There is no significant difference between the attitudes of male and female B.Ed. student teachers of DMCTE and RKSDCE towards teaching profession.
3. There is no significant difference between the attitudes of arts and science student teachers of DMCTE and RKSDCE towards teaching profession.
4. There is no significant difference between the overall attitudes of DMCTE and RKSDCE towards teaching profession.

**Delimitation of the study:** The study was delimited to the attitudes of Pre-Service and In-Service student teachers of DMCTE and RKSDCE towards teaching profession during the session of 2019 - 2020.

**METHODOLOGY**: The descriptive survey method was employed in the proposed study. P**opulation:** All the B.Ed. student teachers of D.M college of Teacher Education,Imphal and R.K Sanatombi Devi College of Education Imphal constituted the population of the present study. S**ample:** For the present study, the investigator used stratified random sampling techniques to choose the sample of the study. Distribution of the sample of the study is shown below:

**Table No:1: Showing The Distribution Of The Sample:**

| D. M. College Of Teacher Education, Imphal | | | | R.K. Sanatombi College Of Teacher Education | | | | Total |
|---|---|---|---|---|---|---|---|---|
| DMCTE-40 | | | | RKSDCE-40 | | | | 80 |
| Male-20 | | Female-20 | | Male-20 | | Female-20 | | |
| Arts 10 | Science 10 | Arts 10 | Science 10 | Arts 10 | Science 10 | Arts 10 | Science 10 | |

**Tools Used:** For the present study the investigator constructed a self-developed questionnaire for the purpose of collecting the views of B.Ed. student teachers of DMCTE and RKSDCE towards the teaching profession. This questionnaire consisted of 25 questions relating to identify the professional attitudes of the student teachers.

The questionnaire contained 25 items under the 3 parameters of teaching effectiveness as per NCTE norms namely:

1. **Competency.**
2. **Commitment and**
3. **Performance.**

The dependent variables during the data collection were:

1. Gender (male / female ) student teachers of DMCTE and RKSDCE
2. Discipline in which they study ( arts/ science)

**Time duration for data collection**: the duration of 30 minutes was given to all the student teachers of the two colleges in order to choose the right answer however most of the trainees were responded within less than 30 minutes.

**Scoring Key:** The scoring key of the questionnaire provided to the student teachers of the two colleges was in the form of 2 points scale (yes/no) under Thurnstone scale.

**Statistical Techniques:** The collected data was put in tabular form to make the process analysis easier. For the analysis and interpretation, the following statistical techniques were used:

1. Percentage.
2. T – Ratio/ T- test and
3. Graphical representation and interpretation.

**THE ANALYSIS AND INTERPRETATION OF THE RESULT IS PRESENTED IN FOUR SECTIONS:**

**OBJECTIVE -1: To Find Out The Overall Teaching Attitudes Of B.Ed. Trainees Of DMCTE And RKSDCE Towards Teaching Profession.**

| SL. NO. | Q.NO. | RIGHT RESPONSE | % | WRONG RESPONSE | % |
|---|---|---|---|---|---|
| **(a) COMPITENCY** | | | | | |
| 1. | 1. | 79 | 98.75 | 01 | 01.25 |
| 2. | 2. | 80 | 100.00 | 00 | 0/000 |
| 3. | 3. | 75 | 93.75 | 05 | 06.25 |
| 4. | 4. | 74 | 92.5 | 06 | 07.50 |
| 5. | 5. | 79 | 98.75 | 01 | 01.25 |
| 6. | 6. | 80 | 100.00 | 00 | 00.00 |
| 7. | 7. | 80 | 100.00 | 00 | 0.000 |
| 8. | 8. | 78 | 97.50 | 02 | 02.50 |
| 9. | 9. | 80 | 100.00 | 00 | 00.00 |
| 10. | 10. | 80 | 100.00 | 00 | 00.00 |
| 11. | 11. | 78 | 97.50 | 02 | 02.50 |
| 12. | 12. | 62 | 77.50 | 18 | 22.50 |
| 13. | 13. | 76 | 95.00 | 04 | 05.00 |
| 14. | 14. | 31 | 38.75 | 49 | 61.25 |

| | | | | | |
|---|---|---|---|---|---|
| **(b) COMMITMENT** | | | | | |
| 15. | 15. | 79 | 98.75 | 01 | 01.25 |
| 16. | 16. | 80 | 100.00 | 00 | 00.00 |
| 17. | 17. | 80 | 100.00 | 00 | 00.00 |
| 18. | 18. | 80 | 100.00 | 00 | 00.00 |
| 19. | 19. | 80 | 100.00 | 00 | 00.00 |
| 20. | 20. | 80 | 100.00 | 00 | 00.00 |
| **(c) PERFORMAMNCE** | | | | | |
| 21. | 21. | 80 | 100.00 | 00 | 00.00 |
| 22. | 22. | 80 | 100.00 | 00 | 00.00 |
| 23. | 23. | 80 | 100.00 | 00 | 00.00 |
| 24. | 24. | 80 | 100.00 | 00 | 00.00 |
| 25. | 25. | 80 | 100.00 | 00 | 00.00 |
| **OVERALL** | | **76.44** | **95.55%** | **03.56** | **04.45%** |

**Table No. 2: Showing the Overall Level of Attitudes of B.Ed. Trainees Of Two Colleges**




**OVERALL CONCLUSION:** It can be concluded that the overall level of teaching attitude of B.Ed. trainees of two colleges comes at 76.44 (95.55%), which is very high as the overall average in term of teaching attitude of B.Ed. trainees towards teaching profession. It is therefore, the **first hypothesis** constructed for testing "There **is no significant overall level of attitudes of all student teachers of two colleges"** is

rejected as the result is so high at 95.55%. However, the lowest level has found in the parameter of competency as compare to others aspects of teaching attitude.

**OBJECTIVE- 2: To compare the attitudes of male and female student teachers of DMCTE and RKSDCE.**

**Table No: 3: To Compare The Attitudes Of Male And Female Student Teachers Of DMCTE And RKSDC:**

| Sl. No. | N | Sex | Mean | SD | SED | T- test | df |
|---|---|---|---|---|---|---|---|
| 1 | 40 | Male | 23.67 | 0.78 | 1.98 | 03.56 | 78 |
| 2 | 40 | Female | 22.77 | 1.40 | | | |

**@ Remark – significant**

**INTERPRETATION:** It can be observed from the above table No: 2 that the level of teaching attitudes of B. Ed trainees of two colleges between male and female are found to have mean score of 23.67 and 22.77 with standard deviation of 0.78 and 1.40. The ratio of the two mean score comes out to be with standard error of 1.98 which is greater than the level of significance at 0.01. Therefore the second hypothesis of the study "There is no significant difference between the level of the attitudes of male and female" trainees of the two B. Ed colleges is rejected as there is difference between the level of teaching attitudes found between male and female student teachers of these colleges. The level of teaching attitudes of male and female are found at the average of 23.67 (94.68%) and 22.77 (91.08%).

**OBJECTIVE-3 To compare and attitudes of arts and science student teachers of DMCTE and RKSDCE towards teaching profession.**

**Table No: 4: Showing the comparison of teaching attitudes of arts and science student teachers of DMCTE and RKSDC towards teaching profession.**

| Sl. No. | N | Subject | Mean | SD | SED | T-test | df |
|---|---|---|---|---|---|---|---|
| 1 | 40 | Science | 23.31 | 1.19 | 0.24 | 0.69 | 78 |
| 2 | 40 | Arts | 23.12 | 1.24 | | | |

**@Remark: Insignificant**

**INTERPRETATION:** It can be observed from the above table No: 3 that the level of teaching attitudes of science and Arts student teachers of DMCTE and RKSDC are found to have mean score of 23.31 and 23.12 with standard deviation of 01.19 and 01.24.The ratio of the two mean scores comes out to be with standard error of 0.24, which is greater than the level of significance at 0.01. Therefore the 3rd hypothesis of the

study **"There is no significant difference between the attitudes of science and Arts student teachers of DMCTE and RKSDCE towards teaching profession" is accepted** as there is no difference between the level of teaching attitudes found between science and arts student teachers of the two B.Ed. colleges.
In addition, the level of teaching attitudes of science and arts are found at the average of 23.31(93.24%) and 23.12(92.48%), which are very high teaching attitude.

**OBJECTIVE-4 : To compare the overall attitude of DMCTE and RKSDC towards teaching profession.**

**Table No. 5: Showing the comparison of teaching attitudes of student teachers of DMCTE and RKSDC towards teaching profession.**

| SL.NO. | N | College | Mean | SD | SED | T-test | df |
|---|---|---|---|---|---|---|---|
| 1 | 40 | RKSDCE | 23.50 | 0.78 | 1.98 | 1.69 | 78 |
| 2 | 40 | DMCTE | 23.05 | 1.47 | | | |

**@Remark: Insignificant**

**INTERPRETATION:** It can be observed from the above table that the level of teaching attitudes of student teachers of DMCTE and RKSDCE are found to have mean score of 23.50 and 23.05with standard deviation of 0.78 and 1.47. The ratio of the two scores comes out to be with the standard error of 1.98 which is greater than the level of significance at 0.01. Therefore the **fourth hypothesis** of the study **"There is no significant difference between the overall level of teaching attitudes towards teaching profession'' of DMCTE and RKSDC is accepted** as there is no difference between the level of teaching found between the trainees of the two B.Ed. colleges. The level of teaching attitudes of DMCTE and RKSDC are found at the average of 23.5(94%) and 23.05 (92.2%).

**MAIN FINDING OF THE STUDY**:

1. It can be concluded that the overall level of teaching attitude of B.Ed. trainees of two colleges comes at 76.44 (95.55%) which is very high. It is therefore, the **first hypothesis** constructed for testing "There is no significant overall level of attitudes of all student teachers of two colleges" is rejected as the result is so high at 95.55%. However, the lowest level has found in the parameter of competency as compare to others aspects of teaching attitude.

2. The **second hypothesis** of the study "There is no significant difference between the attitudes of male and female" trainees of the two B. Ed colleges is rejected as there is difference between the level of teaching attitudes found between male and female student teachers of these colleges. The level of teaching attitudes of male and female are found at the average of 23.67 (94.68%) and 22.77 (91.08%).

3. The **3rd hypothesis** of the study "There is no significant difference between the attitudes of science and Arts student teachers of DMCTE and RKSDCE towards

teaching profession" is accepted as there is no difference between the level of teaching attitudes found between science and arts student teachers of the two B.Ed. colleges.

4. The **fourth hypothesis** of the study "There is no significant difference between the overall level of teaching attitudes towards teaching profession'' of DMCTE and RKSDCE is accepted as there is no difference between the level of teaching found between the trainees of the two B.Ed. colleges.

**REMEDIAL MEASURE SUBJECT TO THE HYPOTHESIS OF THE STUDY:**

1. In regards to first hypothesis of the study, that "There **is no significant overall level of attitudes of all student teachers of two colleges"** is rejected as the result is so high at 95.55%. However, the lowest level has found in the **parameter of competency** as compare to others aspects of teaching attitude. More improvement is required in this regards.

2. In connection with the **2nd hypothesis** of the study, it can be suggested that both male and female student teachers of the two colleges need to improve the level of teaching attitude towards teaching profession as average level of teaching attitude has found out at 23.67 (94.68%) and 22.77 (91.08%) respectively.

3. As far as the **3rd hypothesis** of the study the attitude of both science and arts student teachers of two colleges have a high positive attitude towards teaching profession at the percentage of more than 92%. But it also suggested that teaching attitudes of the student teachers of the two colleges need to improve more.

4. In relation to **4th hypothesis** of the study it can be suggested that teaching attitudes of student teachers of the two colleges need improvement. Because the average teaching attitude level of the two colleges came out only 92% of the total score.

**REMEDIAL MEASURES FOR OVER ALL IMPROVEMENT OF TEACHING ATITUDE OF TEACHERS TRAINEES OF B.ED COLLEGE:**

Attitudes of student teachers towards teaching profession are an area of research concerned with the relationship between the teacher's performance and student's achievement i.e. if the teachers possess positive attitudes towards teaching profession and having a high teaching skill then he or she will give her best practice and strategies to meet the challenging demands of his career, which involves imparting knowledge and developing essential skills in the students. The present educational scenario of the new millennium has become prone to stressing more on quality than on quantity whether it is teaching or research or evaluation or management in all fields of life. The quality of education depends to a great extent on the quality of the teacher; unless we bring quality in teacher we cannot expect quality in education.

Hence attitudes of teachers towards teaching profession can do an effective work. Positive attitudes towards teaching profession can enable the teacher to perform their

normal duty and social duty in a competent way. They can work for the welfare of the students with dedication and devotion. It a necessity for different section of teachers may be at school, college and universities. However the attainment of quality will be a mirage without adequate knowledge of the attitudes of teachers towards teaching profession who will disperse the knowledge.

This study brought out to the forefront of all student teachers commitment, satisfaction, and professional self- esteem; perceive status and interest to stay in teaching profession in DMCTE and RKSDCE. From the present study and their findings it had been concluded that student teacher generally possess positive attitude towards teaching profession but need to improve in competency level as it found low in competency of the student teachers.

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# AN EVOLUTION FROM FRAILTY TO FORTITUDE: MAN'S SUBTLE WAR WITH HIS OWN FRAIL NATURE AS SEEN IN MALAMUD'S 'THE ASSISTANT'

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## Abstract

Malamud, though a writer who produced serious novels, he is regarded as the most renowned Jewish-American writer, who had his word too on the effects of the ugly truth of the historical depressing movements of his society. In his novel 'The Assistant', he did not fail to bring his often repeated element of his characters search towards something better and the transcendence of their characters too. The main character is portrayed by Malamud with bare truth of how frail and flimsy his character is, who is often is driven by uncontrollable carnal desires. But the character is also described in a way wherein he gains sympathy from the side of the readers, when he is shown to have a deep innate desire to win his battle against his frail character. Towards the end he is shown as evolved to the one who is full of Fortitude.

**Keywords:**Anti-Semitism, Jewish Literature, Malamud, The Assistant, Transcendence.

The most acclaimed Jewish-American author, Bernard Malamud, is viewed as one of the most conspicuous writer, who can be classified as well known personas in the Jewish American writing. This scholarly sort of literature has birthed from the recorded development in the history that began in the year 1930s. This sort of composing is outstanding for its change of sad and comic components. Brooklyn conceived writer, paid attention to up composing when he began to catch wind of the revulsions of the Hitler drove Holocaust amidst World War II. He likewise began to peruse with extraordinary intrigue the Jewish convention and history. Practically the entirety of his works can be said tinged with the impacts left by those nearby readings of the aforementioned points.

Aside from various books, he additionally gave his hand a shot composition of short stories as well. He likewise packs up surprisingly numerous honours during his profession, comprehensive of, the most acclaimed Pulitzer prize, Gold Medal of the American Academy and Institute of Arts and Letters, and two or three National Book Awards. Also, as in the standard way, Malamud's fiction consistently implores a tender affirmation of the confinements and guarantees of human life that can help associate the complex alienations inside and in the midst of men.

Malamud's fiction is typically sorted out around moral issues and emergencies of development. He consolidates authenticity and imagery, just as disaster and satire, regularly with the assistance of legendary and model underpinnings. He utilizes dream that is once in a while extraordinary however which all the more frequently, as in The Assistant, gives practical happenings a nature of enchantment and custom.

From his Jewish foundation, Malamud determines a harsh diversion that regularly shows up in the self-joke of his characters yet it is additionally sympathetic to oneself as well as other people. His merciful beautiful reasonableness mixes with a feeling of beauty accomplished through torment. Malamud has announced that "All men are Jews," without a doubt an analogy for the comprehensiveness of estrangement, enduring, and the ethical impulse for men to make the absolute best of their lives inside the constraints and ambiguities of human presence. This ethical impulse is a strict assignment in that it requests an equivalent work for the salvation of oneself as well as other people; to be sure, one is inconceivable without the other. Malamud, nonetheless, has once in a while made explicit Jewish social settings, more often than not liking to look at the strains of Jews uncontrolled in gentile environment.

In his second novel, ‘The Assistant’, Malamud came back to the avenues of his childhood and, as though roused by the need to determine an extreme good essentialness from sorts of enduring he once saw, he shows us a youngster's effective commencement to the requests and cutoff points of life under abusive conditions.

Malamud utilizes ‘The Assistant’ to address a portion of the themes from ‘The Natural’ yet sets the novel in a migrant setting with solid Jewish primary characters. The tale figures out how to summon the

convention of Yiddish legends while keeping up Malamud's preparation in old-style writing and theory. The fundamental character of the novel, Morris Bober, for instance, can be deciphered from the two customs. A few pundits have indicated Morris Bober being an adaptation of the schemiel, a conventional model from Yiddish old stories who goes about as an amusing saint, utilizing light amusingness and incongruity to mellow a generally brutal world. Simultaneously, different pundits have recommended Morris Bober as the exemplification of the existential "I-THOU" reasoning portrayed by Bober's nearby namesake, Martin Buber. Both of these elucidations appear to be fitting and they show that Malamud's tale mirrors his ethnic familial foundation, while additionally keeping up the scholarly convention in which he was prepared. Malamud consistently protested being known as a "Jewish writer," since he has discovered the term excessively restricting. Malamud's primary reason as an essayist, as he clarifies, was "to shield human progress from obliterating itself". All things considered, he worked for humanism—and against scepticism".

The Assistant recounts to the tale of a foreigner food merchant, Morris Bober, who lives and works in Brooklyn, New York. Bober emigrated from Russia in his adolescent years and met his significant other Ida in New York. Their basic food item as of late has fallen on tough occasions because another store has opened over the road and is taking their clients. To remain above water, the Bobers additionally depend upon the wages of their little girl, Helen who fills in as a secretary.

On the opening day of the novel, two men burglarize Morris' basic food item and thump him oblivious with a hit to the head. Following his damage, a man named Frank Alpine lands in the area. Forthcoming has originated from a harsh life in the West to begin once more. At the point when Morris re-opens the store, Frank shows up every morning to assist him with dragging in the overwhelming milk containers. In the long run, Frank inquires as to whether Morris would let Frank work for nothing so Frank could gain proficiency with the exchange. Morris says no and Frank vanishes. Not long after Morris sees that a quart of milk and two rolls are taken from his conveyances every morning. Following seven days, Morris cautions the police since he can't discover the guilty party. On the following day, Morris discovers Frank Alpine resting in his basement. Plain confesses to taking the milk and

bread out of craving. Morris feeds Frank and gives him a chance to rest in the basic food item for the evening. The following morning, Morris slips while hauling in the milk and goes out. Straight to the point salvages him at that point puts on the food merchant's cover and starts working in the store.

During the two weeks that Morris recoups, Frank figures out how to acquire substantially more cash than Morris had done. At the point when Morris returns, Frank moves upstairs to a little room off a condo that an Italian couple, the Fusos, lease. Since business is so fruitful, Morris, in the long run, needs to pay Frank. Straight to the point feels remorseful about being paid in light of the fact that obscure to the food merchant, Frank has been taking cash. Moreover, it was he and Ward Minogue, a kid whose father is a nearby analyst, who had ransacked the staple.

Helen as of late lost her virginity to Nat Pearl a neighbourhood Jewish kid whose guardians possess a sweet store and who is going to Law School, yet she disregarded him in the wake of discovering that he just needed sex. The other nearby Jewish kid in the city, Louis Karp, recommends that Helen wed him, yet she isn't intrigued. Candid courts Helen by meeting her at the library, which she visits two times every week. In the end, they start getting to know one another and even kiss. At the point when Frank recommends that they contact more, Helen reveals to him that she can't engage in sexual relations with somebody except if she is certain that she adores him.

Morris Bober appreciates working with Frank and the two men recount stories to one another during the day. At some point, Morris begins to associate Frank with taking since incomes don't rise to what Morris imagines that they ought to be. He starts watching Frank intently. Blunt, simultaneously, is overwhelmed by his feeling of remorse and chooses to reimburse all the cash he has taken. He puts six dollars back in the register one day, yet when he understands that he will require some cash for that night, he takes a dollar back. Morris gets him and is shattered. All things considered, he requests Frank to leave.

That night, Helen goes to meet Frank late in the recreation centre. She has concluded that she cherishes him and will have intercourse with him. At the point when she gets to the recreation centre, an alcoholic Ward Minogue, whom she knows from grade school, attempts to assault

her. Straight to the point shows up and protects her, however, continues to assault her himself.

The next day, Morris Bober nods off in his loft with the radiator dim, flooding his rooms with gas and practically killing himself. Blunt and Nick Fuso spare him. Morris contracts pneumonia and needs to go to the medical clinic. Candid keeps the store open for the weeks when Morris is wiped out. Business is horrendous in light of the fact that two Norwegians have quite recently revived the contending basic food item and every one of the clients have gone there. Straight to the point gives the majority of his own reserve funds to the basic food item and works throughout the night at an alternate activity to keep it above water. In any case, when Morris comes back to the shop he makes Frank leave. Morris himself at that point attempts to spare the business by securing another position, however, he can't. A baffling man seems one evening offering to torch the store with the goal that Morris can gather the protection cash, yet Morris turns him down. Later Morris attempts to light such a fire himself, yet almost consumes himself to death before Frank shows up and safeguards him. Morris again requests Frank out.

One night, Ward Minogue, who has been determined to have diabetes and who is acting frantically, sneaks into the Karp's alcohol store through a crushed spirit window. In the wake of getting alcoholic, Ward unintentionally sets the store ablaze. Karp's store and building are destroyed. The following day, Karp, who has protection, offers to purchase Morris' store and staple so he can revive. Morris feels glad and goes out to scoop snow for the people on foot, despite the fact that he neglects to wear his jacket. Soon thereafter, he falls wiped out and bites the dust three days after the fact from pneumonia.

After Morris' passing, Frank Alpine begins running the store. He works throughout the night at an alternate activity and has a go at everything to make the store work, yet circumstances are difficult. In any case, he concludes that he needs to pay for Helen to go to school. Toward the finish of the book, Helen has turned out to be friendlier to Frank and appears to be prepared to acknowledge his idea of educational cost. Straight to the point he has changed absolutely ending up totally legit and particularly like Morris Bober, whose store and ways of thinking he presently grasps. In his last demonstration, Frank Alpine goes to the

medical clinic, has himself circumcised and after Passover turns into a Jew.

All through the novel it is seen how frail the characteristic built up of the main character Frank is portrayed by the Novelist. When he is frail, he struggles to the core to reframe his moral and ethical standard to that which is acceptable to the society in which he lives in. Despite the fact that he has stolen from the grocery of Bober, only out of poverty and hunger, he is viewed as an example of the every other normal Jack or John of the public. When the weak internal framework of the people is viewed with speculative eyes then all might appear loose and immoral but with a humanistic eye it would be a pathetic view.

Whatever is the stories' woven pattern, the way the character transcends from a frail character to the one which is remade with fortitude and moral strength. Frank's change in the behavioural patterns towards the end shows how he paves his own ways towards a one which is straight in the moral perception. It is also noted that when he took up the responsibility of the store itself after the demise of the then owner, it made him to change his entire standard of his living itself. He even started to take up his master as his role model and even went in to the extreme of becoming a proper Jew by undergoing Circumcision. This change can be viewed as a pattern created in his life that puts everything in an order of the life which was always battered by his frail carnal nature.

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# GENETIC VARIABILITY IN YIELD AND YIELD RELATED TRAITS IN SOME MAIZE (Zea mays L.) GENOTYPES IN EASTERN HARARGE, ETHIOPIA

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## ABSTRACT

Twenty five maize genotypes were evaluated in randomized complete block design for genetic variability and association between agronomic traits at Haramaya, HU campus. Data were collected on 20 quantitative traits. The analysis of variance showed that the mean squares due to genotype were highly significant ($p<0.01$) for all trait studied, which indicates the existence of sufficient genetic variability and the potential for selection and improvement for the traits. The high phenotypic and genotypic coefficients of variations were observed for PHT, EHT, KT, AGM/ha and GY/ha. Also the difference between genotypic and phenotypic coefficients of variation were low in the traits for days to75% maturity, leaf width, ear diameter, number of rows per ear and harvest index indicating less environmental influence on these traits. High heritability estimates were obtained from days to75% maturity, days to silking, plant height, leaf width, number of nodes per plant, 1000-kernels weight, kernels texture, above ground biomass, grain yield per hectare and internodes length. These traits, therefore, may respond positively due to selection. Estimates of genetic advances as percent of mean at 5% selection intensity ranged from 3.6% for number of plant at harvest to 76.4% for above ground biomass. Genotypic correlation coefficients were found to be higher in magnitude than that of phenotypic correlation coefficients, which clearly indicated the presence of inherent association among various traits. At phenotypic level days to silking, days to maturity, plant height, ear height, number of ears at harvest, internodes length, ear length, days to anthesis, leaf width and number of nodes per plant was observed to have positive and highly significant ($P<0.01$) correlation with grain yield per hectare and negative and highly

significant (P<0.01) correlation with harvest index. However, low and positive phenotypic association were observed between number of ears at harvest and plant height, number of nodes per plant , days to maturity, days to silking and days to anthesis. Path coefficient analysis at phenotypic level based on grain yield as dependent variable revealed that days to anthesis, days to maturity, ear height, leaf width, number of nodes per plant, number of ears at harvest, above ground biomass and harvest index showed positive direct effect. The genotypic path analysis also indicated that above ground biomass and harvest index showed positive and significant correlation, therefore, these traits are more important than other traits for the genetic improvement of maize for yield.

## 1. INTRODUCTION

The center of origin of maize is the Mesoamerican region probably in the Mexican highlands, from where it spread to the rest of the world (Paliwal, 2000 and Farnham, 2003). Archaeological records and phylogenetic analysis suggest that domestication began at least 6,000 years ago (Piperno and Flannery, 2001; Matsuuka, 2002). Maize spread around the world particularly to the temperate zones after European discovery of the Americas in the 15$^{th}$ century, (Paliwal, 2000 and Farnham, 2003).

Maize is one of the most important crops in the world. It is used as a human food, livestock feed, for the different alcoholic and none alcohol drinks production, building material, and as fuel. It is also used to produce medicinal products such as glucose as well as an ornamental plant (Bekric and Radosavljevic, 2008).

Maize was introduced to Ethiopia by the Portuguese in the 16$^{th}$ or 17$^{th}$ century (Haffnagel, 1961). Since its introduction, it has gained importance as a food and feed crop.

Maize growing areas in Ethiopia are broadly classified into four ecological zones based on altitude and annual rainfall. These are the high altitude moist zone, which receive 1200 to 2000mm annual rainfall with an altitude of 1700 to 2400 meters above sea level (m.a.s.l), the mid-altitude moist zone (1200-2000 mm annual rainfall with an altitude of 1000 to 1700 m.a.s.l), the low–altitude moist zone with less than 1000

m.a.s.l and 1200 -1500 mm annual rainfall), and the moisture stress zone with 500 to 1800 m.a.s.l and less than 800 mm annual rainfall. Currently, it is a major crop in Ethiopia in terms of production, consumption and income generation for human beings. The total annual production and productivity exceed all other cereal crops, though it is surpassed by teff in area coverage (EARO, 2000).

Maize breeding in Ethiopia has been ongoing since the 1950's and has passed through three distinctive stages of research and development (CIMMYT, 1998). These are from 1952 to 1980, the main activities were the introduction and evaluation of maize materials from different part of the world for adaptation to local condition, from 1980 to 1990, the work was focused on evaluation of inbred lines and development of hybrid and open-pollinated varieties, and from 1990 to the present, the main activities were (a) extensive inbreeding and hybridization, (b) development of early maturing or drought tolerant cultivars, and (c) collection and improving of maize with adaptation to highland agro ecologies. As a result various improved hybrids and open-pollinated varieties were released for large-scale production, especially for mid-altitude zones. The high land maize breeding program was started in 1998 in collaboration with the international maize and wheat improvement center (CIMMYT, 1998).

The main goal of all maize breeding programs is to obtain new open pollinated varieties (OPVs), inbred lines and from them hybrids and synthetics that will outperform the existing cultivars with respect to a number of traits. In working toward this goal attention needs to be paid to grain yield as the most important agronomic traits (CIMMYT, 1998).

Grain yield is a complex quantitative trait that depends on a number of factors. It's highly influenced by environmental conditions; has complex mode of inheritance and low heritability. Because of this, during selection for grain yield, attention is given first to determine mean values, components of variance and the heritability of yield related traits in order to establish the best selection criteria (Mohamed, 1993)

Besides, knowing the correlations between the traits is also of great importance for success in selection to be conducted in breeding

programs, and analysis of correlation coefficient is the most widely used one among numerous methods, (Yagdi and Sozen, 2009).

Success in any crop improvement or breeding program depends upon the selection of suitable parents, a thorough knowledge of genetic variability, heritability and type of gene action. In addition traits upon which selection of parents is based should be known. Relatively higher estimates of genotype coefficient of variation for grain weight, plant height, ear placement, kernel rows per ear and number of grains per row along with high heritability suggest that the selection can be effective for these traits (Rezaei, 2004).

A number of studies in maize have been conducted to elucidate the nature of association between yield and its components which identified traits like ear length, ear diameter, kernels per row, ears per plants, 100-seed weight and rows per ear as potential selection criteria in breeding program aimed at high yield. Some studies have been undertaken on seed maize production in different parts of Ethiopia (Rezaei, 2004).

According to Yoseph, (2005) who reported in his study on phenotypic diversity for morphological and agronomic traits in traditional Ethiopian highland maize accessions, highland maize varieties may be grouped into a number of completely or partially isolated populations, which may be adapted to different highland conditions. Legesse, (2007) also reported in his study on genetic diversity of maize inbred lines by AFLP Markers that seven pairs of AFLP primers identified 499 scorable fragments out which 81.7% were polymorphic and the diversity varying from 0.35 to 0.71. The above are among the limited studies made on maize genetic diversity in Ethiopia. The currently proposed study involves maize germplasm which were not used by other researchers for similar studies and will contribute positively to the area of study. Thus, this study was undertaken to find out the nature and magnitude of genetic variability for different traits in maize genotypes with specific objectives to:-

- Estimate the nature and magnitude of genetic variability for the yield and yield related traits in maize genotypes.
- Estimate the phenotypic and genotypic coefficient of variation, heritability and genetic advance of some agronomical traits.

- Assess the extent of association between traits among themselves and yield.

## SUMMARY, CONCLUSION AND RECOMMENDATIONS

### Summary and Conclusion

The progress of crop improvement program depends on the choice of the breeding material, the extent of variability and the knowledge of quantitative traits with yield and yield related traits. In view of this, a study was conducted with the objective to assess the genetic variability and association between agronomic traits in some maize genotypes.

Analysis of variance showed the presence of highly significance differences among the tested genotypes for the 20 traits considered which indicates the existence of sufficient genetic variability and there was less coefficient of variation in all of the traits indicating good precision in the conduct of the experiment.

The ranges of mean values for most of the traits were large showing the existence of variation among the tested genotypes. Phenotypic coefficients of variation (PCV) were found to be higher than genotypic coefficients of variation (PCV) for all traits. The two values differed slightly indicating less influence of the environmental factors. The highest phenotypic and genotypic coefficients of variations were observed for plant height, ear height, above ground biomass, grain yield per hectare and kernels texture. Days to75% maturity, leaf width, ear diameter, no. of row per ear had the least phenotypic and genotypic coefficients of variation.

Higher heritability values were obtained for days to75% Maturity, days to silking, plant height, ear height ,leaf width, number of node per plant, number of tassel branch,1000-kernels weight ,kernel texture ,above ground biomass, grain yield per hectare, internodes length and moderate estimates of heritability were observed for number of ear at harvest ,number of rows per ear, harvest index, number of kernels per rows, ear diameter and ear length .

Genetic advance expressed as percentage of mean (GAM) was high for days to silking, days to anthesis, ear height, plant height, kernel texture, internode length, above ground biomass and grain yield per hectare. Low estimates of genetic advances expressed as percentage of mean were

observed for harvest index, and number of ear at harvest, number of plant at harvest and number of ear per plant.

Grain yield showed positive and significant genotypic association with days to anthesis, days to silking, days to75% maturity, plant height, ear height, leafwidth,1000-kernels weight, number of node per plant ,above ground biomass ,inter node length ,and ear length. At phenotypic level days to silking, days to Maturity, plant height, ear height, number of ear at harvest, internodes length, ear length, days to anthesis, leaf width and number of nodes per plant was observed to have positive and highly significant ($P < 0.01$) correlation with grain yield per plant and have negative and highly significant ($P < 0.01$) correlation with harvest index.
Plant height indicated positive and highly significant associations with ear height, number of nodes per plant, internodes length, ear length, leaf width, above ground biomass per hectare and showed negative and highly significant correlation with harvest index.
The path coefficient analysis at phenotypic level based on grain yield as dependent variable revealed that days to anthesis, days of maturity, ear height, leaf width, number of node per plant, number of ear at harvest, above ground biomass and harvest index showed positive direct effect.
The maximum positive genotypic direct effect ingrain yield was observed in above ground biomass yield followed by harvest index, internode length, number of kernels per row, number of ears at harvest and leaf width.
The genotypic path analysis also indicated that negative direct effects were recorded for days of silking, number of kernels per row, number of plant at harvest and ear height.

### 5.2. Recommendations

The result indicated the existence of genetic variability in the maize genotypes studies and this can be exploited in the breeding program. It can also be seen that genotypes BH-660 and BH-661 from among the hybrid varieties and Gibe-1, Gibe-2, Pop-22, Alemaya composite from among the open pollinated varieties gave good high grain yield under Haramaya condition indicating their potential usefulness.

Thus, based on the results obtained the following could be recommended.

- To use plant height, maturity traits, above ground biomass as selection criteria for yield improvement in maize.
- To utilize of genetic variability observed for future maize improvement program and
- Seed production and distribution can also be recommended of the above identified varieties to farmers in Haramaya area.

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# मानव-चिन्तन शक्ति अनबूझे सवालों पर निरन्तर चिन्तनशील-भगवान बुद्ध का अमर इतिहास

**भूमिका-**

चिन्तन के इतिहास में महाकारूणिक भगवान बुद्ध का स्थान सर्वोपरि है। मानव सभ्यता के इतिहास में ईश्वर का सन्देश देने हेतु उनके पुत्र का अभी अवतार नहीं हुआ था और न ही खुदा का संदेश लेकर कोई पैगम्बर ही धरती पर अवतरित हुआ था।

मानव-चिन्तन शक्ति अनबूझे सवालों पर निरन्तर चिन्तशील थी। आर्यावर्त में आरण्यकवासी अग्निहोत्री अपनी तय और ज्ञान से इन अनबूझे सवालों का उत्तर पाने की पूर्ण कोशिश कर रहे थे, परन्तु अभी तक 'गीता का प्रादुर्भाव नहीं हुआ था और न ही 'बाईबिल' और 'कुरान' प्रकाश में आई थी। भारतीय चिन्तन परम्परा में तीन वेदों की उत्पत्ति हो चुकी थी और विचारों के इस युग में इस भू-भाग पर कई वाद प्रचलन में आ चुके थे। सारी दुनिया में कर्मोवेश चार वर्गों का

प्रकटीकरण हो चुका था। भारतीय समाज में वे क्षत्रिय, ब्राह्मण, वैश्य और शूद्र नाम से संज्ञावान हो चुके थे। मानव-मस्तिष्क को मेधा की जिज्ञासा के बुलबुले अपने पूर्ण यौवन में थे, ऐसे उथल पुथल के विचार जगत व व्यवस्थित होते समय में लोक परलोक जन्म मरण कर्म और कर्मफल तथा कर्त्ता और नियन्ता के सवालों से मनुष्य का मन कौतूहल से भरा था इन सभी परिस्थितियों और मानसिक बाध्यताओं ने संस्कृति के लिए नया रास्ता खोल दिया था। ऐसे समय में मानव सभ्यता की एक मानव के रूप में 'महामानव' की प्राप्ति हुई, जो सारी दुनिया की आलोक बनकर विश्व में दे दीप्यमान हुआ और सारी दुनिया को प्रकाशित किया भारत का सिरमौर बनाने वाले इस विश्व आलोक भगवान बुद्ध का जन्म लगभग 563 ई. पूर्व कपिलवस्तु में लुम्बिनी वन में वैशाख पूर्णिमा के दिन हुआ था।

**सिद्धार्थ के जन्म और उस समय की परिस्थिति**

सिद्धार्थ के जन्म का कथानक विविधाताओं से भरा पड़ा है। परन्तु यह एक सर्वसम्मत सत्य हे कि वे न तो किसी ईश्वर के अवतार थे और न ही किसी खुदा के पैगम्बर थे वे मानव पुत्र थे और मानवता उनका पैगाम था। इतिहास बताता है कि उनके जन्म के समय में भारत में जहाँ एक और सामन्ती राजशाही पनप रही थी, वहीं प्रजातन्त्रीय प्रणाली भी आजामई जा रही थी। समकालीन राजनीति का राज्य 'गण' के नाम से विख्यात था और ऐसे ही सोलह ''जनपदीप गणराज्य भारत में अपनी समृद्धि के लिए प्रसिद्ध थे। उनमें से एक 'शाक्य' गणराज्य भी था। शाक्यों की राजधानी 'कपिलवस्तु' थी गण के अधिपति को गणपति या राजा कहा

जाता था। शाक्य गण में प्रजातन्त्र प्रणाली थी और उनके राज्य में सुख और समृद्धि थी। राजा शुद्धोदन की रानी का नाम महामाया था, 'महामाया' अपने मैके देवदाह के लिए सुसज्जित पालकी में रवाना हुई, बीच रास्ते में लुम्बिनी वन-पड़ता था शाल वृक्षों से हरा भरा यह वन में महामाया को प्रसव वेदना की अनुभूति हुई। इसी वन में शाक्य वंश के पुत्ररत्न की प्राप्ति हुई यही शाक्य सिंह आगे जाकर विश्व आलोक बुद्ध कहलाये।

राजा शुद्धोधन राजकुमार की प्रवृत्तियाँ, उम्र और उनके बारे में की गई भविष्यवाणियों को लेकर चिन्तित थे। समय बीतता गया, राज कुमार वैवाहिक जीवनमें बंध चुके थे, परन्तु उनका मन फिर भी ध्यान सुख में लगा ही रहता था, शुद्धोधन के मन में अन्तर्द्वन्द्व की आग तेज हो चुकी थी।

संन्यासी सिद्धार्थ एक बेहतर मार्ग की खोज में चल दिये वह अपने उद्यान, खेत, आचार्य आलार-कालाम के आश्रम में की गई साधना पर चिन्तन करते हुए इस निष्कर्ष पर पहुँचे कि इस साधना के द्वारा ही वे परम सत्य को पा सकते है अत: वे घोर तपस्या के लिये निकल पड़े और यह निश्चय किया कि अब वे किसी आश्रम में नहीं जायेंगे राजगृह में कुटी बनाकर तपस्या की साधना करने की ठानी थी। उनका शरीर मुर्झा गया आँखे धँस गई शरीर हड्डियों का कंकाल मात्र रह गया इस आत्म दमन से भी उन्होंने मार्ग को नहीं पाया उनकी साधना का वर्णन बौद्ध साहित्य में बड़े ही मार्मिक ढंग से किया गया है। पीपल के वृक्ष के नीचे तपस्या करते हुये सात सप्ताह गुजर चुके थे पूर्णिमा का चन्द्रमा आज फिर

अपनी चांदनी में खिल रहा था चन्द्रमा की बढ़ती कला के साथ ही बोधिसत्व का ज्ञान पूर्ण हो रहा था। उनको अचानक आन्दातिरेक हुआ सद्धर्म की प्राप्ति हो गई उन्होंने पाया–धम्म सत्य है अन्तिम सत्य है जीवन का अस्तित्व अवधि रूपी कड़ी से गुरू होता है जीवन के विकास की कड़ियाँ गिनी, उन्हें स्थिर किया– वे द्वादश निदान के रूप में व्यक्त हुई। उन्होंने पाया कि अविधा या अज्ञान से इस संसार रूपी सागर में रचनात्मक और सुव्यवस्थित उत्तेजन होते हैं जिनसे बोध या भावनाएँ उपजती है। ये छः अवयवी छः आयतनों– पाँच इन्द्रियों और मन (बुद्धि) का विश्वास करते है छः आयतन वस्तुओं के स्पर्श में आते हैं। अस्तित्व की तृष्णा वस्तुओं से मोह पैदा करती है, मोह स्वार्थ का वर्धन और पुनः ग्रहण करता है स्थार्थ नये जन्मों में जारी रहता है। स्वार्थ जनित पुनर्जन्म दुख जरा, रोग और मृत्यु के कारण है। वे विलाप चिन्ता और निराशा उत्पन्न करते हैं।

उन्होंने इनके अस्तित्व के बाद निवृत्ति का मार्ग अवधारित किया और चार आर्य सत्यों को पहचाना और प्रतीयसमुत्पाद का अभिज्ञान प्राप्त कर निर्वाण प्राप्त किया। वे अब सम्यक् सम्बुद्ध हो गये। तथागत बुद्ध ने बुद्धत्व प्राप्त करते समय ये उदान गाथाये कही जन्म जन्मान्तर से मैं निरन्तर संसार में दौड़ रहा हूँ शरीर रूपी घर बनाने वाले की खोज में जन्म रूपी श्रृंखला में पड़ता जा रहा हूँ। हे घर बनाने वाले मैनें तुझे देख लिया है अब तू पून शरीर रूपी घर को नहीं बना सकेगा तेरी सभी कड़ियां गई है और शिखर भी बिखर गया है चित्त संस्कार रहित हो गया है और तृष्णा निर्मूल हो गई है।

बुद्ध ने उपदेशों का सार एक शब्द धम्म में आ जाता है मोटे रूप में 'धम्म' शब्द पालि भाषा का तकनिकी शब्द है और भगवान बुद्ध के सिद्धान्त का मूल केन्द्रबिन्दू है।

बौद्ध धर्म में एक और महत्वपूर्ण सत्य निश्चित रूप से उभरता है और वह है- जो बाहर या मानसिक क्रियाएँ हें वे बिना कारण के नहीं है सभी के लिए कुछ ना कुछ कारण अवश्य रहता है। किसी कारण के बिना किसी भी घटना का आविर्भाव नहीं होता है कारणता के इस सिद्धान्त को बौद्ध धर्म में प्रतीत्यसमुत्पाद के नाम से जाना जाता है, प्रतीत्यसमुत्पाद के नियम में बारह अंग है और तीन काण्ड (भाग) है।

बारह अंग इस प्रकार है ⟶ अविधा ⟶ संस्कार ⟶ विज्ञान ⟶ नामरूप⟶ षडायतन⟶ स्पर्श⟶ वेदना⟶ तृष्णा⟶ उपादान भव ⟶ जरामण।

इसके तीन (काण्ड) भाग होते हैं-

अविधा और संस्कार - अतीत पूर्व भव में

जाति और जरामण - अपर भाव में अर्थात भविष्यत् भव में

शेष मध्य के आठ अंग यथा विज्ञान, नामरूप, षडांपतन, स्पर्श वेदना, तृष्णा, उपादान और भव में अर्थात् वर्तमान भव में व्यवस्थित है

**सिद्धार्थ से बुद्ध बनने की यात्रा (ज्ञान प्राप्ति यात्रा)**

ज्ञान की खोज में सिद्धार्थ सर्वप्रथम वैशाली पहुँचे यहाँ वे अलाम् कलाम के आश्रम में गए यहाँ पर तप की क्रिया उपनिषदों की ब्रघ विद्या की शिक्षा प्राप्त की।

वैशाली से राजगीर के पास रूद्रकराम पुत्र आश्रम पहुचे यहाँ पर उन्होंने भोग का ज्ञान प्राप्त किया। राजगीर से उरूवेला गए एवं मोहना तथा निरंजना नदी संगम पर 6 वर्ष तक तपस्या की एवं मोहना तथ्ज्ञा निरंजना नदी संगम पर 6 वर्ष तक तपस्या की परन्तु ज्ञान प्राप्ति नहीं हुई बाद में उन्होंने सुजाता नामक स्त्री से खरीर खाकर अपना व्रत तोड़ा।

35 वर्ष की आयु में निरंजना नदी के किनारे बैशाख पूर्णिमा की रात्री में पीपल वृक्ष के नीचे सत्य एवं ज्ञान की प्राप्ति हुई।

**अनोम नदी**– घर त्यागने के बाद घोड़े एवं सारथी को छोड़ा

**वैशाली**– अलार कलाम से तप क्रिया एवं उपनिषद के ज्ञान की प्राप्ति।

**राजगीर**– रूद्रकराम पुत्र से योग ज्ञान की प्राप्ति

**उरूवेला**– निरंजना नदी तट पर बैशाख एवं ज्ञान का आलोक प्राप्त।

ज्ञान प्राप्ति के बाद उरूवेला का यह क्षेत्र बोधगया एवं सिद्धार्थ बुद्ध कहलाये।

धर्मचक्रप्रवर्तन– गौतम बुद्ध के ज्ञान की प्राप्ति के बाद प्रथम उपदेश एवं दीक्षा दिए जाने की घटना धर्मचक्र प्रवर्तन कहलाती हैं नोट– गौतम बुद्ध ने अपना

पहला उपदेश एवं दीक्षा आदि पतन सारनाथ में दिए इनका उल्लेख संयुक्त निकाय में मिलता है प्रथम उपदेश में ही गौतम बुद्ध ने चार आर्य सत्यों को बताया।

चार आर्य सत्य- 1. दुख - दुख है

2. दुख समुदय - दुख का कारण है
3. दुख निरोध - दुख का निदान है
4. दुख निरोध गामिनी प्रतिवदा - दुख निदान के उपाय- अष्टांगिक मार्ग इसका संबंध चौथे आर्य सत्य से है।

प्रथम आर्य सत्य - दुख प्रथम आर्य सत्य है के अनुसार संसार में सभी वस्तुएँ दुखमय है प्रथम आर्य सत्य में जन्म एवं मरण के चक्र को दुख का मूल कारण बताया गया है।

दुसरा आर्य सत्य - दुख समुदाय दुसरे आर्य सत्य के दुख उत्पन्न करने का मूल कारण तृष्णा को बताया गया है।

तीसरा आर्य सत्य - दुख निरोध गामिनी प्रतिपदा चौथे आर्य सत्य में गौतम बुद्ध ने दुख के उन्मूलन का मार्ग बताया है यही अष्टांगिक मार्ग कहलाते हैं।

**समयक् दृष्टि** - वस्तुओं को वास्तविक स्वरूप का ध्यान रखना।

**समयक् संकल्प** - आसक्ति, द्वेष, हिंसा से मुक्त विचार।

**सम्यक् वाचा** - अप्रिय वचनो का परित्याग

**सम्यक् कर्मान्त** - दान, दया, सत्य, अहिंसा, सत्कर्मो का अनुसरण

**सम्यक् अजीव** – सदाचार के नियमों के अनुकूल जीवन जीना

**सम्यक् व्यायाम** – विवेकपूर्ण प्रयत्न करना

**सम्यक् समाधि** – मन अथवा चित्र का एकाग्रता

**बौद्ध संघ की स्थापना** – गौतम संघ का संगठन गणतांत्रिक प्रणाली पर आधारित था। संघ में प्रवेश पाने के लिए कम से कम 15 वर्ष की आयु का होना आवश्यक था माता-पिता की आज्ञा आवश्यक थी।

संघ के सदस्य / अनुयाई दो वर्गों में बँटे थे।

1. भिक्षु / भिक्षुणी – वे संन्यासी जीवन वाले लोग थे।
2. उपासक / उपासिकाएँ – ये ग्रहस्थ जीवन में रहकर बौद्ध धर्म अनुसरण करने वाले लाग थे।

संघ की सदस्यता सभी जातियों के लिए सुलभ थी। संघ में प्रवेश के समय त्रिरत्न (बुद्ध, संघ, धम्म) में विश्वास करने की शपथ लेनी होती थी।

बौद्ध भिक्षुओं के लिए आवश्यक दस शील (सिद्धान्त)

- ❖ दूसरे के धन की इच्छा न करना।
- ❖ झूठ नहीं बोलना
- ❖ हिंसा से दूर रहना
- ❖ मादक द्रव्यों का सेवन न करना

- ❖ व्यभिचार नहीं करना
- ❖ संगीत एवं नृत्यों में भाग नहीं लेना
- ❖ सुगंधित द्रव्यों का उपयोग नहीं करना
- ❖ असमय भोजन नहीं करना
- ❖ सुखप्रद विस्तर पर नहीं सोना
- ❖ किसी प्रकार के द्रव्य का संचय न करना

**संघ के अधिकारी** – नवकम्मिक : निर्माण से संबंधित अधिकारी

भण्डागारिक – खान पान से संबंधित अधिकारी

कप्पिकारक – क्रम करने वाला अधिकारी

चीवन – वस्त्रागार का अधिकारी

आरम्भिक – आराम से संबंधित अधिकारी

चैत्य एवं विहार में अंतर– चैत्य एक प्रकार की समाधि स्थल थे इन समाधि स्थलों में महापुरुषों को शवदाह के बाद उनके घातु अवशेषों को सुरक्षित रखने के लिए इन समाधियों में भूमि के अन्दर गाढ दिया जाता था एवं ऊपर एक भव का निर्माण किया जाता था ये उपासना के केन्द्र थे।

विहार – चेत्यो के पास ही बौद्ध धर्म के भिक्षुओं को रहने के लिए आवास स्थानों का निर्माण कर दिया जाता था ये आवास स्थान ही विहार कहलाते थे ये आवास के केन्द्र थे।

बौद्ध धर्म के दर्शन- बौद्ध दर्शन क्षणिकवादी है। बौद्ध दर्शन अन्त शुद्धिवादि है बौद्ध दर्शन कर्मवादी है कर्म का आशय कादिक कामीक व मानसिक चेष्टाओं से है।

बुद्ध के शिष्य - तपस्तु व मल्लिक (प्रथम दो अनुयाई) पंचवर्गीय ब्राह्मण, सारिपुत्र, मौदगल्लापन, राहुल (पुत्र), नंद, सौतेला भाई, उपालि, आनन्द, जीवक, बिम्बिसार, अजातशत्रु, प्रसेनजित, महाकश्यप।

बुद्ध की प्रमुख शिष्याएँ- महा प्रजापति गौतमी (सौतेली माँ) यशोधरा (पत्नि), नंदा सौतेली बहन, आम्रपालि, विशाखा क्षेमा, मल्लिका।

बौद्ध धर्म के संरक्षक राजा- बिम्बिसार, अजातशत्रु मगध के राजा, प्रसेन्नजित कोशल के राजा, उदयन वत्स नरेश, प्रघोत्त अवन्ति नरेश, अशोक व दशरथ मौर्य वंश कनिष्क कुजाण वंश, हर्षवर्धन पुज्यभूति वंश, सहसी वंश, पाल वंश।

**बौद्ध धर्म की लोकप्रियता के कारण**- धार्मिक वाद विवाद से अलग रहा इस कारण जनसामान्य आकर्षित वर्ण व्यवस्था की निन्दा करने से निम्न वर्गों का समर्थन प्राप्त, बौद्धसंघ सभी जातियों के लिए खुला था। ब्राह्मणवाद के विरोधी लोगों का बौद्ध धर्म की ओर रूचि बुद्ध का व्यक्तित्व व उपदेश प्राणाली उपदेश की भाषा पालि जनसाधारण की भाषा थी। संघ की स्थापना, महत्वपूर्ण शासकों का सहयोग इत्यादि।

बौद्ध धर्म की विशेषताएँ और इसके प्रसार के कारण – बौद्ध संघ का दरवाजा हर किसी भी जाति का क्यों न हो, संघ में प्रवेश का अधिकार स्त्रियों को भी था जिससे उन्हें पुरुषों की बराबरी प्राप्त होती थी ब्राह्मण धर्म की तुलना में बौद्ध धर्म अधिक उदार और अधिक जनतांत्रिक था।

**अनीश्वरवाद**– बौद्ध धर्म ईश्वर की सत्ता को नहीं मानता है इसके अनुसार संसार कर्मो का चक्र है। यह कार्य चक्र ना ही कही से शुरू हुए है और न ही कभी खत्म होगे। यह कार्य किसी और ने नहीं अपितु मनष्यु ने ही शुरू किए है।

**शून्यतावाद**– शून्यता महायान बौद्ध संप्रदाय का मुख्य दर्शन माना जाता है। इसके अनुसार संसार की किसी भी वस्तु पर किसी का कोई अधिकार नहीं है सभी पदार्थ या वस्तुएं सत्ताहीन है इस दर्शन के अनुसार मनुष्य अपने कर्मो को पूरा कर उसी प्रकार मोक्ष और शन्ति प्राप्त करता है जैसे तेल और वाती समाप्त होने पर दीपक शांत हो जाता है।

**अनात्मवाद** – अनात्मवाद सिद्धान्त इस बात पर प्रकाश डालता है कि आत्मा जैसे कोई चीज नहीं होती जिसे हम आत्मा समझते हैं वह दरअसल आंतरिक चेतना है।

**क्षाणिकवाद**– संसार में कोई भी चीज सदैव के लिए नहीं रहती जो इंसान जन्म लेता है वह मरता अवश्य है जो पेड़ फल देता है वह खत्म भी हो जाता है कमया हुआ पैसा खर्च भी हो जाता है यानि जीवन में कोई भी चीज कुछ क्षण के लिए ही रहती है।

जो समाज में चेतना को पैदा करता है ज्ञान के विभिन्न उपागमों में से धर्म भी एक है धर्म एक महत्वपूर्ण व्यवस्था है और ज्ञान का एक साधन है। बुद्ध के उपदेशों का सार एक शब्छ धम्म से आ जाता है धम्म शब्द पालि भाषा का तकनीकी शब्द है, बुद्ध ने धम्म को उदघाटित किया, जगत में प्रकाशित किया, यह निर्विवाद है भगवान बुद्ध द्वारा उपदिष्ट धम्म वस्तुतः हमारे अस्तित्व की व्याख्या प्रस्तुत करता है भगवान बुद्ध ने मानव अस्तित्व की व्याख्या प्रस्तुत करता है भगवान बुद्ध ने मानव अस्तित्व के मूल तत्वों की खोज की उनमें अन्तर्भूत नियमों और उपनियमों की जानकारी प्राप्त की और आम लोगों को उनकी भाषा में समझाया।

बुद्ध ने अनुयायीयों के मुख्य स्थान- लुम्बिनी यह स्थान नेपाल की तराई में ईसा पूर्व 563 में राजकुमार सिद्धार्थ गौतम का जन्म यही हुआ था हालाँकि, यहाँ के बुद्ध के समय के अधिकतर प्राचीन विहार नष्ट हो चुके हैं केवल सम्राट अशोक का एक स्तम्भ अवशेष के रूप में इस बात की गवाही देता है कि भगवान बुद्ध का जन्म यहाँ हुआ था इस स्तम्भ के अलावा एक समाधि स्तुप में बुद्ध की एक मूर्ति है

**बोधगया**- करीब छः साल तक जगह-जगह और विभिन्न गुरूओं के पास भटकने के बाद भी बुद्ध को कही परम ज्ञान न मिला इसके बाद वे गया पहुँचे आखिर मे उन्होंने प्रण लिया कि जब तक असली ज्ञान उपलब्ध नहीं होता, वह पिपल वृक्ष के नीचे से नहीं उठेंगे इसके बाद करीब छह दिन छह रात एक पिपल

वृक्ष के नीचे भूखे प्यासे तप किया आखिर में उन्हें परम ज्ञान का बुद्धत्व उपलब्ध हुआ सिद्धार्थ गौतम अब बुद्धत्व पाकर आकाश जैसे अनंत ज्ञानी हो चुके थे जिस पिपल वृक्ष के नीचे वह बैठे उसे बोधि वृक्ष यानि ज्ञान का वृक्ष कहा जाता है उसी गया को बोधगया के नाम से जाना जाता है।

**कुसीनगर**– बौद्ध अनुयाईयों का बड़ा पवित्र स्थल है भगवान बुद्ध कुशीनगर में ही महापरिनिर्वाण को प्राप्त हुए कुशीनगर के समीप हिरण्यवती नदी के समीप बुद्ध ने अपनी आखिरी सांस ली।

**दीक्षा भूमि** – नागपुर महाराष्ट्र राज्य के नागपुर शहर में स्थित पवित्र एवं महत्वपूर्ण बौद्ध तीर्थ स्थल हे बौद्ध धर्म विद्वावान बोधिसत्व डॉ. बाबासाहब अम्बेड़कर ने भारत में बौद्ध धर्म का पुरुत्थान किया, यहीं पर डॉ. अम्बेड़कर ने बौद्ध धर्म की दिक्षा ग्रहण की बौद्ध धर्म पूर्णत: वैज्ञानिक और परिपूर्ण का भण्डार है, जो प्रत्येक वैज्ञानिक के मस्तिष्क एवं सामान्यजन की मेधा को सन्तुष्ट करने में सक्षम है हमने भौतिक पदार्थ या द्रव्य की व्याख्या बौद्ध धर्म के अनुसार की जिसमें यह पाया कि हमारा शरीर भौतिक पदार्थों की सूक्ष्मतय इकाई से बना है।

अभिधम्म साहित्य में मन और शरीर के बारे में कई मान्यताएँ विशेष स्थान रखती है बौद्ध धर्म के अनुसार चार ही परमार्थ है वे इस प्रकार है चित्त, चेतसिक, रूप निब्बाण बौद्ध वाङ्मय में आत्मा तथा परमात्मा ने तो व्यवहार सत्य है और न ही परमार्थ सत्य है रूप का वर्णन हम पहले ही कर चुके है, एवं चित्त तथा चेतसिक का वर्णन अभिधम्म कोश के अनुसार ही करने का प्रयत्न करेंगे। चित्त,

विज्ञान और मन आदि ऐसे शब्द है जो बौद्ध साहित्य में जगह–जगह आये है कोई भी प्रवृत्त चित्त अनेक चेतसिकों में से कम या वेश कुछ चेतसिकों या चैतो का समूह ही है। चित्त या मन कहते उसी को है जिसमें चेतसिक रहते हैं चित्त और चेतसिक या चित्ता और चैत के उत्पत्ति, विरोध, आलम्बन, वस्तु आदि एक ही होती है बिना चित्त के चेतसिक देखने में नहीं आते हैं। और बिना चेतसिकों के कही भी प्रवृत्त चित्त देखने में नहीं आता है। इसलिए चित्त और चेतसिकों के बीच कही भी कोई पार्थक्य की रेखा खींचना सहज नही हैं।

**मन आत्मा नहीं**– बौद्ध दर्शन में आत्मा नाम के किसी तत्व की स्वीकारोक्ति नहीं है बौद्ध साहित्य के अनुसार आत्मा का अस्तित्व नहीं है आत्मा शब्द संसार का सामान्य प्रयोग है।

स्कन्ध जड़ है और इनके अतिरिक्त चेतन सत्ता वाला कूटस्थ आत्मा नहीं है चेतना विज्ञान आदि के लिये बौद्ध धर्म में कूटस्थ आत्मा नहीं है चेतना विज्ञान आदि के लिये बौद्ध धर्म में मन मनस आदि शब्दों का प्रयोग हुआ है यह मन या चित्त बौद्ध धर्म में परमार्थ है परन्तु यह आत्मा नहीं है। मन का कोई भी घटक आत्मा नहीं है मन अपनेआप में कोई स्कन्ध भी नहीं है यह अरूपी स्कन्धों का पूंजीभूत है जो अपनी विषयवस्तु से अलग नहीं है साधारण रूप में हम यों कह सकते हैं कि मन एक ऐसा पर्दा है जो चैत या चेत्तसिकों या इन तत्वों से बनता है और इनके अलग भी उसकी सत्ता है वह एक तत्व है।

**मन के घटक**– मन के संगठन में स्कन्धों में से चार स्कन्ध वेदना, संज्ञा, संस्कार और विज्ञान प्रधान है अत: मन की वास्तविक स्वरूप रचना को जानने के लिए इनको जानना जरूरी है।

**वेदना स्कन्ध**– हमारे व्यवहार का जो संवेदना पक्ष है उसको इस स्कन्ध के रूप में संगृहीत समझना चाहिये वेदना क्या है? इसकी परिभाषा करते हुए अभिधम्म कोश में आचार्य बसुबन्धु कहते है कि वेदना अनुभव है। जब कोई वस्तु सुखकारी प्रभाव पैदा करती है तो सुख वेदना है, जब वस्तु दुखकारी प्रभाव पैदा करती है तो अदुखासुख वेदना कहते हैं।

**संज्ञा स्कन्ध**– मन या चित्त की रचना करने वाला दूसरा तत्त्व है संज्ञा स्कन्ध। जो हमारे व्यवहार पक्ष के प्रत्यक्षीकरण प्रक्रियाओं से सम्बन्धित है अभिधम्मकोश की कारिका में इसे इस प्रकार से कहा जाता है।

**संस्कार स्कन्ध**– मन के जो घटक अभी तक बताये गये हैं, वे तथा विज्ञान स्कन्ध के अलावा जो घटक है वे बौद्ध मनोविज्ञान में संस्कार स्कन्ध की व्याख्या पाते हैं।

**विज्ञान स्कन्ध**– मन के निर्माण में चौथे महत्वपूर्ण घटक विज्ञान स्कन्ध है। बौद्ध धर्म में चित्त, मन और विज्ञान एक ही अर्थ के वाचक है, परन्तु आधुनिक मनोविज्ञान की दृष्टि से बौद्ध धर्म में उनके सूक्ष्म भेद भी दर्शाया गया है।

**निष्कर्षत:**– बोधि की प्राप्ति से लेकर महापरि निर्वाण–पर्यन्त करूणा के अनन्त सागर भगवान बुद्ध संसार के प्राणियों के कल्याण के लिए अपने मार्ग का

उपदेश देते रहे बोधि की प्राप्ति के पश्चात् प्रारम्भ में ही उन्हें इस प्रकार की धारणा उत्पन्न हुई कि अपने द्वारा खोजे गये मार्ग को विश्व को बताया। बुद्ध के ये उपदेश मौखिक ही थे उपदेश के समय उपस्थित स्मृतिमान तथा बहुश्रुत भिक्षु इन्हें याद कर लेते थे बुद्ध के परिनिर्वाण के पश्चात् इनके संग्रह की आवश्यकता हुई तो त्रिपिटक रूप में ये संग्रहित हुए त्रिपिटक का अर्थ होता है तीन पिटारियाँ बुद्धवचन की भाषा बुद्ध ने किसी विशेष भाषा का आग्रह न करके बुद्धवचनों को अपनी-अपनी भाषा में सीखने और धारण करने की अनुमति प्रदान कर दी थी। पालि शब्द को भाषा के अर्थ की अनुमति प्रदान कर दी थी। पालि शब्द को भाषा के अर्थ की अनुमति प्रदान कर दी थी। पालि शब्द को भाषा के अर्थ में व्यवहृत करते हैं और इसमें बौद्ध-धर्म के थेरवाद का सम्पूर्ण त्रिपिटक एवं अनुपिटक साहित्य प्राप्त है। प्रारम्भ में यह शब्द मूल बहुवचन अथवा त्रिपिटक के लिए प्रयुक्त होता रहा और बाद में यह उस भाषा का घोतक हो गया जिसमें बुद्धवचन प्राप्त है। इस प्रकार भाषा के अर्थ में पालि शब्द का प्रयोग नवीन ही है, विशेषकर उन्नीसवीं शदी से इसका व्यापक प्रचार ही रहा है आज भी जिस भाषा को पालि की संज्ञा से अभिहित करते हैं इसका परम्परा से प्राप्त नाम मागधी है।

हम प्राचीन भारतीय आर्यभाषा के विकास-क्रम पर विचार करे तो इसी निष्कर्ष पर पहुँचते हैं कि वैदिक भाषा निरन्तर विकास पथ पर अग्रसर होती गई। जितनी ही भाषा बदलती गई उतना ही हमारे परवर्ती पूर्वजों की अपने पूर्वजों की भाषा और कृतियों के प्रति अधिक लोकोत्तर श्रद्धा बढ़ती गई और उन्होंने इसकी

रक्षा के अनेक उपाय किये फिर भी बोलचाल की भाषा आगे बढ़ती ही गई समय बीतने के साथ लोगों को इसकी चिन्ता हुई कि इस भाषा को कैसे सजीव तथा सुरक्षित रखा जाए इसलिए उन्हें वेद मन्त्रों को कैसे सजीव तथा सुरक्षित रखा पद जटा धन आदि नाना क्रम से उच्चारण तथा कंठस्थ करके सुरक्षित किया वहाँ उस भाषा की भीतरी बनावट के लिए अपनी-अपनी शाखा के प्राप्ति शाठप बनाये। तब बुद्ध छठी शताबदी में उत्पन्न हुए इन्होंने साहित्यिक भाषा को छोड़कर प्रचलित तथा उपयुक्त होने से लोकभाषा में ही लोगों को उपदेश दिया कुछ लोगों ने बुद्धवचनों को प्राचीन भाषा को ही अपनाया और आगे यथासंभव प्रयत्न उसे अधिक स्थाई भाषा में उसे सुरक्षित करने का प्रयास किया।

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# ॥ऋग्वेदस्य वैश्विकसन्देशः॥

## ॥ कृण्वन्तो विश्वमार्यम् ॥

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पीठिका –

वेदाः वैश्विकजनमानसमुद्दिश्य प्रवृत्ताः सन्ति । तत्र मानवेभ्यः संस्काराणां ज्ञापनं, विधि-निषेधपूर्वकं तेषाम् आचरणम्, तेन चित्तशुद्धिः, विश्वबन्धुत्वभावना, लक्ष्यसिद्धिः इत्यादिप्रकारेण मानवानाम् आत्यन्तिकसुखं प्रापयितुं वेदाः प्रवृत्ताः सन्ति । अत्र भेदभावनायाः लवलेशोऽपि न दृश्यते ।सामान्येन वेदाः कर्मादिषु प्रवृत्ताः भवन्तीति जानीमः किन्तु लक्ष्यमुद्दिश्य प्रवृत्तौ मध्ये अनेके मानवोपयोगिविचाराः स्पष्टीकृताः । मानवसङ्कुलस्य उद्धर्तुकामाः क्रान्तदर्शिनः ऋषयः धर्ममार्गप्रवर्तनाय अभ्युदयनिःश्रेयसात्मकं मार्गद्वयं तैः दृष्टैः मन्त्रैः उपदिष्टवन्तः ।तान् मन्त्रान् विविच्य पश्यामश्चेत् तत्र बहुविधाः मन्त्राः उपलभ्यन्ते यथा - संस्कारबोधकाः (गुणाधानेन दोषापनयम्) मन्त्राः, विवाहोपयोगिनः, संवादसूक्तानि, अक्षसूक्तानि, मण्डूकसूक्तानि, दानस्तवनसूक्तानि इत्यादीनि लैकिकविषयबोधकानि प्रसिद्धानि सन्ति । मन्त्रोक्तप्रकारेण यदि वयं अस्माकं जीवने संस्कारान्विताः भवेम तर्हि राष्ट्रदृष्ट्या सुसंस्कारवन्तः प्रजाः, अध्यात्मदृष्ट्या च चित्तशुद्धिद्वारा पुरुषार्थप्राप्तिः भविष्यति ।

- Key Words –
  - लौकिकविषयबोधकमन्त्रेषु विभागः
  - बृहद्देवतोक्तप्रकारेण मन्त्रविभागः
  - मन्त्रेषु संस्कारबोधनम्
  - दानप्रशंसा
  - संवादसूक्तानि
  - बृहद्देवतोक्तप्रकारेण मन्त्रेषु विभागः -

स्तुतिः प्रशंसा निन्दा च संशयः परिदेवना । स्पृहाशीः कत्थना याञ्चा प्रश्नः प्रैषः प्रवह्लिका ॥
नियोगश्चानुयोगश्च श्लाघा विलपितं च यत् । आचिकख्यासाथ संलापः पवित्राख्यानमेव च ॥.....
भूतं भव्यं भविष्यं च पुमान् स्त्री च नपुंसकम् । एवं प्रकृतयो मन्त्राः सर्ववेदेषु सर्वशः ॥[1]

[1] बृहद्देवता – ३५-४०

इत्येते अर्थाः मन्त्रसमूहेषु कदाचित् एकस्याम् ऋचि, अर्धर्चि, एकस्मिन् पादे वा अभिव्यक्ताः भवन्ति । यत्र शब्दोच्चारेण वस्तु निर्देशः क्रियते तत्र नामपदमिति मनीषिणः कथयन्ति । तदुक्तम् –

शब्देनोच्चारितेनेह येन द्रव्येण प्रतीयते । तदक्षरविधौ युक्तं नामेत्याहुर्मनीषिणः ॥[2]

- लौकिकविषयबोधकमन्त्रेषु विभागः :-

१) विवाहसूक्तानि
२) और्ध्वदैहिकसूक्तानि
३) ऐतिहासिकसूक्तानि
४) दानस्तवनसूक्तानि
५) मण्डूकसूक्तानि
६) आभिचारिकसूक्तानि
७) संवादसूक्तानि
८) अक्षसूक्तानि

इत्येतानि सूक्तानि लौकिकानि इति विमर्शकाणाम् अभिप्रायः । अत्र विवाहादिसंस्कारसम्बद्धाः विषयाः जीवनसम्बद्धाः च उच्यन्ते । यास्काचार्यरचिते निरुक्ते मन्त्रदर्शनप्रकरणे स्तुतिः, निन्दा, आशीर्वादः, शपथः, अभिशापः इत्यादिरुपेण मन्त्राणां विविधत्वं प्रदर्शितवन्तः । मन्त्राः यथा अपूर्वविषयान् (अदृष्टविषयान्) बोधयन्ति तथैव दृष्टविषयकबोधकाः अपि भवन्ति । लौकिकाः विषयाः नाम मानवेभ्यः संस्कारबोधकाः, दानस्तुतयः इत्यादयः अन्तर्भवन्ति । सर्वेषां जनानां हितमेव काङ्क्षयन्, सर्वानपि जनान् सन्मार्गे प्रवर्तयन् दुष्टमार्गात् च निवर्तयन् अस्ति वेदः। स्तुतिरूपार्थवेदवाक्यैः सत्कार्यं कर्तुं स्व आस्तिकान् जनान् चोदयति, तथा निन्दारूपार्थवेदवाक्यैः दुष्टकार्यात् आस्तिकान् जनान् निवर्तयति । अतः विध्यर्थवाक्येन प्रवर्तको भवति, निषेधवाक्येन निवर्तकोऽपि भवति वेदः ।अतः वेदस्य व्युत्पत्तिं विद्वांसः एवं दर्शितवन्तः :-"विद्यन्ते ज्ञायन्ते लभ्यन्ते वा एभिः धर्मादिपुरुषार्थाः इति वेदाः"[3] इति विद्-धातुनिष्पन्नत्वात् वेदस्य ज्ञानार्थत्वं,लाभार्थत्वं च दर्शितं ऋग्वेदप्रातिशख्ये । वेदभाष्यकारेण सायणाचार्येणापि अयमेवाभिप्रायः प्रकटितः स्वीयायाम् ऋग्वेदभाष्यभूमिकायाम् – 'इष्टप्राप्त्यनिष्टपरिहारयोः अलौकिकमुपायं यो ग्रन्थो वेदयति स वेदः'[4] इति । वेदस्य स्वरूपविचारे बहवः विचाराः प्रकटिताः विद्वद्भिः, सर्वप्रथमं बौधायन-आपस्तम्बप्रभृतिभिः सूत्रकारैः "मन्त्रब्राह्मणयोः वेदनामधेयम्"[5] इति मन्त्रब्राह्मणात्मकं स्वरूपं वेदस्य इति निर्धारितम् ।

ये आस्तिकाः जनाः वेदस्य प्रामाण्यम् अभ्युपगच्छन्ति तेषामपि क्वचित् वेदविषये अन्यथा प्रतिपत्तिः दृश्यते, यथा – वेदः केवलं यज्ञयागादिकं बोधयति, वेदमन्त्राः केवलं देवताराधनेषु एव प्रयुज्यन्ते, तन्मन्त्राः अपरादिक्रियासु उपयुज्यन्ते, आत्मज्ञानप्राप्त्यर्थं केवलं विद्यन्ते वेदाः इति । एतादृशं ज्ञानम् अस्माभिः सर्वथा न निराक्रियते यतः किन्तु वास्तविकज्ञानार्थमेव प्रयतते । वेदे यथा आत्मज्ञानम्, दर्शनम्, यज्ञाः, संस्कारादिक्रियाः उच्यन्ते तथा अत्यन्तलौकिकाः विषयाः अपि प्रतिपाद्यन्ते । एवं लौकिकानि सूक्तानि सन्ति चेदपि अत्र साक्षात् कृषिमेवाभिलक्ष्य सूक्तानि न सन्ति, अर्थात्

[2] बृहद्देवता - ४२

[3] ऋग्. संहिता भाष्य.भूमिका.

[4] ऋग्. संहिता भाष्य.भूमिका

[5]ऋग्. संहिता भाष्य.भूमिका.

अन्यं विषयं द्वारीकृत्य एतत्सम्बद्धाः विचाराः प्रकटिताः सन्ति ।कृष् धातुना व्युत्पन्नोऽयं कृषिशब्दः विलेखने, व्याकर्षणे इत्यस्मिन् अर्थे रूढः अस्ति । अधुना परम्परया यत्र कृषेः स्तवनं कृतं तदिदानीं पश्यामः – ऋग्वेदे विशेषेण दशमे मण्डले दानस्तवनपराः मन्त्राः सन्ति । तत्र अन्नमुखेन दानस्य महत्वं कथयन् कृषेः प्रामुख्यं वर्णयति । अस्य सूक्तस्य अन्नमेव देवता, भिक्षुर्नामाङ्गिरसः ऋषिः यथा –

o उच्चा दिवि दक्षिणावन्तो अस्थुर्ये अश्वदाः सहते सूर्येण । हिरण्यदा अमृतत्त्वं भजन्ते वासोदाः सोमप्रतिरन्त आयुः ॥ [6]

अयं मन्त्रः दानस्य महत्वं कथयन् दानकर्तुः सद्गतिं सूचयति । यतः अस्माकं परम्परायां प्राचीनकालादपि विद्वांसःधर्मान्तर्गतत्वेन दानं स्तुन्वन्ति स्म । ऋषयः वेदे दानमेवं स्तुन्वन्ति – दानमिति सर्वाणि भूतानि प्रशंसन्ति दानान्नाति दुश्चरं तस्माद्दाने रमन्ते ……..दानं यज्ञानां वरूथं दक्षिणा लोके दातारं सर्वभूतान्युपजीवन्ति दानेनारातीरपानुदन्त दानेन द्विषन्तो मित्रा भवन्ति दाने सर्वं प्रतिष्ठितं तस्माद्दानं परमं वदन्ति ।[7] एवं दानेन समाजः सुस्थितौ भवति, अस्मान् द्विषन्तः जनाः अपि मित्रा भवन्ति, दानेन कर्ता सद्गतिमपि प्राप्नोति इति ।

➢ संवादसूक्तानि –

ऋग्वेदे यथा कानिचन् सूक्तानि (दार्शनिकसूक्तानि) तत्त्विकविवेचनस्य आधारभूतानि सन्ति तथैव कानिचन सूक्तानि आधुनिक-काव्यनाटकादिभ्यः आधारभूतानि सन्ति । तान्येव सूक्तानि संवादसूक्तानि इति कथयन्ति । ऋग्वेदे बहूनि संवादसूक्तानि उपलभ्यन्ते यथा – यम-यमी संवादः, पुरूरव-उर्वशी संवादः, विश्वामित्र-नदी संवादः, सरमा – पणी संवादः, अग्नि – देवता संवादः, वसिष्ठ – इन्द्र संवादः, अगस्त्य – लोपामुद्र संवादः इत्यादीनि सुक्तानि प्रसिद्धानि सन्ति ।

यम-यमी संवादे चतुर्दशमन्त्राः सन्ति । यमयमिनौ उभावपि वैवस्वतः सन्तानौ आस्ताम् । तावुभावपि एकदा मन्दप्रकाशस्थद्विपमेकम् आगतवन्तौ । तत्र कामवशगा यमी यमे अनुरक्ता सती तं यमं बहुभिः शब्दैः प्रलोभनं करोति ।किन्तु यमः धीरः विवेकी तां निराकरोति । आवामुभावपि सहजन्मानौ एतादृश कामवासनया अनर्थं न कुर्वः इति बुद्धिं कथयति । तदुक्तम् –

औ चित्सखायं सख्या ववृत्यां तिरः पुरूचिदर्णवं जगन्वान् ।
पितुर्नपातमा दधीत वेधा अधिक्षमि प्रतरं दीध्यानः ॥[8]
गर्भे नु नौ जनिता दम्पती कर्देवस्त्वष्टा सविता विश्वरूपः ।
न किरस्य प्रमिनन्ति व्रतानि वेद नावस्य पृथिवी उत द्यौ ॥[9] इति ॥

[6] ऋग्. संहिता भाष्य.भूमिका – १०/१०७/२

[7] यजु.आरण्यकम् – ४/१००, १०१

[8] ऋग्. सं – ०५/१०/०१

[9] ऋग्. सं – ०५/१०/०५

पुरूरवा – ऊर्वशी संवादे कामेन पीडितः विरहतप्तः पुरूरवा दिव्याप्सरां ऊर्वशीं पश्यति । अप्सरा स्त्री ऊर्वशी वर्षचतुष्टयं दाम्पत्यमपि करोति । गर्भवती अप्सरा पुरूरवं त्यक्त्वा गच्छति । ततः अस्य विरहः प्रारभ्यते । मन्त्राः च –

किमेता वाचा कृणवा तवाहं प्राक्रमिषमुषसामग्रियेव ।

पुरूरवः पुनरस्त्वं परेहि दुरापना वात इवाहमस्मि ॥[10] इति ।

इषुर्न श्रिय इषुधेरसना गोषा शतसा नरं हिः ।

अवीरे क्रतौ वि दविद्युतन्नोरा न मायुं चितयन्त धुनयः ॥[11] इति ॥

एवं संवादसूक्तमाधारीकृत्य एव कान्तसम्मितादिकं प्रवृत्तमिति जानीमः । एवं स्वस्थसमाजस्य निर्माणार्थं ऋग्वेदस्य योगदानं महदस्ति ।

- विवाहसूक्तम् –

ऋग्वेदस्य दशमे मण्डले सूर्यसूक्तमिति प्रसिद्धम् अस्ति । इदं सूर्यसूक्तमेव विवाहसूक्तमिति प्रसिद्धम् अस्ति । अत्र अस्माकं देशस्य अनेकेषु संस्कारेषु अन्यतमं विवाहसंस्कारः वर्णितः अस्ति । अस्मिन् सूक्ते सूर्यपुत्र्याः सूर्यायाः सोमस्य च विवाहवर्णनं कृतं वर्तते । अस्य सूक्तस्य सवितृपुत्री सूर्या एव ऋषिः भवति । सूक्तारम्भे वरस्य सोमस्य वर्णनं कृतम् । यथा –

सोमेनादित्या बलिनः सोमेन पृथिवी मही । अथो नक्षत्राणामेषामुपस्थे सोम आहितः ॥[12] इति । वधू सूर्या विवाहानन्तरं एवं स्वपतिगृहं प्रविशति –

मनो अस्या अन आसीत् द्यौरासीदुतच्छदिः । शुक्रावनड्वाहावास्तां यदयात्सूर्या गृहम् ॥[13] इत्यादिप्रकारेण गृहप्रवेशसन्दर्भः, विवाहस्य उद्देश्यम् च वर्णितम् । अत्र केचन मन्त्राः उल्लिख्यन्ते –

इह प्रियं प्रजया ते समृध्यतां । अस्मिन् गृहे गार्हपत्याय जागृहि ।[14]

सुमङ्गलीरियं वधूरिमां समेत पश्यत । सौभाग्यमस्यै दत्वायाथास्तं विपरेतन ॥[15] इति ।

गृह्णामि ते सौभगत्वाय हस्तं मया पत्या जरदष्टिर्यथासः । भगो अर्यमा सविता पुरन्धिः मह्यं त्वा दुर्गार्हपत्याय देवाः ॥[16] इत्यादिप्रकारेण विवाहक्रमान्, तस्य माहात्म्यं सर्वं अस्मिन् सूक्ते विवृतमस्ति ।

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[10] ऋग्. संहिता – १०/९५/०२

[11] ऋग्. संहिता – १०/९५/०३

[12] ऋग्. संहिता – १०/८५/०२

[13] ऋग्. संहिता – १०/८५/१०

[14] ऋग्. संहिता – १०/८५/२७

[15] ऋग्. संहिता – ०१०/८५/३३

[16] ऋग्. संहिता – १०/ ८५/३६

एवं वेदः विश्वस्तेभ्यः मानवकुलेभ्यः गुणाधानेन दोषापनयनं कुर्वन् , समग्रमानवकुलानि सुसंस्कारवन्ति करोति । एवं 'यत्र विश्वं भवत्येक नीडम्', 'समानी व आकूतिः', 'स्वस्ति पन्थामनुचरेम' इत्यादिप्रकारेण शतशैः मन्त्रैः मानवकुलस्य स्वास्थ्यम्, सुखम्, एकत्वम् च बोधयति ।

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# आचार्य विनोबाभावे के नेतृत्व में चलाये गए भूदान-यज्ञ पर श्रीलाल शुक्ल जी के विचार ।

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**Abstract**

श्रीलाल शुक्ल जी हिन्दी साहित्य के प्रमुख साहित्यका, भारतीय लोकतांत्रिक व्यवस्था में हजारों किस्म की विसंगतियों ओर विडम्बनाओं को क़रीब से देखते रची गाई एक दुर्लभ कृति ''बिसामपुर का संत ''है। श्रीलाल शुक्ल ने विनोबा भाव के नेतृत्व में चालर्य गए भूदान यज्ञ और ग्रामदान आंदोलन आदि इस पृष्ठभूमि में लिखा गया है। यह एक बेजोड़ उपन्यास '' बिसामपुर का संत ''है, इस पर भूदान - यज्ञ आदि पर शुक्ल जी के विचार कुछ इस प्रकार के हैं।

**1. विषय** - भावे की प्रेरणा से जयप्रकाश नारायण जैसे कई बडे समाजवदी नेता इस आंदोलन से जुडे भूदान आंदोलन का उद्देश्य पुरे देश का शद्धार करना था जिसमें समाज में सबको साथ लेकर आगे बढना था। भूदान आंदोलन सिर्फ भूमि का वितरण नही था बल्कि एक प्रक्रिया थी जिसके अंतर्गत समाज के सभी वर्गों के हितों की रक्षा की गयी थी।

**2. भूदान, ग्रामदान, उद्योगदान, जीवनदान और विचारदान वाले विनोबाभावे का जीवन और व्यक्तित्व परिचय**

विनोबा भावे जी का समय 11.9.1895 से 15.11.1982 तक माना जाता है। विनायक नरहरि भावे को 'विनोबा' का यह नाम महात्मा गांधी ने दिया था, नई पीढ़ी के लोग अकमर इस बात का यकीन नहीं कर पाते कि भारत जैसे देश में लोगों ने अपने ही गांव-समाज के भूमिहीन लोगों के लिए जमींने दान में दी होंगी। भारत के मौजूदा सामाजिक, राजनीतिक और वैचारिक वातावरण को देखते हुए सचमुच उनके लिए यह यकीन करना आसान भी नहीं है। लेकिन भारत और विनेबा के जीवन की इस सच्ची कहानी से गुजरना उनके लिए भी कम रोमांचक नहीं होगा।

विनोबा के व्यक्तिगत जीवन के बाकी प्रसंगों की कहानी फिर कभी परिचय के रूप में भी अभी केवल इतना कि गणित और वैज्ञानिक अध्यात्म को अपने जीवन और चिंतन का आधार बनाने वाले विनोबा एक मौलिक विचारक, आजीवन शिक्षक और अहिंसक कर्मयोगी थे। किसी ने उन्हें आचार्य विनोबा कहा, तो किसी ने संत विनोबा और कईयों ने तो उन्हें ऋषि विनोबा और बाबा विनोबा तक कहकर संबोधित किया, लेकिन भारतीय समाज के एक बडे हिस्से के लिए वे केवल उनके अपने विनोबा रहे। गांधीजी के जाने के बाद भारतीय समाज के सभी तबकों ने जिस पर सहज और सबसे अधिक भरोसा किया, जिसकी तरफ मार्गदर्शन के लिए देखा, वह निर्विवाद रूप से विनोबा ही कहे जा सकते हैं। ऐतिहासिक शख्सियतों का मूल्यांकन आनेवाली पीढियों के लिए आसान नहीं होता क्योंकि इसके लिए महज दस्तावेजी सबूत ही काफी नहीं होते, इसके लिए तटस्थता, विनम्रता, वैचारिक अनेकांतता और गहरी संवेदनशीलता के साथ-साथ स्वयं अपने जीवन के स्तर पर भी अनुभूतिजन्य प्रयोगशीलता की जरूरत होती है । विनोबा के जीवन को देखने के लिए 'श्रद्धा' और 'भक्ति' के प्रचलित नमूनों से ऊपर उठना होगा, क्योंकि विनोबा स्वयं ही ऐसा सोचते थे । उन्होंने किसी को भी उपना गुरू मानने और किसी को भी अपना चेला बनाने से इनकार कर दिया था।

**3.भूदान यज्ञ की समिधा - ''बिसामपुर का संत''**

भूदान यज्ञ की चर्चा, शास्त्रों, स्मृतियों, पुराणों आदि में न मिलेगी। आचार्य विनोबा भावे उसके आदि प्रस्तोता थे, वही उसके आदि प्रस्तोता थे, वही उसके पहले अधीष्ठाता वही यजमान थे। इस यज्ञ के बारे में सादिश था - 'हवा और धूप एक की नही, सबकी है। वैसे ही जमीन भी। 'कुछ दिन पहले तेलंगाना के छोटे खेतिहरों और खेत मजदूरों ने ऐलान किया था कि अब वह नहीं, उकने खेत भी जाग गए हैं। दान पात्र में दो गावों का ब्यौरा दिया गया था। इसमें से आधे से ऊपर जमीन ऊसर-बंजर - बीहड थी।

भूदान यज्ञ के दिनों सर्वोदय के लिए अनेक नौजवानों ने अपने जीवन का दान कर दिया था। सन् 1950-51 में साम्यवदियों के नेतृत्व में भूपतियों के खिलाफ किसानों का व्यापक आन्दोलन चल रहा था। हालकि भूदान आंदोलन गांवों में एक जटिल आर्थिक और सामाजिक दुर्व्यवस्था को कोई उल्लेखनीय व्यावाहारिक और स्थाई समाधान नही दे पाया

श्रीलाल शुक्ल ने भूदान आंदोलन का संकेतात्मक संदर्भ 'सूनी घाटी का सूरज' तथा 'रागदरबारी' में दिया है, किंतु उसकी सटीक समीक्षा ''बिसामपुर का संत'' में की है। वह समीक्षा उपन्यास में कुछ इस प्राकर प्रस्तुत है - एक ओर हिंसा और लाभ के ऊपर सौहार्द और सहज मानवीय उदारता की विजय के रूप में देखा गया है और इस रूप में उसे सामाजिक विषमता के निवारण का एक अमोध अस्त्र समझा गया है दूसरी और प्रगति विरोधी क्रान्ति विरोधी और बडे भूस्वामियों का पोशक मानकर इसकी अपेक्षा की गई है। पूरी कहानी भूदान यज्ञ और कुंवर जयंती प्रसाद सिंह के इर्द - गिर्द धूमती है।

**4.भूदान आंदोलन का इतिहास** (( Bhoodan Andolan History in Hindi))

देश में स्वतंत्रता के बाद सामान्य कृषक वर्ग को कई समस्याओं का सामना करना पड़ा था, जिसमें भूमि की कमी काफी बड़ी समस्या थी, इसके समाधान हेतु ही भूदान आंदोलन अस्तित्व में आया, ये आंदोलन कोई एक दिन, महीने या वर्ष तक चलने वाला आंदोलन नहीं था, इसमें पूरा एक दशक लगा था । इस मिशन की चर्चा देश के बाहर भी हुयी थी और इसे काफी सराहना भी मिली। आंदोलन के संस्थापक विनोबा भावे के बारे में न्यूयॉर्क टाईम्स में भी छपा था ।

कब शुरू हुआ था?(when did started) 18 अप्रैल 1951 को

कहां शुरू हुआ था? (Where did started)नालगोंडा क्षेत्र में

किसके नेतृत्व में हुआ था ?Who was the founder and leader of this movement) विनोबा भावे

**5.भूदान आंदोलन का उद्देश्य** (Objectives of the Bhoodan Movement)

भूदान आंदोलन का उद्देश्य पूरे देश का उद्धार करना था जिसमें समाज में सबको साथ लेकर आगे बढना था। भूदान आंदोलन सिर्फ भूमि का वितरण नही था बल्कि एक प्रक्रिया थी जिसके अंतर्गत समाज के सभी वर्गों के हितों की रक्षा की गयी थी। भावे ने कहा था कि हम समाज की आर्थिक समस्याओं के कम करना चाहते हैं। भूदान आंदोलन का लक्ष्य देश के पिछडे और शोषित वर्ग को मुख्यधारा में लाना था।

सामाजिक और राजनीतिक परिप्रेक्ष्य में देख जाए तो इस आंदोलन का घोषित उद्देश्य शक्ति का विकेंद्रीकरण करना था, जिसमें गाँव-गाँव तक शक्ति की पहुँच हो, सबका संपति पर अधिकार हो और मजदूरी इत्यादि मामलों में किसी भी तरह की असमानता नहीं हो।

**6.किसने शुरू किया था ?**(Who started it)

आचार्य विनोबा भावे ने भूदान आंदोलन की शुरूआत की थी, विनोबा जी ने गांधीजी के साथ स्वतंत्रता संग्राम में भाग लिया था और लगभग ५ वषज्ञ जेस में बिताये थे। गांधीजी की हत्या के बदा भावे को ही उनका उत्तराधिकारी माना जा रहा था लेकिन उनके उद्देश्य काफी अलग थे, उन्होंने देश के गरीब और भूमि विहीन वर्ग के हितों की रक्षा

की जिम्मेदारी ली थी। भावे ने उनके आदर्शों और सिद्धांतों को आगे बढाते हुए भूमि सुधार कार्यों में विशेष योगदान दिया था । 1951 में भूदान आंदोलन के लिए विनाबा भावे ने हजारों मीलों की पदयात्रा की थी और भू-दाताओं से जमीन दान करने की अपील की थी। भावे की प्रेरणा से जयप्रकाश नारायण जैसे कई बडे समाजवादी नेता इस आंदोलन से जुडे।

**7.भूदान आंदोलन कब और कैसे शुरू हुआ था ?**(When and where did Bhoodan Andolan started)

अ) 18 अप्रैल 1951 को जब विनोबा भावे ने नालगोंडा श्रेत्र के पोचामपेली गाँव में प्रवेश किया जहां कम्युनिस्ट का कब्जा था, तो वहां के भूमि विहीन और पिछडे वर्ग के लोगों ने उनका स्वागत किया, विनोबा ने अछूत कहे जाने वाले लोगों से संवाद बढाया तो उन्होंने भावे को कहा कि यदि उन्हें कुछ भूमि दी जाए तो उनकी स्थिति बेहतर हो सकती हैं, लेकिन सरकार उनके लिए ऐसा कुछ नहीं कर रही हैं। इसके बाद जब वो लोग उनसे ८० एकड जमीन से जुडी समस्टा के बारे में दिशा - निर्देश लेने आये तो विनोबा ने ये सुझाव दिया कि यदि सरकार जमीन की समस्या हल नहीं कर पा रही दो ग्रामीण एक -दूसरे की मदद कर सकते हैं। इस तरह रामचन्द्र नाम के व्यक्ति ने अपनी भूमि दान की, और उनसे प्रेरित हो अन्य भू-मालिकों ने भी १०० एकड़ जमीन दान करने का वादा किया।

आ) 1951 में तीसरी वार्षिक सर्वोदय कांफ्रेंस शिवारामपल्ली में हुयी थी, ये गाँव हैदराबाद से थोडी दूर पर स्थित था। उस समय तेलांगना में कम्युनिस्ट विद्रोह चल रहा था, जिसमें धनी भू-मालिको द्वारा गहीबों के शोषण का विरोध हो रहा था । 11 अप्रैल 1951 को 24 घंटे चली कांफ्रेंस में ये निष्कर्ष निकला कि विनोबा देश में उन क्षेत्रों का दौरा करेगे, जहाँ पर कम्युनिज्म ज्यादा हैं। उस समय ये एक बहुत ही बड़ा और साहसिक निर्णय था ।

इ) आंध्रप्रदेश में घटित हुयी इस आकस्मिक घटना ने भूदान आंदोलन की नींव रख दी । भावे ने कहा कि लालच ही भूमि पत एकत्व अधिकार कारण हैं यदि लोगों में लालच कम हो जाए तो ना केवल सबकी मदद की जा सकेगी।

**8.आंदोलन का प्रसार** (The Movement Expands)

अ) पहली बार हुए भूदान ने विनोबा को पूरे देश में इस आंदोलन को आगे बढाने को प्रेरित किया। अगले कुछ वर्षों में भावे ने इस आंदोलन को एक नई दिशा दी, और उन्हें काफी सफलता भी मिली । भावे ने गाँव-गाँव पद-यात्रा की, जब वो किसी गाँ में पहुँचते तो वो भू-मालिकों से उनकी कुल सम्पति की जानकारी लेते और उन्हें भू-दान के लिए प्रेरित करते। भू-मालिक उपनी इच्छा से कुछ भूमि विनोबा भावे को दे देते और भावेजी अपने कार्यकर्ताओं की सहायता से इस भूमि का पुनःवितरण करवाते। इस तरह भूदान कार्यकर्ताओं की देखरेख में प्राप्त हुयी भूमि वापिस जरूरतमंदों में बांटी जाती थी। इससे गरीब किसान जमींदार या सरकार पर निर्भर होने की जगह अपने लिए काम करने को सक्षम हो जाते थे।

आ) कुछ लोगों का मानना था कि दान दी जाने वाली जमीन बंजर, पथरीली और कृषि के लिए अनुपयुक्त था, लेकिन आंदोलन के अनुसार कोई भी जमीन अनुपयोगी नहीं थी । बावे कहते थे कि भूमि की उपयोगिता से कही ज्यादा ये जरूरी हैं कि लोग एक दूसरे की मदद के लिए आगे आ रहे हैं, और अपनी संपति समाजिक कारणों के लिए दान कर रहे हैं, और यही तो क्रान्ति का बीजारोपण हैं। वैसे भी खहाब गुणवता वाली जमीन का उपयोग चारागाह, वनीकरण और बेघर लोगों को बसाने में किया जा सकता है।

इ) इस तरह भूदान से शुरू हुयी बात ग्रगमदान तक पहुंची और कई लोग गाँव के गाँव दान करने को आगे आये, वास्तव में ये सब सर्वोदय अभियान का हिस्सा था, जिसमें समाज के हर वर्ग के नवजीवन का उदय हो रहा था।

ई) भारत के लगभग ५० मिलियन भूमि-विहीन कृषकों के लिए विनोबा जी ने ५० मिलियन एकड भूमि दान करने का लक्ष्य बनाया था दिससे कि १ एकड भूमि प्रत्येक किसान को मिल सके। यदि कोई किसान का परिवार ५ सदस्यों वाला हो तो ऐसे परिवार के हिस्से में ५ एकड भूमि आ सके । उन्होंने भूमि संपन्न लोगों से आह्वान किया कि

वो अपनी भूमि का छठा हिस्सा भूमि - हीनों को दान कर दे। एक अनुमान के अनुसार उस समय लगभग ३०० मिलियन एकड़ कृषि युक्त भूमि थी जिसे दान दिया जा सकता था ।

**9.आंदोलन की समाप्ति**

विनोबा भावे ने भूमि विहीन लोगों के लिए पूरे देश में भूमि-वंचितों तक भूदान आंदोलन पहुंजाने का निर्णय किया था, इसलिए जो आंदोलन निजी स्तर पर शुरू हुआ था वो राष्ट्रीय आंदोलन बन गया। लेकिन १९७१ की शुरूआत में इसका महत्व बदलने लगा एव भूदान की जगह ग्रामदान का चलन बढा, इस दान में किसी गाँव का अधिकतर हिस्सा ग्रामीणों में सभी परिवारों को बराबर बाँट दिया जाता था, हालांकि भूदान तब भी हो रहा था लेकिन कम हो गया था।

वैसे भूदान आंदोलन गैर-आदिवासी इलाकों में नहीं पहुंच सका था, इसलिए भी समय के साथ कमजोर हो गया था। हालांकि आंदोलन में कई उतार-चढाव आये लेकिन १९६९ में भूदान तक लगभग ४ मिलियन एकड भूमि दान की जा चूकी थी।

इसके अतिरिक्त संपतिदाव, श्रमदान, जीवनदान (आंदोलन में अपना जीवन देना), साधनदान (कृषि कार्यों के लिए साधन-उपकरण दान देना) जैसे कई कार्यक्रम हुए। वैसे संपति दान भूदान के साथ शुरू नही हुआ था लेकिन भूमि विहीन लोगों के पास इस भूमि पर काम शुरू करने के लिए साधन नही थे इसलिए संपतिदान अस्तित्व में आया। आचार्यजी ने कहा कि वो शुरू से जानते थे कि ये समस्या आयेगी, लेकिन जडों को मजबूत करना जरूरी होता हैं, शाखाएं स्वतः निकल आती हैं, और ये बात सबको पता थी कि समस्या की जड भूमि की कमी होना है। इस तरह भूदान आंदोलन से ना केवल भूमि विहीन लोगों को भूमि की कमी होने हैं। इस तरह भूदान आंदोलन से ना केवल भूमि विहीन लोगों को भूमि मिली बल्कि गाँधीवादी विचारधारा का विस्तार भी हुआ।

**उपसंहार**

भारतीय लोगतांत्रिक व्यवस्था में हजारों किस्म की विसंगतियों और विडम्बानाओं को करीब से देखते रची गई अनेक दुर्लभ कृतिय इन के समकालीन जीवन में सर्वोत्तम उपन्यास, व्यंग्य-निबंध रचनाऐ और आलोचना, निबंध आदि के हिंदी सुप्रसिद लेखक श्री लाल शुक्ल जी के बारे में शोध प्रबंध प्रस्तुतकर एम. फिल. पि.एचडि उपाधि पाकर एक शोधार्थी के रूप में मेरा जन्म भी सार्थक हुई ।

बिसामपुर का संत समकालीन जीवन की ऐसी महागाथा है जिसका फलक बडा विस्तीर्ण है जो एक साथ कई स्तरों पर चलती है। एक ओर यह भूदान आंदोलन की पृष्ठभूमि में स्वांतत्योत्तर भारत में सत्ता के व्याकरण और उसी क्रम में विनोबा भावे के नेतृत्व में चलाये गए भूदान यज्ञ और ग्रामदान आंदोलन का प्रसंग आया है ।

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# EFFECT OF YOGIC PRACTICES ON SELECTED HEALTH RELATED PHYSICAL FITNESS AND PHYSIOLOGICAL VARIEBLES OF HIGH SCHOOL BOYS

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## Introduction

Importance of physical fitness is nurtured only when man exhibits his innocence to stand as a complete individual in the society. The society believes that to lead successful life one should attain victories in all his ventures. But success should not be assessed through number of victories; it should be assessed only through pains and problems that you overcome.

It is only through physical fitness one can achieve the conservation of energy, during work, sense of humor, the reality of personality. Apart from being gaining mental toughness to face even failures as a part of victory, which definitely plays a major role in our life which everybody expects to meet success for the ultimate satisfaction?

A sound mind in a sound body is man's most precious possession. Physical fitness develops the organic fitness is the basis of dynamic and creative activity. By participating in vigorous physical activities, physical strength and organic vigour can be improved to a large extent. The building of physical strength helps one to have good endurance to withstand strain and be efficient in the performance of activities.

## Statement of the Problem

The purpose of this study was to assess the effect of yogic practices on selected health related physical fitness and physiological variables among high school boys.

## Hypothesis

It was hypothesized that there would be significant improvement due to 12 weeks yogic practices on selected health related physical fitness variables flexibility, cardiovascular endurance muscular endurance and body mass index of high school boys.

## Methodology

The purpose of the study was to find out effect of yogic practices on selected health related physical fitness and physiological variables among high school boys . 30 High school boys from Z.P. High School, Lingapuram, Ramakuppam Mandal, Chittoor District (A.P) were randomly selected as subjects and their age was between 12 and 15 years. They were assigned into two groups of which one group served as yogic practices groups, and the other group served as control group.

**Dépendent Variables**

**Health Related Physical Fitness Variables**

1. Flexibility
2. Cardiovascular Endurance
3 .Muscular Endurance

4.Body Mass Index

**Physiological Variables**

1.Systolic Blood Pressure
2.Diastolic Blood Pressure
3.Resting Pulse Rate
4.Respiratory Rate

**Independent Variables**

1.Yogic practices

**Experimental Design**

The study was formulated as a true random group design, consisting of a pre-test and post-test. The subjects (n=30) were randomly assigned to two equal groups of 15 High school boys in each. The groups were assigned as Experimental Groups and control group respectively. Pre tests were conducted for all the subjects on selected health related physical fitness and physiological variables such as flexibility, cardiovascular endurance, muscular endurance and body mass index, systolic blood pressure, diastolic blood pressure, resting pulse rate and respiratory rate. The experimental group participated in yogic practices for a period of 12 weeks.The post tests were conducted on the above said dependent variables after a period of yogic practices. The differences between the initial and final scores on selected variables were considered as the effect of 12 weeks yogic practices. To test statistical significance of the differences, ANCOVA was employed. In all cases 0.05 level was fixed as significance to accept or reject the formulated hypotheses

**Criterion Measures**

1. Flexibility was measured using sit and reach test.
2. Cardio vascular endurance was measured through 12 minutes run/ walk test.
3. Muscular Endurance was measured through sit ups.
4. Systolic Blood Pressure and Diastolic Blood Pressure were measured through Sphygmomanometer and stethoscope.
5. Resting pulse rate was measured by counting pulses at radial artery using the fingers in a minute.
6. Respiratory rate was measured by counting the number of times the chest is raising in a minute.

**Results on Flexibility**

**Table I**
**Computation of Analysis of Covariance On Flexibility**

| Speed Avg | Experimental group | Control group | Source of Variance | Sum of Squares | Df | Mean Squares | Obtained F |
|---|---|---|---|---|---|---|---|
| Pre Test Mean | 5.53 | 6.13 | Between | 2.70 | 1 | 2.70 | 0.46 |
| | | | Within | 163.47 | 28 | 5.84 | |
| Post Test Mean | 8.80 | 6.60 | Between | 36.30 | 1 | 36.30 | 7.26* |
| | | | Within | 140.00 | 28 | 5.00 | |
| Adjusted Post Test Mean | 9.02 | 6.38 | Between | 51.50 | 1 | 51.50 | 27.09* |
| | | | Within | 51.32 | 27 | 1.90 | |
| Mean Diff | 3.27 | 0.47 | | | | | |

Table F-ratio at 0.05 level of confidence for 1 and 28 (df) =4.19, 1 and 27(df) =4.21 .* Significant

The pre-test mean on experimental group was 5.53, and control group was 6.13 and the obtained F value was 0.46, which was less than the required F value of 4.19 to be significant. Hence, it was not significant and the groups were equal at initial stage.
The comparison of post-test means, experimental group 8.80 and control group 6.60 proved to be significant at 0.05 level as the obtained F value 7.26 was greater than the required table F value of 4.19 to be significant at 0.05 level.
Taking into consideration the initial and final mean values adjusted post-test means were calculated and the obtained F value of 27.09 was greater than the required F value to be significant 4.21 and hence, there was significant difference. Thus, it was proved that experimental group gained mean difference on physiological variable, Flexibility 3.27 was due to yogic practices given to stressed software executives was found to be significant at 0.05 level.

**Results on Cardiovascular Endurance**

**Table II**
**Computation of Analysis of Covariance On cardiovascular Endurance**

| | Experimental Group | Control Group | Source of Variance | Sum of Squares | Df | Mean Squares | Obtained F |
|---|---|---|---|---|---|---|---|
| Pre Test Mean | 1818.00 | 1856.67 | Between | 11213.33 | 1 | 11213.33 | 0.64 |
| | | | Within | 488423.33 | 28 | 17443.69 | |
| Post-Test Mean | 1969.33 | 1885.00 | Between | 53340.83 | 1 | 53340.83 | 4.69* |
| | | | Within | 318493.33 | 28 | 11374.76 | |
| Adjusted Post Test Mean | 1971.34 | 1882.99 | Between | 57233.44 | 1 | 57233.44 | 4.93* |
| | | | Within | 313213.88 | 27 | 11600.51 | |
| Mean Diff | 151.33 | 28.33 | | | | | |

Table F-ratio at 0.05 level of confidence for 1 and 28 (df) =4.19, 1 and 27(df) =4.21 .* Significant

The pre-test mean on experimental group was 1818.00, and control group was 1856.67 and the obtained F value was 0.64, which was less than the required F value of 4.19 to be significant. Hence, it was not significant and the groups were equal at initial stage. The comparison of post-test means, experimental group 1969.33 and control group 1885.00 proved to be significant at 0.05 level as the obtained F value 4.69 was greater than the required table F value of 4.19 to be significant at 0.05 level.Taking into consideration the initial and final mean values adjusted post-test means were calculated and the obtained F value of 4.93 was greater than the required F value to be significant 4.21 and hence, there was significant difference. Thus, it was proved that experimental group gained mean difference on physiological variable, Cardiovascular Endurance 151.33 was due to yogic practices given to stressed software executives was found to be significant at 0.05 level.

**Results on Muscular Endurance**

**Table III**
**Computation of Analysis of Covariance on Muscular Endurance**

| | Experimental Group | Control | Source of Variance | Sum of Squares | Df | Mean Squares | Obtained F |
|---|---|---|---|---|---|---|---|
| Pre Test Mean | 35.60 | 36.67 | Between | 8.53 | 1 | 8.53 | 0.36 |
| | | | Within | 668.93 | 28 | 23.89 | |
| Post Test Mean | 38.07 | 35.73 | Between | 40.83 | 1 | 40.83 | 2.00 |
| | | | Within | 571.87 | 28 | 20.42 | |
| Adjusted Post Test Mean | 38.49 | 35.31 | Between | 74.60 | 1 | 74.60 | 12.86* |
| | | | Within | 156.58 | 27 | 5.80 | |
| Mean Diff | 2.47 | -0.93 | | | | | |

Table F-ratio at 0.05 level of confidence for 1 and 28 (df) =4.19, 1 and 27(df) =4.21 .* Significant

The pre-test mean on experimental group was 35.60, and control group was 36.67 and the obtained F value was 0.36, which was less than the required F value of 4.19 to be significant. Hence, it was not significant and the groups were equal at initial stage. The comparison of post test means, experimental group 38.07 and control group 35.73 proved to be insignificant at 0.05 level as the obtained F value 2.00 was lesser than the required table F value of 4.19 to be significant at 0.05 level. Taking into consideration the initial and final mean values adjusted post test means were calculated and the obtained F value of 12.86 was greater than the required F value to be significant 4.21 and hence, there was significant difference. Thus, it was proved that experimental group gained mean difference on physiological variable, Muscular Endurance 2.47 was due to yogic practices given to stressed software executives was found to be significant at 0.05 level.

**Results on Body Mass Index**

**Table IV**
**Computation Of Analysis of Covariance on Body Mass Index**

| | Experimental group | Control | Source of Variance | Sum of Squares | Df | Mean Squares | Obtained F |
|---|---|---|---|---|---|---|---|
| Pre Test Mean | 19.94 | 19.79 | Between | 0.17 | 1 | 0.17 | 0.77 |
| | | | Within | 6.21 | 28 | 0.22 | |
| Post Test Mean | 19.20 | 19.75 | Between | 2.32 | 1 | 2.32 | 15.18* |
| | | | Within | 4.29 | 28 | 0.15 | |
| Adjusted Post Test Mean | 19.14 | 19.80 | Between | 3.17 | 1 | 3.17 | 60.01* |
| | | | Within | 1.43 | 27 | 0.05 | |
| Mean Diff | -0.74 | -0.03 | | | | | |

Table F-ratio at 0.05 level of confidence for 1 and 28 (df) =4.19, 1 and 27(df) =4.21 .* Significant

The pre test mean on experimental group was 19.94, and control group was 19.79 and the obtained F value was 0.77, which was less than the required F value of 4.19 to be significant. Hence, it was not significant and the groups were equal at initial stage. The comparison of post test means, experimental group 19.20 and control group 19.75 proved to be significant at 0.05 level as the obtained F value 15.18 was greater than the required table F value of 4.19 to be significant at 0.05 level. Taking into consideration the initial and final mean values adjusted post test means were calculated and the obtained F value of 60.01 was greater than the required F value to be significant 4.21 and hence, there was significant difference. Thus, it was proved that experimental group gained mean difference on physiological variable, Body mass index -0.74 was due to yogic practices given to stressed software executives was found to be significant at 0.05 level.

**Results on Blood Pressure**

**Table V**
**Computation of Analysis of Covariance of Systolic Blood Pressure**

| | Experimental Group | Control | Source of Variance | Sum of Squares | Df | Mean Squares | Obtained F |
|---|---|---|---|---|---|---|---|
| Pre Test Mean | 122.20 | 119.47 | Between | 56.03 | 1 | 56.03 | 1.06 |
| | | | Within | 1484.13 | 28 | 53.00 | |
| Post Test Mean | 120.13 | 120.87 | Between | 4.03 | 1 | 4.03 | 0.08 |
| | | | Within | 1409.47 | 28 | 50.34 | |
| Adjusted Post Test Mean | 118.83 | 122.17 | Between | 80.73 | 1 | 80.73 | 37.94* |
| | | | Within | 57.45 | 27 | 2.13 | |
| Mean Diff | -2.07 | 1.40 | | | | | |

Table F-ratio at 0.05 level of confidence for 1 and 28 (df) =4.19, 1 and 27(df) =4.21 .* Significant
The pre test mean on experimental group was 122.20, and control group was 119.47 and the obtained F value was 1.06, which was less than the required F value of 4.19 to be significant. Hence, it was not significant and the groups were equal at initial stage. The comparison of post test means, experimental group 120.13 and control group 120.87 proved to be insignificant at 0.05 level as the obtained F value 0.08 was lesser than the required table F value of 4.19 to be significant at 0.05 level. Taking into consideration the initial and final mean values adjusted post test means were calculated and the obtained F value of 37.94 was greater than the required F value to be significant 4.21 and hence, there was significant difference. Thus, it was proved that experimental group gained mean difference on physiological variable, Systolic Blood Pressure -2.07 was due to yogic practices given to stressed software executives was found to be significant at 0.05 level.

**Results on Systolic Blood Pressure**

**Table VI**
**Computation of Analysis of Covariance on Systolic Blood Pressure**

| | Experimental Group | Control | Source of Variance | Sum of Squares | Df | Mean Squares | Obtained F |
|---|---|---|---|---|---|---|---|
| Pre Test Mean | 122.20 | 119.47 | Between | 56.03 | 1 | 56.03 | 1.06 |
| | | | Within | 1484.13 | 28 | 53.00 | |
| Post Test Mean | 120.13 | 120.87 | Between | 4.03 | 1 | 4.03 | 0.08 |
| | | | Within | 1409.47 | 28 | 50.34 | |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Adjusted Post Test Mean | 118.83 | 122.17 | Between | 80.73 | 1 | 80.73 | 37.94* |
| | | | Within | 57.45 | 27 | 2.13 | |
| Mean Diff | -2.07 | 1.40 | | | | | |

Table F-ratio at 0.05 level of confidence for 1 and 28 (df) =4.19, 1 and 27(df) =4.21 .* Significant
The pre test mean on experimental group was 122.20, and control group was 119.47 and the obtained F value was 1.06, which was less than the required F value of 4.19 to be significant. Hence, it was not significant and the groups were equal at initial stage.The comparison of post test means, experimental group 120.13 and control group 120.87 proved to be insignificant at 0.05 level as the obtained F value 0.08 was lesser than the required table F value of 4.19 to be significant at 0.05 level.Taking into consideration the initial and final mean values adjusted post test means were calculated and the obtained F value of 37.94 was greater than the required F value to be significant 4.21 and hence, there was significant difference. Thus, it was proved that experimental group gained mean difference on physiological variable, Systolic Blood Pressure -2.07 was due to yogic practices given to stressed software executives was found to be significant at 0.05 level.

**Results on Diastolic Blood Pressure**

**Table VII**
**Computation of Analysis of Covariance on Diastolic Blood Pressure**

| | Experimental Group | Control | Source of Variance | Sum of Squares | Df | Mean Squares | Obtained F |
|---|---|---|---|---|---|---|---|
| Pre Test Mean | 84.87 | 82.73 | Between | 34.13 | 1 | 34.13 | 1.37 |
| | | | Within | 698.67 | 28 | 24.95 | |
| Post Test Mean | 82.47 | 83.60 | Between | 9.63 | 1 | 9.63 | 0.41 |
| | | | Within | 661.33 | 28 | 23.62 | |
| Adjusted Post Test Mean | 81.46 | 84.60 | Between | 70.39 | 1 | 70.39 | 42.45* |
| | | | Within | 44.77 | 27 | 1.66 | |
| Mean Diff | -2.40 | 0.87 | | | | | |

Table F-ratio at 0.05 level of confidence for 1 and 28 (df) =4.19, 1 and 27(df) =4.21 . * Significant
The pre test mean on experimental group was 84.87, and control group was 82.73 and the obtained F value was 1.37, which was less than the required F value of 4.19 to be significant. Hence, it was not significant and the groups were equal at initial stage.The comparison of post test means, experimental group 82.47 and control group 83.60 proved to be insignificant at 0.05 level as the obtained F value 0.41 was lesser than the required table F value of 4.19 to be significant at 0.05 level.Taking into consideration the initial and final mean values adjusted post test means were calculated and the obtained F value of 42.45 was greater than the required F value to be significant 4.21 and hence, there was significant difference. Thus, it was proved that experimental group gained mean difference on physiological variable, Diastolic Blood Pressure -2.40 was due to yogic practices given to stressed software executives was found to be significant at 0.05 level.

**Results on Resting Pulse Rate**

**Table VII**
**Computation of Analysis of Covariance on Resting Pulse Rate**

| | Experimental Group | Control | Source of Variance | Sum of Squares | Df | Mean Squares | Obtained F |
|---|---|---|---|---|---|---|---|
| Pre Test Mean | 84.60 | 83.13 | Between | 16.13 | 1 | 16.13 | 0.49 |
| | | | Within | 931.33 | 28 | 33.26 | |
| Post Test Mean | 82.13 | 83.93 | Between | 24.30 | 1 | 24.30 | 0.78 |
| | | | Within | 868.67 | 28 | 31.02 | |
| Adjusted Post Test Mean | 81.45 | 84.62 | Between | 74.16 | 1 | 74.16 | 36.93* |
| | | | Within | 54.22 | 27 | 2.01 | |
| Mean Diff | -2.47 | 0.80 | | | | | |

Table F-ratio at 0.05 level of confidence for 1 and 28 (df) =4.19, 1 and 27(df) =4.21 .* Significant
The pre-test mean on experimental group was 84.60, and control group was 83.13 and the obtained F value was 0.49, which was less than the required F value of 4.19 to be significant. Hence, it was not significant and the groups were equal at initial stage.The comparison of post-test means, experimental group 82.13 and control group 83.93 proved to be insignificant at 0.05 level as the obtained F value 0.78 was lesser than the required table F value of 4.19 to be significant at 0.05 level.Taking into consideration the initial and final mean values adjusted post-test means were calculated and the obtained F value of 36.93 was greater than the required F value to be significant 4.21 and hence, there was significant difference. Thus, it was proved that experimental group gained mean difference on physiological variable, Resting Pulse rate -2.47 was due to yogic practices given to stressed software executives was found to be significant at 0.05 level.

**Results on Respiratory Rate**

**Table VIII**
**Computation of Analysis of Covariance on Respiratory Rate**

| | Experimental Group | Control | Source of Variance | Sum of Squares | Df | Mean Squares | Obtained F |
|---|---|---|---|---|---|---|---|
| Pre Test Mean | 18.27 | 18.73 | Between | 1.63 | 1 | 1.63 | 0.09 |
| | | | Within | 519.87 | 28 | 18.57 | |
| Post Test Mean | 16.73 | 19.07 | Between | 40.83 | 1 | 40.83 | 3.31 |
| | | | Within | 345.87 | 28 | 12.35 | |
| Adjusted Post Test Mean | 16.92 | 18.88 | Between | 28.79 | 1 | 28.79 | 45.10* |
| | | | Within | 17.24 | 27 | 0.64 | |
| Mean Diff | -1.53 | 0.33 | | | | | |

Table F-ratio at 0.05 level of confidence for 1 and 28 (df) =4.19, 1 and 27(df) =4.21 . * Significant The pre test mean on experimental group was 18.27, and control group was 18.73 and the obtained F value was 0.09, which was less than the required F value of 4.19 to be significant. Hence, it was not significant and the groups were equal at initial stage. comparison of post-test means, experimental group 16.73 and control group 19.07 proved to be insignificant at 0.05 level as the obtained F value 3.31 was lesserr than the required table F value of 4.19 to be significant at 0.05 level.Taking into consideration the initial and final mean values adjusted post-test means were calculated and the obtained F value of 45.10 was greater than the required F value to be significant 4.21 and hence, there was significant difference. Thus, it was proved that experimental group gained mean difference on physiological variable, Respiratory Rate -1.53 was due to yogic practices given to stressed software executives was found to be significant at 0.05 level.

**Conclusions**

It was concluded that 12 weeks yogic practices significantly improved selected health related physical fitness variable, such as flexibility , cardiovascular endurance , muscular endurance, body mass Index, systolic blood pressure, diastolic blood pressure, resting pulse rate, resting pulse rate, respiratory rate of high school boys.

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శ్రీపాద సుబ్రహ్మణ్యశాస్త్రి (23-04-1891 -- 25-02-1961) కవి, పండితులు, వైద్యులు, పత్రికాధిపతి, సంపాదకులు, నాటకకర్త, నటుడు, నాటక ప్రయోక్త, అవధాని, నవలాకారుడు, వ్యాసకర్త, బహుగ్రంథకర్త అన్నింటినీ మించి తెలుగు కథకుడు. తొలి తరం కథారచయితల్లో ఒకరు.

శుద్ధ శ్రోత్రియ కుటుంబంలో శాస్త్రిగారు శ్రీ లక్ష్మీపతి సోమయాజులు, మహాలక్ష్మీ సోదెమ్మ దంపతులకి 23-04-1891 న నేటి తూర్పుగోదావరి జిల్లా రామచంద్రాపురం తాలూకాలోని పొలమూరు గ్రామంలో జన్మించారు. వీరి తండ్రి వేదం, శ్రౌతం, జ్యోతిష్యం, స్మార్తం, ధర్మశాస్త్రం, మంత్రశాస్త్రంలో గొప్ప పేరున్నవారు. ఆంగ్లచదువులు స్వధర్మ నష్టమని వీరి భావన. అలాగని తెలుగునిచేరదీయలేదు. ఇంట్లో అంతా సంస్కృతమే. కూడుబెట్టే భాష సంస్కృతమేనని వీరి నమ్మకం. అందుకే శాస్త్రిగారిని మూడవ తరగతిలోనే 'బడి' మాన్పించారు. కులవిద్యలు కూటికనవసరమని 'వైదిక విద్య'లో ప్రవేశపెట్టారు. తెలుగు, ఇంగ్లీషు చదువుకోవాలనే బలమైన వీరి కోరికకు తండ్రి, చిన్నన్నలు అడ్డుగోడగా నిలిచారు. వీరి పెద్దన్న గారి ప్రోత్సాహంతో తెలుగు వచనం, కావ్యాలు చదవడం మొదలుపెట్టారు. వీరేశలింగంగారిని, బ్రహ్మసమాజ సిద్ధాంతాలని చదివిన మీదట కులవిద్యల మీద నిరసన పెరిగింది. తెలుగు మీద పద్యం కంటే వచనం మీద ఇష్టం పెరిగింది. చిన్నప్పటి నుంచే కథలు రాయాలనే కోరిక మెండుగా ఉన్నా 1915 నాటికి కథరాసే అవకాశం అనుకోకుండా వీరికి కలిగింది. 'ఆంధ్రపత్రిక'లో పనిచేసే కోటంరాజు పున్నయ్య పత్రిక కోసం అప్పటికప్పుడు ఒక కథ రాసివ్వమంటే ఒక గంట వ్యవధిలో రాసిచ్చారు. దానిపేరు 'ఇరువురమొక్కచోటికే పోదము' ఇది వీరి తొలికథ.

మొత్తంగా వీరివి 75 కథలు ఇందులో 65 సాంఘీకాలు, 10 చారిత్రకాలు అని, వీరి కథల మీద పరిశోధన చేసిన 'చామర్తి కనకయ్య' గారు చెప్తారు. మొదట్లో సరళ గ్రాంథికంలో రచనలు చేసినా, తర్వాత పూర్తి వ్యావహారికంలో కథలు రాశారు. తెలుగుతనానికి చిరునామాగా మారారు. జాతి కథకునిగా గుర్తింపు పొందారు.

ఆత్మాభిమానం మెండుగా గల మనిషి వ్యక్తిగతంగానూ, సాహిత్య, కళారంగాల్లోనూ మచ్చలేని జీవితం వీరిది. సున్నిత మనస్కులు, విశాల భావాలు గలవారు, కొన్ని విషయాల్లో చాలా ఖచ్చితమైన మనిషి. ముఖ్యంగా తెలుగు భాషంటే వల్లమాలిన మమకారం కలిగిన వీరి 'శుభీకే శిర ఆరోహ!' అనే కథ హిందీ ఆధిపత్యాన్ని నిరసించేదే. అవకాశమున్న ప్రతిచోటా తెలుగుభాష, సంస్కృతుల గొప్పతనాన్ని తెలియజేస్తారు. పరాయిభాషల ఆధిపత్యాన్ని నిరసిస్తారు. అందుకే 'తెనుగు భాషలో మధురాతి మధురమైన తెనుగు భాషలో - నా జాతివాళ్ళు చిన్నచూపే చూస్తూ ఉండినా, మాధుర్యం గుర్తించి శక్తిన్నీ అవగాహన చేసుకుని పాశ్చాత్యులు కూడా ముక్తకంఠంతో కీర్తించిన నా మాతృభాషలో కలం పట్టి నాలుగు బంతులు

రాసే అదృష్టం నాకు కలిగింది' అని తెలుగు కథలు రాసి మురిసిన వారు, మనం మురుసుకునేలా చేసినవారు శ్రీపాద.

తెలుగు భాషలోని తీయదనం స్త్రీల దగ్గరే ఉందంటూ "జాతీయమైన తెలుగు భాష కావాలంటే స్త్రీల దగ్గరే నేర్చుకోవాలి, మర్యాదగల తెలుగు భాష కావాలంటే మళ్ళీ క్షత్రియ రమణుల దగ్గర నేర్చుకోవాలి, మరో దారి లేదు" అంటారు. ఇటువంటి తెలుగులో తెలుగు కథానిక/కథ జీవనదిలా కొనసాగుతోంది. ప్రాచీన కాలం నుంచి, పాశ్చాత్య సాహిత్య ప్రభావం పడిన దగ్గర నుంచీ కథగా, కథానికగా ప్రవహిస్తూనే ఉంది. ఇతర జాతులకి, దేశాలకి ఎంతో కథావాఙ్మయ భిక్ష పెట్టిన గడ్డ, భారతగడ్డ. భారతీయ కథా సాహిత్యంలో తలమానికంగా చెప్పే 'గుణాఢ్యుని', 'బృహత్కథ' తెలుగు నేలపై పురుడుపోసుకుంది. అటువంటి తెలుగు నేలపై ఎంతో కథాసాహిత్యం పరిఢవిల్లుతూనే ఉంది. అసలు కథ చెప్పడం, వినడం మానవ స్వభావంలో ఒక భాగం అందుకే కథ మనిషి జీవితంతో పెనవేసుకుపోయింది. ప్రతిభావంతులైన కథకులు తమ కథల ద్వారా వారి కాలం నాటి సమాజాన్ని చిత్రించారు. తనను తాను దిద్దుకోటానికి సమాజాలకి అవి పాఠాలుగా నిలిచాయి. వారు భావితరాలకి ఆదర్శంగా నిలిచారు. అటువంటి తెలుగు కథకుల్లో శ్రీపాద ఒకరు. ఆధునిక తొలి తెలుగు కథగా 'దిద్దుబాటు' ఆ కథకునిగా గురజాడ తెలుగు కథానికకు మేలుకొలుపు పాడారు. వారి ఆశయాలకు కొనసాగింపా? అన్నట్లు శ్రీపాద సుబ్రహ్మణ్యశాస్త్రి గారి కథలు నిలుస్తాయి.

శ్రీపాద తమ కథలను 'చిన్నకథ' లనే పిలిచారు. కథ, కథానిక లన్న పేరు వాడలేదు. వీరి కథలు పెద్దవిగా ఉండటం వలన కొందరు విమర్శకులు వీటిని 'పెద్దకథలు' అన్నారు. 'చిన్న నవలలు' అనీ, 'నవలిక' అని కొందరు పిలిచారు. ఏమైనా శ్రీపాద వారి కథలు లక్షణపరంగా సంప్రదాయకథలు,ఆధునిక కథానికల కలబోతగా ఉంటాయి.

కథా వస్తువుని ఎంచుకోవడం, కథను నడిపించటంలో వీరిది ప్రత్యేకశైలి. సామాజిక సమస్యలని గుర్తించి వాటి నేపథ్యంలో కథావస్తువును ఎంచుకోవడం వీరి చాలా కథలు ఈ కోవకిందకి వస్తాయి. అయితే ఎక్కడా సంఘటనలే కథను కల్పించినట్లు అనిపించదు. కథ ఎంపికకు మూలమైన ఆ సంఘటనలే కథలో సహజంగా ఇమిడి పోయేలా అల్లుకోవడం, సన్నివేశాలు కల్పించుకోవడం వీరి ప్రతిభకు నిదర్శనం. అయితే కొన్ని కథలు అప్పటి వాస్తవ సంఘటనలని ఆధారం చేసుకుని రాశారు. ఉదా. 'అన్నంతపనీ జరిగింది' కథలో వ్యావహారిక భాషని సమర్థిస్తూ రాసిన ఈ వాక్యాలు కల్పించినట్లుగాక సహజంగా కథలో అమరిపోయేలా ....." అదేనోయ్! వ్యావహారికం దేశం అంతటా అప్పుడే పాకిపోయింది కాదూ! మహాదిట్టమైన వాడోయ్ గిడుగు రామమూర్తి పంతులు. నవీన వాఙ్మయ నిర్మాతలయిన యువకులనందర్నీ తోపు చేసుకున్నాడు పంతులు. ముసలి తలకాయలు గ్రాంథికమో అంటూ యెంత గోలపెడితే మాత్రం ఆ వాదం యింకెన్నాళ్ళ నిలుస్తుందీ! మా అమ్మాయిక్కూడా రామమూర్తి పంతులు వాదమే నచ్చింది...." అంటూ వ్యావహారిక భాష ప్రాముఖ్యాన్ని దాని 'చేవ'ని, పెద్దల ప్రయత్నాలని, గ్రాంథిక వాదులగోలని నేర్పుగా ప్రస్తావిస్తారు. అలాగే 'శుభకే శిర ఆరోహ!" అనే కథలో హిందీ భాష, సంస్కృతులు తెలుగుపై సాగించే పెత్తనాన్ని ఎత్తిచూపి ఎద్దేవా చేస్తారు. అలాగే 'ఇలాంటి తవ్వాయి వస్తే' కథతో కింది కులాలు మతాలు మారటం, గౌరవం కోసం, రక్షణకోసం ప్రయత్నించటం వివరిస్తారు. ఇటువంటి కథలతో పాటు మిగతా కథల్లో కనిపించే అంశాలు చూద్దాం... వైదిక బ్రాహ్మణ కుటుంబాల్లోని స్త్రీలు, రెడ్డి, వెలమ, క్షత్రియ స్త్రీలు కనిపిస్తారు. వీరితో చిన్నవాళ్ళ, పెద్దవాళ్ళు, దాసీలు, సంసారులు, వేశ్యలు, వితంతువులు, రాణివాసం వారు పలు తెరగులు. వీరి సమస్యలని

పలుకోణాల నుండి చిత్రించారు. ముఖ్యంగా స్త్రీల శ్రమకి గౌరవం లేకపోవడం, పురుషాధిపత్య సమాజంలో స్త్రీల పరిస్థితి కింది కులాలు అభ్యున్నతి, ప్రేమ వివాహాలు మనుషుల కోసం మతం, శాస్త్రాలు, దేవుళ్ళు ఉపయోగపడాలి గాని, వాటికోసం మనుషులు అన్నట్లు ఉండకూడదంటారు. మనిషికి గుణం ముఖ్యం గాని కులం కాదు అంటారు. ఇలా వీరు ఆనాడు లేవనెత్తిన పలు సమస్యల్లో కొన్ని లేవు. కొన్ని అట్లానే ఉన్నాయి. ముఖ్యంగా స్త్రీల విషయం.

ఇంటిపని, వంటపని, పిల్లల్ని కనడం, పెంపకం పూర్తిగా స్త్రీలచే అనే భావం నేటి సమాజంలో ఇంకా ఉంది. సాంకేతికంగా వచ్చిన అభివృద్ధి జరిగి అందుబాటులోకి వచ్చిన 'గ్రైండర్స్', 'మిక్సీలు', 'వాషింగ్‌మెషిన్', 'కిచెన్‌వేర్' ఇలాంటికి స్త్రీల పని భారాన్ని తగ్గిస్తున్నా పనిమాత్రం స్త్రీలదే. ఆధునిక కాలంలో ఉద్యోగ బాధ్యతలు చూసుకుంటూనే ఇంటిపని చూసుకోవాలి. శ్రీపాద ఆనాడే స్త్రీ పురుషుల సంబంధాలలోని అసమానతలు, స్త్రీల శ్రమ దోపిడిని చక్కగా క్రమబద్ధీకరించిన కుటుంబ వ్యవస్థలోని పురుషుల స్వార్థాన్ని, స్త్రీల స్వార్థాన్ని, స్త్రీలలో ఉండే రకరకాల మనస్తత్వాలు, అధికారం చెలాయించాలనే పురుషాధిపత్య భావజాలాన్ని చెప్పి స్త్రీలకు మేలు కలిగించే మార్గాన్ని సూచిస్తారు. ఇల్లాలు ఇంటిపని భారంగా భావించదు. పైగా తనవారికోసం తను పని చేసుకుంటున్నందుకు ఆనందం కూడా ఉంటుంది. అయితే ప్రేమగా, ఇష్టపూర్వకంగా స్వేచ్ఛగా పనిచేయడం వేరు. ఆ పనులు ఆమె, ఆడపిల్లలు తప్ప మగపిల్లలు, మగవాళ్ళు చేయడం నామోషి అనడం, అది ఆడవాళ్ళ పనే అనడం నిర్బంధం అవుతుంది. శ్రీపాదకథల్లో ఈ రెండురకాల పని అంటే పరాయికరణకు గురైన, గురికాని ఆడవాళ్ళ శ్రమకి మధ్య తేడాను చూపిస్తారు. ఆ కాలంలో వితంతువుల సమస్య తగ్గినా ఇంట్లో స్త్రీలకి తప్పటం లేదు. ఇటువంటి ఒకటి రెండు కథలని స్త్రీ సమస్యల నేపథ్యంలోంచి చూద్దాం.

**కొత్తచూపు** ఈ కథ పూర్తిగా కొత్త పద్ధతిలో నడిచింది. ఇంగ్లీషు చదువులు, ఆత్మరక్షణ విద్యలు, పెళ్ళి విషయంలో అమ్మాయికి స్వేచ్ఛ ఉండటం నలుగురులో స్వేచ్ఛగా తమ అభిప్రాయాలు చెప్పగలగడం ఈ కథలో చూస్తాం. నవంబరు 1948లో ఈ కథ అచ్చులో వచ్చింది. "ముదితల్ నేర్వరాని విద్యగలదే ముద్దార నేర్పించినన్" అని మన పెద్దలు చెప్పిన మాటకి లక్ష్యప్రాయంగా రాసిన కథా అనిపిస్తుంది. 'ఆకాశంలో సగం' అని మావో అన్నట్లు. స్త్రీలు అన్ని రంగాల్లో రాణించాలని ఆనాడు శ్రీపాద ఉద్దేశించి రాసిన కథ ఇది.

ఈ కథలో ప్రధాన పాత్ర 'అన్నపూర్ణ'. ఈమె రామశాస్త్రి, రాజేశ్వరిల ఏకైక కుమార్తె. తల్లిదండ్రులు ఈమెను ఆధునిక పద్ధతుల్లో పెంచారు. వైదిక కుటుంబాల్లో కట్టుబాట్లు దాటుకుని ముందుకు రావాలని పైకి కనిపించే వాస్తవం. కాని ఆడపిల్లలని తక్కువగా చూడకుండా వాళ్ళని చదివించాలి అని ఆనాటి సమాజానికి శాస్త్రిగారి సూచన. అందుకే పట్నంలో ఉంచి ఇంగ్లీషు చదివిస్తాడు. అలాగే వీరముష్టి సుబ్బయ్య దగ్గర అన్నపూర్ణకి 'సాముగరిడీలు' నేర్పిస్తారు. పురుషాధిపత్య సమాజంలో స్త్రీలు ఆత్మరక్షణ విద్యలు నేర్చుకోవడం చాలా అవసరం అని ఆనాడు వారు రాసిన విషయాలు నేడు స్పష్టంగా కనిపిస్తున్నాయి. ఊరంతా తనని చూసి నవ్వినా పట్టించుకోకుండా తన దగ్గర పెరిగే మగపిల్లలతో అన్నపూర్ణ చేత కుస్తీ చేయిస్తాడు.

పెళ్ళి విషయంలో మగపెళ్ళివారు కోరేకోరికలకు అంతు ఉండదు. ఏకపక్షంగా ఆడపెళ్ళివారిపై ఆధిపత్యం చెలాయిస్తుంటారు. పెళ్ళికూతురికైతే మాట్లాడే స్వేచ్ఛ తక్కువే. ఇటువంటి వాటి మీద తిరుగుబాటు చేస్తాడు. శ్రీపాద ఈ కథలో అన్నపూర్ణ చేత...." ఇప్పుడు వరయోగ్యత నిర్ణయించవలసినవారు.... మీ

వంటి తలపండిపోయిన వృద్ధులు కారు". తెనుగు కన్యలం మేమిప్పుడు చూసుకోవలసినవరయోగ్యత చక్కదనం కాదు, చదువూ కాదు. ఐశ్వర్యం కానేకాదు. ఇవన్నీ తెనుగు యువతిని బానిసనిచేశాయి. ఈ లక్షణాలున్న తెనుగు యువకులింత వరకూ చక్రవర్తులుగా చెలామణీ అయినారు, కాని అలాంటి వారిక వివాహానికి అర్హులుకారు". బతికినంతకాలమూ జీవితంలో స్త్రీలు తమతో సహకరించుకోవాలంటే యువకులిప్పుడు గడించుకోవలసిన యోగ్యతలు, శౌర్యం, బలపరాక్రమాలు, తెగబడి యుద్ధంచేసే ధైర్యం ..... ఇలా పెళ్ళిపెద్దల ముందు ధైర్యంగా మాట్లాడుతుంది. తానాశించినట్లు తయారైన కూతురిని చూసి రామశాస్త్రి గర్వపడతాడు. తల్లి పొంగిపోతుంది. కొడుకు ఉద్ధరించేవాడు. కూతురు పరాయిది అనే భావన పోయి ఆడపిల్లలని మగపిల్లలతో సమానంగా పెంచాలని సూచిస్తాడు. 'స్త్రీలు వంటింటి కుందేళ్ళు కాదు' అని సూటిగా చెప్తాడు. కచ్చితమైన జవాబ్దూ 1928లో రాసిన ఈ కథలో 'పూర్ణ' ప్రధాన పాత్ర. చిట్టెమ్మ, సీతారామయ్య, జానకిరామయ్యా ముఖ్యపాత్రలు. ఇందులో ప్రధాన అంశం. మనుషుల జీవితాలు బాగుపడటానికి శాస్త్రాలు, మతాలు, పనిచేయాలి గాని మనుషులు సుఖంగా లేకుండాజేసే ఈ ఆచారాలు, శాస్త్రాలు ఎందుకూ అని ప్రశ్నిస్తాడు.

మనుష్యులను అన్నివిధాల విడతీసిన శాస్త్రాలు యింకా లోకంలో యెక్కడేనా వున్నాయా?". ఈ కర్మ భూమిలో ఈ పుణ్యభూమిలో - సారం విరిగిపోయిన యీ చౌటిపర్రలో తప్ప మరెక్కడా లేవు". "బావా! ఇంకెందుకూ? వెధవలూ మళ్ళీ పెళ్ళాడితే పనికిరాని మతం వెధవలుంటే పనికొస్తుందా? వొకదారీ తెన్నులేని మతాన్ని లక్ష్యపెట్టడం యెందుకూ?....." అని..... నావంటి వాళ్ళంతా యీదుర్గతి దేవుడు కలిగించిందే అనుకుంటున్నారు గాని మనుష్యులు అందులోనూ మొగాళ్ళు - వేదశాస్త్రాలు చదువుకున్న బ్రాహ్మలు కలిగించిందని తెలుసుకున్నారంటే వాళ్ళవుసురు తగిలి యీ దేశంఅంతా వొక్కక్షణంలో బుగ్గయిపోతుంది....." అని హెచ్చరిస్తాడు.

అలాగే సాగర సంగం కథలో అంటరాని కులాలుగా చెప్పే మాలమాదిగల మధ్య ప్రేమపెళ్ళికి కులం అడ్డుగా నిలిస్తే ప్రేమ ముఖ్యం మనుషులు ముఖ్యం కులం కాదని పెళ్ళి జరిపిస్తాడు. అలాగే వెలమలు, రెడ్లు, క్షత్రియ బ్రాహ్మణ మొదలైన కులాల్లోనూ ప్రేమ పెళ్ళిళ్ళు జరిపిస్తారు.

వీరి కథల్లో స్త్రీ పాత్రలు చాలా ఉన్నతంగా, ఆదర్శంగా ఉంటాయి. వీరి మొదటి కథ "ఇరువుమొక్కచోటికేపోదము"లో వెంకమ్మ ప్రేమపాశములో బంగారమ్మ, ప్రణయ తపస్సులో సుబ్బమ్మ, ప్రణయభంగంలో సరసు, 'కన్యాకాలేయత్నాద్వరితా'లో రంగనాయికి, జానకి, అన్నపూర్ణకథలో ఉన్నతమైన స్త్రీపాత్రలుంటాయి. ఇది ఒక పార్శ్వమైతే ప్రధాన పురుష పాత్రలు స్త్రీల అభ్యున్నతికి తోడ్పాడునందించేవిగా ఉంటాయి.

వీరి కథల్లో బాగా ప్రాచుర్యం పొందిన కథలు చాలా ఉన్నాయి. అన్నింటిలోనూ స్త్రీల సమస్యలని చిత్రించారు. మచ్చుకి రెండు కథలని మాత్రం స్థూలంగా ప్రస్తావించాను. స్త్రీల అభ్యున్నతికికృషిచేసిన తొలితరం కథారచయితలోల వీరొకరు.

**ఉపయుక్త గ్రంథ సూచి -**

శ్రీపాద సుబ్రహ్మణ్యశాస్త్రి కథలు. 1,2,3 భాగాలు.

శ్రీపాద సుబ్రహ్మణ్యశాస్త్రి కథలు. అనుభవాలూ, జ్ఞాపకాలూ.

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# AGE RELATED ALTERATIONS IN ANTIOXIDANT ENZYMES AND OXIDATIVE ENZYMES IN THE BRAIN TISSUE IN RESPONSE TO EXERCISE TRAINING

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## ABSTRACT

This current study was undertaken to investigate the effects of exercise training on the antioxidant defense system in young and old rats. The activity of antioxidant defense system parameters namely superoxide dismutase (SOD), glutathione-s-transferase (GST), uric acid (UA), glucose 6 phosphate dehydrogenase (G6PDH), succinate dehydrogenase (SDH), and glutamate dehydrogenase (GDH) were assayed in the brain tissue. The activities of SOD, GST, G6PDH, SDH and GDH are decreased with advancement of aging. Where as UA level is increased in aged rats, than that of young rats. However with exercise training these parameters were increased. Exercise training to these rats reversed the contrary effects of aging in aged rats, which could be an important in alleviating the pathological consequences of aging. Based on the data obtained in this study, it is suggested that 2 months exercise training increases antioxidant defense enzymes, decreases oxidative damage and reduces the adverse effects of aging in the brain of rats. So, exercise is beneficial during aging process.

## INTRODUCTION

Aging has been defined as the sum of all changes produced with the passing of time, determining a decline in the morphological integrity and functional capacity of the endocrine, nervous and immune systems, together with a decrease in their ability to maintain homeostasis. Cell damage caused by free radicals appears to be a major contributor to aging and to degenerative diseases of aging such as cancer, cardiovascular disease, cataracts, immune system decline, and brain dysfunction[1,2]. Aging is associated with a progressive decline in muscle performance, characterized by decreased muscle strength and endurance capacity in both humans and animals[3]. Aging is

characterized by an increased production of ROS in tissues, which results in the decreament of antioxidant enzymes [4].

Exercise is recognized as an important activity for healthy life style and is recommended throughout life by scientists and clinicians[5]. Exercise training improves the physiological and functional capacity in the elderly peoples[6]. The benefits of regular physical exercise include reduce risk of cardiovascular disease, cancer, osteoporosis and diabetes[7]. It is well known that regular performed moderate exercise has many beneficial effects, whereas, acute exercise can produce significant damage in the tissue[8].

Animal tissues are constantly coping with high reactive oxygen species, such as super oxide anion, hydroxyl radicals, hydrogen peroxides and other radicals generating during numerous metabolic reactions[9]. The generation of small amount of free radicals appears to have an important biological function, but oxidative stress is caused by excess production of reactive oxygen species [10]. To protect the cell and organ system of the body against reactive oxygen species, mammal cells are well equipped with highly sophisticated and complex defense mechanisms known as antioxidant defense mechanism. Antioxidant defense systems protect cellular homeostasis from oxidative disruption by reactive molecules generated through the reduction of molecular oxygen. The efficient functionality of these mechanisms requires the concerted action of the individual systems. These defense systems also have to be in concert with the components responsible for the repair processes of oxidatively damaged molecules in order in the cell integrity [11].

So far, various age related changes have been investigated in antioxidant enzyme and oxidative enzyme capacity in rat tissues. However it must be stressed that these experimental results are inconsistent[12]. It is also unaware that exercise training could provide the protective effect to the aged brain. Hence, in this study, we determined the role of exercise training on antioxidant enzymes and oxidative enzymes in the brain tissue of rats.

## MATERIALS AND METHODS

### Animal care and maintenance

Wistar strain male albino rats of two different age groups, that is, young (3 months n=12) weighing 170±10 g and old (18 months n=12) weighing 240±10, were used in the present investigation. This study was approved by the Institutional Animal Ethics Committee (Regd. No. 438/01/a/CP CSEAI dt.17.07.2001; resolution number 9/IAEC/SYU/ 2001/dt. 04.03.2002). The rats in the 3-month age group were considered as "younger" and the 18-month age group were considered as "older" or adult rats as per the life span of Wistar strain. The rats were housed in

clean polypropylene cages, six rats per cage and maintained under hygienic conditions, temperature controlled room (27±2°C) with a photoperiod of 12-h light and 12-h dark cycle. The rats were fed with standard laboratory chow (Hindustan Lever Ltd, Mumbai, India) and water *ad libitum.*

**Grouping of animals**

Age matched rats were divided into 4 (Young and Old rats ) groups of six in each group and treated as follows: i) Normal Control, ii) Exercise training.

**Group I - Normal Control (NC) :** Six young rats were put on a six-channel, motor driven treadmill for 5 days / week for a period of 2 months and given 2 m/ mm exercise for 5 min for equivalent handling, and also the rats received normal (0.9%)saline orally via orogastric tube.

**Group II - Normal Control (NC) :** Six old rats were put on a six-channel, motor driven treadmill for 5 days / week for a period of 2 months and given 2 m/ mm exercise for 5 min for equivalent handling, and also the rats received normal (0.9%)saline orally via orogastric tube.

**Group III - Exercise Training (Ex T) :** Six young rats were given exercise training on a six-channel, motor driven treadmill for 5 days / week for a period of 2 months.

**Group IV - Exercise Training (Ex T) :** Six Old rats were given exercise training on a six-channel, motor driven treadmill for 5 days / week for a period of 2 months at the running speed of 23m / mm 30 mim at a constant gradient of 7.5%. Treadmill was custom-built at University Scientific Instrumentation Center (USIC)- Sri Venkateswara University Campus.

After completion of 2 months treatmentthe animals were sacrificed by cervical dislocation and the brain tissue was excised at 4.C.

The tissues are washed with ice-cold saline, immersed in liquid nitrogen and immediately stored in deep freezer at -80. C for further biochemicalanalysis. The selected antioxidant enzymes such as superoxide dismutase (SOD), glutathione s transferase (GST), uric acid (UA), glucose 6 phosphate dehydrogenase (G6PDH), succinate dehydrogenase (SDH) and glutamate dehydrogenase (GDH) were monitored by the methods of Misra and Fridovich, (1972), Habig *et al.*,(1974), Martinek (1970), Lohr and Waller (1965), as modified by Mastanaiah *et al.,* (1978), Nachlas *et al.,* (1960) as suggested by Prameelamma and Swami (1975) Lee and Lardy (1965) respectively. Where as total proteins was estimated by the method of Lowry *et al*, (1951).

The data has been analyzed by using SPSS (Version 13.5; SPSS Inc., Chicago, IL, USA) and M.S. Office, Excel Software for the significance of the main effects (factors), and treatments along with their interactions. The data has been compared using one way ANOVA with Dunnett's multiple comparison test and differences were considered significant at $p < 0.001$.

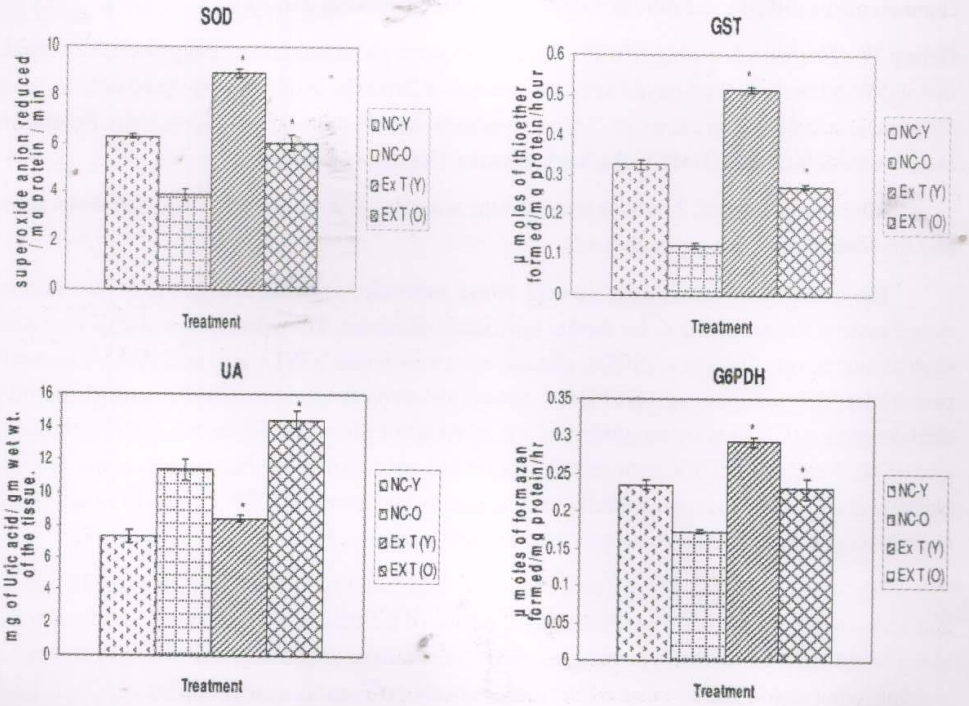
## Results

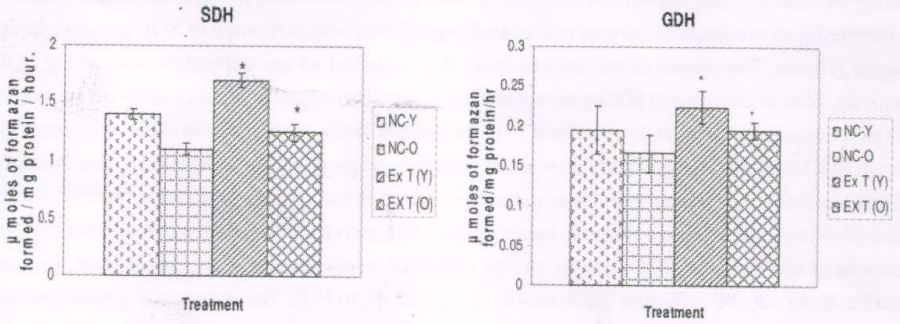
Figure 1 depicts the activities of SOD, GST, UA, G6PDH, SDH, and GDH. In aged rats these parameters activities were decreased than that of young rats, except UA level. However with exercise training all these parameters activities were increased.

In this investigation the activity of SOD observed as a foot marker of oxidative stress, was dropped with advancement of age and elevated with exercise training. Exercise induced elevation of SOD content even in old (56%) and Young (42%) animals promotes the antioxidant status brain.

Figure I shows that as age advances GST activity was decreased in brain tissue. But with exercise training GST activity is significantly increased in both age (Young 74 %, Old 82%) groups of brain tissue.

**Fig 1: Changes in SOD, GST, UA, G6PDH, SDH and GDH** activities in the brain tissue of Normal Control (NC), Exercised (Ex T) (23 m / min, 30 min/day, 5 days/week for 2 months), rats of two age groups. i,e Young (Y), and Old (O).






UA level was less in young animals compared to old animals in brain tissue. We report that significant elevation ($p<0.001$) in UA level due to exercise. The percent elevation of UA was more in old rats (26%), than of young rats (15%).

As result of age, the activity of G6PDH was decreased in brain compared to their young rats. In the present study a significant ($p<0.001$) augmentation of G6PDH activity in brain (24%) in young rats, and (32%) in old rats was observed with exercise training when compared to their respective normal controls.

SDH activity was greater in young rats, than that of old rats. We report that significant elevation ($p<0.001$) in SDH activity due to exercise. The percent elevation of SHD was more in (21%) in young rats. The same trend was also observed in old exercised rats (13%).

In this investigation the activity of GDH observed as a foot marker of oxidative stress, was dropped with advancement of age and elevated with exercise training. Exercise induced elevation of GDH content even in old (17%) and Young (14%) animals promote the antioxidant status brain. In the present study, the GDH activity in the brain tissue was decreased in old age rats than young rats.

**Discussion**

The effects of exercise on free radical production and the antioxidant system in the elderly have been widely investigated. However, it has not yet been studied how exercise affects the oxidant-antioxidant balance. We have therefore focused our attention on how the activities of antioxidant enzymes (SOD, GST, UA) and oxidative enzymes (G6PDH, SDH, GDH) in various tissues are affected in aged rats, which had performed treadmill exercise for two months.

Among various antioxidant enzymes, SOD is thought to be one of the major enzymes which protects against tissue damage caused by the potentially cytotoxic reactivities of radicals [13]. In this

study we reported that, age related decrease in SOD activity was observed in brain tissue, indicates either reduced synthesis of enzyme or elevated degradation or in activation of SOD enzyme during aging process. The results of the present study demonstrated an age dependent decrease in SOD activity. Similar decrease in SOD was reported by several investigators in mitochondria[14], in human skeletal muscle[15] and in rat myocardium [16]. In the present study, in response to exercise training the brain SOD exhibited a significant increase in both the age groups when compared to that controls. The increase in the enzyme activity as more pronounced in the younger age group. Several studies demonstrated that exercise training increase the SOD activity in heart, liver, lung and skeletal muscle of rat[17] because SOD activity can be increased with increase in $O_2 \cdot \hat{I}$ production. In most tissues there may be sufficient SOD activity to convert $O_2$ to $H_20_2$. Nevertheless, rigorous training is shown to increase SOD activity even in brain[18]. The observed increase in SOD activity in the brain of exercise-trained rats reflects the ability of this tissue to scavenge excess $O_2 \cdot \hat{I}$ in response to adaptation due to training. Sawada and Carlson reported that super oxide radical formation increases with age, therefore a decreased protection against toxic radical may have serious consequences for aging tissues[19]. Previously several scientists reported that an acute bout of exercise increases the SOD activity in various tissues including brain [20, 21].

Glutathione-s-transferase (GST) is a group of multifunctional proteins and has an important role in the detoxification of numerous xenobiotics [22]. The activity of GST was significantly decreased in the brain of older rats when compared to younger rats indicating the age dependent alterations in the activity of the enzyme. The increased accumulation of oxidative damage evident in the brain with age may be caused by a decline in cellular repair capacity or antioxidant status rather than increased oxidant production per se [23]. Ji & Fu reported that cellular antioxidant defense plays a more crucial role at advancing age[24]. The results of the present study showed an age dependent decline of the activity of GST. Similar age-dependent decrease in the activity levels of GST was reported by [25]. Several studies reported that exercise training significantly increased the antioxidant enzyme activities in the heart of mice and rats [26]. Sen *et al.* reported elevated activity levels of hepatic GST in the rat after exhaustive exercise[27]. Earlier reports on the skeletal muscle, hepatic and lung GST of rat showed similar induction in response to exercise training [28]. This induction of GST might be aimed at countering the oxidative stress that prevailed during exercise. The hyperoxic condition by the enhanced respiratory rate during exercise training might be the causative factor for the induction of GST with exercise training. The results of the present study showed elevated activity of brain GST with exercise training in both the age groups of rats, indicating the possible activation of the enzyme or its synthesis in response to exercise training, since GST is an inducible enzyme. Husain & Somani reported similar increase in the activity levels of GSTs in the plasma of rat with exercise training [29].

Uric acid function as a potential antioxidant has been recently emphasized. Its antioxidant property was first reported by [30]. Uric acid effective in quenching the hydroxyl and superoxide anion radicals. In this present study, uric acid levels were significantly increased in aged rats. In aged rats, exercise increases antioxidant enzymes in brain tissue [31]. An increased uric acid level with exercise training was reported by [32]. The mechanism of the exercise induced increase in uric acid content is thought to be the marked inhibition of renal clearance of urate by the lactate and b-hydroxy butyrate that accumulate during exercised training [33]. A high amount of uric acid level with exercise training suggests that free radical toxicity due to aging was countered effectively by uric acid, there by preventing the lipid peroxidation and tissue damage. Exercise training has the capacity to raise uric acid levels, which likely augments the antioxidative defense system, thereby protecting the brain tissue against oxidative-stressed condition during aging.

Glucose-6-phosphate dehydrogenase (G-6-PDH or G6PD) is the enzyme of the pentose phosphate pathway that is responsible for the generation of NADPH, which is required in many detoxifying oxygen derived free radicals [34]. In the present investigation the brain of older rats showed depleted activity of G-6-PDH suggesting decreased conversion of glucose-6-phosphate to 6-phospho-gluconate leading to reduced formation of NADPH in HMP shunt. A decrease in G-6-PDH activity in old rat brain could also be attributed to the reduced availability of NADP. The activity of G-6-PDH depends on SH groups in its active site. The decrease in sulfhydral groups, observed in the muscles of aging rats [35] supports the view that the activities of SH dependent enzymes including G-6-PDH are possibly decreased. A decrease in G-6-PDH activity affects RNA synthesis and nucleic acid metabolism, which is of vital importance for growth and regeneration. Exercise induced elevation of G-6-PDH activity was noticed in several studies [36]. In the present study G-6-PDH activity was increased on exercise training rats for the active participation of HMP pathway to overcome energy crisis and to generate reduced NADP for detoxification of free radicals in aged rat brain tissues. This increase was more pronounced in the younger rats when compared to older rats. The important function of HMP shunt is to produce NADPH which may act as an alternate source of energy to overcome energy crisis, which is prevailing in the cell systems due to altered citric acid cycle operation during physical stress. In other words the stepped up G-6-PDH activity may be interpreted, as a functional adaptation to meet the energy demands of the animal under exercise induced stress. The common feature of the tissue under stress conditions is a general elevation in the activities of NADP dependent dehydrogenases, and reduction in the activities of NAD dependent dehydrogenases. This is obvious, since one of the major functions of HMP shunt is to provide reduced NADP required for the detoxification of free radicals [37]. Kihlstrom reported an increase in the heart G-6-PDH activity during endurance training.

Succinate dehydrogenase (SDH) is a marker enzyme of mitochondria in the tissues. In this present study the specific activity of SDH was dramatically decreased with advancement of age. Similar age related decrease in SDH activity was reported by [38]. Age related decrease in the SDH activity was noticed in the brain tissue of rats reflects a general decline in oxidative potential of senescent tissues due to marked structural changes in mitochondria such as enlargement, matrix vacuolation and shortened cristae with the advancement of age as reported by [39]. The decrease in the SDH activity may also be due to diversion of TCA cycle intermediates such as a-ketoglutarate, for the conversion into glutamate and glutamine to counter the toxic effects of ammonia produced during aging there by depleting TCA cycle intermediates [40]. Where as with exercise training the SDH activity was increased in both age group rats. The increased SDH activity during exercise training indicates increased aerobic efficiency of the brain tissue. The present results are also attesting with the previous findings of [41, 42] who reported the significant increased levels of SDH activity with exercise in different tissues of both young and old rats. Stuewe *et al.,* reported that chronic exercise training induces many mitochondrial enzymes and enhanced mitochondrial proteins turnover which may also contribute to elevated SDH activity [43]. Gurumurhty et.al also reported the increased SDH activity in muscle and hepatic tissues respectively with response to endurance exercise training in both young and old albino rats. The increased activity of SDH in young rats with endurance exercise training program suggests increased mitochondrial oxidative potential and energy synthesis, utilization of carbohydrates and fats as substrates.

Glutamate dehydrogenase (GDH) is a homohexameric mitochondrial matrix enzyme that catalyses the reversible oxidative deamination of glutamate to a-ketoglutarate plus free ammonia using either NAD or NADP as a co-factor. The enzyme is expressed at high levels in liver, brain, pancreas and kidney but low in muscle. Aging is accompanied by a gradual deterioration of cell functions, mitochondrial dysfunctions and accumulation of protein damage have been proposed to contribute aging process [45]. As age advances, mitochondrial respiration also decreases in the tissues. In old age rats, due to lack of co-ordination among TCA cycle intermediate products the GDH activity may be decreased. Due to lack of sufficient availability of glutamate concentration at cellular levels the activity of glutamate dehydrogenase may also decreased in the tissues. In the present investigation, we reported that in exercise trained rats GDH activity was increased. This elevation of GDH activity indicates its contribution to enhanced a-ketoglutarate, which subsequently enter into TCA cycle. The increased GDH activity may be due to the sufficient availability of intracellular glutamate, which is released from ammonia and act as a substrate to the GDH. Glutamate dehydrogenase utilizes the NAD or NADP as a co-substrate to catalyze the reversible oxidative deamination of glutamate to a-ketoglutarate and free ammonia [46]. The elevation of GDH in the cells

help in supply of more amount of a-ketoglutarate to TCA cycle in order to compensate the energy crisis during exercise induced stress conditions. However with advancement of aging the GDH activity was decreased.

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# AMELIORATIVE POTENTIAL OF VITAMIN C IN SODIUM FLUORIDE (NAF) INDUCED TOXICITY IN FISHES: A STUDY WITH REFERENCE TO ANTIOXIDANT ENZYMES

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**ABSTRACT**
A study was undertaken to investigate the effect of Vitamin C on the toxicity of NaF in fishes. The fishes were divided into four groups and treatment was given for 30 days as per the experimental protocol. Antioxidant enzymes like Super oxide dismutase (SOD), catalase (CAT), ascorbic acid (AA), uric acid (UA) and thiobarbituric acid reactive substances (TBARSs) levels are estimated in liver tissue. Antioxidant enzymes decreased and TBARSs levels increased in NaF intoxicated fishes. However, these toxic effects of NaF were significantly reduced when the fishes were treated with the Vitamin C. This indicated that Vitamin C might play a role in reducing the toxic effect of NaF in fishes.

**KEYWORDS**: Antioxidant enzymes, Fishes, NaF, Vitamin C.

## INTRODUCTION

Fluoride in small doses has influence by inhibiting dental caries while in higher doses it causes dental and skeletal fluorosis (Shanthakumari *et al.*, 2004). Fluoride enter the body through drinking water, food, toothpaste and other dental products; drugs and fluoride dust and fumes from industries using fluoride containing salt and hydrofluoric acid (Shulman and Wells, 1997). Recent studies revealed that fluoride induces excessive production of oxygen free radicals, and might cause the depletion of antioxidant enzymes (Chlubek, 2003).Increased free radical generation and lipid peroxidation are proposed to mediate the toxic effects of fluoride on soft tissues (Rzeuski *et al.*, 1998).

Antioxidants are substances that are efficient to trap ROS and so maybe competent of decreasing oxidative damage. The use of antioxidants as therapeutic agents to treat diseases. The administration of antioxidant compounds have many protective effects. Exogenous sources of antioxidants are those that can be obtained from the diet. These can include Vitamin E (tocopherols), ascorbic acid (Vitamin C), carotenoids and flavonoids. In addition to dietary antioxidants, endogenous antioxidants also play a vital role in regulating ROS production and can be either enzymatic or non-enzymatic.

The present study was an attempt to evaluate the toxic effect of sodium fluoride and possible ameliorative role of Vitamin C in fishes.

## MATERIALS AND METHODS

### Animals

**Fish Acclimation**: Fishes were transported to laboratory under ordinary conditions. Fishes were divided into four groups, each containing ten fishes and placed in a fiber glass aquarium, size: 36cmx 18cm x 15cm containing ground water. Air pumps and filters were used to aerate the aquarium water by circulating it. All control and treated fish were fed with commercial pellet once a day. Water in aquaria was changed after every two days. Chemical analysis of water was done according to standard methods.

*Channa punctatus* ranging in length from 12±15cm and having a body weight of 30±35gm were obtained from the local fresh water resources and were maintained in large aquaria for 7 days to acclimatize them to the laboratory conditions. Chlorine free water was used which was changed at regular intervals. The values of some of the parameters of the water used were hardness 180ppm, pH 7.5±0.2, temperature 25±2c0.
The fishes were divided into 4 groups of 10 fishes in each group.
1. Normal Control (NC): Fishes are treated with normal ground water for 30 days.
2. NaF Control (NF C): Fishes are treated with NaF (100 ppm) for 30 days.
3. Vitamin C treatment (Vit c t): Fishes are treated with Vitamin C (100 ppm) for 30 days.

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4. NaF + Vitamin C (NF + Vit C): Fishes received Na F (100 ppm) and Vitamin (100 ppm) for 30 days.
The liver tissues are collected after the 30days of treatment.

**RESULTS**

Effect of Sodium Fluoride on hepatic antioxidant enzymes SOD, CAT, ascorbic acid and uric acid levels decreased in NaF intoxicated fishes. Administration of Vitamin C alone caused significant ($P < 0.05$) increase in the activities of SOD, CAT, ascorbic acid and uric acid levels compared to control rats. In addition, a significant recovery relating to SOD, CAT, ascorbic acid and uric acid was observed in response to the treatment with Vitamin C in NaF fishes. (Table 1).

**Table 1. Effect of Vitamin C on the antioxidant enzymes in NaF intoxicated fishes**

| | NC | NaF | Vit C | Na F + Vit C |
|---|---|---|---|---|
| SOD (Superoxideanion reduced/mg rotein/min ) | 14.06±1.612 | 8.02±1.214 | 15.86±2.418 | 12.84±1.82 |
| CAT (µm of hydrogen peroxide degraded /mg protein/min) | 28.02±2.14 | 14.62±1.48 | 32.04±0.32 | 22.14±2.86 |
| AA (mg ascorbic acid/g wet weight of the tissue) | 1.12±0.212 | 0.82±0.012 | 2.4±0.384 | 1.42±0.814 |
| UA (µm of uric acid/g wet weight of the tissue) | 1.6±0.10 | 1.02±0.036 | 1.8±0.246 | 1.4±0.028 |
| MDA (µm of malondialdehyde /gram) | 98.12±4.628 | 180.28±6.216 | 94.06±4.82 | 126.04±6.264 |

Our results indicated that the levels of thiobarbituric acid reactive substances(TBARSs) is significantly ($P < 0.05$) increased in liver of fishes treated with NaF (Table 1). Treatment with Vitamin C alone caused significant ($P < 0.05$) decrease in liver TBARS compared to control. In addition, Vitamin C supplementation in NaF fishes reduced the elevation of TBARS. (Table 1)

**DISCUSSION**

Fluorosis is a well-defined clinical entity characterized by toxic effects of high-fluoride intake on teeth, bones and soft tissues (Krishnamachari, 1976).

This is the first report on the effect of vitamin c in sodium fluoride intoxicated fishes. The present study exhibits the toxic effects of sodium fluoride on antioxidant enzymes in fishes. The present investigation also suggests sodium fluoride alters antioxidant enzymes, however Vitamin C supplementation protected the fishes from NaF intoxication. Hence, Vitamin C may be used as protective agent against many toxic substances in aquatic conditions.

SOD is an important antioxidant enzyme found in nearly all living cells exposed to oxygen. CAT is a very important enzyme in protecting the cell from oxidative damage by reactive oxygen species (ROS).Ascorbic acid is a potent water-soluble antioxidant enzyme involved with radical chain-breaking and regeneration of tocopherol from tocopheroxy radicals. Uric acid, a important antioxidant for humans, birds, reptiles, and some primate species, that scavenges singlet oxygen, peroxy radicals, and hydroxyl radicals and has been studied extensively in many physiological and pathological systems.

In the present study, SOD, CAT, AA and UA activities are decreased in Naf intoxicated fishes. It is proposed that there is an increased oxidative stress in Fluorosis and decreased in SOD and CAT in the red blood cells (RBC) of fluoride-in

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toxicated rats (Shivarajashankara *et al.*, 2001).In another study, decreased SOD and CAT activities in rat upon ingestion of sodium fluoride for 14 days were observed (Vani and Reddy, 2000). The decreased activities of SOD and CAT may be a response to increased production of hydrogen peroxide and superoxide by excessive production of free radicals. Many reports suggested that NaF supplementation causes excessive production of toxic free radicals which scavenges free radicals thus antioxidant enzymes came to rescue, hence these antioxidant enzymes activities decreased in NaF fishes (Liu et al., 2003). However Vitamin C treatment recovered all these antioxidant enzymes near normal levels.

Some studies suggest the use of antioxidants and antioxidant rich foods for the management of fluorosis (Susheela, 1999) and also for the beneficial effects of antioxidants as antidotes for fluoride toxicity (Chinoy *et al.*, 1994). Therefore, the purpose of the present study is to find out the ameliorating potential of Vitamin C on sodium fluoride-induced reactive oxygen species (ROS) and lipid peroxidation. Treatment with Vitamin C significantly increased SOD, CAT, AA and UA in NaF intoxicated fishes. The increased lipid peroxidation in NaF in fishes as found in the present study may be due to the inefficient anti-oxidant system. The elevated lipid peroxidation is responsible for the formation of lipid hydroperoxides in membrane and would result in damage of the membrane structure and inactivation of membrane bound enzymes. Elevated oxidative stress due to this imbalance leads to liver tissue injury through oxidized proteins and augmented levels of lipid peroxidation, as indicated by increased TBARS contenting NaF in the present study. Vitamin C treatment significantly reduces this enhanced lipid peroxidation. The anti-oxidant compounds and other pharmacological compounds of plants may inhibit the production of free radicals, and reduced the products of lipid peroxidation (Table 1).

## CONCLUSION

From the above study, we conclude that Vitamin C supplementation protected liver tissue in NaF intoxicated fishes. To the best of our knowledge this is the first reported data on the effect of Vitamin C in Na F fishes and also with reference to the antioxidant enzymes. However, further research is needed, for the better understanding of the mechanism of action of vitamin C by which it modulates anti-oxidant enzymes in toxicity condition.

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Research Article

# Phytochemical Screening and Antimicrobial Evaluation of *Ocimum sanctum* : A study with reference to Pharmacological aspect

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**ABSTRACT**

The Phytochemical analysis of medicinal plants are gaining importance due the production of the new drugs from plants. The objective of the present research work was to investigate the presence of the phytochemical constituents and to study the bactericidal effect of *Ocimum sanctum* (OS). Phytochemical screening analyses was determined by using standard protocol methods. The antibacterial activities of OS were estimated by disc diffusion method against different bacterial strains. The results revealed that OS was found to be the predominant occurrence of phytochemicals like flavonoid, phenol, tannins, reducing sugar, glycosides, steroids and terpenoids, while starch resins, are absent. Ethanolic extract of the OS hold promises as a potential source of pharmaceutically important phytochemicals and also have strong antibacterial activity against Escherichia coli, Staphylococcus aureus and other strain than aqueous extract. Hence, the present investigation proves that O*cimum sanctum* can be applied as antimrobial agent against bacterial diseases.

Keywords: Phytochemical screening, Antibacterial screening, *Ocimum sanctum*

## INTRODUCTION

Medicinal plants have many potentially active phytochemicals which used to cure various ailments. These plants play beneficial role in healthcare system by protecting human beings from the adverse effects of diseases and other complications. [1]. Medicinal plants are the reservoirs of potentially useful chemical compounds which could serve as newer leads and clues for modern drug design [2]. Medicinal plants have been screened in many countries as antimicrobial agents and tissue protective drugs. The screening of plant extracts for antimicrobial activity has shown that plants are potential source of novel antimicrobial compounds [3].India is one of the oldest, richest and most diverse cultural traditions associated with the use of medicinal plants. During the last two decades, the pharmaceutical industry has made immense progress in pharmacological and chemical researches all over the world in an effort to discover new plant drugs. This leads to screening, isolation and estimation of compounds from many medicinal plants. *Ocimum sanctum* is one of important herb which is used in India. It has many pharmacological properties like antioxidant, antidiabetic, antiulcer, antinflammatory [4]. Hence, the present study was designed to screen the phytochemicals and antimicrobial activity of *Ocimum sanctum*.

## Materials and methods

### Collection of Plant Materials

The leaves of *Ocimum sanctum* were collected from Tirupati, A.P, India and identified by the Dr. Madhav Chetty, Department of Botany, SV University, Tirupati. Voucher specimen of *Ocimum sanctum* No 1183 was deposited in the Botany department.

### Chemicals and reagents

All chemicals used were of analytical grade and were purchased from Sigma–Aldrich, Merck and. All chemicals and reagents were used without further purification.

### Preparation of Plant Materials:

The sample of *O. sanctum* leaves was weighed on Shimadzu Electronic Balance. The stems were dried in an oven at 50-60ºC. The dried leaf are cooled at room temperature and weighed again on the same electronic balance. .

### Ethanolic extraction

100 grams of air-dried powder was taken in 1000 ml of ethanol in a conical flask, plugged with cotton wool and then kept for 24 hours. After 24 hours the supernatant was collected, this procedure was repeated thrice, until the residue turns to colure less.

The solvent was evaporated to make the final volume one fourth of the original volume with the help of rotavapour and the final metahnolic extract was stored at -10ºC.

**Aqueous extraction**

100 grams of air-dried powder was added to 1000 ml of water and soaked for 24 hours. It was then filtered through filter paper. The supernatant was collected, this procedure was repeated thrice, until the residue turns to colure less. The solvent was evaporated to make the final volume one fourth of the original volume with the help of rotavapour and the final aqueous extract was stored at -10ºC.

A portion of the leaf powder was subjected to phytochemical analysis, using standard chemical tests. Phytochemical screening of the crude extract was carried out employing standard methods and tests.

1. Test for Alkaloids (Wagner's reagent)

A fraction of extract was treated with 3-5drops of Wagner's reagent (1.27g of iodine and 2g of potassium iodide in 100ml of water) and observed for the formation of reddish brown precipitate (or) coloration.

2. Test for Terpenoids (Salkowski Test)

0.5 gram of each extract was added to 2 ml of chloroform. Concentrated sulphuric acid (3 ml) was carefully added to form a layer. A reddish brown colouration of the interface indicates the presence of terpenoids.

3. Test for Tannins

About 0.5 gram of the extract was boiled in 10 ml of water in a test tube and then filtered. A few drops of 0.1% ferric chloride was added and observed for brownish green or a blue-black coloration.

4. Test for Saponins (Foam test)

To 2ml of extract add to 6ml of water in a test tube. The mixture was shaken vigorously and observed for the formation of persistent foam that confirms the presence of saponins.

5. Test for Cardiac glycosides (Keller Kelliani's test)

5ml of each extract was treated with 2ml of glacial acetic acid in a test tube and a drop of ferric chloride solution was added to it. This was carefully underlayed with 1ml concentrated sulphuric acid. A brown ring at the interface indicated the presence of deoxysugar characteristic of cardiac glycosides. A violet ring may appear below the ring while in the acetic acid layer, a greenish ring may form.

6. Test for Phenols (Ferric chloride test)

A fraction of the extracts was treated with aqueous 5% ferric chloride and observed for formation of deep blue or black colour.

7. Test for reducing sugars (Fehling's test)

The extract (0.5 g in 5 ml of water) was added to boiling Fehling's solution (A and B) in a test tube. The solution was observed for a colour reaction.

8.Test for Flavonoids

To portion of the dissolved extract, a few drops of 10 % ferric chloride solution was added. A green or blue colour indicates the presence of phenolic nucleus.

9. Test For Resins

10 ml of petroleum ether extract was obtained in a test tube, the same amount of cupper acetate solution was added and the mixture was shaken vigorously and allowed to separate, a green colour indicates the presence of resins.

10. Sterols and Steroids (Salkowski's Test)

One ml of extract was treated with 2 ml of chloroform and equal amount of concentrated sulphuric acid was added, upper layer is turns to red indicates the presence of the sterols and steroids.

**Table 1: Phytochemicals analysis of *Ocimum sanctum***

| S.No | Phytochemical Constituents | Ethanolic Extract | Aqueous Extract |
|---|---|---|---|
| | | Stem | Stem |
| 1. | Phenolic Compounds | + | + |
| 2. | Saponins | - | - |
| 3. | Flavonoids | + | + |
| 4. | Terpenoids | + | + |
| 5. | Alkaloids | + | + |
| 6. | Tannins | + | - |
| 7. | Cardioglycosides | + | + |
| 8. | Steroids | + | + |
| 9. | Reducing Sugars | - | - |
| 10. | Anthraquinones | - | - |
| 11. | Resins | - | - |

**Collection of Text Organism**

Human pathogens culture of *Escherichia coli* (*E. coli*), *Staphylococcus aureus* (*S. aureus*), *Bacillus subtilis* and *Psudomonas aeruginosa* in this study were obtained from the Microbiology Laboratory of Sri Venkateswara University, Tirupati, Andhra Pradesh, India. All cultures were maintained in nutrient broth at 37ºC and maintained on nutrient agar slants at 4ºC.

**Determination of Zone of Inhibition**

The antibacterial activity studies are assessed by agar well diffusion method. Standard antibiotic streptomycin was used as positive control. Four bacterial strains were used for screening the antimicrobial activity of *Ocimum sanctum*. *Escherichia coli, Staphylococcus aureus, Bacillus subtilis* and *Pseudomonas aeroginosa* stock cultures were collected from department of Microbiology Sri Venkateswra University Tirupati, A.P, India. These organisms were cultured in nutrient agar medium prepared by autoclaving 2.5 gram nutrient agar in 100 ml of distilled water and incubated at 37ºC for 24h. Inoculate the testing microorganisms on agar plate by using inoculation wire loop. The discs were prepared by using sterilized what man (grade no.1) filter paper. The discs are rinse in different concentrations (10,20,30% w/v) of ethanolic and aqueous extracts of OS and those were placed on inoculated agar plates, then the plates were incubated at 37ºC for 24h. The tests were performed three times and the zones of inhibition were measured for by using a ruler and the results were recorded in mm.

**Results**

**Qualitative phytochemical screening**

In the present study, we investigated the phytochemical screening of *Ocimum sanctum* in ethanol and aqueous extract. The ethanolic extract of OS showed the presence of many phytochemicals. flavonoids, phenol, tannins, glycosides, terpenoids, steroids, alkaloids and absence of starch, anthraquinone, resins, and saponins. In the case of aqueous extract flavonoids, phenol, terpenoids, alkaloids, gcardiolycosides and absence of anthraquinone, resins, reducing sugars, tannins and saponins. (Table 1).

**Antimicrobial activity of *Ocimum sanctum***

The antimicrobial activity of ethanolic and aqueous extracts of OS was investigated by using agar diffusion method against selected human pathogens such as *Staphylococcus sp, Escherichia coli, Bacillus subtilis* and *Pseudomonas aeroginosa*. These four different pathogens have also tested with commercially available antibiotic like Streptomycin and results were indicated in Table 2. OS extracts used against the pathogenic organisms have showed varied degree of antimicrobial activity against the pathogens.

The result indicates that the ethanol leave extract showed more effective result than the aqueous extract with significant inhibition against *Pseudomonas aeroginosa* in well diffusion and poison plate. Thus, it was evident that the organic extracts were more effective than aqueous extract.

So, it is suggested that *Ocimum sanctum* may be recommended as antimicrobial agent against pathogens.

**Table 2: Antimicrobial Activity of Ocimum sanctum (Zone of inhibition in millimetres)**

| **Bacterial Species** | **Zone of Inhibition** (mm) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | **Ethanolic Extract** | | | | **Aqueous Extract** | | | |
| | S.mycin | 50mg/*l* | 100mg/*l* | 200mg/µ*l* | S.mycin | 50mg/*l* | 100mg/*l* | 200mg/*l* |
| Escherichia coli | 78mm | 13mm | 13.5mm | 15mm | 60mm | 12mm | 13.5mm | 14.2mm |
| Staphylococcus aureus | 72mm | 12mm | 12.5mm | 14.5mm | 68mm | 11mm | 12mm | 13.5mm |
| Bacillus subtilis | 66mm | 0mm | 0mm | 1.2mm | 60mm | 0mm | 0mm | 0.6mm |
| Psudomonas aeruginosa | 63mm | 12mm | 16mm | 18mm | 69mm | 10mm | 11mm | 11.5mm |

## Discussion

This study was conducted to investigate the phytochemical characteristics and antimicrobial activities of OS. Phytochemical constituents are secondary metabolites of plants which contribute significantly towards the biological activities of medicinal plants such as hypoglycemic, antidiabetic, antioxidant, antimicrobial, antiinflammatory, anticarcinogenic, antimalarial, anticholinergic, antileprosy activities etc. [5]. Phytochemical constituents such as tannins, flavonoids, alkaloids and several other compounds serve as defense mechanism against predation by many microorganism, insects and herbivores. The curative properties of medicinal plants are perhaps due to the presence of various secondary metabolites such as alkaloids, flavonoids, glycosides, phenols, saponins, steroids etc [6]. The preliminary phytochemical screening may be useful in the detection of the bioactive principles and subsequently may lead to the drug discovery and development of new drugs. Further, these tests facilitate their quantitative estimation and qualitative separation of pharmacologically active chemical compounds [7].The pharmacological properties of OS are able to determine the presence of flavonoids, alkaloids, steroids, triterpenes, glycosides, and tannins. The flavonoids were the common group of compounds found in all plants and play a major role in metabolism (Shirley 2001). The biological functions of flavanoids apart from its antioxidant properties include protection against allergies, inflammation, free radicals, platelet aggregation, microbes, ulcers, hepatoxins, viruses and tumors [8]. It also helps in managing diabetes induced oxidative stress. Flavonoids in OS act as antioxidant and free radical scavenger, which prevent oxidative cell damage [9,10].Alkaloids are secondary metabolites containing low molecular weight substances and show variety of biological functions. The alkaloids are used to design the anticancer and analgesic medicines [11]. Uses of specific photochemical presence in plants are an advantage to human being and it reduces the side effects of toxic substances formed by many metabolic reactions.Numerous studies have confirmed that steroids are responsible for cholesterol-reducing properties. Steroids also help in regulating the immune response. Steroids are present only in OS which is supposed to be of maximum medicinal value Steroids also help in regulating the immune response [12].Terpenoids exhibit various important pharmacological activities i.e., anti-inflammatory, anticancer, anti-malarial, inhibition of cholesterol synthesis, anti-viral and anti-bacterial activities [13]. Phenolic compounds are some of the mot widespread molecules among plant secondary metabolites, are known to act as natural antioxidants . Tannins have amazing stringent properties. They are known to hasten the healing of wounds and inflamed mucous membrane [14] Terpenoids have been found to be useful in the prevention and therapy of several diseases, including cancer. Terpenoids are also known to possess antimicrobial, antifungal, antiparasitic, antiviral, anti-allergenic, antispasmodic, antihyperglycemic, antiinflammatory and immunomodulatory properties [15]. In addition, terpenoids can be used as protective substances in storing agriculture products as they are known to have insecticidal properties as well [16]. Alkaloids are used as anaesthetic agents and are found in medicinal plants [17].Plant derived compounds received interest in the past few decades because of their potential antimicrobial activities. The phytochemicals of medicinal plants improve the health status of people and so it is used in pharmaceutical and nutraceutical products of commercial importance [18]. The results of antibacterial assay of OS extracts are presented in the table 2. OS contains unique constituents which differ from one extract to another, hence the type and extent of their medicinal property also differs. The presence of phytochemical components like alkaloid, terpenoids, tannin and steroids in ethanol extract may have good anti-inflammatory activities, antibacterial activity. The zone of inhibition increased with an increase in the concentration of the extracts in the well. The study revealed that ethanolic extract of OS is very effective against *Staphylococcus sp, Escherichia coli, Bacillus subtilis* and *Pseudomonas aeroginosa*. In nut shell, it can be concluded that the phytoconstituents of methanol extracts of OS can be used as antimicrobial agent. Antimicrobial activity of OS in different extract was shown in Table 2 and compared with different concentrations. The ethanolic extract showed highest antibacterial activity than aqueous extract. Ethanolic extract of OS worked against pathogenic bacteria responsible for common infections of skin, urinary, and gastrointestinal tracts. OS contains alkaloids, which are responsible for the strong antibacterial activities. The antimicrobial activity of OS may be due to the presence of many phytochemicals.

## Conclusion

The present study clearly indicates that *Ocimum sanctum* have many phytochemical constituents. The antimicrobial efficacy of *Ocimum sanctum* leaves indicates that the plant possess potent antimicrobial properties as well. As *Ocimum* is widespread in India, it can be recommended as an easily available and renewal source of antimicrobial agent instead of synthetic chemicals. It is quit safer to use as an herbal medicine as compare to chemically synthesized drug. The presence of many bioactive compounds in high concentration justifies that the OS can be used for various ailments by traditional practitioners. However, isolation of individual phytochemical constituents and subjecting it to pharmacological activity will definitely give fruitful results.

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# THE PARADIGM OF ENTRY INTO HOST - CONCERNS IN DEVELOPING ANTIVIRALS FOR COVID-19

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## ABSTRACT

Corona Virus Disease – 19 (COVID-19) that appeared first in December 2019 has become a pandemic within a short span of time. It is posing many questions to the scientific community, challenging food and health security. As on April 3, 2020 the number of cases approached one million worldwide. There have been massive thermal screening, quarantines, social distancing and lockdowns world over. While there is spread of many falsifications around corona virus infections, scientists have been engaged in research to find out a solution to control the pandemic, prevent the spread and treat the affected successfully. Intensive research is needed to elucidate the transmission routes and pathogenic mechanism of novel emerging corona virus diseases. It is also required to elucidate the possible drug targets to develop effective preventive and therapeutic measures. In this backdrop, the present paper reviews the available literature, with emphasis on virus entry in to the host and possible development of effective therapies using manipulation of receptor proteins as first step prevention.

Key words: COIVD-19; Pandemic; Entry into host; Receptors.

**Introduction:**

Corona viruses affect mammals and birds. These viruses cause respiratory tract infections in human beings, which range from symptoms of cold to SARS, MERS. Symptoms in other species vary. As against many viruses, development of a vaccine has been difficult.Corona viruses are spherical, large and pleomorphic having a diameter around 120nm. The envelop consists of a lipid bilayer where in the structural proteins are anchored. These include the membrane, envelop and spike proteins. The viral spike peplomers, which are surface proteins give its characteristic ‘crown’ like appearance, hence the name ‘corona’ virus (Image 1). Subsets of corona viruses are found to have shorter projections that function as Haemaglutinin Esterase (HE).

The nucleocapsid present inside the envelop is formed by copies of nucleocapsid protein which are bound to the positive sense ssRNA genome. The virus, when it is outside the host,is protected by envelop, membrane protein and nucleocapsid. SARS-CoV-2, responsible for COVID-19 pandemic, also has mushroom shaped protein spikes which render the virus the ability to bind and fuse to human cells, gaining entry into the host.

Four of the seven strains of human coronaviruses studied are known to produce the generally mild symptoms of the common cold:

1. Human corona virusOC43 (HCoV-OC43)
2. Human corona virusHKU1
3. Human corona virusNL63 (HCoV-NL63, New Haven coronavirus)
4. Human corona virus229E (HCoV-229E)

Three other strains produce severe symptoms, which include

1. Middle East respiratory syndrome-related corona virus (MERS-CoV), previously known as *novel coronavirus2012* and *HCoV-EMC*
2. Severe acute respiratory syndrome corona virus (SARS-CoV or "SARS-classic")
3. Severe acute respiratory syndrome corona virus2 (SARS-CoV-2), previously known as 2019-nCoV or "novel coronavirus2019"

The coronaviruses HCoV-229E, -NL63, -OC43, and -HKU1 continually circulate in the human population and cause respiratory infections in adults and children world-wide.

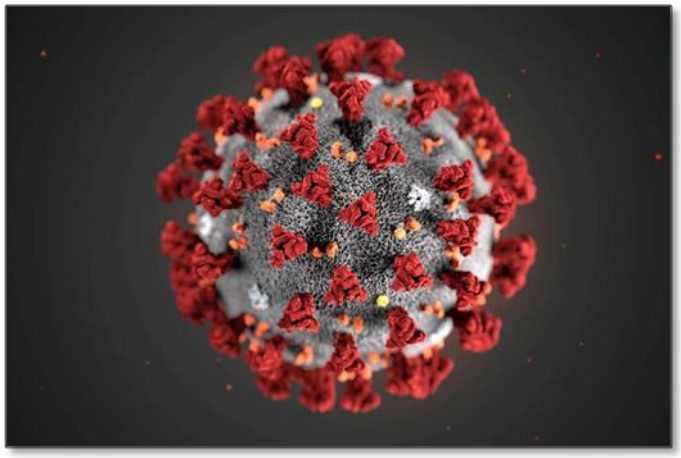


Image 1: The ultrastructural morphology exhibited by the SARS-CoV-2
(Center for Disease Control and Prevention on January 29, 2020)

**Infection of a coronavirus**

When the viral spike glycoprotein binds its complementary host cell receptor, infection occurs. Once attached, host cell protease cleaves the receptor attached spike-protein. Virus enters the host cell by endocytosis or fusion of viral envelop with host cell membrane. Availability of host cell protease, cleavage and activation determine the entry of virus into the host cell. Viral genome enters the host cell cytoplasm once the virus particle is uncoated immediately after entry. The corona virus RNA genome attaches to host ribosome with a high degree of specificity, which is due to the presence of a 3' poly adenylated tail and 5' methylated cap. The initial overlapping open reading frame of the virus genome is translated to form a long polypeptide chain, which has its own protease sequence to cleave it into multiple non-structural proteins.

**Human to human transmission**

The issue of concern about corona viruses is their ability to get transmitted from human to human individuals. The transmission occurs among close contact by droplet infection. affected people transmit during incubation period. The infectivity, tissue tropism and species range of the corona virus is largely dependent on the interaction of spike proteins with complementary host cell receptors. For example, SARS corona virus infection takes place by attachment to angiotensin converting enzyme 2 (ACE2) receptor.

**Coronavirusdisease 2019 (COVID-19)**

A pneumonia outbreak was reported in December 2019 in Wuhan City, Hubei Province, China. On 31 December 2019, after ruling out a number of etiological agents including SARS Corona Virus & MERS Corona Virus, the outbreak was traced to a novel strain of coronavirus,which was given the interim name 2019-nCoV by WHO.Genome analysis reveals that 2019-nCoV belongs to *Sarbecovirus* subgenus, *Betacoronavirus* genus of the subfamily *Orthocoronavirinae* in the family *Coronaviridae* of the suborder *cornidovirineae* of the order *Nidovirales.*It was later renamed as SARS-CoV-2 by the International Committee on Taxonomy of Viruses.The outbreak was declared a Public Health Emergency of International Concern on 30 January 2020. On 11 February 2020, WHO announced a name for the new coronavirus disease - COVID-19.

As of 03 April 2020, there have been at least 46764confirmed deaths and more than 932166 confirmed casesworldwide and the epidemic curve is on steep rise (Image 2).The Wuhan strain of Corona Virus is identified to have approximately 70% genetic similarity to the SARS-CoV. The virus has a 96% similarity to a bat coronavirus, so it is widely suspected to originate from bats as well.




Image 2: The COVID-19 pandemic as on 03.04.2020 (courtesy: WHO dashboard)

**The viral capsid and viral entry into the host:**

Viral capsids are generally stable to protect the genome inside and play different roles in the host-virion interactions. Envelop- associated proteins play crucial role in binding to receptors, membrane fusion, uncoating and receptor modification, all of which are vital for virus replication. Studies on fusion proteins reveal their importance in viral entry and release. Priming of viruses is a very important aspect, which should be probed into to identify potential drug targets. Priming, which involves conformational changes in surface proteins, facilitates viral uptake and infection of target cells. Release of viral genome into the cytoplasm of the host cell is one crucial area where scientific intervention can lead to discovery of potential therapeutic agents. For example, priming of influenza viruses involves endosome membrane disruption based on activation of hemagglutinin molecule. Inhibition of enzyme cascade may prove efficient therapy for prevention of virus infection and infestation.

Virus-host relationship may form a crucial area for scientific studies because virion attachment and entry into the host cell is the most important stage for virus multiplication. Viral envelops act as fusion machines to facilitate viral entry into host cells. For example, fusion of

influenza virus depends on consecutive binding of gp120 to CD4 and the chemokine receptors. The fusogenic domain is in gp41 and the fusion peptide is formed at the nacent amino peptide formed by cleavage of gp160 precursor. Premature triggering of the fusion peptide will result in an inactive virus. Crystallized gp41 complex shows conspicuous structural homology with the influenza hemagglutinin. It is noteworthy that the fusogenic confirmation of influenza hemagglutinin is induced by low pH. Such subtle areas may form crucial points of research to combat infections.

**COVID-19 entry into the host**

Studies revealed that the spike protein of the SARS-CoV-2 that causes COVID-19 has a good affinity (10-20 times to that of SARS virus) and binds to the host cell receptor known as angiotensin -converting enzyme 2 (ACE2) and this serves as the entry point into human cells. When compared to SAARS corona virus, the novel corona virus has high human-to-human transmissibility because of this higher affinity. Studies to employ SARS specific antibodies to prevent novel corona virus infection did not yield results. It is also revealed that the spike protein has 98% sequence similarity to that of bat corona virus.

Corona viruses have the largest genomes of all RNA viruses. These comprise of cis-acting RNA elements which warrant the replication of viral RNA. These cis-acting elements form a minor fraction of the total viral genome. RNA secondary structures of these cis-acting regions are well-understood. But, how the cis-acting structures and sequences interact is not yet understood. Infectious corona virus assembly selection of viral genomic RNA from a pool of non-viral and viral RNA present in the cell. Studies revealed that seven to ten viral mRNAs are synthesized in infected cells and the full-length genomic RNA alone is packaged into corona virus particles. There are studies which revealed the involvement of cis-acting and trans-acting viral factors in encapsulation and packaging. The molecular mechanisms of genome selection and packaging will form a critical area where in scientists can develop anti-viral agents for diagnostics and therapeutics. Also, understanding the atomic level structure of the novel corona virus – 2019 spike protein may augment development of potent vaccines.

**Discussion and conclusion:**

The SARS-Sprotein is a type I transmembrane protein, which comprises 1,255 aminoacids and contains 23 consensus signals for N-linked glycosylation. S protein is synthesized in the secretory pathway of infected cells.It contains an N-terminal signal sequence, which mediates import of the nascent protein into the endoplasmic reticulum, where the protein is folded and modifiedwith mannose-rich carbohydrates. Upon transport of the protein into the Golgi apparatus, most, if not all, of the high-mannose carbohydrates are processed into complex glycans. A novel dibasic ER retrieval motif in the cytoplasmic tail of SARS-S promotes accumulation of the S protein at the ER–Golgi intermediate compartment and the Golgi region the sites where progeny particles are assembled. Formation and budding of new particles are driven by the membrane protein (M), the envelope protein (E) and the nucleocapsid protein (N);interactions with the M protein might facilitate S protein incorporation into particles.The domain organization of SARS-S resembles that of several well-characterized viral membrane proteins, such as influenza virus hemagglutinin (HA) and human immunodeficiency virus (HIV) envelope protein (Env). These proteins employ comparable strategies to facilitate fusion of viral and host cell membranes and are termed class I fusion proteins.They are distinguished from class II fusion proteins, found, forexample, on flavi- and alphaviruses, by their distinct spatial organization and theparticular configuration of the functional elements required for fusion with targetcells: class I fusion proteins are inserted perpendicular to the viral membrane andcontain an N-terminal surface unit (SU) and a C-terminal transmembrane unit(TM). The globular SU interacts with cellular receptors, while the TM promotes. The position of the S protein open reading frame in the SARS-CoV genome is indicated in the upper panel. Coronavirus S proteins exhibit a domain organization characteristic for class Ifusion proteins. A signal peptide is located at the N-terminus and mediates import of the nascent protein into the secretory pathway of infected cells. The surface unit S1 contains a receptor binding domain (RBD), which allows engagement of cellular receptors for infectious entry. The transmembrane unit (S2) harbors functional elements pivotal to membrane fusion: a fusion peptide, two helical regions, and a

transmembrane domain. Proteolytic cleavage into the S1 and S2 subunits by host-cell proteases is formed.

The cellular entry of SARS-CoV-2 is a multistep process which involves the formation of several transient intermediates. All structures participating in the entry cascade are potential targets for inhibitors and the feasibility of several approaches to prevent entry. The S protein can also be targeted by lectins, which bind glycans on the S protein and thereby block viral entry In summary, the approaches described above, particularly combinations thereof, should allow development of compounds suitable for effectively preventing or combating future outbreaks of SARS-CoV-2.

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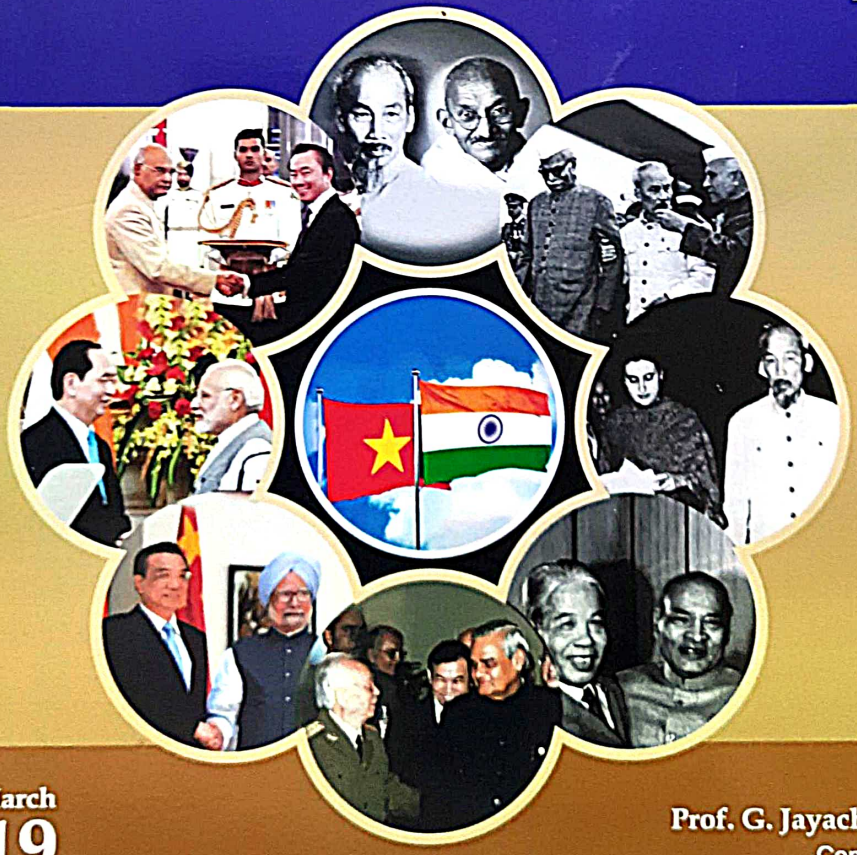
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UGC Centre for Southeast Asian and Pacific Studies
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*International Conference on*

# India-Vietnam Relations through the Prism of Gandhian and Ho Chi Minh Philosophies

18-19 March 2019

## Session-wise Programme

### 18 March 2019

**Breakfast** : 7.45am – 8.30am (at Hotel Pai Viceroy)

| 9.00am – 11.00am: INAUGURAL SESSION | |
|---|---|
| **Venue** | **Hotel Pai Viceroy (Orion Hall)** |
| **President** | **Prof. VVN Rajendra Prasad,** Vice-Chancellor, Sri Venkateswara University, Tirupati |
| **Inauguration** | **H.E. Amb. Pham Sanh Chau,** Vietnamese Ambassador to India, New Delhi |
| **Keynote Address** | **Amb. Ranjit Rae,** Former Ambassador to Vietnam, Ministry of External Affairs, New Delhi |
| **Guest of Honour** | **Lt General PR Shankar** PVSM, AVSM, VSM, Former Director General Artillery, Professor of Practice IIT Madras |
| **Guest of Honour** | **Dr. Upendra Choudhury,** Director, ICSSR, New Delhi |
| **Special Invitee** | **Prof. Le Van Toan,** Chairman of the Scientific Committee and Founding Director General of Centre for K Studies, Hanoi |

**11.00am – 11.15am Tea Break**

| 11.15am – 1.00pm : Session I | | |
|---|---|---|
| **Venue** | | **Hotel Pai Viceroy (Orion Hall)** |
| **Chairman** | | **Prof. A. Lakshmana Chetty** |
| **Theme** | | **India-Vietnam: History, Culture and Philosophy** |
| **11.15-11.30** | **Prof. K. Raja Reddy** | India-Vietnam: Burgeoning Partnership |
| **11.30-11.45** | **Prof. V. Suryanarayan** | Reflections on Third Indo-China War |
| **11.45-12.00** | **Prof. Le Van Toan** | Vietnam-India Relationship: Looking Back and Pondering |
| **12.00-12.15** | **Prof. Tridib Chakraborty** | Mahatma Gandhi and Ho Chi Minh: The Converging Destiny of Means and Ends |
| **12.15.12.30** | **Dr. Sonu Trivedi** | Gandhian and Ho Chi Minh Philosophies: The Ideological Link in India-Vietnam Relations |
| **12.30-1.00** | Discussion | |

# Trends in India's trade with Vietnam: An Empirical Analysis

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**Abstract**

*India and Vietnam share close to half a century of relations with the establishment of formal diplomatic ties that began in 1972 between India and the then-North Vietnam. The relations were derived from common historical linkages as colonies of Western powers striving to achieve independence. Bilateral ties between India and Vietnam have got strengthened in recent years with a focus on regional security issues and trade. The adoption of the 'Look East Policy', imbued with the economic element, marked an important turning point in India-Vietnam economic relations. Vietnam has played an important role in India's "Act East" policy, which was enunciated as an upgrading of the earlier 'Look East Policy' and also she has been a crucial partner in sub-regional, regional and multilateral forums. The need for economic development increased the importance of bilateral economic and commercial linkages between both the countries. These efforts received fillip from regional arrangements, as for example, ASEAN-India cooperation and Mekong - Ganga Cooperation. India is Vietnam's fifth largest trading partner in ASEAN; Vietnam holds the 19th position worldwide for India, both the countries made conscious efforts to expand the areas of economic cooperation and to increase the volume of trade and investment. India's total trade comprising exports and imports skyrocketed from the abysmal level of US $0.24 billion to the magnificent level of US $12.27 billion between the years 2001 and 2017. India and Vietnam will explore "substantive and practical measures" to achieve the bilateral trade target of $15 billion by 2020. Currently, India has 182 investment projects worth US $816 million in Vietnam, while Vietnamese businesses have a mere seven projects worth some US $6 million in India. The present paper reviews the performance of India's merchandise trade with Vietnam during 2000-01 to 2015-16 on the basis of the data released by the Ministry of Commerce and Industry, Government of India.*

*(302 words)*

**KEY WORDS:** ASEAN, Trade, Growth Rates, Commodity and Act East Policy

Several regional economic groups have emerged in different parts of the world particularly after 1950s. One such regional groups that has made rapid strides in terms of degree of economic integration and geographical coverage is "Association of South East Asian Nations" (ASEAN) among the countries of South East Asia. The Association of Southeast Asian Nations, or ASEAN, was established on 8th August 1967 in Bangkok, the capital of Thailand, with the signing of the ASEAN Declaration (Bangkok Declaration) by the founding members of ASEAN, namely Indonesia, Malaysia, Philippines, Singapore and Thailand. Brunei Darussalam then joined the Association on 8th January, 1984, Vietnam on 28th July 1995, Lao PDR and Myanmar on 23rdJuly,1997 and Cambodia on 30th April 1999. The ten member states of ASEAN hope that the regional co-operation among these members could help in exploiting the existing resources in the region fully. ASEAN is a unique example for regional co-operation and development. It is most successful inter-governmental organization in the developing world today. In the words of Kofi Annan, former Secretary General, UNO, ***"Today, ASEAN is not only a well-functioning, indispensable reality in the region, it is a real force to be reckoned with far beyond the region. It is also a trusted partner of United Nations in the field of development".***

India's relations with Vietnam are marked by growing economic and commercial engagement. India is now among the top ten trading partners of Vietnam. In recent times, political contacts have strengthened as reflected in several high level visits by leaders from both sides. Trade and economic linkages continue to grow. India's thrust under the 'Look East' policy combined with Vietnam's growing engagement within the region and with India has paid rich dividends. Vietnam is an important regional partner in South East Asia. India and Vietnam closely cooperate in various regional forums such as ASEAN, East Asia Summit, Mekong – Ganga Cooperation, Asia Europe Meeting (ASEM) besides UN and WTO.

Trade and other Areas along with defence and strategic ties, India has attempted to boost economic relations with Vietnam. Sri.NarendraModi's policy navigation from "Look East" to "Act East", which essentially aims to strengthen ties with the extended neighborhood of the Asia Pacific region and to expand ties between India and Vietnam to the level of "Comprehensive Strategic Partnership", makes Vietnam extremely critical in India's eastward outreach. Vietnam on its part has actively supported the Act East Policy as it facilitates India's larger role in the region. Also, Vietnam is ASEAN's Coordinator for ASEAN-India Dialogue Relations from 2015 to 2018, which can be utilised to further increase the cooperation. India is now among Vietnam's top ten trading

partners and during Sri. NarendraModi's 2016, which is expected to further boost bilateral trade between them. India-Vietnam economic ties date back to 1978 when both countries signed.

The two countries also expanded cooperation in areas such as space exploration and cyber security. New Delhi and Hanoi signed the Inter Governmental Framework Agreement for the exploration of outer space for peaceful purposes, and agreed to conclude the Implementing arrangement between the Indian Space Research Organisation and the Vietnam Ministry of Natural Resources and Environment on the establishment of a Tracking and Data Reception Station and a Data Processing Facility in Vietnam under the India-ASEAN Space Cooperation. A Memorandum of Understanding on cyber security was also signed between Vietnam's Ministry of Public Security and India's Ministry of Electronics and Information Technology; and the two countries also facilitated the transfer of equipment to the Indian-funded Indira Gandhi High-Tech Crime Laboratory. India has also established a satellite tracking facility in Ho Chi Minh City. Although termed a civilian facility, it could provide strategic benefits such as the tracking of Chinese movement in the sea, in case of a threat. It has been planned and implemented by the Indian Space Research Organization. Conclusion Collaborating on regional security, defence, and trade engagements, India and Vietnam have managed to build a strong partnership over the last few years. Given their mutual convergence, it is likely that this relationship will only grow stronger. There remains much to do, for instance India can help Vietnam is also a prospective market for India's defence exports, which still remains under-exploited. Beyond that, there is significant scope to explore in the economic realm on areas such as energy, mineral exploration, agro-processing, healthcare, IT, and education, among others, which will help to boost existing ties. Cultural and people-to-people exchanges need to be strengthened further as there is significant goodwill that can be leveraged by the two states. Overall, this is a relationship that is poised to take off in the coming years, led by political leaderships in the two countries determined to make this relationship truly strategic in orientation.

**India's Trade with Vietnam:**

Bilateral trade between India and Vietnam has seen continuous growth over the past few years. India is now among the top ten trading partners of Vietnam. Over the past 16 years there has been a steady increase in the trade volume between India and Vietnam. Eventually it crossed the 10,000cr. Mark in the year 2009-10. This is a major achievement, in light of the fact that one decade ago; in 2000-01 the total trade was Rs. 1088.64 cr. In the last five years there has been a continuous growth in the bilateral trade.

Vietnam is ASEAN country with which India has favorable trade balance. The relevant details are furnished in Table -1.

**Table-1: India's Exports to and Imports from Vietnam and World** (Rs in crores)

| Year | Exports | Imports | Exports to World | Imports from World | 2 as %age of 4 | 3 as %age of 5 | Balance of Trade | Trade Balance as % of total trade |
|---|---|---|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| 2000-01 | 1032.02 | 56.62 | 203571.01 | 230872.76 | 0.12 | 0.36 | 975.4 | 89.60 |
| 2001-02 | 1040.51 | 90.19 | 209017.97 | 245199.71 | 0.14 | 0.73 | 950.32 | 84.05 |
| 2002-03 | 1632.81 | 141.23 | 255137.27 | 297205.87 | 0.14 | 0.55 | 1491.58 | 84.08 |
| 2003-04 | 1886.01 | 175.6 | 293366.74 | 359107.66 | 0.14 | 0.52 | 1710.41 | 82.96 |
| 2004-05 | 2498 | 388.65 | 375339.52 | 501064.54 | 0.14 | 0.36 | 2109.35 | 73.07 |
| 2005-06 | 3057.86 | 581.69 | 456417.86 | 660408.9 | 0.11 | 0.35 | 2476.17 | 68.04 |
| 2006-07 | 4446.23 | 758.61 | 571779.28 | 840506.31 | 0.11 | 0.42 | 3687.62 | 70.85 |
| 2007-08 | 6451.28 | 698.07 | 655863.52 | 1012311.69 | 0.11 | 0.32 | 5753.21 | 80.47 |
| 2008-09 | 7949.47 | 1862.26 | 840755.05 | 1374435.55 | 0.12 | 0.14 | 6087.21 | 62.04 |
| 2009-10 | 8673.97 | 2459.11 | 845533.64 | 1363735.54 | 0.12 | 0.45 | 6214.86 | 55.82 |
| 2010-11 | 12045.07 | 4847.59 | 1142921.92 | 1683466.95 | 0.13 | 0.28 | 7197.48 | 42.61 |
| 2011-12 | 18084.98 | 8323.25 | 1465959.39 | 2345463.24 | 0.18 | 0.28 | 9761.73 | 36.96 |
| 2012-13 | 21562.84 | 12594.42 | 1634318.83 | 2669161.95 | 0.18 | 0.29 | 8968.42 | 26.26 |
| 2013-14 | 33253.25 | 15568.62 | 1905011.08 | 2715433.9 | 0.25 | 0.31 | 17684.63 | 36.22 |
| 2014-15 | 38317.85 | 18398.04 | 1896348.41 | 2737086.57 | 2.02 | 0.67 | 19919.81 | 35.12 |
| 2015-16 | 34616.91 | 16763.11 | 1714617.7 | 2488007.47 | 2.02 | 0.67 | 17853.8 | 34.75 |

Source: Website: http://commerce.nic.in/eidb/Default.asp (from 2000-01 to 2015-16)

It could be seen from the table that India's exports to Vietnam soared from Rs. 1,032.02crores to Rs. 34,616.91crores registering a magnificent 33.54 fold increase between 2000-01 and 2015-16. India's imports from this country, on the other hand, a skyrocketed by 296 times from Rs. 56.62 crores to Rs. 16,763.11crores. Thus both in magnitude and growth, the performance of imports from Vietnam were higher than that of exports. The same conclusion is reiterated by the ratio analysis. As could be seen from the table, India's exports to Vietnam as a proportion of her total global exports put up a spurt from 0.12 per cent in 2000-01 to 2.02 per cent in 2015-16. On the other hand, India's imports from Vietnam as a proportion of her total global imports rose sharply from 0.36 per cent to 0.67 per cent amidst wide fluctuations. In view of rising trends in both exports and imports both in absolute and relative terms, India had a comfortable position on her balance of trade. The India's positive trade balance with Vietnam

notched up from Rs.975.4crores to Rs. 17,853.8 crores in absolute terms but in relative terms the ratio decelerated from 89.60 per cent to 34.75 per cent during the study period in view of higher growth rates of imports as compared to exports.

Thus, both in magnitude and growth, the performance of imports from Vietnam was higher than that of exports. The same conclusion is reiterated by the ratio analysis. In view of relatively higher level of exports as compared to imports in absolute and relative terms, India had been in a comfortable position on her balance of trade. The India's positive trade balance with Vietnam notched up from Rs.975.4crores to Rs. 17,853.8 crores in absolute terms but declined from 89.60 per cent to 34.75 per cent in relative terms during the study period. The analysis of growth rates of India's trade with Vietnam as presented in Table.1A revealed excellent performance in both exports and imports. India's imports from this country grew by robust 51.22 per cent as compared to exports that put up a handsome 29.84 per cent growth per annum during the period under study. Both these growth rates were statistically significant at one per cent probability levels as confirmed by the computed 't' test statistics for exports (38.25) and imports (27.99) that were higher than the theoretical 't' test statistic value of 3.250. Also exports had a lower SEE of b value (0.007) and higher $R^2$ value (0.99) as compared to the corresponding values of 0.015 and 0.98 for imports.

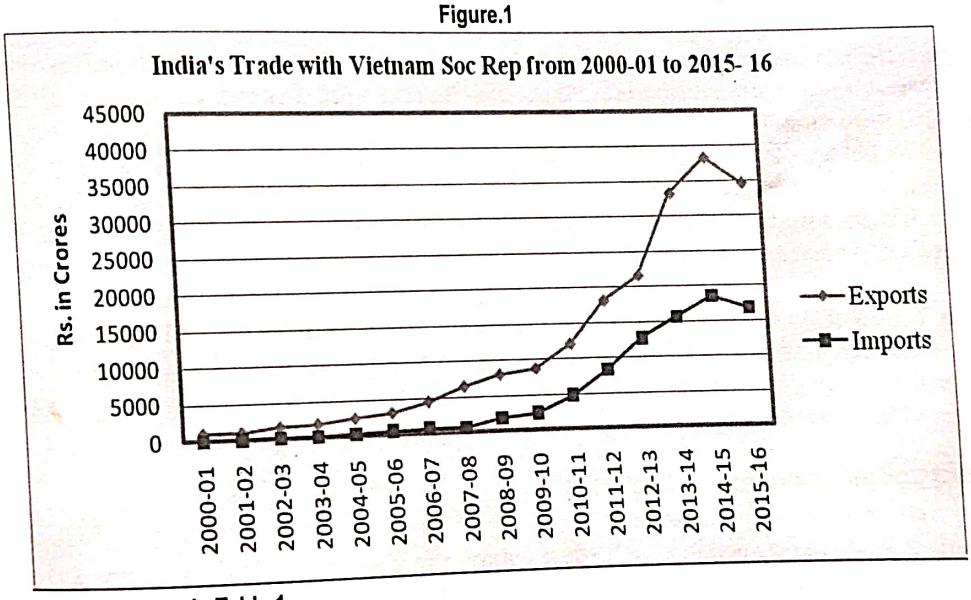
**Table.1A: Growth of India's Trade with Vietnam Soc. Rep., during 2000-01 to 2015-16**

| Variable | CAGR% | $R^2$ | SEE of b-value | t-value |
|---|---|---|---|---|
| Exports | 29.84 | 0.99 | 0.007 | 38.25 |
| Imports | 51.22 | 0.98 | 0.015 | 27.99 |

Source: Table.1

Thus India's exports to Vietnam performed well as compared to her imports from Vietnam in several respects. Figure.1 highlights the excellent performance India's trade with Vietnam in terms of line charts.

**Figure.1**




**Source: Computed for data in Table.1**

## GROWTHRATES OF MAJOR COMMODITY GROUPS OF INDIA'S EXPORTS TO VIETNAM

From the discussion of India's trade with Vietnam in chapter five, it was inferred that Vietnam is one of the most important and emerging India's trade partner within ASEAN region because India's exports to Vietnam grew by reliable and splendid 29.84 per cent and that India's imports from Vietnam surged by dependable and marvelous 51.22 per cent per annum during the period 2000-01 and 2015-16. India has also been enjoying positive trade balance with her trade with Vietnam. Given the scenario of overall trade, an attempt is made here to further probe to analyse the growth pattern of India's top 10 exports and imports items in her trade with Vietnam and relative shares of top ten commodity groups. Table.2 incorporates the necessary information on the growth rates, mean, standard deviation and coefficient of variation relating to India's exports to Vietnam.

**Table.2: Growth Rates of Top – 10 Commodities of India's Exports to Vietnam Soc Rep During the period from 2000-01to 2015-16**

| S. No | HS Code | Commodity | CAGR% | $R^2$ | t-cal value | Mean (Rs in crores) | SD (Rs in crores) | CV % |
|---|---|---|---|---|---|---|---|---|
| 1 | 23 | Residues and waste from the food industries; prepared animal fodder | 9.56 | 0.27 | 2.31 | 70.39 | 754.89 | 59.42 |
| 2 | 30 | Pharmaceutical products | 15.12 | 0.97 | 24.03 | 451.00 | 301.41 | 66.83 |
| 3 | 39 | Plastic and Articles Thereof | 12.33 | 0.76 | 6.70 | 383.52 | 248.68 | 64.84 |
| 4 | 84 | Nuclear reactors, boilers, machinery and mechanical appliances; parts thereof. | 28.67 | 0.86 | 9.65 | 375.10 | 415.09 | 110.66 |
| 5 | 40 | Rubber and Articles Thereof | 12.20 | 0.60 | 5.20 | 109.52 | 71.57 | 65.34 |
| 6 | 72 | Iron and Steel | 17.67 | 0.62 | 4.84 | 459.12 | 537.80 | 117.13 |
| 7 | 38 | Miscellaneous chemical products | 16.44 | 0.85 | 8.94 | 236.64 | 152.09 | 64.27 |
| 8 | 29 | Organic Chemicals | 16.07 | 0.94 | 15.40 | 248.98 | 161.94 | 65.04 |
| 9 | 3 | Fish and Crustaceans, Molluscs and other Aquatic invertebrates | 42.76 | 0.76 | 6.65 | 1580.01 | 2420.13 | 153.17 |
| 10 | 52 | Cotton | 40.59 | 0.93 | 14.33 | 653.53 | 821.42 | 125.68 |

Source: http://commerce.gov.in/EIDB.aspx

It is observed from the table that out of the top ten export commodity groups listed in the table, Fish and Crustaceans etc., (HS Code: 03) registered the highest growth rate of 42.76 per cent, closely followed by Cotton (HS Code: 52) with a growth rate of 40.59 per cent. The growth rates of these commodity groups were statistically significant at one per cent probability level. Next to these two commodity groups, the high tech commodity group viz., Nuclear Reactors, Boilers etc., (HS Code: 84) registered the highest growth rate of 28.67 per cent followed by Iron and Steel (HS Code:72) with a growth rate of 17.67 per cent.

The high growth rate of all the above four commodity groups was also associated with high levels fluctuations in terms of Coefficient of Variation ranging from 111 per cent to 153 per cent. The other export commodity groups that have registered double digit growth rates during the study period were Miscellaneous Chemical products (HS Code: 38) with a growth rate of 16.44 per cent, Organic Chemicals (HS Code: 29) with a growth rate of 16.07 per cent, Plastic and articles thereof (HS Code: 39) with a growth rate of 12.33 per cent, Rubber and articles thereof (HS Code: 40) with a growth rate of 12.20 per cent.Thus, out of 10 commodity groups, the only commodity group that has registered the single digit statistically insignificant growth of 9.56 per cent was the commodity group Residues and wastes from the food industries etc., (HS Code: 23).

The $R^2$ value of this commodity group was also very low. The commodities that have registered the growth rates between 10 per cent and 20 per cent, by and large, were subjected to relatively less degree of fluctuations in terms of coefficient of variation. The mean values of top 10 export commodity groups from India to Vietnam varied between a low of Rs.70.39 crores to Rs.1580 crores during the period under consideration.

**GROWTHRATES OF MAJOR COMMODITY GROUPS OF INDIA'S IMPORTS FROM VIETNAM**

The growth rates of India's imports from Vietnam during the period from 2000-01 to 2015-16 along with $R^2$ values, computed t-values, mean, standard deviation, coefficient of variation are furnished in Table.3. A cursory glance at the table indicates that when compared to the export growth rates, the import growth rates from Vietnam were relatively high. Among the listed top 10 import commodity groups, the Hi-tech commodity group viz., Electrical Machinery and Equipment etc., (HS Code: 85) registered the reliable and fabulous growth of 71.30 per cent per annum followed by Rubber and articles thereof (HS Code: 40) with a tremendous growth rate of 56.58 per cent, Footwear, Gaiters etc., (HS Code: 64) with a magnificent growth rate of 45.60 per cent, Plastic and articles thereof with an amazing growth rate of 40.66 per cent. It is important to note that the $R^2$ and computed t-values of all these commodity groups were all very high indicating the dependable and sustainable growth of these commodity groups in the future.

At the other extreme, the commodity group Lac, Gums, Resins etc., (HS Code: 13) exhibited negative growth of -18.21 per cent during the period under consideration. Though another commodity group Other Base metals, cermets etc., (HS Code: 81) registered reasonably higher growth rate of 18.26 per cent per annum, the growth was not statistically significant and also the $R^2$ value was very low. The mean value of India's top ten commodity groups from Vietnam varied between a low of Rs.4.29 crores in the case of Lac, Gums etc., and a high of Rs.2047.67 crores in the case of Electrical machinery etc. It should, however, be noted that

the fluctuations in the quantum of imports from the country were very high and were above 100 per cent indicating that the standard deviation values of the commodity groups were higher than the corresponding mean values. This implies that there are wide fluctuations in the year to year India's imports from Vietnam. Nevertheless, the growth rates of imports of all the commodity groups from Vietnam were statistically significant at one per cent probability level except in the case of one commodity group viz., Other Base metals etc. (HS Code: 81).

**Table.3 : Growth Rates of Top – 10 Commodities of India's Imports from Vietnam Soc Rep During 2000-01 to 2015-16**

| S. No | HS Code | Commodity | CGR% | $R^2$ | t-cal value | Mean (Rs in crores) | SD (Rs in crores) | CV % |
|---|---|---|---|---|---|---|---|---|
| 1 | 9 | Coffee, Tea, Mate and Spices | 27.90 | 0.922 | 12.83 | 404.83 | 435.64 | 92.93 |
| 2 | 13 | Lac; Gums, Resins and other vegetable saps and extracts | -18.21 | 0.44 | 3.37 | 4.29 | 4.31 | 99.54 |
| 3 | 85 | Electrical machinery and equipment and parts thereof; sound recorders and reproducers, television image and sound recorders and reproducers, and parts. | 71.30 | 0.957 | 17.66 | 2047.67 | 2883.82 | 71.01 |
| 4 | 39 | Plastics and articles thereof | 40.66 | 0.817 | 7.89 | 79.77 | 104.31 | 76.47 |
| 5 | 33 | Essential oils and Resinoids; perfumery, cosmetic or Toilet preparations | 51.76 | 0.95 | 16.37 | 86.63 | 129.53 | 66.88 |
| 6 | 40 | Rubber and Articles Thereof | 56.58 | 0.94 | 15.13 | 362.46 | 504.31 | 71.87 |
| 7 | 81 | Other Base Metals; Cermets; Articles Thereof. | 18.26 | 0.31 | 2.53 | 3.36 | 4.87 | 68.99 |
| 8 | 38 | Miscellaneous chemical products | 37.11 | 0.97 | 22.74 | 38.36 | 42.99 | 76.22 |
| 9 | 64 | Footwear, Gaiters and the like; parts of such Articles | 45.60 | 0.96 | 17.82 | 75.02 | 98.42 | 89.23 |
| 10 | 29 | Organic Chemicals | 26.16 | 0.64 | 5.04 | 28.18 | 18.57 | 151.75 |

Source: http;//commerce.gov.in/EIDB.aspx

**SHARES OF TOP 10 EXPORT COMMODITIES TO VIETNAM**

Having discussed the growth of India's top 10 export and import commodity groups from Vietnam, an attempt is made to analyse their relative shares in total exports and imports. Table.4 incorporates the information on the shares of top ten export commodity groups in India's exports to Vietnam during the period from 2000-01 to 2015-16.

**Table.4: Shares of Top Ten Commodities in India's Exports to the Vietnam Soc Rep**

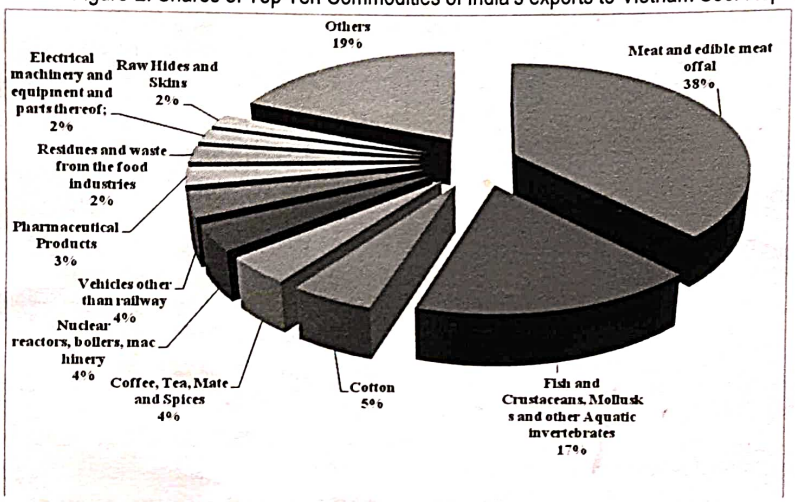
| S. No. | HS Code | Commodity | % Share in 2000-01 | Rank | % Share in 2015-16 | Rank |
|---|---|---|---|---|---|---|
| 1 | 23 | **Residues and waste from the food industries; prepared animal fodder** | **18.11** | **1** | **2.54** | **8** |
| 2 | 30 | **Pharmaceutical Products** | **14.87** | **2** | **2.76** | **7** |
| 3 | 39 | **Plastics and articles thereof** | **13.65** | **3** | **1.83** | **12** |
| 4 | 84 | **Nuclear reactors, boilers, machinery and mechanical appliances; parts thereof.** | **8.03** | **4** | **3.90** | **5** |
| 5 | 40 | **Rubber and Articles Thereof** | **6.98** | **5** | **0.34** | **28** |
| 6 | 72 | **Iron and Steel** | **5.92** | **6** | **1.33** | **14** |
| 7 | 38 | **Miscellaneous chemical products** | **5.33** | **7** | **1.26** | **15** |
| 8 | 29 | **Organic Chemicals** | **4.66** | **8** | **1.59** | **13** |
| 9 | 3 | **Fish and Crustaceans, Molluscs and other Aquatic invertebrates** | **4.52** | **9** | **16.76** | **2** |
| 10 | 52 | **Cotton** | **3.19** | **10** | **4.99** | **3** |
| | | Total | 85.26 | – | 37.3 | – |

Source: Computed for the data obtained from, commerce.nic.in/eidb/ecom.asp

It could be seen from the table that the top 10 India's export commodity groups to Vietnam accounted for an overwhelming proportion of 85.26 per cent of India's exports to Vietnam in the year 2000-01.However, over the years there has been marked change in the commodity composition of India's exports to Vietnam. As could be observed from the table in the year 2015-16, the top listed commodities in the table could account for only 37.3 per cent of total exports to the country. Except two commodity groups

viz., Fish and Crustaceans etc., (HS Code: 03) and Cotton (HS Code: 52), all other commodity groups have lost their shares drastically over the period of time. While the former commodity group could increase its share dramatically from 4.52 per cent to 16.76 per cent and rank from 9th to 2nd, the latter commodity group could marginally gain its share from 3.19 per cent to 4.99 per cent and rank from 10th to 3rd between the years 2000-01 and 2015-16. Three other notable commodities, that have retained their ranking within the top 10 even after losing their export shares, were Residues and wastes from the food etc., (HS Code: 23 which has lost its share from 18.11 per cent to 2.54 per cent and the rank from 1st to 8th), Pharmaceutical Products (HS Code: 30) which has lost its share from 14.87 per cent to 2.76 per cent and rank from 2nd to 7th and Nuclear Reactors, boilers etc., (HS Code: 84) which has lost its share from 8.03 per cent to 3.90 per cent and rank from 4 to 5). *The fall in the importance of India's hi-tech export products like Nuclear Reactors, boilers etc., (HS Code: 84) and Pharmaceutical Products (HS Code: 30) is a cause for concern.* Thus out of the top 10 export commodities five commodities slipped out of the top ten-list and in their place new commodity groups have entered. **Appendix Table-1** provides the details of the new commodity groups that have entered into India's export basket to Vietnam and their relative shares. These 10 commodity groups constituted about 81 per cent of the total exports shipped to Vietnam in the year 2015-16. The structure India's exports to Vietnam in the year 2015-16 are vividly represented in the form of Pie Diagram in Figure-2.

Figure-2: Shares of Top Ten Commodities of India's exports to Vietnam Soc. Rep. during 2015-16




## SHARES OF TOP - 10 IMPORT COMMODITIES FROM VIETNAM

The analysis of growth of India's imports from Vietnam in the earlier section indicated that all the commodities except one commodity group registered positive and high rates of growth. What is the effect of the growth rates on the relative shares of these commodity groups over the period of time? Table.5 provides the information on the relative shares of top ten India's import commodities from Vietnam during two years viz., 2000-01 and 2015-16.As could be observed from the table, out the top commodities two commodity groups viz., Electrical machinery and Equipment etc., (HS Code: 85) and Rubber and articles thereof (HS Code: 40) that have registered the highest and the second highest growth rates during the period 2000-01 and 2015-16 have markedly improved their relative shares respectively from 9.89 per cent to 31.40 per cent and from 5.43 per cent to 6.11 per cent.

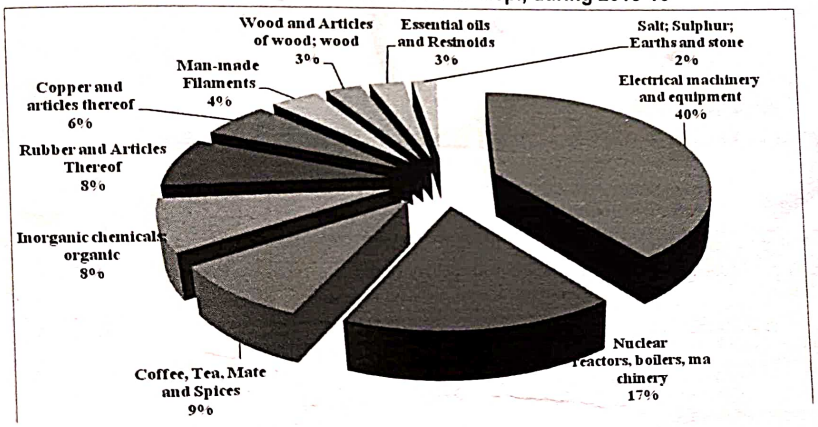
These two commodity groups occupied the first and fifth ranks respectively in the year 2015-16. In view of enormous rise in the relative share of the first commodity group, viz., Electrical machinery and Equipment etc., (HS Code: 85) from about 9 per cent to 31 per cent, the relative shares of other commodity groups have dwindled over the years even though they have achieved higher rates of growth. It is matter of appreciation to note that India has been importing essential manufactured commodities like electrical machinery and equipment, Rubber and articles thereof from Vietnam. On the other hand, India has been curtailing the imports of primary products such as coffee, Tea, mate etc., (HS Code: 09) whose share has fallen drastically from 34.54 per cent to 6.94 per cent, lac, Gums, Resins etc., (HS Code: 13), whose share has also decelerated sharply from 14.46 per cent to 0.02 percent, Miscellaneous Chemical products (HS code: 38) whose share has decelerated from 3.54 per cent to 0.74 per cent), plastic and articles thereof (HS Code: 39) whose share has come down from 8.42 per cent to 1.67 per cent, Essential Oils and Resinoids etc., (HS code: 33) whose share declined from 5.71 per cent to 2.37 per cent and Organic Chemicals (HS Code: 29) which has lost its share from 1.88 per cent to 0.21 per cent.

**Table.5:** Shares of Top Ten Commodities in India's Imports from Vietnam Soc. Rep

| S. No. | HS Code | Commodity | % Share in 2000-01 | Rank | % Share in 2015-16 | Rank |
|---|---|---|---|---|---|---|
| 1 | 9 | Coffee, Tea, Mate and Spices | 34.54 | 1 | 6.94 | 3 |
| 2 | 13 | Lac; Gums, Resins and other vegetable saps and extracts | 14.46 | 2 | 0.02 | 61 |
| 3 | 85 | Electrical machinery and equipment and parts thereof; sound recorders and reproducers, television image and sound recorders and reproducers, and parts. | 9.89 | 3 | 31.40 | 1 |
| 4 | 39 | Plastics and articles thereof | 8.42 | 4 | 1.67 | 12 |
| 5 | 33 | Essential oils and Resinoids; perfumery, cosmetic or Toilet preparations | 5.71 | 5 | 2.37 | 9 |
| 6 | 40 | Rubber and Articles Thereof | 5.43 | 6 | 6.11 | 5 |
| 7 | 81 | Other Base Metals; Cermets; Articles Thereof. | 3.94 | 7 | 0.01 | 67 |
| 8 | 38 | Miscellaneous chemical products | 3.54 | 8 | 0.74 | 20 |
| 9 | 64 | Footwear, Gaiters and the like; parts of such Articles | 1.92 | 9 | 1.66 | 13 |
| 10 | 29 | Organic Chemicals | 1.88 | 10 | 0.21 | 35 |
| | | Total Share | 89.74 | – | 51.13 | – |

Source: Computed for the data obtained from, commerce.nic.in/eidb/ecom.asp accessed on 08.06.2017

**Figure-3: Shares of Top Ten Commodities of India's Imports from Vietnam Soc Rep., during 2015-16**




All these commodity groups together accounted for only 51.13 per cent of total imports from Vietnam in the year 2015-16. This implies that other new commodity groups have entered in to India's import commodity basket and thereby India's imports structure has been more diversified in the year 2015-16 as compared to the year 2000-01. The details of new and diversified India's import basket from Vietnam in the year 2015-16 are furnished in the **Appendix Table-II**. At the same time, the details of India's import structure from Vietnam in the year 2015-16 are furnished in the form of Pie Diagram in Figure-3.

**Conclusion:**

India's has been initiating economic liberalisation since 1991 and Vietnamsince 1986. The economic reforms initiated by DoiMoiin Vietnam had created massive opportunities for commercial exchanges and cooperation in such areas as agriculture processing and technology and knowledge-based industries such as IT, biotechnology, oceanography and Space. Vietnam is focussing its attention on restructuring its economy by enhancing science and technology adoption where India can help Vietnam to a great extent. India's exports to Vietnam increased by 30 per cent whereas her imports from Vietnam rose by 51 per cent during 2000-01and 2015-16. The share of Vietnam in India's total exports to world varied from 1.11 per cent to 2.02 per cent and the share of imports from the country as a proportion of India's total imports ranged between a low of 0.14 per cent and 0.67 per cent during 2000-01and 2015-16. India has all along been getting positive trade balance with Vietnam in view of higher exports and relatively lower imports.Finally, both the countries need to understand their strengths and opportunities in their bilateral economic relations and

act accordingly. In a short period of time, it will be impossible for Vietnam to bridge the trade balance, which is currently in India's favour. Vietnam's attention therefore, must be focused on attracting investment from India, which Vietnam needs, to fuel its growing economy. At the same time, India in its endeavour to become a global economic player needs to strengthen its economic relations with Vietnam through increased interaction with physical, commercial, investment, and trade linkages to venture into the larger Asia-Pacific.

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www.asean.org


**Appendix Table - I**

**Shares of Top Ten Commodities in India's Exports to the Vietnam Soc Rep In the year 2015-16**

| S.No | HS Code | Commodity | % Share in 2015-16 | Rank |
|---|---|---|---|---|
| 1 | 2 | Meat and edible meat offal | 37.95 | 1 |
| 2 | 3 | Fish and Crustaceans, Mollusks and other Aquatic invertebrates | 16.76 | 2 |
| 3 | 52 | Cotton | 4.99 | 3 |
| 4 | 9 | Coffee, Tea, Mate and Spices | 4.09 | 4 |
| 5 | 84 | Nuclear reactors, boilers, machinery and mechanical appliances; parts thereof. | 3.90 | 5 |
| 6 | 87 | Vehicles other than railway or tramway rolling stock, and parts and accessories thereof. | 3.82 | 6 |
| 7 | 30 | Pharmaceutical Products | 2.76 | 7 |
| 8 | 23 | Residues and waste from the food industries; prepared animal fodder | 2.54 | 8 |
| 9 | 85 | Electrical machinery and equipment and parts thereof; sound recorders and reproducers, television image and sound recorders and reproducers, and parts. | 2.15 | 9 |
| 10 | 41 | Raw Hides and Skins (other than Fur skins) and leather | 1.99 | 10 |
| **Total** | | | **80.95** | -- |

Source: Computed for the data obtained from, commerce.nic.in/eidb/ecom.asp.

## Appendix Table - II

**Shares of Top Ten Commodities in India's Imports from Vietnam Soc Rep in the year 2015-16**

| S.No | HS Code | Commodity | % Share in 2015-16 | Rank |
|---|---|---|---|---|
| 1 | 85 | Electrical machinery and equipment and parts thereof; sound recorders and reproducers, television image and sound recorders and reproducers, and parts. | 31.40 | 1 |
| 2 | 84 | Nuclear reactors, boilers, machinery and mechanical appliances; parts thereof. | 13.11 | 2 |
| 3 | 9 | Coffee, Tea, Mate and Spices | 6.94 | 3 |
| 4 | 28 | Inorganic chemicals; organic or inorganic compounds of precious Metals, of Rare-Earth Metals, or Radi. Elem. or of isotopes. | 6.53 | 4 |
| 5 | 40 | Rubber and Articles Thereof | 6.11 | 5 |
| 6 | 74 | Copper and articles thereof | 4.50 | 6 |
| 7 | 54 | Man-made Filaments | 3.20 | 7 |
| 8 | 44 | Wood and Articles of wood; wood charcoal | 2.43 | 8 |
| 9 | 33 | Essential oils and Resinoids; perfumery, cosmetic or Toilet preparations | 2.37 | 9 |
| 10 | 25 | Salt; Sulphur; Earths and stone; Plastering materials, Lime and Cement. | 1.74 | 10 |
| | | **Total** | **78.32** | **–** |

Source: Computed for the data obtained from, commerce.nic.in/eidb/ecom.asp.

# Dissolution test Method and HPLC analysis for Pantoprazole Pellets dosage forms.

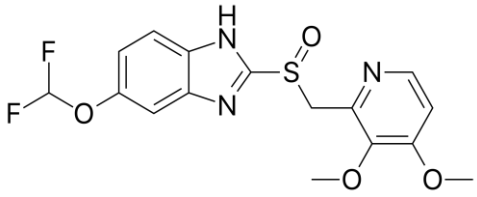
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**ABSTRACT:** Pantoprazole belongs to benzimidazole group. It is a proton pump inhibitor, used for the treatment of gastric and duodenum ulcers. It undergoes degradation in acid medium of the stomach, can be coated with enteric coating polymer that will safely deliver the drug in the small intestine. A simple dissolution test method for Pantoprazole pellets dosage forms has been proposed and HPLC analytical method was developed for the measurement of Pantoprazole pellets dosage forms with Detector .The chromatographic system consists of 4.0mm x 12.5CM, 5µ Packing L7 column, an gradient mobile phase of 340 ml of Acetonitrile+660ml phosphate buffer. The flow rate is 1ml /minute and elute is tested at 280nm.The pantoprazole was eluted 4.569min with no interfering peak from additives used for preparation dosage forms. The method was linear over the range of 10-125µg/ml pantoprazole. The dissolution test was conducted in 6.8 phosphate buffer, 900ml with paddle RPM at 100.Dissolution was found to be NTL 75% in 45 minutes. The proposed method was applied successfully for the measurement of Pantoprozole content in pellets dosage forms

Key words: Dissolution tester, HPLC, Pantoprazole Pellets dosage forms, RPM, Mobile phase

1. INTRODUCTION: IUPAC name of pantoprazole is "6-(difluoromethoxy)-2-[(3,4-dimethoxypyridin-2-yl)methylsulfinyl]-1H-benzimidazole".It is a substituted benzimidazole specified for the short-term treatment (up to 16 weeks) in the healing and symptomatic relief of erosive esophagitis. Pantoprazole is a proton pump inhibitor (PPI) that suppresses the final step in gastric acid production[1], it is due to lipophilic weak base that crosses the parietal cell membrane and enters the acidic parietal cell canaliculus where it becomes protonated, producing the active metabolite sulphenamide, which forms an irreversible covalent bond with two sites of the H+/K+-ATPase enzyme located on the gastric parietal cell, thereby inhibiting both basal and stimulated gastric acid production[2].

**Structure of Pantoprazole:**



2. Materials and Methods:

2.1 Instruments: Dissolution tester make Electrolab India (p)L.t.d, High performance liquid chromatograph shimadzu 2010 Rheoodyne injector with 100µl loop.L.C solutions computer based software is used.

2.2.Chemicals: Working standard pantoprazole procured from M/S Angels Pharma India Private Limited, Acetonitrile, HPLC grade(make E-Merck) ,Methylene chloride, Methanol (HPLC GRADE), Ammonia, Isopropyl alcohol(HPLC GRADE), Ethanol AR, Disodium tetraborate AR, Dibasic Sodium phosphate AR, Hydrochloric acid AR, Sodium Hydroxide AR, Monobasic sodium phosphate AR, Potassium dihydrogen orthophosphate and purified water.

2.3. Drug release

Acid resistance stage:

| | |
|---|---|
| Medium | : 0.1 N Hydrochloric acid; 500mL |
| Apparatus | : USP-II |
| Rpm | :100 |
| Time | : 2 hours |

Buffer stage

| | |
|---|---|
| Medium | : 6.8 phosphate buffer, 900ml |
| Apparatus | : USP-II |
| Rpm | : 100 |
| Time | : 30min. |

2.4**Requirements:**

**Instruments:** A suitable High Performance Liquid Chromatography consisting of a pump, a UV-VIS detector, sample injector, controller and integrator or equivalent software. The system is equipped with 4.6mm x 250mm, Inertsil ODS 3V or Equivalent. Dissolution apparatus, pH meter

**Reagents;** Methylene chloride, Methanol (HLC GRADE), Ammonia, Isopropyl alcohol(HLC GRADE), Ethanol AR, Disodium tetra borate AR, Dibasic Sodium phosphate AR, Hydrochloric acid AR, Sodium Hydroxide AR, Monobasic sodium phosphate AR, Acetonitrile (HLC GRADE), Potassium di hydrogen orthophosphate and purified water.

2.5 Solution Preparation:

Preparation of 0.01M of Disodium borate:
Weigh about 3.84g of Disodium tetraborate and make up to 100mL using wate, mix well.
0.1NHCI Preparation:
Take about 8.5ml of Hydrochloric acid and make up to 1000ml using water, mix well.

2N HCI Preparation:
Take about 17.0ml of Hydrochloric acid and make up to 100ml using water, mix well

2N NaOH Preparation
Weigh about 8.0g of NaOH and make up to 100ml using water, mix well.

pH 10.4 Buffer preparation:
0.235 M Dibasic sodium phosphate-Dissolve 33.36g of anhydrous sodium phosphate in 100ml of water. And adjust with 2N sodium Hydroxide to pH of 10 .4 ± 0.1

pH 6.8 Phosphate buffer preparation:
Add 400ml of 0.1N hydrochloric acid to 320 ml of pH 10.4, 0.235 M Dibasic sodium phosphate and adjust with 2N Hydrochloric acid or 2N sodium hydroxide, if necessary, to a pH of 6.8±0.05. Dilute 250ml of this solution with water to 1000ml.

pH 7.6 Phosphate Buffer preparation:
Dissolve 0.178g of monobasic sodium phosphate and 4.49g of dibasic sodium phosphate in 1000ml of water. Adjust with 2N Hydrochloric acid or 2N sodium hydroxide, if necessary, to a pH 7.6±0.1. Dilute 250ml of this solution with water to 1000ml.
Mobile phase preparation:
Transfer 340 ml of Acetonitrile to a 1000ml volumetric flask, dilute with pH 7.6 phosphate buffer to volume, and pass through a membrane filter having a 0.5um or finer porosity,. Make adjustments.
Diluents:-
Dissolve 7.6g of sodium borate dehydrates in about 800ml of water. Add 1.0g of edentate Disodium, and adjust with 50% sodium hydroxide solution to a pH of 11.0±0.1. Transfer the solution to a 2000ml volumetric flask, add 400ml of dehydrated alcohol, and dilute with water to volume.

Solution A- Prepare a filtered and degassed solution of 6.0g of glycogen in 1500ml of water. Adjust with 50% sodium hydroxide solution to a pH of 9.0, and dilute water to 2000ml.

Solution B- Use a filtered and degassed mixture of acetonitrile and methanol(85:15)

Mobile phase – Use variable mixture of solution A and solution B as directed for chromatographic system. Make adjustments if necessary.

3.0 Acid Stage Dissolution solutions preparation:

Standard solution:
Accurately weigh about 50 mg of Pantoprazole WS, in to a 250ml volumetric flask, dissolve in 50 ml of alcohol, dilute with 0.01M sodium borate solution to volume and mix. Transfer 10.0ml of this solution into a 100ml volumetric flask, add 20ml of alcohol, dilute with 0.01M sodium borate solution to volume and mix well.

Test solution:
Transfer 500ml 0.1N HCI solution in dissolution jar maintains the temp. $37.0^0C \pm 0.5^0C$ and accurately weigh 235.0mg of sample (pellets) transfer in to the jar. Start the dissolutions system. After 2 hours, filter the dissolution medium containing the pellets on the sieve, and rinse them aperture of not more than 0.2mm. after 2 hrs collect the pellets on the sieve, and rinse them with water.
Using approximately 60ml of 0.01M sodium borate solution, carefully transfer the pellets quantitatively to a 100ml volumetric flask. Sonicate for about 20minutes until the pellets are broken up. Add 20ml of alcohol to the flask, dilute with 0.01M sodium borate solution to volume, and mix. Dilute the an appropriate amount of this solution with 0.01M sodium borate at about 3000rpm for 5 minutes. Final Concentration 10µg/ml.

4.0 Buffer stage:
Medium: pH 6.8 phosphate buffer, 900ml
Proceed as directed for acid resistance stage with a new set of pellets from the same batch. After 2 hours, add 400 ml of 0.235M dibasic sodium phosphate to the 500ml of 0.1N hydrochloric acid medium in the vessel. Adjust, if necessary, with 2 N hydrochloric acid or 2 N sodium hydroxide to a pH 6.8 ±0.05.

ApparatusUSP-II : 100rpm
At the end of 30 minutes, determine the amount of Pantoprazole dissolved in pH 6.8 phosphate buffer by employing the following method.

Dissolution Calculation:

$$\frac{\text{Sample area}}{\text{Std area}} \times \frac{\text{std dilution}}{\text{sample dilution}} \times \frac{100}{Assay} \times \text{Stand purity} = \text{---------}\%$$

5.0. Chromatographic parameters:

| | |
|---|---|
| Column | : 4.0mm x 12.5CM, 5 µ Packing L7 |
| Detector | : UV-Vis Detector |
| Wave length | : 280nm |
| Flow rate | : 1.0ml/minute |
| Injection volume | : 20 µL |
| Run time | : 12 minutes |

| Time (Minutes) | solution A % | solution B % | Elution |
|---|---|---|---|
| 0-20 | 88-40 | 12-60 | linear gradient |
| 20-21 | 40-88 | 60-12 | linear gradient |
| 21-25 | 88 | 12 | isocratic |

System suitability:

Inject blank and record the chromatogram. Examine the chromatogram for any extraneous peaks. There should be no interference from the blank at the retention time of analyte peak. Inject standard solution five times and calculate the relative standard deviation (RSD) for area of the analyte peak. The relative standard deviation for five injections of Pantoprazole should not be more than 2.0%.

Separately: Inject equal volume (about 20µL) of the standard preparation and the test preparation into the chromatograph, record the chromatograms, and measure the peak area response. Calculate the quantity, in mg of Pantoprazole by the given formula

Dissolution Calculation:

$$\frac{\text{sample area}}{\text{Std area}} \times \frac{\text{std Dilution}}{\text{sample dilution}} \times \frac{100}{\text{Assay}} \times \text{std purity} = _____\%$$

6. Assay:

6.1 Requirements:

Instrument: A suitable high performance Liquid chromatograph consisting of a pump, a UV-VIS detector, sample injector, controller and integrator or equivalent software. The system is equipped with 4.6mm x 250mm, inertsil ODS 3V or Equivalent, Dissolution apparatus and pH Meter.

Reagents: Methanol (HPLC GRADE), Phosphorouspentixide, ammonia, hydrochloric acid AR, sodium hydroxide AR, Monobasic sodiumphospahte, Acetonitrile, (HPLC GRADE) and purified water.

6.2 pH 7.6 Phosphate Buffer preparation:
Dissolve 0.718g of monobasic sodium phosphate and 4.49g of dibasic sodium phosphate in 1000ml of water. Adjust with 2N Hydrochloric acid or 2N sodium hydroxide, if necessary, to a pH of 7.6$\pm$ 0.1. Dilute 250ml of this solution with water to 100ml.

6.3 Mobile phase preparation:
Transfer 340ml of acetonitrile to a 1000ml volumetric flask, dilute with pH 7.6 phosphate buffer to volume, and pass through a membrane filter having a 0.5um or finer porosity. Make adjustments.

Diluent: Dissolve 7.6 g of sodium borate dehydrates in about 800ml of water. Add 1.0g of edentate Disodium, and adjust with 50% sodium hydroxide solution to a pH of 11.0$\pm$0.1. Transfer the solution to a 2000ml volumetric flask, add 400ml of dehydrated alcohol, and dilute with water to volume.

Blank solution: Take mobile phase as blank.

6.4 Chromatographic parameters:

Column : 4.0mm x 12.5CM, 5µ Packing L7
Detector : UV-Vis Detector
Wave length : 280nm
Flow rate : 1.0ml/minute
Injection volume : 20µL
Run time : 12 minutes

Procedure:

| Time (Minutes) | solution A % | solution B % | Elution |
|---|---|---|---|
| 0-20 | 88-40 | 12-60 | Linear gradient |
| 20-21 | 40-88 | 60-12 | Linear gradient |
| 21-25 | 88 | 12 | isocratic |

Standard preparation- Dissolve, by sonicating an accurately weighed quantity of Pantoprazole WS in diluent, and quantitatively, and stepwise if necessary, with diluents to obtain a solution having known concentration of about 0.2mg per mL.

Sample preparation- Weigh and mix the contents, Transfer an accurately weighed portion of the mixture about 235mg of Pantoprazole, to a 100mL volumetric flask, add about 50ml of membrane filter having 0.45µm of fine porosity. (Note – Bubbles may form just before bringing the solution to volume. Add a few drops dehydrated alcohol to dissipate the bubbles if the persist for more than few minutes.)

Blank solution: Take mobile phase as blank.

Procedure:
Separately inject equal volume (about 20µl) of the standard preparation and the test preparation into the chromatograph, record the chromatograph, and measure the peak area responses. Calculate the quantity, in mg of Pantoprazole by the given formula

$$\text{Assay calculation: } \frac{\text{sample area}}{\text{Std area}} \times \frac{\text{standard dilution}}{\text{sample dilution}} \times \text{std purity} = _____\%$$

**Recovery studies:** To study the linearity, accuracy and precision of proposed method, recovery experiments were carried out known quantities of standard at two different levels were added to the pre analyzed sample, the recovery was estimated to be more than 99%.

**Conclusion:** The proposed method is simple rapid and no where involves use of complicated sample preparation. High percentage of recovery shows that the method is free from interference of the excipients used in the semi formulations. Therefore method can be useful in routine quality control analysis.

**7. Acknowledgement**

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Materials Research Express

**ACCEPTED MANUSCRIPT**

# Influence of fuel nature on dye adsorption efficiency of solution combustion derived zinc oxide nanoparticles: A comparative study

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# Influence of fuel nature on dye adsorption efficiency of solution combustion derived zinc oxide nanoparticles: A comparative study

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## *Abstract*

The present work demonstrates the use of coffee husk extract as a fuel (otherwise an agro waste) for the synthesis of nano zinc oxide (ZnO) by one step solution combustion synthesis. We also show the comparative studies of coffee husk extract (green fuel) derived nano ZnO (CHZnO) and sugar (chemical fuel) derived nano ZnO (SZnO) as an adsorbent for Congo red dye removal. Synthesized ZnO nanoparticles were characterized using XRD, SEM, TEM, FTIR, and BET. The adsorption characteristics were investigated with respect to changes in pH, temperature, initial dye concentration, adsorbent dose and contact time. CHZnO exhibited higher adsorption capacity (76 mg/g) compared to SZnO (56 mg/g). The equilibrium adsorption data were analyzed using various isotherm models (Langmuir, Freundlich, Temkin, and Dubinin-Radushkevith) and thermodynamic parameters. Among the models studied, Langmuir isotherm fitted well with experimental equilibrium data ($R^2$>0.99). Adsorption kinetics was found to follow pseudo-second order with the highest $R^2$ value. Intraparticle or pore diffusion was the major rate controlling step in the adsorption process. The present study demonstrates the potential application of agro-based bio-waste as a novel fuel in the synthesis of nanomaterials for use as efficient adsorbents in water treatment.


Keywords: Coffee husk extract, nano ZnO, Adsorption, Congo Red, Intraparticle diffusion

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## *Introduction*

Textile industry ranks first in the usage of dyes for colouration of fibres. However, low levels of dye-fibre fixation results in more than 50% of dyes being lost in the effluent stream of these industries [1]. The complex aromatic structure of dyes resists them from aerobic digestion. This increases the problem of degradation and poses severe problems to the aquatic life, food web and causes damage to the aesthetic nature of the environment [2,3]. Most of the dyes may be carcinogenic, mutagenic or teratogenic, cause allergic dermatitis, skin irritation etc. and pose a serious threat to human health. To control the negative effects of dyes on the living system and water quality, it is necessary to completely remove or minimize the concentration of dyes to permissible limits prior to their discharge [4,5].

Several physical, chemical, and microbial methods like adsorption, coagulation, flocculation, biodegradation, chemical oxidation, reverse osmosis, membrane filtration, electrochemical methods etc. have been reported for the removal of dyes in the effluent [4,6,15,7–14]. However, due to the complexity of the dye-containing wastewater stream, there is no single technique capable of providing complete remediation for such streams [16]. Among the various methods, adsorption process has been found to be superior in terms of its effectiveness, flexibility, simplicity, and ease of operation. Adsorption also removes the dye molecule as a whole and leaves no harmful fragments in the effluents [11,17]. Adsorptive removal of pollutants from wastewater has been extensively studied using activated carbon, zeolites, biomaterials, polymers etc. However, owing to factors like low efficiency, high cost, recycling difficulty and lower adsorption rates of various adsorbents used, it is crucial to develop more efficient and cost-effective adsorbents for removal of pollutants from wastewater in industrial scale [18,19]. Metal and metal oxide nanoparticles, due to their small size, larger surface area, high adsorption efficiency, and other multifunctional properties, have gained great attention over conventional adsorbents in decontamination of wastewater [16,20,21]. Among numerous metal oxides used, ease of large-scale synthesis with economic viability has made zinc oxide nanoparticles ideal adsorbent in water decontamination applications [22]. Extensive literature is available on the utilisation of ZnO nanoparticles as a photocatalyst for removal of organic pollutants, however, its use as adsorbant is limited [12,23–29]. Adsorptive removal of Acid Black 210 [30], Reactive black 8 [31], Remazol Brilliant Blue R[30,32], Victoria Blue B [21], Congo red [19,22,33], Brilliant green [33], Ionic dyes [34], Methyl orange [35], Methylene blue [35,36], Rhodamine 6G [35], Rhodamine B [37], acid orange 7 [37], RuN3 [38], malachite

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green [22] dyes using zinc oxide nanoparticles synthesised by different routes have been reported.

Among the various routes of nanoparticle synthesis, solution combustion method is a simple one-step process that requires lesser time and energy [39–41]. This method also yields homogenous and crystalline oxide products of high purity. Fuel used in the solution combustion synthesis is important among various experimental parameters because it has a tremendous effect on the exothermicity and amount of gases that evolve during the auto-combustion process. These parameters have significant effect on morphology, phase and particle size of the oxide products [42,43]. From the recent reports, it is evident that most commonly used fuels for combustion synthesis are carbohydrates and amines that have the capability of chelating with metal ions of desired metal oxides [39]. In spite of various reports on the use of different chemicals as fuels, use of eco-friendly, bio-derivative extracts as fuels are limited. The main objective of this research is therefore, to utilize extract of coffee husk, an agro waste generated during dry processing of coffee beans, as a sustainable fuel for the synthesis of ZnO nanomaterial (CHZnO) through solution combustion method. Coffee husk extract could play an important role as fuel because it is rich in biomolecules such as carbohydrates (58-85%), proteins (8-11 %), polyphenols, tannins etc. [44]. Some of these biomolecules contain amine groups which possess good chelating properties and helps in combustion [45]. The use of coffee husk extract as novel fuel for the synthesis of metal oxides could be a greater contribution to the field of nanomaterial synthesisand opens up a new avenue in the utilization of bio-waste as one of the reactants (fuel) for nanomaterial synthesis.

In the present study, adsorption efficiency for removal of Congo red using green-fuel derived CHZnO was compared with chemical-fuel derived SZnO. Effect of process parameters such as adsorbent dose, solution pH, initial dye concentration, temperature and time were studied in batch mode. The equilibrium adsorption data were analyzed with various kinetic and thermodynamic models and experimental data were modelled with various isotherms to understand the mechanism of Congo red adsorption on ZnO nanoparticles.

## Materials and Methods

### *Materials*

Zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$, 99 % purity) and Congo red ($C_{32}H_{22}N_6Na_2O_6S_2$, $\lambda_{max}$-497 nm, Figure) were procured from S D Fine-Chem Limited, Mumbai. All chemicals were of



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analytical grade and used without further purification. Coffee husk was collected from Allana Coffee Curing Works, Hassan (13.0753° N, 76.1784° E), India. Double distilled water was used throughout the experiments. The structure of Congo red is given in Figure S1.

***Preparation of Coffee Husk extract***

Coffee husk was manually cleaned to remove foreign materials and dried in hot air oven at 40 ºC till a constant mass was achieved. Dried coffee husk was ground in a domestic mixer and powdered. 15 g of powder was boiled in 250 ml of water for 1 h with reflux arrangement. The extract was filtered to remove the residues and refrigerated for further experiments.

***Synthesis of ZnO nanoparticles***

To study the effect of fuel on morphology and adsorption capacity of nanoparticles, zinc oxide was prepared using coffee husk extract as green fuel and sugar as chemical fuel. For coffee husk extract mediated synthesis of ZnO, 2.97 g zinc nitrate hexahydrate was dissolved in 10 ml of coffee husk extract and diluted with 10 ml of double distilled water. The resulting redox mixture was stirred for 1 h using a magnetic stirrer to obtain a homogeneous solution. This mixture was kept in a preheated muffle furnace at 500±10 ºC. The reaction mixture underwent thermal dehydration followed by flame type combustion with the evolution of a large amount of gases. Milky white fluffy mass of nanocrystalline ZnO nanoparticles was obtained. The experiment was repeated for different volumes of coffee husk extract (20, 30, 40, 50 ml and 60 ml) to optimize the fuel quantity. The same protocol was used for chemical fuel mediated synthesis of ZnO nanoparticles using a stoichiometric ratio of zinc nitrate hexahydrate and sugar. The obtained ZnO nanoparticles using coffee husk extract and sugar were named as CHZnO and SZnO respectively.

***Characterization of ZnO Nanoparticles***

Powder X-ray diffraction (XRD) characterization of the ZnO nanoparticles was carried out using (Rigaku's, Smartlabs, Japan) rotating anode Cu Kα (1.5406 Å). The accelerating voltage and current were 30 kV and 40 mA respectively. The XRD patterns were collected in the 2θ range 10° to 70° with a step size of 0.02°. Scanning electron micrographs (SEM) were recorded to investigate the surface morphology using JEOL (JSM-840A) instrument. TEM analysis was



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performed using JEOL JEM-301 machine operated at 200 kV. The surface area and porosity of the adsorbent were determined using a MicrotracBEL, Japan, Automatic specific surface area/pore size distribution measurement. The FTIR spectroscopic studies of the adsorbent have been carried out on a Perkin Elmer spectrometer (Spectrum 1000) with KBr pellets.

***Determination of Zero Point Charge***

The zero-point charge of the adsorbent was determined by solid addition method described elsewhere [38,39]. A Series of 50 ml 0.01 N NaCl solution was taken in 250 ml conical flask and solution pH was adjusted between 2 and 12 using 0.01 N NaOH and 0.01 N HCl. 0.01 g of ZnO nanoparticles was added to these solutions and kept in an orbital shaker at 150 rpm to equilibrate for 48 h. Final pH of the solution after 48 h was measured and the zero-point charge was obtained from the plot of the change in pH (final pH – initial pH) Vs initial pH.

***Batch Adsorption studies***

To assess the performance of the adsorbent, batch mode of adsorption experiments was conducted in 250 ml conical flasks with 50 ml of Congo red solution agitated at 150 rpm in an orbital shaker. Effect of adsorbent dosage (5-50 mg), pH (6-12), initial dye concentration (100-800 mg/L), temperature (30-60 $^{o}$C) and time (5-120 min) were systematically investigated. Initial pH was adjusted using sodium hydroxide (0.1 N) or hydrochloric acid (0.1 N). Post-interaction, solutions were centrifuged at 15000 rpm for 5 min to remove the adsorbent. The absorbance of the supernatant solution was recorded at 497 nm wavelength. The dye removal efficiency, equilibrium capacity of adsorption ($q_e$) and adsorption capacity at time t ($q_t$) are calculated using equations,

$$\text{Dye removal efficiency (\%)} = \frac{100\,(C_i - C_e)}{C_i} \quad \text{or} \quad \frac{100\,(C_i - C_t)}{C_i} \qquad \text{Equation (1)}$$

$$q_e = \frac{(C_0 - C_e)\,V}{m}, \text{ mg/g} \qquad \text{Equation (2)}$$

$$q_t = \frac{(C_0 - C_t)\,V}{m}, \text{ mg/g} \qquad \text{Equation (3)}$$

where $C_i$ is the initial dye concentration (mg/L), $C_e$ or $C_t$ is dye concentration left in solution after equilibrium or kinetic time, $V$ is the volume of dye solution (L) and $m$ is the mass of adsorbent (g).



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### *Statistical Analysis*

Adsorption experiments were carried out in duplicates and average values were used for modelling of isotherm and kinetics data. Linear regression analysis of models was performed in Microsoft Excel® 2016 and the suitable models were selected based on the values of the coefficient of correlation ($R^2$) calculated using the following expression,

$$R^2 = \frac{\sum(q_{e,pre,i} - q_{e,exp,avg})^2}{\sum(q_{e,pre,i} - q_{e,exp,avg})^2 - \sum(q_{e,pre,i} - q_{e,exp,i})^2} \quad \text{Equation (4)}$$

where $q_{e,exp,i}$ and $q_{e,pre,i}$ are experimentally measured and model predicted adsorbate solid phase concentration on adsorbent at any observation i respectively. $q_{e,exp,avg}$ is average of experimentally measured observations and N is the number of observations [46].

## Results and Discussion

### *Characteristics of ZnO Nanoparticles*

XRD patterns of nano ZnO prepared with different volumes (10-60 ml) of coffee husk extract fuel are shown in Figure 1. XRD pattern of all the samples prepared indicated pure ZnO with hexagonal structure without any impurity phases within the concentration range of the fuel studied. All the diffraction planes can be readily indexed to standard data (JCPDS: 72-0627) [47]. However, the XRD diffraction peaks showed differences in peak height and width for samples prepared with the varying concentration of coffee husk extract fuel. With an increase in the volume of fuel, the peak width is found to increase and the intensity of diffraction peaks are significantly reduced. This might be attributed to reduced exothermicity when excess fuel is used due to the fact that part of energy during combustion is used up for oxidation of carbon moiety present in the fuel [43]. From the XRD pattern, it is evident that beyond 30 ml of fuel, there is a significant decrease in the crystallinity of the ZnO nanoparticles. On the other hand, when the volume of coffee husk extract is < 30 ml, the diffraction patterns show broad peaks with relatively less intensity. This suggests that when the fuel volume is < 30 ml, the crystallinity of the ZnO obtained is not sufficient enough due to fuel deficient conditions. 30 ml of coffee husk extract fuel which resulted in nano ZnO with appreciable crystallinity, is therefore chosen as the optimised concentration of fuel. Further, XRD pattern of ZnO prepared with sugar as fuel is shown in Figure 2. which indicates wurtzite structure ZnO particles devoid of

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impurities. It is worth noticing that the crystallinity of the ZnO prepared with sugar as fuel is found to be significantly higher than that with coffee husk extract fuel. This might be due to higher exothermic nature of the reaction when sugar is used as fuel resulting in a better crystalline product. To evaluate the average crystallite size of the samples, Scherrer's peak broadening method was employed using Scherrer equation [48,49]. The average crystallite size for CHZnO and SZnO was found to be 12 nm and 24 nm respectively.

Scanning electron microscopic images of CHZnO and SZnO is shown in Figure 3 (a) and (b) respectively. From the micrographs, it is evident that SZnO nanoparticles showed well-formed particles with a varying size and the agglomeration of the particles resulted in the formation of interconnected particle clusters. Discontinuous nature of agglomerated particles resulted in the creation of voids in the structure. On the other hand, the surface morphology of the CHZnO has clusters of agglomerated mass and individual particles are not clearly distinguishable. The extent of agglomeration is found to be greater in CHZnOcompared to SZnO. It is worth noticing that in CHZnO varying sizes of agglomerated clusters are formed on flaky type morphology.. The difference in the size of agglomerated clusters can be attributed to the uneven distribution of heat during combustion reaction [50] and higher agglomeration in the coffee husk extract derived samples might be due to smaller particle size compared to that of sugar derived samples.

Transmission electron microscopy (TEM) of ZnO nanoparticles prepared by coffee husk extract and sugar as fuels is shown in Figure 4 (a) and (b) respectively. Figure 4(a) indicates predominantly spherical particles with a few irregular shaped particles. The size of the particles is found to be varying between 10 and 40 nm in diameter. However, TEM micrographs of CHZnO coffee husk extract derived ZnO nanoparticles (Figure 4 b) shows that all the particles are near spherical in nature with average size ~15 nm. The extent of agglomeration in CHZnO is found to be greater than that of SZnO. The obtained TEM result is consistent with SEM analysis and the reason for higher agglomeration might be due to smaller particles that readily agglomerate in order to reduce the higher surface energy.

Among the many important characterizations for nanopowders, specific surface area (SSA) is essential for evaluating the applicability for various engineering applications. It is well established and recorded fact that SSA ($m^2/g$) of powder samples depends on various other parameters such as size, morphology, size distribution, and synthesis methodology. In addition to this, porosity is also one crucial factor that significantly affects the SSA. It is well-known fact

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that solution combustion derived products possess high porosity due to the liberation of gaseous byproducts during the exothermic reaction [45]. Further, the heat generated during exothermic combustion reaction is sufficient enough for the nucleus formation but too short for the grain growth. This will lead to the formation of particles in the nano-regime and hence higher surface area for combustion derived products [42]. The surface area and pore size distribution of the samples CHZnO and SZnO are evaluated from $N_2$ adsorption-desorption isotherms and are given in Figure 5(a) and (b) respectively. The BET surface areas of CHZnO and SZnO are found to be 38 and 29 $m^2/g$ respectively. The reduced surface area for SZnO can be attributed to the reduced particle size compare to that of CHZnO, which is also evident from TEM analysis. The reasons for variation in particle size are discussed in PXRD and TEM sections. The pore size distribution is calculated using the Barrett–Joyner–Halenda (BJH) model and indicates that pore size distribution is in the range of 10 - 30 nm with a maximum at about 11 nm.

***Effect of Adsorbent dosage***

The effect of adsorbent dosage on the removal of Congo red dye using zinc oxide nanoparticles was studied with an initial dye concentration of 20 mg/L at neutral pH and the results obtained are shown in Figure 6. With an increase in adsorbent dosage, the percentage dye removal is found to increase. Percent removal of dye was 32 % with 0.1 g/L of CHZnO and reached a maximum of 96 % at 0.7 g/L dosage. In contrast, use of SZnO as adsorbent showed 26 % (minimum) and 83 % (maximum) removal when the dosage was 0.1 and 0.9 g/L respectively. The increase in dye removal efficiency with dosage can be attributed to the increase in adsorption sites. The greater adsorption capacity of CHZnO compared to SZnO can be attributed to smaller particle size and larger surface area of CHZnO compared to SZnO which are evident from TEM and BET surface area results (Figure 4 and 5).

***Effect of pH***

Adsorption of pollutants on to solid particles greatly depends on the solution pH, which significantly influences absorbent surface charge and ionization degree of pollutants [51,52]. The effect of pH on Congo red adsorption on ZnO nanoparticles was studied in the pH range 6 and 10.5 (Figure 7). The studies were not carried below pH 6 because of shift in $\lambda_{max}$ of the dye.



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The dye removal efficiency of CHZnO nanoparticles varied from 83 % to 78 % in the pH range 6 to 8, and decreased significantly beyond pH 8. The dye removal efficiency of SZnO nanoparticles also decreased significantly beyond pH 7. The experimentally determined zero-point charge for CHZnO and SZnO is pH 7.55 and pH 7.35 respectively (Figure 8). At pH above the zero-point charge, adsorbent surface acquires a negative charge and develops a repulsive force against anionic Congo red dye resulting in decreased removal efficiency. Based on the pH experiments the optimum pH for dye removal was considered to be pH 7 and further experiments are carried out at this pH.

***Adsorption Isotherms***

It is important to develop a correlation for the equilibrium data to optimize the design of adsorption system. The interaction between adsorbate and adsorbent can be better explained using equilibrium adsorption isotherm. Experimental equilibrium data were fitted with four isotherms namely Langmuir, Freundlich, Temkin and Dubinin-Radushkevitch isotherms and the equations for these models are presented below (Equation 5-11):

Langmuir Isotherm:

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \quad \text{Equation (5)}$$

$$R_L = \frac{1}{(1 + K_L C_0)} \quad \text{Equation (6)}$$

Freundlich Isotherm:

$$q_e = K_f C_e^{1/n} \quad \text{Equation (7)}$$

Temkin Isotherm:

$$q_e = \frac{RT}{b_T} \ln(K_T C_e) \quad \text{Equation (8)}$$

.

Dubinin-Radushkevitch Isotherm:

$$q_e = q_{DR} e^{-K_{DR}\varepsilon^2} \quad \text{Equation (9)}$$

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \quad \text{Equation (10)}$$

$$E = \frac{1}{\sqrt{2K_{DR}}} \quad \text{Equation (11)}$$

where $q_{max}$ (mg/g) is maximum saturated monolayer adsorption capacity; $K_L$ (L/mg), Langmuir constant related to the affinity between adsorbent and adsorbate; $R_L$ (Dimensionless), separation factor; $K_f$ (mg/g) (L/mg), Freundlich constant; n, Freundlich intensity parameter; $K_T$ (L/mg), equilibrium binding constant; $b_T$( J/mol), Temkin isotherm constant related to the heat of sorption; $q_{DR}$ (mg/g), adsorption capacity; $K_{DR}$ ($mol^2/kJ^2$), constant related to sorption energy; ε,



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Polanyi potential; R (kJ $K^{-1}$ $mol^{-1}$), gas constant (8.314 $\times 10^{-3}$); T (K), absolute temperature; E (kJ/mol), mean adsorption energy.

Model constants and $R^2$ values of selected isotherms are given in Table 1. According to the results obtained, the Langmuir isotherm model has the highest $R^2$ value and fitted best with experimental equilibrium data obtained for both the adsorbents in the temperature range studied (30 to 60 $^oC$). Langmuir isotherm model explains the formation of monolayer adsorption of adsorbate molecules on the surface of the adsorbent with the absence of lateral interaction or steric hindrance between adsorbate molecules [46]. The obtained results indicated a decrease in the maximum adsorption capacity, $q_{max}$, which could be attributed to the exothermic nature of adsorption process. Langmuir constant, $K_L$, also decreased with increase in temperature indicating that affinity between adsorbate and adsorbent deceased with an increase in temperature. The maximum adsorption capacity of Congo red on CHZnO and SZnO was found to be 77 and 52 mg/g respectively. The adsorption capacities of CHZnO and SZnO are compared with the other adsorbents reported in literature and tabulated in Table 2. As evident from Table 2, CHZnO is a promising adsorbent for removal of Congo red from wastewater compared to the other reported nanomaterial-based adsorbents.

The predicted $q_{max}$ values obtained from the Langmuir model are closer to the experimental values compared to the $q_{max}$ predicted by other isotherm models. In addition to the Langmuir constant ($K_L$), favourability of adsorption process was also identified using the separation factor, $R_L$ [61]. This separation factor signifies the nature of adsorption process depending on the values of $R_L$. $R_L>1$, $R_L=1$, $0<R_L<1$ and $R_L=0$ indicate to unfavourable, linear, favourable and irreversible adsorption process respectively. Effect of temperature and concentration on $R_L$ values are depicted in Figure 9 (a) and (b). In the present study $R_L$ values are found to be in the range $0<R_L<1$ indicating that the adsorption process is favourable.

***Adsorption Kinetics and Mechanism of adsorption***

In general any adsorption process involves three important steps: (a) transfer of adsorbate molecules from bulk phase to adsorbent surface - film diffusion or external diffusion (b) movement of adsorbate molecules from outer surface of adsorbent to the pores - intraparticle or pore diffusion (c) attachment of adsorbate molecule to the adsorption site [62]. Film diffusion and pore diffusion are transport steps that lead to the adsorption process and the last step is the reaction step where adsorbate molecules bind to the adsorptive sites. In the adsorption process, the reaction step is rapid compared to transport steps. So it is critical to evaluate the kinetic



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parameters to understand the performance of adsorbent and estimate the rate-limiting step in the process [63]. Two reaction models and two diffusion based models were employed to study the kinetics of Congo red adsorption on ZnO nano-adsorbents. The details of the selected models are presented below:

**Pseudo First Order**

$$q_t = q_e\left(1 - e^{-k_1 t}\right) \quad \text{Equation (12)}$$

**Pseudo Second Order**

$$q_t = \frac{q_e^2\, k_2\, t}{1 + k_2\, q_e\, t} \quad \text{Equation (13)}$$

**Weber-Morris Intra-particle Diffusion**

$$q_t = k_d\, t^{1/2} + C \quad \text{Equation (14)}$$

**Bangham**

$$\log\left\{\log\left(\frac{C_o}{C_o - q_t\, m}\right)\right\} = \log\left(\frac{k_o\, m}{2{,}303\, V}\right) + \propto \log(t) \quad \text{Equation (15)}$$

where qe (mg/g) is adsorption capacity at equilibrium; qt (mg/g), adsorption capacity or concentration of solute in a solid phase at time t (min); $k_1$ ($min^{-1}$), pseudo first-order rate constant; $k_2$ (g/mg. min), pseudo-second-order rate constant; $k_d$ (mg/g x $t^{1/2}$), intraparticle rate constant; C (mg/g), constant associated with the thickness of the boundary layer; $C_o$ (mg), amount of initial adsorbate in the liquid phase; m (g), amount of adsorbent; V(L) is the volume of solution used in the batch adsorption; $k_0$ (L $g^{-1}$) and α (<1) are the Bangham's equation parameters [62,64].

The kinetic model parameters and $R^2$ values obtained at various concentrations are summarised in Table 3. Based on the $R^2$ values, pseudo-second-order model fitted well with experimental kinetic data indicating Congo red adsorption on nano ZnO follows the pseudo-second-order model. Further, this is also supported by the values of $q_e$ that are found to be closer to the experimental values. It is worth noticing that with an increase in dye concentration from 20 to 60 mg/L, adsorption capacities for CHZnO and SZnO were found to increase by a factor ~48 % and ~53 % respectively (Figure 10 (a) and (b)).

Mere reaction models are not sufficient to identify the diffusion mechanism during the adsorption process. Therefore, Weber-Morris intraparticle diffusion and Bangham diffusion models were employed to explain the diffusion rate-limiting step [65]. From Table 3, it can be



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noted that the value of intercept C of Weber-Morris model is found to be away from zero indicating that this model is not suitable to predict the rate-limiting step. Further, if intraparticle diffusion is the only rate-limiting step in adsorption has been confirmed by Bangham model. Higher correlation of desired linear fit in the double logarithmic plot shows that intraparticle diffusion is the rate-limiting step in the adsorption of Congo red on ZnO nanoparticles [66]. From the obtained experimental results, it is also observed that the diffusion rate increased with increase in concentration. An increase in initial concentration will produce a higher concentration gradient which will eventually cause faster diffusion and quicker adsorption (Ofomaja, 2010). Thus one may infer that intraparticle diffusion is the significant rate-limiting step in the adsorption of Congo red on nano ZnO.

***Thermodynamic Studies***

Development of efficient batch adsorption process for removal of pollutants from aqueous solution is significantly reliant on various thermodynamic parameters such as Gibbs free energy ($\Delta G$), enthalpy change ($\Delta H$), entropy change ($\Delta S$), isosteric heat of adsorption ($\Delta H_X$), mean free energy per molecule of adsorbate ($E_d$) etc. These parameters are also critical in predicting the nature of adsorption; either physisorption or chemisorption [59]. Thermodynamic parameters were computed using the following equations:

$$\Delta G^0 = -RT \ln K_c \qquad \text{Equation (16)}$$

where R is a universal gas constant (8.314 x $10^{-3}$ kJ $mol^{-1}$ $K^{-1}$) and $K_c$ is dimensionless equilibrium constant derived from Langmuir coefficient $K_L$ using Equation 17.

$$K_C = M_w \times 55.5 \times 1000 \times K_L \qquad \text{Equation (17)}$$

Where $M_W$ is molecular weight of Congo red (696 g/mol), factor 55.5 is the number of moles of pure water per litre[67,68].

The relationship between $\Delta G^o$, $\Delta H^o$ and $\Delta S^o$ is described as follows:

$$\Delta G^o = \Delta H^o - T\Delta S^o \qquad \text{Equation (18)}$$

Substituting Equation (16) in Equation (18) one can obtain well know van't Hoff equation given in Equation (3)

$$\ln K_c = \frac{-\Delta H^o}{R}\frac{1}{T} + \frac{\Delta S^o}{R} \qquad \text{Equation (19)}$$



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The values of $\Delta H^o$ and $\Delta S^o$ are determined using the plot of $\ln K_C$ Vs 1/T. Thermodynamic parameters calculated for both the adsorbents are tabulated in Table 4. A negative value of $\Delta G$ confirms that adsorption of Congo red on ZnO nanoparticles is a spontaneous and feasible process. A negative value of $\Delta H$ confirms the adsorption process is exothermic and indicates that adsorption efficiency of the adsorbent decreases with increase in temperature. The values of $\Delta H$ in the range of -20 to 0 kJ/mol infer that hydrogen bonding forces may play a vital role in the adsorption of Congo red on ZnO nanoparticles [69]. The magnitude of the $\Delta H$ value indicates that adsorption of Congo red dye on ZnO nanoparticles is physical in nature [70].

Isosteric heat of adsorption is another important thermodynamic parameter used to characterize and optimize the adsorption process. It is also a crucial parameter in the design of adsorption separation process and provides insights into the surface energy heterogeneity of adsorbent. The isosteric heat of adsorption at constant surface coverage is calculated using an integrated form of Clausius–Clapeyron equation given below:

$$\ln C_e = -\left(\frac{\Delta H_X}{R}\right)\frac{1}{T} + C \qquad \text{Equation (20)}$$

where C is the constant.

From Table 5, it is found that $\Delta H_X$ values for both the adsorbents at various temperatures are below 80 kJ/mol and is attributed to the occurrence of physisorption process [71]. The decrease in $\Delta H_X$ values at higher solution concentration indicates that ZnO nanoparticles have energetically heterogeneous surfaces. In contrast, a constant value of the heat of adsorption is attained in the adsorbents which have homogenous surfaces [70,72]. From Table 5 it is evident that at low adsorbent concentrations, heat of adsorption values are found to be higher but when the adsorbent concentrations are higher these values are found to be lower. This can be explained based on the adsorbate-adsorbent interactions. These interactions results in high adsorption heat values whereas the interaction between adsorbate and adsorbate molecules leads to lower values of heat of adsorption [71].

## Stability Studies of Adsorbents

Stability of the adsorbents after use in adsorption experiments are significant in order to utilise them for real time applications. To evaluate the stability of the ZnO adsorbent after adsorption the samples were characterized by XRD, FTIR and EDAX techniques. From the XRD results it



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is evident that there is no significant variation in the diffraction pattern before and after adsorption experiments for CHZnO (Figure S2). All the diffraction peaks and peak positions are unaltered after the adsorption experiments. Therefore, it can be inferred that ZnO adsorbent after adsorption experiment is found to be stable. Further, FTIR spectra recorded for both CHZnO and SZnO showed characteristic Zn-O peak ~447 $cm^{-1}$ (Figure S3 and S4). It can be noticed that the characteristic Zn-O bond stretching band is unaltered even after adsorption experiments. This clearly indicates that adsorbent is stable even after adsorption experiments. Similarly, EDAX analysis also showed that except for the additional C peak (due to Congo red adsorption) the other elemental composition remains same (Figure S5).

## Conclusion

In summary, the influence of green and chemical fuel on adsorptive characteristics of solution combustion derived nano ZnO for Congo red as a model pollutant was demonstrated. ZnO nanoparticles synthesized using coffee husk extract (CHZnO) showed smaller particles size compared to that synthesized with sugar (chemical fuel) (SZnO). Adsorption studies clearly demonstrated that pH, adsorbent dose, initial dye concentration, temperature and time have a significant effect on dye removal. CHZnO showed higher adsorption efficiency with adsorption capacity ~ 77 mg/g. Langmuir isotherm model regressed well with experimental equilibrium data for both the adsorbents in the temperature range studied. Separation factor ($R_L$) calculated to be in the range $0<R_L<1$ indicates favourability of the adsorption process. Hydrogen bonding forces might play a vital role in the adsorption of Congo red on ZnO nanoparticles since the values of $\Delta H$ was in the range of -20 to 0 kJ/mol. Modelling of experimental data with various diffusion based kinetic models to understand the mechanism of adsorption indicated that intraparticle or pore diffusion was the major rate controlling step. This study demonstrates the promising application of agro-based bio-waste as fuel in combustion synthesis for the preparation of efficient adsorbents for water treatment.

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## Declaration of conflicting interest

The author(s) declared no conflict of interest.

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**Table 1: Isotherm model parameters for adsorption of congo red on ZnO Nanoparticles**

| Model | Temperature, K | Model Constants | | | Model Constants | | |
|---|---|---|---|---|---|---|---|
| | | Qmax | $K_L$ | $R^2$ | Qmax | $K_L$ | $R^2$ |
| **Langmuir** | | | | | | | |
| | 303 | 76.9231 | 0.7222 | 0.9972 | 52.0833 | 0.2602 | 0.9997 |
| | 313 | 75.7576 | 0.2288 | 0.9959 | 49.5050 | 0.1841 | 0.9994 |
| | 323 | 74.0741 | 0.1519 | 0.9907 | 46.7290 | 0.1639 | 0.9998 |
| | 333 | 78.7402 | 0.0706 | 0.9943 | 42.9185 | 0.1410 | 0.9996 |
| **Freundlich** | | **n** | **$K_F$** | | **n** | **$K_F$** | |
| | 303 | 6.1350 | 41.3015 | 0.9181 | 3.7453 | 17.9376 | 0.8876 |
| | 313 | 4.3440 | 28.7460 | 0.9222 | 3.4953 | 15.0353 | 0.9486 |
| | 323 | 3.9526 | 24.2933 | 0.9862 | 3.3727 | 13.4006 | 0.9306 |
| | 333 | 2.5740 | 13.4019 | 0.9817 | 3.3069 | 11.6884 | 0.9336 |
| **Temkin** | | | | | **$K_T$** | **$b_T$** | |
| | 303 | **$K_T$** | **$b_T$** | 0.9361 | 4.9067 | 0.2792 | 0.9361 |
| | 313 | 102.6580 | 0.2799 | 0.9530 | 2.9329 | 0.2872 | 0.9530 |
| | 323 | 7.9196 | 0.2230 | 0.9875 | 2.3342 | 0.3036 | 0.9875 |
| | 333 | 4.0244 | 0.2196 | 0.9954 | 1.8936 | 0.3333 | 0.9954 |
| | | 0.7388 | 0.1642 | | | | |
| **Dubinin-** | | **$K_{DR}$** | **$Q_{DR}$** | **E** | **$K_{DR}$** | **$Q_{DR}$** | **E** |
| **Radushkevitch** | 303 | 0.1811 | 72.0240 | 1.6616 | 0.9048 | 1.4686 | 46.2657 | 0.5835 | 0.9710 |
| | 313 | 1.1339 | 65.9568 | 0.6640 | 0.9433 | 1.8868 | 42.1865 | 0.5148 | 0.9304 |
| | 323 | 1.5516 | 61.0260 | 0.5677 | 0.8753 | 2.7426 | 40.0328 | 0.4270 | 0.9502 |
| | 333 | 6.0147 | 58.3115 | 0.2883 | 0.9016 | 3.7537 | 36.5982 | 0.3650 | 0.9506 |

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**Table 2: Comparison of various adsorbents for adsorptive removal of Congo red.**

| Sl. No. | Nanoadsorbent | Adsorption capacity, mg/gm | References |
|---|---|---|---|
| 1. | $NiFe_2O_4$ | 97.10 | [53] |
| 2. | Hierarchical Ni(OH)2 nanosheets | 82.90 | [54] |
| 3. | Hierarchical hollow $MnO_2$ nanostructures | 80.00 | [55] |
| 4. | α-$Fe_2O_3$ nanorod | 78.13 | [56] |
| 5. | Manganese oxide | 58.13 | [57] |
| 6. | $Fe(OH)_3$ | 49.13 | [58] |
| 7. | Single-crystalline NiO nanosheets | 36.10 | [59] |
| 8. | Hollow Zn–$Fe_2O_4$ nanospheres | 16.10 | [60] |
| 9. | CHZnO | 76.92 | Present Study |
| 10. | SZnO | 52.08 | Present Study |

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**Table 3: Kinetic parameters for adsorption of congo red on ZnO nanoparticles**

| | | CHZnO | | | SZnO | | |
|---|---|---|---|---|---|---|---|
| **Model** | **Concentration** | | | | | | |
| | | **$q_e$** | **$k_1$** | **$R^2$** | **$q_e$** | **$k_1$** | **$R^2$** |
| Pseudo First Order | 20 | 14.1159 | 0.0873 | 0.9166 | 11.5271 | 0.1309 | 0.9536 |
| | 40 | 39.1892 | 0.0499 | 0.9517 | 27.6106 | 0.1078 | 0.9843 |
| | 60 | 46.3166 | 0.0379 | 0.9166 | 30.6521 | 0.0909 | 0.9888 |
| | | **$q_e$** | **$k_2$** | | **$q_e$** | **$k_2$** | |
| Pseudo Second Order | 20 | 39.3701 | 0.0142 | 0.9997 | 21.8818 | 0.0196 | 0.9996 |
| | 40 | 68.0272 | 0.0029 | 0.9978 | 38.7597 | 0.0062 | 0.9993 |
| | 60 | 75.7576 | 0.0020 | 0.9989 | 45.2489 | 0.0054 | 0.9994 |
| | | **$k_d$** | **C** | | **$k_d$** | **C** | |
| Webber-Moris | 20 | 3.0924 | 21.9480 | 0.9047 | 0.9851 | 13.5880 | 0.5434 |
| | 40 | 4.2887 | 32.2930 | 0.9446 | 2.5208 | 16.8250 | 0.7143 |
| | 60 | 5.7794 | 27.6390 | 0.9060 | 2.6518 | 21.3960 | 0.7703 |
| | | **$k_o$** | **A** | | **$k_o$** | **α** | |
| Bangham | 20 | 1.3974 | 0.1687 | 0.9216 | 0.6466 | 0.1420 | 0.9216 |
| | 40 | 0.7635 | 0.1510 | 0.9875 | 0.3493 | 0.1705 | 0.9875 |
| | 60 | 0.4142 | 0.1560 | 0.9670 | 0.3240 | 0.1270 | 0.9670 |

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**Table 4: Thermodynamic parameters calculated for adsorption on ZnO nanoparticles.**

| Temperature, K | CHZnO | | | | SZnO | | | |
|---|---|---|---|---|---|---|---|---|
| | ΔG, kJ/mol | ΔH, kJ/mol | ΔS, kJ/mol K | $R^2$ | ΔG, kJ/mol | ΔH, kJ/mol | ΔS, kJ/mol K | $R^2$ |
| 303.15 | -4.691 | -34.467 | -0.098 | 0.930 | -3.175 | -9.232 | -0.019 | 0.999 |
| 313.15 | -3.614 | | | | -2.991 | | | |
| 323.15 | -3.356 | | | | -2.784 | | | |
| 333.15 | -1.478 | | | | -2.577 | | | |



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**Table 5: Isosteric heat of adsorption calculated from Clausius–Clapeyron equation**

| Adsorbent | | Concentration, mg/L | | | | |
|---|---|---|---|---|---|---|
| | | **20** | **40** | **60** | **80** | **100** |
| **CHZnO** | **$\Delta H_X$, kJ** | 52.152 | 22.988 | 9.847 | 3.761 | 2.179 |
| | **$R^2$** | 0.927 | 0.993 | 0.873 | 0.985 | 0.979 |
| **SZnO** | **$\Delta H_X$, kJ** | 17.182 | 14.812 | 6.943 | 5.069 | 3.409 |
| | **$R^2$** | 0.999 | 0.946 | 0.982 | 0.997 | 0.996 |

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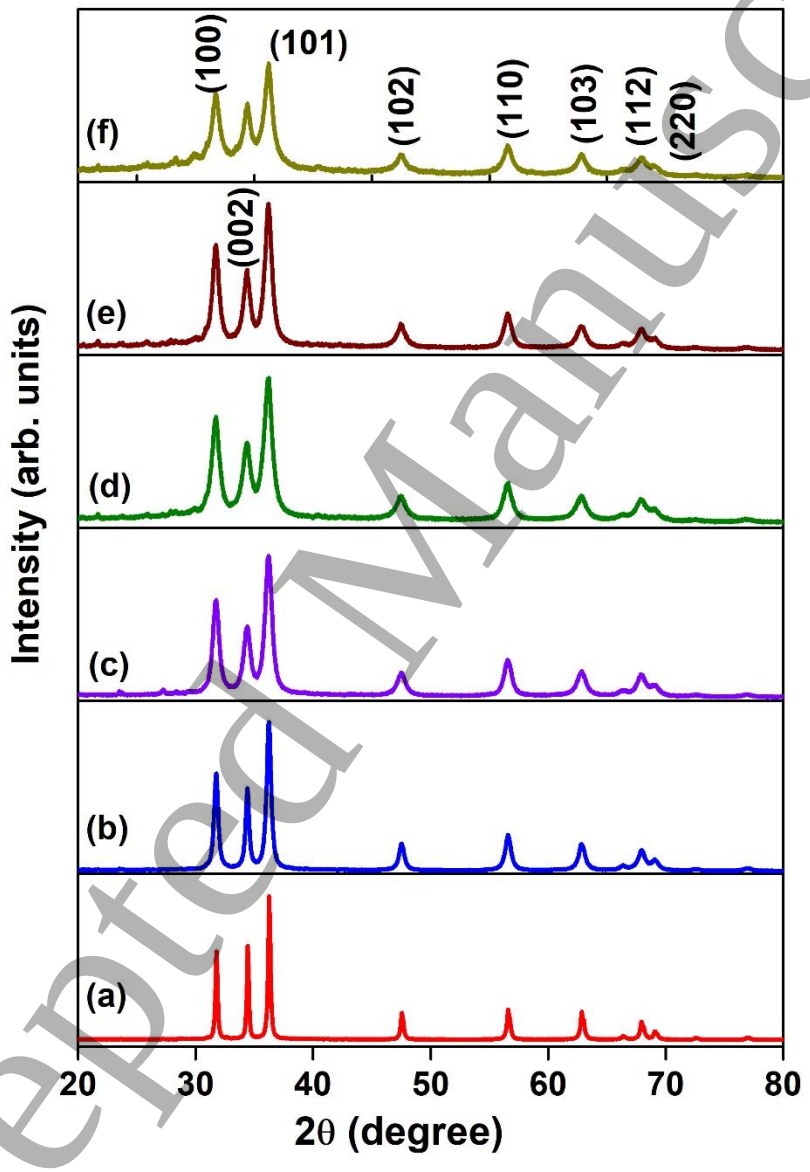



**Figure 1: X-Ray diffraction pattern of CHZnO at various concentration of coffee husk extract (a) 10 ml (b) 20 ml (c) 30 ml (d) 40 ml (e) 50 ml (f) 60 ml**

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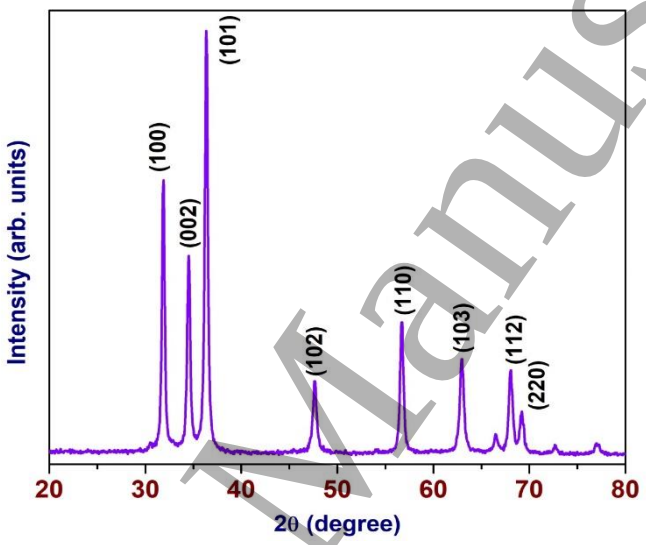



**Figure 2: X-Ray diffraction pattern of SZnO**

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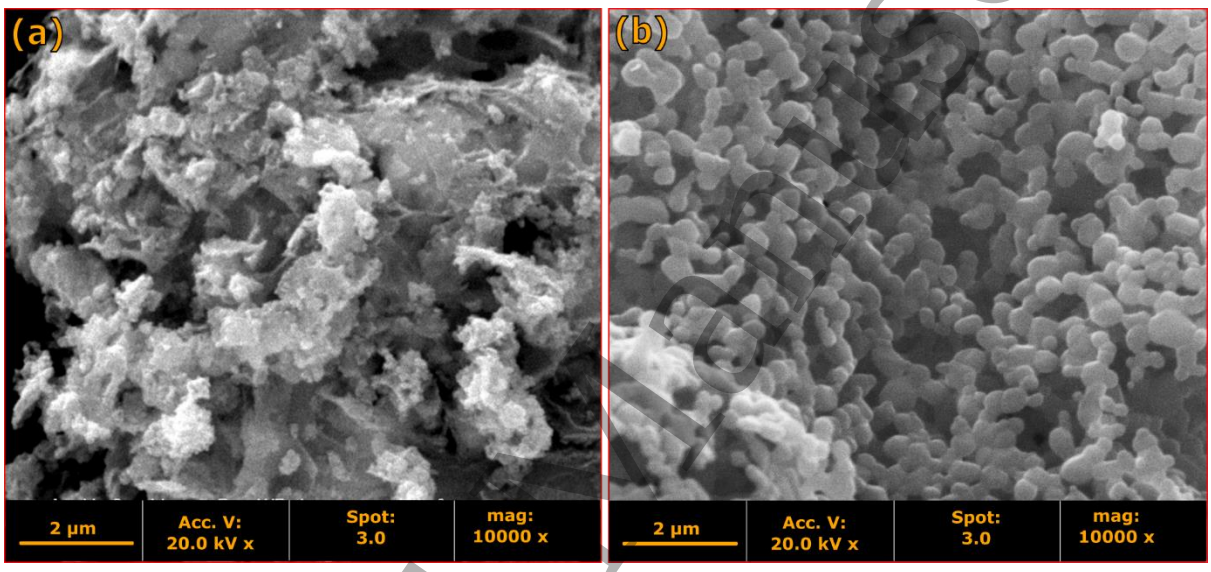



**Figure 3: SEM images of (a) CHZnO (b) SZnO**

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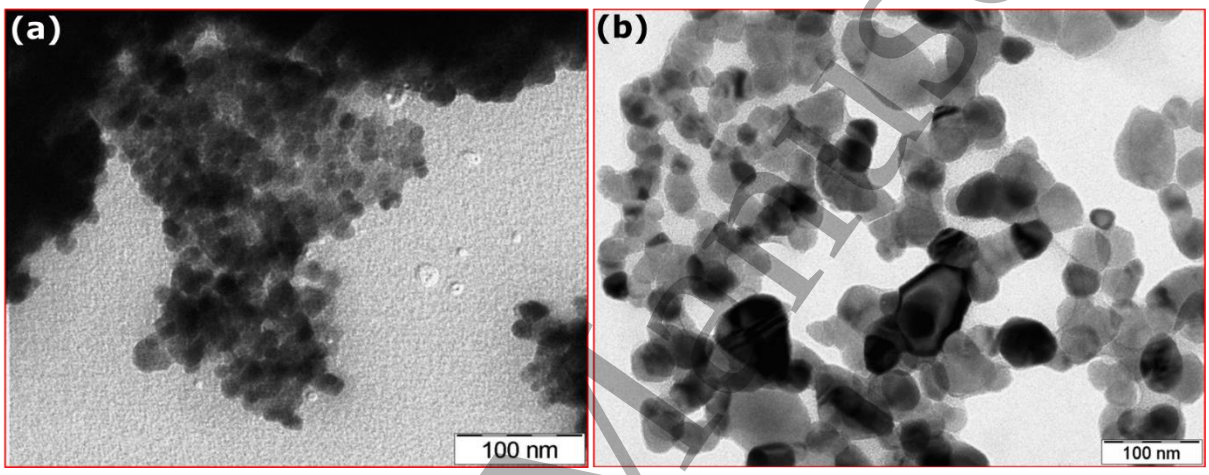



**Figure 4: TEM images of (a) CHZnO (b) SZnO**

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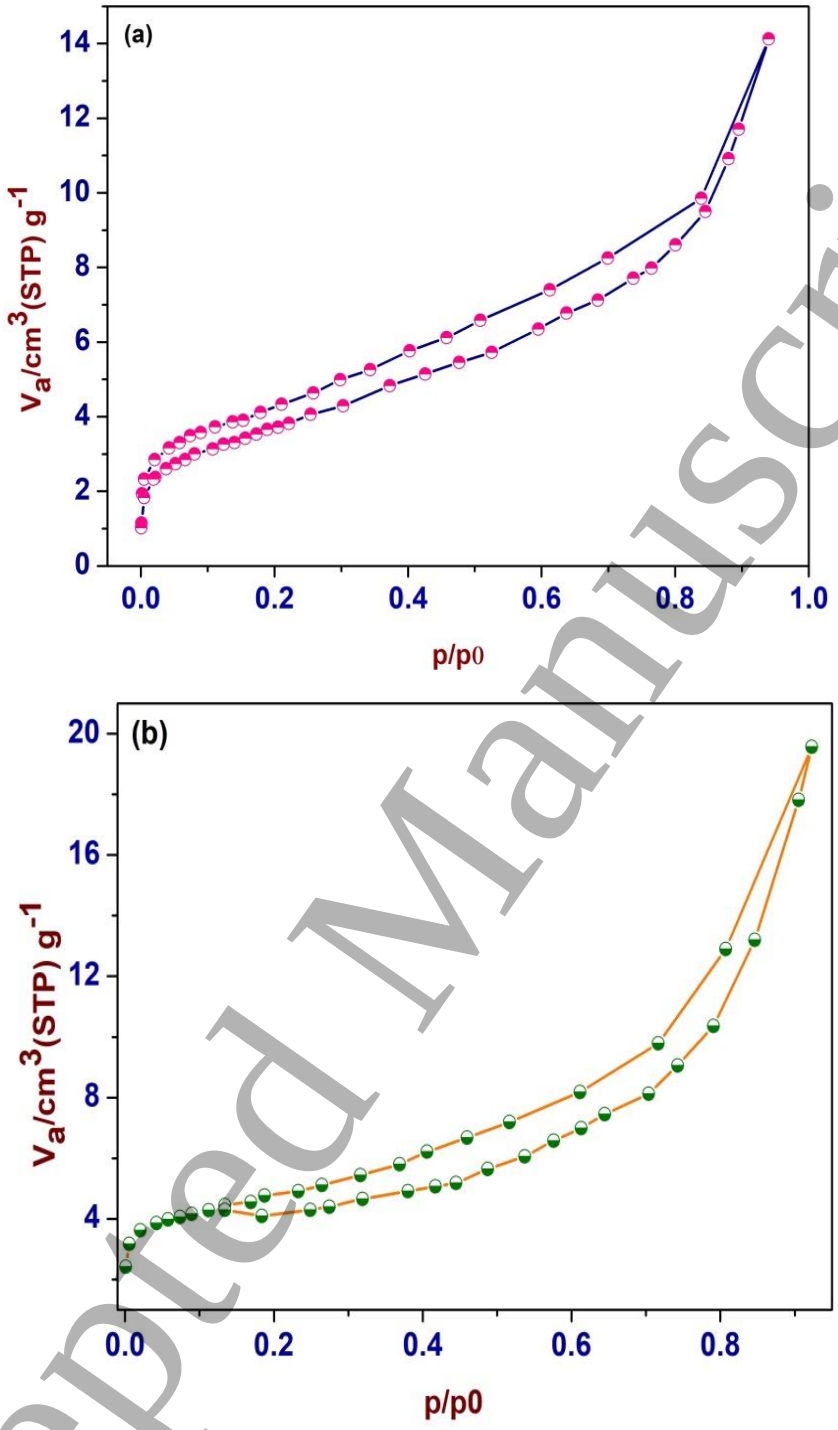



**Figure 5: $N_2$ adsorption-desorption isotherm of (a) CHZnO (b) SZnO**

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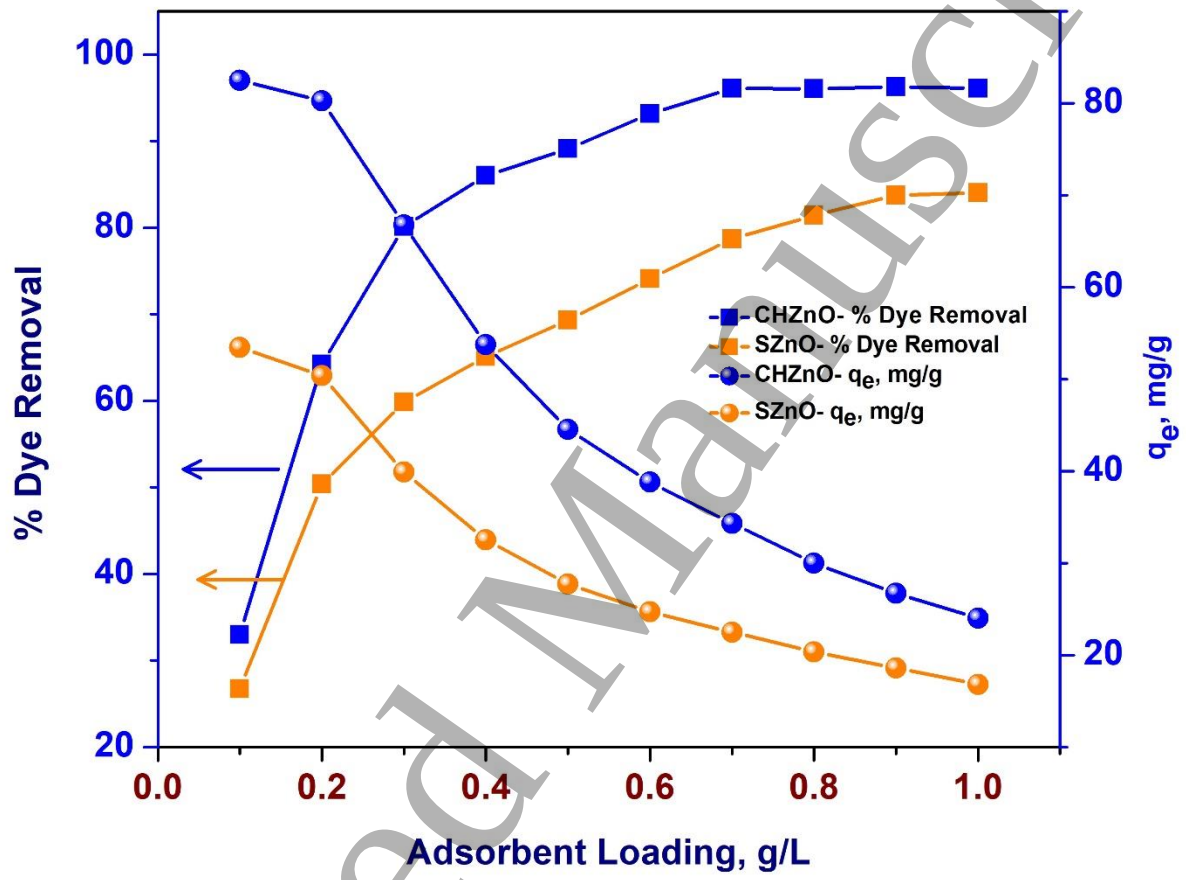



**Figure 6: Effect of ZnO dosage on adsorption of Congo red**

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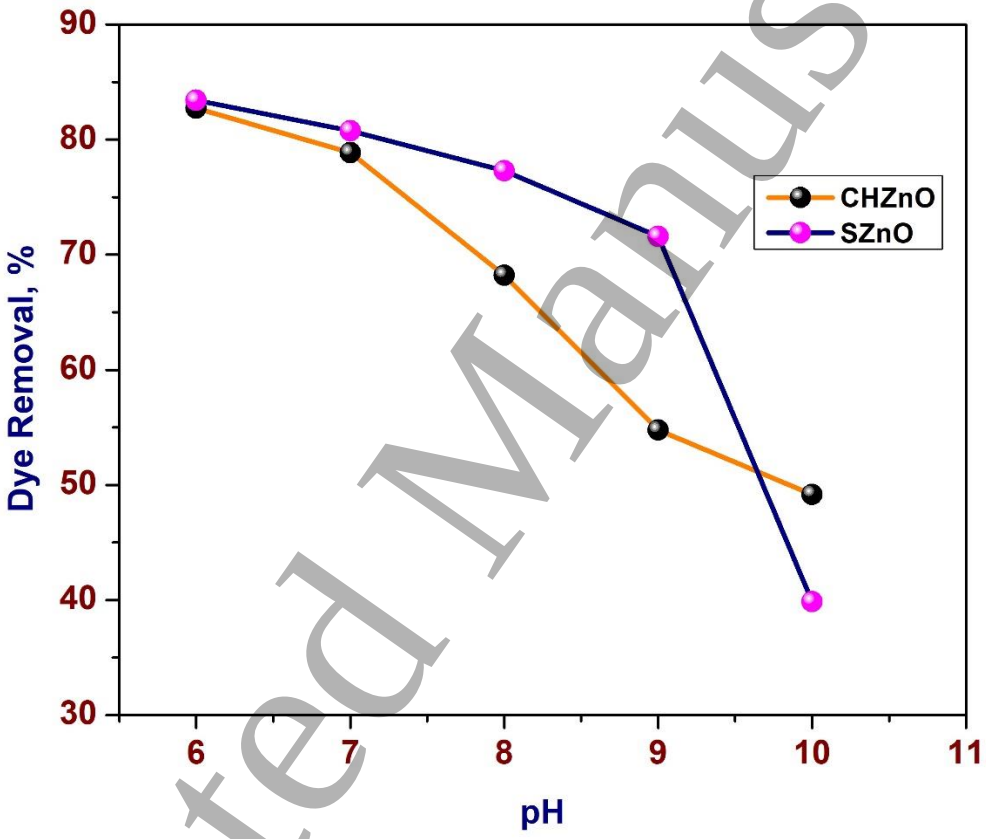



**Figure 7: Effect of pH on adsorption capacity of ZnO nanoparticles**

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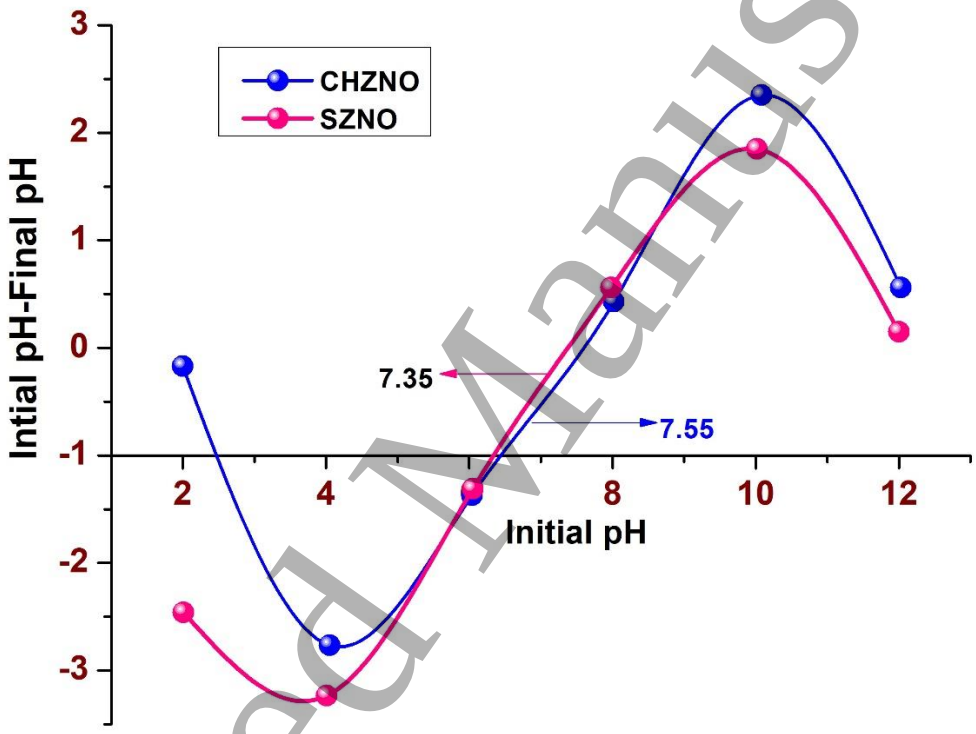



**Figure 8: Zero Point Charge of ZnO nanoparticles**

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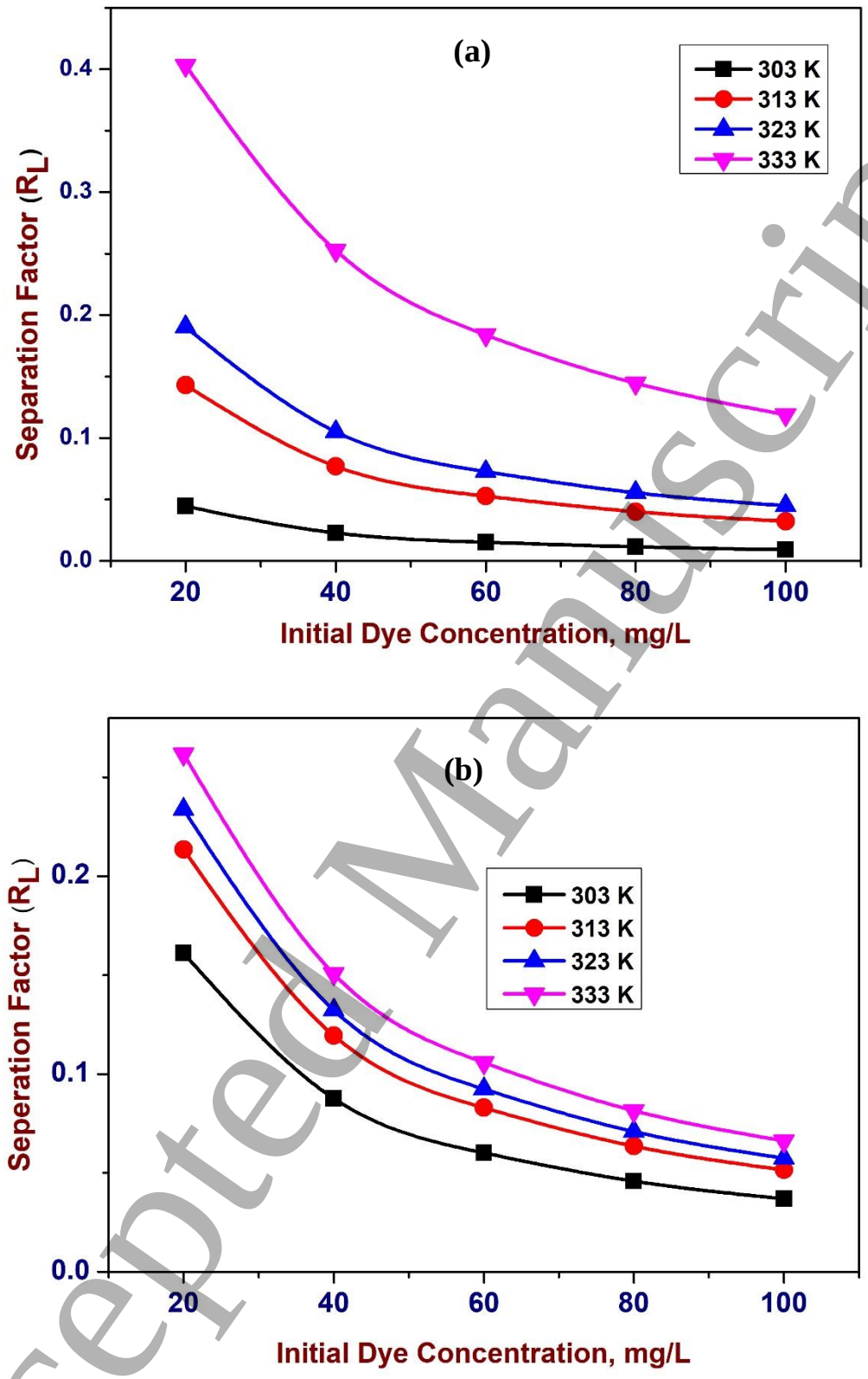



**Figure 9: Separation factor at various temperatures (a) CHZnO (b) SZnO**

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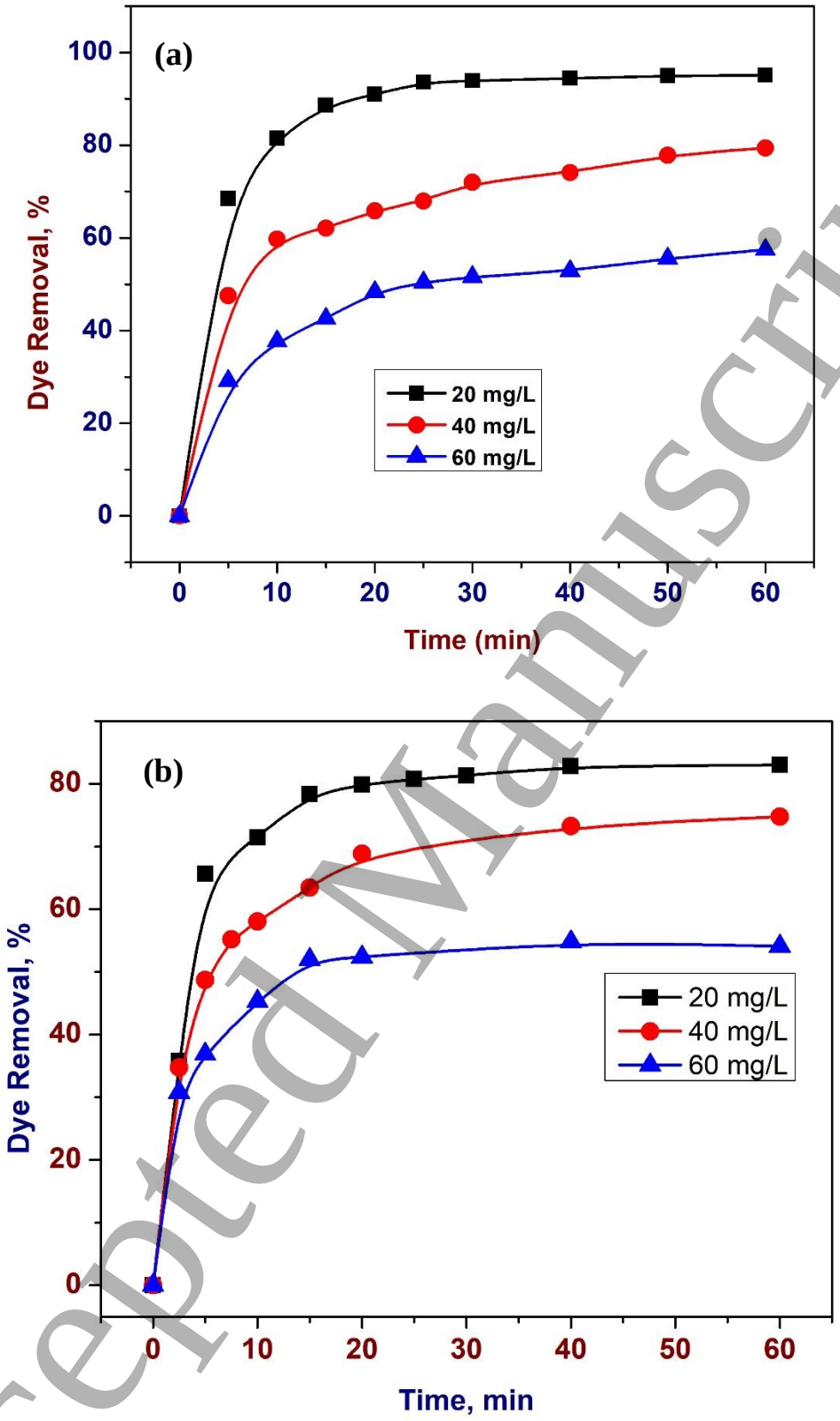



**Figure 10: Effect of time on adsorption of Congo red at various concentration (a) CHZnO (b) SZnO**

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# A NOVEL APPROACH TOWARDS GREEN SYNTHESIS OF ZINC NANO PARTICLES FROM *GUAZUMA ULMIFOLIA* (LAM) FOR THEIR ANTI OXIDANT ACTIVITY STUDY

**Nannapaneni U. R.[a]* and Rayapati S. R.[b]**

(Received 24 September 2018) (Accepted 02January 2019)

**ABSTRACT**

Here we report a novel biological approach for the formation of zinc nanoparticles using *Guazuma ulmifolia* (Lam) leaves. Zinc acetate was reduced with aqueous solution of *Guazuma ulmifolia* leave extracts. X-Ray diffraction (XRD) pattern reveals the formation of zinc nanoparticles, which shows crystallinity. Scanning electron microscopy (SEM) suggested particles size in the range of 46-96nm and spherical shape. UV absorption studies of zinc nano particles showed absorbance at 698nm and FT-IR studies of zinc nanoparticles confirmed the presence of bio active phyto-constituents in the formed nano particles. The DPPH free radical inhibition study confirmed that the synthesized zinc nano particles have potential radical inhibiting activity.

***Keywords***: *Guazuma ulmifolia*, zinc nanoparticles, FT-IR, XRD, SEM, DPPH radical scavenging activity

## INTRODUCTION

It has been demonstrated that many biological systems, including plants algae[1], diatoms[2], bacteria[3], yeast[4], fungi[5], and human cells[6] can transform inorganic metal ions into metal nanoparticles. The advantages of using plant and plant-derived materials for biosynthesis of metal nanoparticles have interested researchers to investigate mechanisms of metal ions uptake and bioreduction by plants, and to understand the possible mechanism of metal nanoparticle formation in plants. Among all other biological synthesis methods, plants and plant extracts appear to be the best options because of cost efficiency, low cost a of cultivation, short production time, safety and low maintenance requirement. In this connection, the present paper deals with the eco-friendly synthesis of zinc nanoparticles by *Guazuma ulmifolia* plant extract.

*Guazuma ulmifolia* (Lam), a West Indian Elm is a medium-sized tree and has been cultivated in India and Sri Lanka for over 100 years, and often planted as shade and ornamental tree elsewhere in the tropics. It is also found in the Caribbean, Mexico, Central America and Colombia, Ecuador, Peru, Bolivia, Paraguay, Argentina, and Brazil[7]. The tree produces small, whitish-cream flowers during the dry season. These develop into odd, woody fruits which look similar to the true Rudraksh, used as beads in *rudraaksh maala* worn by sadhus and saints. Usually, leaves are alternate, in flat plane along long branches, upper side dark green, underside light green-blue. The plant has a long history of herbal use, and is much used in modern herbal medicine in South America. The plant is antibacterial, anti-inflammatory, antifungal, antitussive, antiviral, astringent, blood purifier, cardiac, diaphoretic, digestive, diuretic, febrifuge, haemostatic, hypotensive, oxytocic and vulnerary. Various studies using leaf and bark extracts have clinically demonstrated remarkable antibacterial activity against several disease-causing pathogens, including *Bacillus, Staphylococcus, Streptococcus, E. coli, and Neisseria gonorrhea.* The bark is a rich source of tannins and antioxidant chemicals called proanthocyanidins. In particular, procyanidin B-2 has been shown in various studies to help promote hair growth and alleviate baldness[8].

The plant *G. ulmifolia* is having tremendous medicinal activity and there is no manuscript reported for the synthesis of nano particles using *G. ulmifolia*. Hence, the present work describes the synthesis and DPPH free radical activity study of zinc nano particles using *G. ulmifolia* leaves.

## MATERIAL AND METHODS

### Collection of Plant Material

Fresh leaves of the plant *G. ulmifolia* were collected in the coastal area near Machilipatnam port, Andhra Pradesh, India.

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**Fig. 1: Plant leaves of *Guazuma ulmifolia***




**Fig. 2: The process of synthesis of zinc nano particles a) Zinc acetate solution, b) Plant extract, c) addition of plant extract and metal solution at 0h, d) change in color during the synthesis process after 24h**

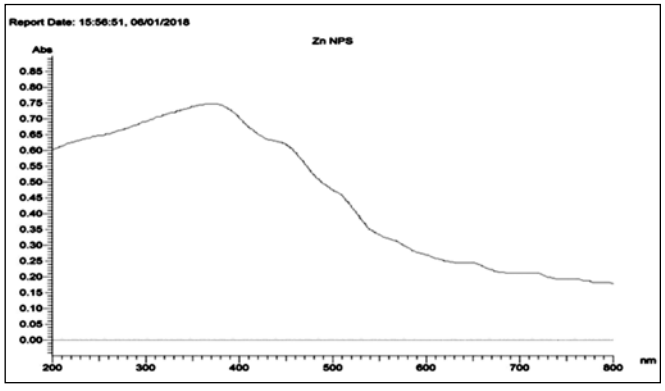



**Fig. 3: UV- visible absorption spectra of synthesized zinc nano particles**

## Collection of the extracts

Collected plant parts were cleaned with water absorbent paper (wet filter paper). Then, it was cut into small pieces, dispensed in 100 mL of sterile distilled water and boiled for one hour at 80$^0$C. Then the extract was collected in separate conical flasks by standard filtration method.

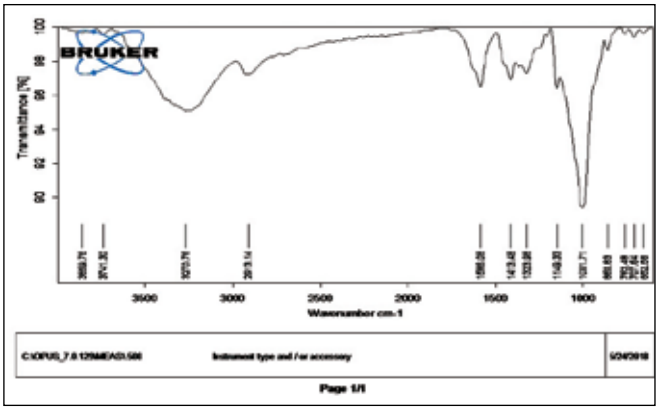



**Fig. 4: FT IR spectrum of synthesized zinc nano particles**

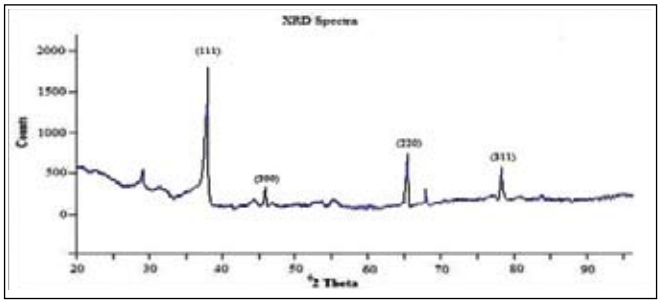



**Fig. 5: XRD spectrum of synthesized zinc nano particles**

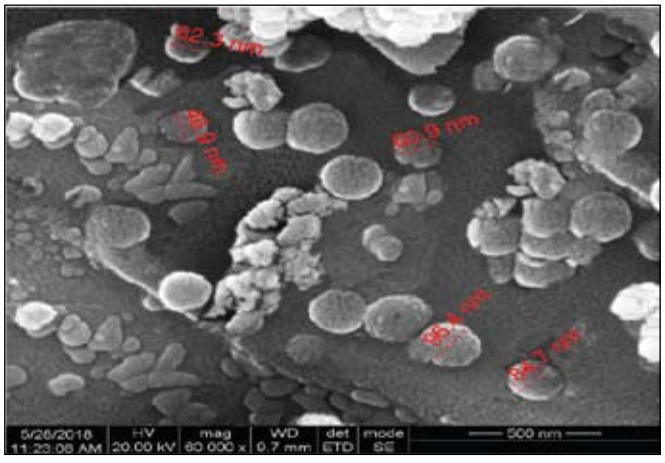



**Fig. 6: Scanning electron microscopy image of synthesized zinc nano particles**

## Preparation of extract

Different parts of the plant like leaves, stem, root, flower and whole plant were used for the synthesis of zinc nano particles. 10 g of different parts of plant powder was dissolved in 100 mL of distilled water separately and boiled under constant stirring using a magnetic stirrer for around 3 h. After cooling, the extract was centrifuged

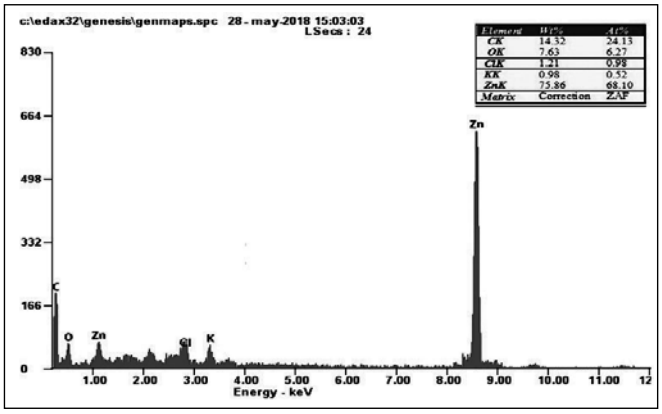



**Fig. 7: EDS of synthesized zinc nano particles**

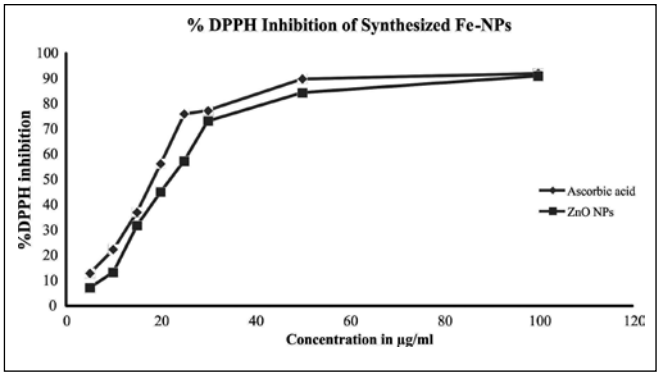



**Fig. 8: DPPH free radical scavenging activity study results**

twice for 10 min to get clear extracts. All the extracts were preserved in air tight container and were used for the synthesis of zinc nano particles.

## Green synthesis of zinc oxide nanoparticles

15 mL of selected plant part extract of *Guazuma ulmifolia* was added to 2.195 g of zinc acetate dihydrate dissolved in 35 mL of distilled water. The reaction mixture was kept on magnetic stirrer for 6h. After 6h, 2 M NaOH (4 g of NaOH pellet in 50 mL of Milli-Q water) was added to the solution and it was placed in incubator at 60°C with magnetic stirring overnight then it was centrifuged at 14,000 rpm for 15 min. Precipitate was subjected to washing with alcohol and distilled water three times each. Precipitate was dried in an incubator at 40–50 °C and fine powder was prepared with the help of ceramic pestle and mortar. The same procedure was fallowed for the synthesis of zinc nano particles using different parts of plant *G. ulmifolia*. The nanoparticles that produced high yield were considered for further characterization and biological activity study.

**Table II: DPPH free radical scavenging activity study results**

| Sr. No | Concentration in µg/mL | Ascorbic acid | Green Synthesis |
|---|---|---|---|
| 1 | 5 | 12.941 | 7.273 |
| 2 | 10 | 22.353 | 13.369 |
| 3 | 15 | 37.112 | 31.765 |
| 4 | 20 | 56.257 | 45.134 |
| 5 | 25 | 75.936 | 57.433 |
| 6 | 30 | 77.326 | 73.155 |
| 7 | 50 | 89.839 | 84.385 |
| 8 | 100 | 91.979 | 91.016 |

## Characterization of synthesized Zinc oxide nanoparticles

The synthesized zinc oxide nanoparticles were characterized using UV-visible, FTIR, EDS, SEM and

**Table I: Color change observed during the synthesis of zinc nano particles**

| Sr. No | Time intervals in Hours | Change observed for Zinc nano particle formation with plant part | | | | |
|---|---|---|---|---|---|---|
| | | Leaves | stem | root | flower | whole |
| 1 | 0 | Light | Light | Light | Light | Light |
| 2 | 1 | Light | Light | Light | Light | Light |
| 3 | 2 | Dark | Light | Light | Light | Dark |
| 4 | 3 | Dark | Light | Dark | Dark | Dark |
| 5 | 4 | Very Dark | Dark | Dark | Dark | Dark |
| 6 | 5 | Very Dark | Dark | Dark | Dark | Very Dark |
| 7 | 6 | Very Dark | Very Dark | Dark | Dark | Very Dark |
| Yield of nano particles | | 26.5mg | 15.7mg | 11.8mg | 9.1mg | 19.2mg |

X-ray diffraction (XRD) techniques. The UV absorption of synthesized zinc nano particles was studied in the range of 500-200 nm. The UV absorption was recorded using Techomp (UV-2301) and the absorption values were re-plotted using UV solution software 2. Fourier transform infrared (FTIR) spectroscopy was studied for determining the functional groups involved in the synthesized ZeNPs on Perkin Elmer FTIR Spectrophotometer with attenuated total reflectance technique. Energy dispersive spectrometer (EDS) conforms the purity of zinc nano particles. Field emission electron microscopy (LEO 1420 VP Compact variable pressure Digital SEM manufactured by Leo Electron Microscopy Ltd) was used for determining the size, shape of the synthesized ZeNPs. X-ray diffraction (Bruker-D4 ENDEAVOR XRD instrument) was used for determining the atomic and molecular structure of a nano crystal.

### DPPH free radical scavenging activity of synthesized zinc nano particles

*In vitro* antioxidant activity was studied by testing the scavenging capacities on 2,2-diphenyl-1- picrylhydrazyl (DPPH) free radical. The nanoparticle solution was lyophilized and converted to a powder, the concentration of the stock solution was 1 mg/mL. Various concentrations of the stock solutions (concentrations of 5-100µg/mL) were mixed with 0.25 mM DPPH in ethanol, to produce a final DPPH concentration of 0.1 mM. The mixture was vigorously shaken and left to stand for 20 min in the dark and its absorbance was measured at 517 nm. Ascorbic acid was used as the standard. The radical-scavenging activities of samples, expressed as percentage inhibition of DPPH, were calculated according to the formula i.e.,

$$\text{Inhibition percentage} = \frac{(\text{Absorbance of control} - \text{Absorbance of sample})}{\text{Absorbance of control}} \times 100$$

## RESULTS AND DISCUSSION

Different parts of *G. ulmifolia* plant extracts were employed for the green synthesis of zinc nanoparticles. The color formed during the addition of different parts of plant extract and zinc metal solution was noted. The color of the zinc acetate and plant extract mixture was gradually changed from light yellow to dark brown, indicating the formation of zinc nanoparticles. The color formed in the metal of leaf extract as green reducing agent produces high yield with less time of 6h. The formation of nano particles in the presence of other plant medicated synthesis show less color change and very less yield was observed, confirming that the formation of nano particles was high in the presence of leaf extract of *G. ulmifolia* as reducing agent. The color changes and the yields of nano particle formation are given in Table I. The nano particles formed using leaf extract produces a very high amount of 26.5mg of nano particles where as flower extract produces a very less amount of 9.1mg. The synthesis of zinc nano particles process is given in Fig. 2. The nano particles formed using leaf extract of *G. ulmifolia* as reducing agent was found to produce high amount of nano particles in less time and hence further studies were carried using nano particles formed using leaf extract of *G. ulmifolia*.

The UV absorption nature of the synthesized nano particles was studied using UV visible spectrophotometer. At a temperature of 35°C, the formation of the nanoparticles was observed with a characteristic plasmon band at 368 nm, which appeared at 30 min reaction time (Fig. 3). No change in absorbance was observed after 6h, indicating the complete conversion of $Zn^{++}$ to Zn. FTIR spectroscopy was employed to determine the possible bimolecular and functional groups involved in reduction, capping and efficient stabilization of newly synthesized zinc nanoparticles. The FTIR spectrum of zinc nano particles are presented in Fig. 4. In the FTIR spectrum of synthesized zinc nano particles, some pronounced absorbance was recorded in the area between 4000 and 500 $cm^{-1}$. Strong band at 1149 $cm^{-1}$, 3741 $cm^{-1}$ and 3270 $cm^{-1}$ confirms the C-O stretch, O-H stretch and H-bonded O-H group in alcoholic compounds confirms the alcoholic compounds in the nano particles. The aromatic carbon=carbon stretching vibration was observed at 1586 $cm^{-1}$ confirms that aromatic alcoholic compounds are involved in the formation of zinc nano particles. The precipitation stage during the reduction process usually involves fast chemical reactions and nucleation kinetics, thus the type of reducer is a significant factor in the particle size distribution of the product. The results previously reported indicated that flavonoids, phenolic compounds and terpenoids may be held responsible for efficient capping and stabilization of obtained nano particles. The X-ray diffraction analyses were carried out to determine the known phase of the zinc nanoparticles. Fig. 5 demonstrates the XRD pattern of the dried synthesized zinc nanoparticles by the *G.ulmifolia* leaf extract. The spectrum exhibited four distinct separate peaks at $2\theta$ of 35.6, 46.2, 65.1 and 79.7 that could be indexed to (111) (200), (220), (311) and (222) planes, respectively. The diffraction peaks data obtained were in accordance with the reports of FCC structure. The mean grain crystalline size of green synthesized zinc oxide nano particles was calculated by employing Debye–Scherrer formula. The average grain crystalline size of zinc nano

particles was estimated to be approximately 70.2nm. A small number of unassigned peaks were also recorded that might be due to the crystallization of bioorganic phases present in *G. ulmifolia* leaf extract on the surface of the zinc nanoparticles.

SEM technique was employed to determine the surface morphology and the topography of synthesized zinc nanoparticles. Fig. 6 shows the size of zinc nanoparticles from 46-96nm, with an average size 70.2nm. SEM image exhibited that the biosynthesized zinc nanoparticles were mostly circular shape. The circular particles were found to be less in size than the irregular particles.

The EDS profile (Fig. 7) shows a strong zinc signal at 8.6eV. The graph also shows the presence of carbon (C), oxygen (O), chloride (Cl) and potassium (K) in the EDS picture of zinc nanoparticles. It has been reported that nanoparticles synthesized using plant extracts are surrounded by a thin layer of some capping organic material from the plant extract and are, thus, stable in solution up to 4 weeks after synthesis. This is another advantage of nanoparticles synthesized using plant extracts over those synthesized using chemical methods.

### Anti-oxidant activity by DPPH method

The antioxidant activity of the synthesized zinc nano particles and ascorbic acid were evaluated using DPPH scavenging assay. The IC50 values of extract, standard and synthesized zinc nano particles are reported in Table II. It can be inferred from the data that synthesized zinc nano particles displayed similar antioxidant activity in comparison to standard ascorbic acid. There was a dose dependent increase in the percentage inhibition (% inhibition) of extracts and synthesized zinc nano particles. DPPH free radical scavenging assay of the synthesized zinc nano particles when compared with the standard ascorbic acid showed promising activity (Fig. 8). It was found that at a concentration of 5-100µg/mL, the bio-conjugated zinc nano particles exhibited better free radical scavenging activity with reference to drug ascorbic acid. These results suggest that at concentrations of 30µg/mL, the synthesized zinc nano particles may serve as potent radical scavengers. All these results suggest that intercalation of bio extracts with zinc nanoparticles can serve as promising antiradical agents.

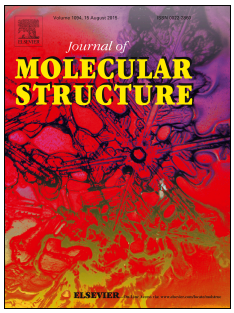
## CONCLUSION

The present work reports the facile, convenient and eco-friendly, *G. ulmifolia* leaves extract mediated green synthesis of bio-conjugated zinc nanoparticles. The characterization with UV–Vis spectroscopy, FT-IR, SEM and EDS analysis authenticate the formation of target zinc nanoparticles. Characterization analysis depicts the stabilization of synthesized zinc nanoparticles by the capping organic materials thereby preventing their agglomeration. The synthesized zinc nanoparticles exhibited promising ability to diffuse the toxic free radicals and can be used as a possible food additive or in nutraceutical and biopharmaceutical industries. It could be concluded that *G. ulmifolia* leaves mediated zinc nano particles can be used efficiently in the production of potential antioxidant and antibacterial zinc nano particles for commercial application.

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Synthesis, conformational, characterisation and reactivity study of 1,7-bis(4-bromophenyl)heptane-1,7-dione

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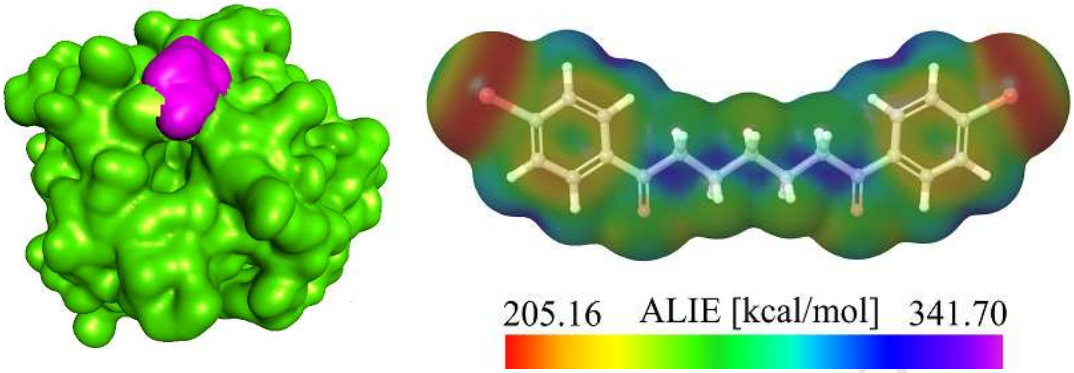
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# Synthesis, conformational, characterisation and reactivity study of 1,7-bis(4-bromophenyl)heptane-1,7-dione

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**Abstract**

In the present study, the title compound 1,7-bis(4-bromophenyl)heptane-1,7-dione (BBPHD) was synthesized according to the procedure described in literature, and its solid state crystal structure was characterised by the single crystal x-ray diffraction study. The complete crystallographic information has been reported in the present work. Physicochemical characterization by various spectral tools such as FT-IR, FT-Raman, $^{1}$H-NMR, $^{13}$C-NMR and UV-visible, have been performed as well and these results have been correlated with the theoretical data. The ground state geometrical optimization of the title compound has been performed using the DFT/B3LYP/6-311++G(d,p) level of theory in gas phase. Extracted molecular structure obtained by x-ray difractometry has been used as the starting molecular structure for geometrical optimizations. Computationally obtained structural and geometric parameters are in good

agreement with the experimentally obtained values. The experimental FT-IR and FT-Raman spectral data were compared with the theoretical spectral data and the complete assignment of vibrational wave numbers has been done on the basis of potential energy distribution (PED). In addition, reactive properties have been addressed on the basis of frontier molecular orbital analysis, global chemical reactivity descriptors, natural bond order (NBO) analysis, nonlinear optical (NLO) properties, molecular electrostatic potential (MEP) and average local ionization energy (ALIE) surfaces. Molecular dynamics (MD) simulations have been used in order to study the influence of water to the title compound. The docked ligand forms a stable complex with feruloyl esterase inhibitor and could be considered as a lead compound for the development of new antioxidant drug.

**Key words:** DFT; Hirshfeld surfaces; ALIE; RDF; Molecular docking.

## 1. Introduction

Owing to their abundance in natural products and pharmacologically active compounds, the significance of halogenated compounds is increasing [1-3]. This class of molecules has been successfully applied for the development of paints, dyes, adhesives, flame retardants, imaging agents in medical diagnosis, hydraulic and heat transfer fluids, refrigerants, solvents and in materials science [4-6]. Halogenated aromatic organic substrates are of great importance for the organic chemistry transformations, especially in the area of cross-coupling chemical reactions [7]. Although the halogenation is frequently followed by toxic chemicals, this procedure is highly developed and frequently used. There are number of advantages when it comes to the employment of halogens for the development of new molecules. For example, the introduction of carbon-halogen bond increases the thermal and oxidative stability, which leads to the lower sensitivity towards the oxidation by the liver P450 detoxification [6]. The same group of authors also indicates that carbon halogen bond increases the biological membrane permeability. Halogenated compounds are especially important in the area of agriculture and halogenation proved to be an important tool for development of efficient agricultural products. Jeschke [8] reports the information that since 2010, 96%of launched agricultural products, including herbicides, fungicides, insecticides/acaricides and nematicides, are containing halogen atoms. Positive effects of halogen atoms and halogen-containing groups are owed to steric and electronic effects [9], polarity of carbon-halogen bond [10] and pKa values effects [8]. One of the most important parameters in terms of pharmacokinetics, molecular lipophilicity, turned out to be adjustable by the substitution with halogen atoms [11]. Recently, Chen et al. [12] reported specific

nematic liquid crystal (LC) whose synthesis is based on the title compound (BBPHD). Taking into account the importance of their work, and importance of BBPHD for the synthesis of some other new specific nematic liquid crystals, we have decided to study BBPHD in details by spectroscopic and computational approaches. Density functional theory (DFT) represents irreplaceable tool for performing efficient and inexpensive computational studies in many areas [13-16]. DFT calculations with the hybrid exchange correlation functional B3LYP (Becke's three parameter (B3) exchange in conjunction with the Lee-Yang-Parr's (LYP) correlation functional) are of particular significance for studying systems comprising of extensive electron conjugation and/or electron lone pairs [17-20]. These structures have been the subject of many experimental and theoretical studies, especially when it comes to understandings of their structure, molecular properties and reaction mechanisms. Computational molecular modelling based on DFT calculations has become practically indispensable tool for evaluation and prediction of various properties of molecules and structures [21, 22], while in this work DFT calculations have been used in order to address global and local reactivity descriptors, including frontier molecular orbitals, MEP and ALIE surfaces and Fukui functions. DFT calculations were also used for confirmation of spectroscopic characterization and elucidation of vibrational specificities. Natural bond orbital (NBO) analysis has also been performed. Because newly synthetized molecules such as BBPHD might find place in the new pharmaceutical products, it is quite possible that they might end up in different water resources [23-27]. The introduction of halogen atoms also increases the persistency of compounds in environment, and in the same time hardening their degradation. This motivated us to also computationally study the degradation properties by calculation of bond dissociation energies for hydrogen abstraction (H-BDE) and stability in water by molecular dynamics (MD) simulations, another very important component of molecular modelling. Solid state crystal structure of BBPHD is elucidated by the single crystal X-ray diffraction studies, while contribution and quantification of various intermolecular interactions in crystal structure has been determined by the Hirshfeld surface analysis.

## 2. Material and methods

### 2.1. General remarks

The synthesis of BBPHD was carried according to the procedure reported in paper by Chen et al. [12]. Colourless prism like suitable crystals used for the structure determination was obtained by slow evaporation of ethanol at ambient temperature. FT-IR spectrum (Fig.S1-

supporting information) of title compound was recorded using the KBr pellets in the range of 4000-600 $cm^{-1}$ region, with the ATR module ALPHA-T Bruker FT-IR spectrophotometer. FT-Raman spectrum (Fig.S2-supporting information) of the title compound was recorded by Bruker RFS 100/s (Germany) using the Nd:YAG laser source, excitation wavelength of 1064 nm and spectral resolution of 2 $cm^{-1}$. $^{1}H$ and $^{13}C$-NMR spectra of the title compound was recorded (in ppm) on Bruker 400MHz spectrometer in $CDCl_3$ as solvent and TMS as internal standard.

**2.2. Data Collection and refinement details**

A suitable prism like crystal was selected and mounted on a Bruker APEX-II CCD diffractometer using the graphite monochromated MoKa ($\lambda$ = 0.71073 Å) radiation and detector (CCD). The crystal was kept at 296(2) K during data collection. The structure was solved using the Olex2 software [28] employing the olex2.solve [29] structure solution program and using the Charge Flipping. The structure was refined with the ShelXL [30] refinement package using the Least Squares minimization. All of the non-hydrogen atoms were revealed in the first difference Fourier map itself and were refined anisotropically. All of the hydrogen atoms were positioned geometrically, with C-H = 0.96 Å for methyl H, C-H = 0.93 Å for aromatic H, and refined using the riding model with $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl hydrogens and $U_{iso}(H) = 1.2U_{eq}(C)$ for aromatic hydrogens. The nitrogen bound hydrogen atom was located in a difference map and was refined isotropically with the bond length restraint of N-H = 0.86(2) Å. All of the geometrical calculations were carried out using the program PLATON [31] within the WinGXsuite [32]. The molecular and packing diagrams were generated using the MERCURY program [33].

**2.3. Computational details**

Molecular structure of BBPHD is extracted from the X-ray structure for computational studies. The molecular geometry optimization, vibrational analysis, frontier orbital analysis (HOMO-LUMO), MEP, surface analysis and Mullikan atomic charges were calculated at DFT/6-311G++(d,p)(5D, 7F) level using Gaussian 09 program package [34]. The assignment and PED analysis of wave number were performed by GaussView5.0 program [35] and GAR2PED software package [36]. For better agreement of calculated wavenumber numbers with experimental values, the wave numbers were scaled by the scaling factor of 0.9613 [37]. Schrödinger Materials Science Suite 2017-3 [38] was also used for computational study of global and local reactive properties of the newly synthetized BBPHD molecule. Particularly, Jaguar 9.7

program [39] has been used for DFT calculations, combined with Desmond program [40-43] for simulations based on molecular dynamics. Computational study based on DFT approach with SMSS has been also done with Becke-Lee, Parr i Yang (B3LYP) [44] exchange-correlation functional with 6-311++G(d,p), 6-31+G(d,p) and 6-311G(d,p) basis sets, in order to respectively obtain ALIE, Fukui functions and bond dissociation energies (BDE). Molecular dynamics simulation has been done with OPLS3 force field [40, 45-47], with simulation time of 10 ns, temperature of 300 K, pressure of 1.0325 bar and cut off radius of 12 Å. System was of isothermal–isobaric (NPT) ensemble class, while the simple point charge (SPC) solvent model [48] was chosen for the modelling of solvent properties. A single BBPHD molecule was placed into the cubic box with approximately 3000 water molecules. Analysis of electron density between atoms has been performed according to the works of Johnson et al. [49, 50], in order to identify formation of intra-molecular non-covalent interactions. Maestro GUI [51] was used for the preparation of input files and analysis of results when Schrödinger Materials Science Suite 2017-3 was employed.

### 2.4 Conformational Analysis

The solid structure of the title compound has been determined, by the X-ray diffraction spectroscopic technique, to be planar with $C_s$ symmetry, but it can be considered as near-$C_{2v}$ as well. Such configuration allows more efficient packing and facilitates the intermolecular interaction between the molecular layers. Very interestingly, the optimized strict $C_{2v}$ structure was verified to be a minimum with all computed frequencies being positive. The two carbonyl groups prefer to point away from the skeleton of the molecule to maintain up to a 6 kcal/mol more stable configuration than when one of them would eclipse any of the $CH_2$ units. Nevertheless, detailed conformational analysis revealed that other possible non-planar (*np*) forms can possibly exist, and their calculated energies are expected to be very comparable with the experimentally reported one. Understanding these conformations is of great importance, as the molecular structure in the crystalline packing could be sensitive to several parameters such as temperature and pressure. To explore the possible stable forms beside the one determined experimentally, detailed conformational analysis at the B3LYP/6-311++G(d,p) has been performed. The internal rotations about the C2-C3, C3-C4 and C5-C6 (Fig.S3-supporting information) were calculated and show three possible non-planar forms (*np*-1, *np*-2 and *np*-3, respectively) within a stability range of less than 1 kcal/mol compared to the $C_s$ form. The large-

amplitude rotation about these bonds exhibits a barrier in a range of 2-3 kcal/mol in the non-condensed phase, indicating the feasibility of the formation of other packing pattern when harsh conditions are applied.

### 2.5. Hirshfeld surfaces

We examined molecular surfaces, packing of molecules in their crystal structure, highlighting the contribution of significant inter molecular interactions between molecules that are responsible for the molecular arrangement in the crystalline state through Hirshfeld surface analysis. Hirshfeld surfaces [52-54] and the related 2D finger print plots (FP) [55-57] are unique for any crystal structure and provide a quantitative measure of the intermolecular interactions on the surface [52, 58]. The Hirshfeld surface analysis and finger print plots of BBPHD was generated by using Crystal Explorer 3.0 software [59] which accepts structure input file in the CIF format. The surfaces are mapped using a fixed colour scale red, white and blue, where red highlights contacts shorter than the sum of van der Waals (vdW) radii which is represented by negative sign values of $d_{norm}$, white for contacts around vdW separation with $d_{norm}$ values equal to zero, and blue for contacts longer than vdW sum with positive sign $d_{norm}$ values.

## 3. Result and discussions

### 3.1. Crystal structure analysis

The title compound crystallizes in orthorhombic space group *Abm2*, with the following unit cell parameters: $a$ = 7.1227(11) Å, $b$ = 42.536(4) Å, $c$ = 5.8126(6) Å and Z = 4. The molecule exhibits crystallographic inversion symmetry located at the C10 carbon atom and there is half-molecule in the asymmetric unit. The molecule is almost planar with root mean squared deviation of all atoms (excluding H-atoms) being 0.076Å. The crystal structure features C2-H2…$\pi_{aryl}$ and C5-H5…$\pi_{aryl}$ interactions, forming a three dimensional grid like architecture. The packing of molecules in the crystal lattice is shown in Fig.S4 (supporting information). The crystallographic data and refinement parameters are summarized in Table 1.

### 3.2. Hirshfeld surfaces

3D Hirshfeld surfaces and 2D finger print analysis illustrations of the title compound (BBPHD) are shown in Fig.5 (supporting information), where surfaces have been mapped over $d_{norm}$ and shape index -1.0-1.0 Å. A red spot close to the H2 hydrogen atom on the $d_{norm}$ surface and the centroid of the aromatic ring arises as a result of C2-H2…$\pi_{aryl}$ interactions present in the crystal. Similarly, a faint red spot close to H5 atom on the $d_{norm}$ surface is due to weak C5-

H5…$\pi_{aryl}$ interactions (Fig.S5a). The dark red spots close to the centroid of the two aromatic rings in the shape index is a result of the two C-H…$\pi_{aryl}$ interactions. The two C-H…$\pi_{aryl}$ interactions are mapped over the $d_{norm}$ surface to support the presence of these interactions (Fig. S5b). The relative contribution of different interactions to the Hirshfeld surface was calculated for BBPHD. It is evident from Fig.S5(c) that the H···H contacts account for about 34.7% of the total Hirshfeld surface area; the remaining contribution was mostly due to C···H (25.8%), O···H (12.4%), Br···H (15.0%), Br···Br (9.3%) interactions and only minor contribution from other interactions.

**3.3. Geometrical parameters**

In the present case the experimental C-C bond lengths are in the range of 1.4104-1.3785 Å and the calculated C-C bond lengths are in the range of 1.4057-1.3727 Å [60]. For the title compound, the C-Br bond length is 1.9237 Å (DFT) and 1.9055 Å (XRD), which is in agreement with the literature data [61]. The C=O bond length (1.1988) agrees with the reported literature values [60]. At C8 position, the bond angles (/DFTXRD) are C3-C8-C9 = 123.5/123.7°, C3-C8-Br1 =119.1/119.2° and C9-C8-Br1 = 117.3/117.1° and the asymmetry in angles is due to the electronegative bromine atom.

**3.4. IR and Raman spectra**

Table 2 contains the wavenumbers (calculated and observed) with vibrational assignments, while the atom labelling is provided in Fig.1. Phenyl rings at C5 and C27 are designated as PhI and PhII, respectively. The carbonyl stretching C=O vibrations [62-64] appear at 1668 $cm^{-1}$ (IR), 1680 $cm^{-1}$ (Raman) and theoretically at 1679 and 1678 $cm^{-1}$. The bands observed at 679, 662 $cm^{-1}$ (IR), 658, 551 $cm^{-1}$ (Raman) and at 678, 667, 553 $cm^{-1}$ (DFT) are assigned as C=O deformation modes [62]. The phenyl C-H stretching modes are assigned at 3081, 3062 $cm^{-1}$ (spectrum), 3079, 3059 $cm^{-1}$ (Raman) and in the range 3082-3064 $cm^{-1}$ based on DFT calculations [62, 65]. The ring stretching modes of the phenyl ring are assigned in the range 1558-1269 $cm^{-1}$ theoretically. The bands observed at 1570, 1530, 1450, 1374 $cm^{-1}$ (IR) and at 1565, 1279 $cm^{-1}$ (Raman) are assigned as the phenyl ring stretching modes. The band at 1042 $cm^{-1}$ (IR), 1042 $cm^{-1}$ (Raman) and 1040 $cm^{-1}$ (DFT) is assigned as the ring breathing mode of the para substituted phenyl ring [65], which is in agreement with the reported values at 1062 $cm^{-1}$ (IR) and 1061 $cm^{-1}$ (DFT) [66]. The in-plane and out-of-plane CH deformations are assigned theoretically in the range 1276-1087 $cm^{-1}$ and 965-788 $cm^{-1}$, respectively. Experimentally, these

modes are assigned at 1156, 1087 $cm^{-1}$ (IR), 1279, 1088 $cm^{-1}$ (Raman) and 963, 815, 801 $cm^{-1}$ (IR), 968, 818, 798 $cm^{-1}$ (Raman). The $CH_2$ stretching modes are assigned in the range 2965-2865 $cm^{-1}$ in IR spectrum, 2965-2877 $cm^{-1}$ in Raman spectrum and in the range of 2962-2873 $cm^{-1}$based on DFT calculations [62,67]. The $CH_2$ bending modes are observed in the ranges 1450-759 $cm^{-1}$ in the IR spectrum and 1440-738 $cm^{-1}$ in the Raman spectrum. According to the DFT calculations, these modes are in the range of 1453-706 $cm^{-1}$. The C-C stretching modes are assigned in the range 1173-780 $cm^{-1}$computationally. Bromine compounds [62] absorb strongly in the region of 635±85 $cm^{-1}$, due to the CBr stretching vibration and in the present case, bands at 615 $cm^{-1}$ (IR), 624 $cm^{-1}$ (Raman) and 616 $cm^{-1}$ (DFT) are assigned to this mode. Varghese et al. [68] reported the CBr stretching mode at 632 $cm^{-1}$ theoretically.

**3.5. NMR spectra analysis**

Chemical shift ($^{1}H$ and $^{13}C$) values of the investigated molecules have been computed with GIAO/B3LYP method [69] and compared with experimental values (Table S1-supporting information). The chemical shift values of $^{1}H$-NMR spectrum of title compound show two ranges; first one is consequence of the chemical shift of aliphatic C-H protons, which occurred in the range of 1.39-2.95/1.29-3.02 ppm (experimental/theoretical). The chemical shift of hydrogen atom attached to carbon near to the carbonyl group is higher than expected. H21, H22, H40 and H41 resonate at high frequency 2.95/3.02 (experimental/DFT), due to influence of carbonyl groups. Second one, around 7.60-7.81/7.69-8.06 (experimental/theoretical) ppm, occurred due to the aromatic protons. Chemical shift values of $^{13}C$-NMR for aromatic carbon atoms in general have values higher than 100 ppm [70,71]. Computational and experimental $^{13}C$ NMR values of carbon atoms of methylene groups of aliphatic chain are in good agreement as well: C17, C36 (24.02/27.40), C13 (28.97/32.69) and C20, C39 (38.37/42.69) ppm (experimental values/computational values). The chemical shift value at 199.26/205.26 ppm (experimental/computational) is assigned to the carbonyl carbon atoms C2 and C24. Signals observed in range of the 128.26-135.82/134.04-153.80 ppm (experimental/computational) correspond to carbon atoms of phenyl rings. From above result shows, the theoretical chemical shifts are good in agreement with experimental findings.

**3.6. Electronic properties and frontier molecular orbital analysis**

Chemical reactivity and kinetic stability of molecules depend upon the energy gap between HOMO and LUMO orbitals. These molecular orbitals are often known as frontier

molecular orbitals (FMOs). Based on the energy gap between frontier orbitals, molecules are frequently classified into soft and hard molecules. Energy gap between frontier orbitals is a critical parameter for prediction of the biological activity and transport properties. Frontier molecular orbitals have been visualized in Fig.S6 (supporting information). It can be seen that HOMO (MO109) is localized mainly at the carbonyl group and partially at the aliphatic chain, while LUMO (MO110) is localized mainly at the benzene ring and partially at the carbonyl group. Based on the HOMO to LUMO transitions, it can be concluded that the transfer of electron cloud occurs mainly from carbonyl group to benzene ring. In the present case, the calculated energy values of HOMO and LUMO are -7.20 eV and -2.16 eV, respectively and the energy gap between HOMO and LUMO is 5.04 eV. The higher the energy gap between HOMO-LUMO is, the harder the molecule is. In order to understand the chemical reactivity of title compound, global reactivity parameters were evaluated by DFT method. Single point calculation was carried out at DFT/6-311++G(d,p) level of theory. Vertical ionization potential (IP) and vertical electron affinity (EA) parameters have been calculated. These parameters were defined according to the following equations:

$$IP = E_{n-1(\text{cation})} - E_{N(\text{neutral})},$$

$$EA = E_{N(\text{neutrail})} - E_{N+1(\text{anion})},$$

where $E_{N+1(\text{anion})}$, $E_{N(\text{neutral})}$ and $E_{N-1(\text{cation})}$ are total energies of anion, neutral and cation forms of investigated molecule, respectively [72, 73]. These parameters were used in order to calculate the values of global reactivity descriptor, summarized in Table S2 of the Supplementary Materials. TD-DFT calculations have been performed at B3LYP/6-311++G(d,p) level of theory, while theoretical UV transitions have been characterized by vertical excitation energies, wavelength and oscillator strength. These results are summarized in Table S3 of the Supplementary Materials. The UV spectrum of the title compound (Fig.S7-supporting information) is characterized by electronic absorption band located at 268 nm, which is the consequence of the transitions: HOMO-1→LUMO and HOMO→LUMO+1(π-π transition).

### 3.7. Nonlinear optical properties

With regards to optoelectronic applications [74], the NLO active materials receive significant attention. Some of the properties that are important for optoelectronic applications can be obtained by DFT calculations and these include dipole moment, polarizability, first and

second hyperpolarizabilities. Respectively, these parameters have been calculated to be 4.102 Debye, $4.149\times10^{-23}$ esu, $6.227\times10^{-30}$ esu and $-71.736\times10^{-37}$ esu. It is interesting to notice that the first hyperpolarizability of the title compound is 31.98 times higher than in the case of urea, revealing possibility of the title compound to possess representative NLO properties, comparable with similar derivatives [75].

### 3.8. Molecular electrostatic potential

Analysis of charge distribution by mapping of MEP to the electron density surface is valuable approach in molecular modelling, when it comes to the biological recognition, hydrogen bonding interactions and visualization of reactive molecular sites [76, 77]. Optimized molecular structure was used for the generation of 3D MEP and 2D counter surfaces plots with rainbow colour scheme (electron reach regions are represented with red colour, while electron poor regions are represented with blue colour). For the title compound MEP took values from– 5.56a.u. (red) to 5.56a.u. (blue). MEP and surface analysis diagram of title compound, Fig.2, show that negative regions are mainly localized over oxygen atoms of the carbonyl groups, indicating the most sensitive sites towards the electrophilic attacks. On the other side, the maximal positive regions are localized over hydrogen atom of the aliphatic chain as well as phenyl rings, indicating sensitivity towards the nucleophilic attacks.

### 3.9. Natural Bond Orbital analysis

Natural bond orbital (NBO) calculations were performed using NBO 3.1 program [78] as incorporatedin the Gaussian09 package. In this case the DFT/SDD level of theory was used in order to understand various second-order interactions, principal interaction summarized in Tables S4 and S5 (supplementary materials). The strong intermolecular hyper conjugative interactions are: $C_2$-$C_5$ from $O_{16}$ of $n_2(O_{16}) \rightarrow \sigma^*(C_2\text{-}C_5)$ which increases the electron density 0.06345e that weakens the respective bond $C_2$-$C_5$ leading stabilization of 16.61 kJ/mol; $C_2$-$C_{20}$ from $O_{16}$ of $n_2(O_{16})\rightarrow\sigma^*(C_2\text{-}C_{20})$ which increases the electron density 0.05561e that weakens the respective bond $C_2$-$C_{20}$ leading stabilization of 17.56 kJ/mol; $C_{24}$-$C_{27}$ from $O_{35}$ of $n_2(O_{35})\rightarrow\sigma^*(C_{24}\text{-}C_{27})$ which increases the electron density 0.06345e that weakens the respective bond $C_{24}$-$C_{27}$ leading stabilization of 16.61 kJ/mol; and $C_{24}$-$C_{39}$ from $O_{35}$ of $n_2(O_{35})\rightarrow\sigma^*(C_{24}\text{-}C_{39})$ which increases the electron density 0.05561e that weakens the respective bond $C_{24}$-$C_{39}$ leading stabilization of 17.56 kJ/mol. The orbital with low occupation number are high energies are $n_2(O_{16})$, $n_2(O_{35})$ with energies -0.27360, -0.27360a.u. and considerable p-characters100,

99.99% and low occupation numbers 1.90859, 1.90859 while the orbital with high occupation numbers and low energies are: $n_1(O_{16})$, $n_1(O_{35})$ -0.68914, -0.68914a.u. and p-characters, 61.77, 61.77 and occupation numbers 1.97457, 1.97457. Thus, a very close to pure p-type lone pair orbital participates in the electron donation to the $\sigma^*(C_2\text{-}C_5)$ orbital for $n_2(O_{16}) \rightarrow \sigma^*(C_2\text{-}C_5)$, $\sigma^*(C_2\text{-}C_{20})$ orbital for $n_2(O_{16}) \rightarrow \sigma^*(C_2\text{-}C_{20})$, $\sigma^*(C_{24}\text{-}C_{27})$ orbital for $n_2(O_{35}) \rightarrow \sigma^*(C_{24}\text{-}C_{27})$, $\sigma^*(C_{24}\text{-}C_{39})$) orbital for $n_2(O_{35}) \rightarrow \sigma^*(C_{24}\text{-}C_{39})$ interactions in the title compound.

### 3.10. ALIE and MEP surface, Fukui functions and non-covalent interactions

Aside of the MEP surface, in this work ALIE values were mapped to the electron density surface in order to identify the molecule sites where electrons are least tightly bound. This enabled us to detect molecule sites that are the most sensitive towards the electrophilic attacks (Fig.3) [79-82]. The analysis of electron density between atoms revealed that the intra-molecular non-covalent interactions in the case of BBPHD molecule didn't form. The lowest ALIE values in the case of BBPHD molecule were calculated in the near vicinity of bromine atoms, with corresponding values of ~205 kcal/mol. On the other side, the highest ALIE values were calculated in the near vicinity of all hydrogen atoms with the corresponding values of ~342 kcal/mol. Additional insights into the local reactive properties of BBPHD molecule were obtained thanks to the calculation of Fukui functions, which are in the case of Jaguar program for DFT calculations obtained by the finite difference approach according to the following equations:

$$f^{+} = \frac{\left(\rho^{N+\delta}(r) - \rho^{N}(r)\right)}{\delta}, \qquad (1)$$

$$f^{-} = \frac{\left(\rho^{N-\delta}(r) - \rho^{N}(r)\right)}{\delta}, \qquad (2)$$

where $N$ represents the number of electrons in reference state of the molecule, while $\delta$ is fraction of electron which default value is set to be 0.01 [83]. After mapping of the values of the Fukui functions to the electron density surface the following corresponding surfaces have been obtained, Fig.4. In general Fukui functions track the changes in electron densities which are consequence of change in the overall charge of the observed molecule. The change in overall molecular charge influences the values of electron density at the molecular surface. By tracking of these changes in electron density, Fukui functions allow detection of molecule sites with electrophilic and nucleophilic properties. In this regard, purple colour for Fukui $f^{+}$ function in

Fig.4a is positive colour and indicates sites with increased electron density after the addition of charge. In Fig.4a it can be seen that blue-to-purple colour is located in the near vicinity of carbon atoms connected with oxygen atoms, which marks them as an electrophilic ones. On the other side, red colour for Fukui $f^-$ function is a negative colour and indicates sites with decreased electron density after the removal of charge. Inspection of Fig.4b indicates that the red colour is located in the central part of the molecule, marking this area as nucleophilic.

### 3.11. Sensitivity towards autoxidation and water

Taking into account the negative environmental impact of the pharmaceuticals, in this work we have also studied the sensitivity of BBPHD molecule towards the autoxidation mechanism [24, 84]. Oxidation mechanism represents one of the most important pathways for degradation of pharmaceuticals [85-88]. Thanks to the correlation between bond dissociation energies for hydrogen abstraction (H-BDE) and sensitivity towards the autoxidation mechanism, computational molecular modelling techniques can be used for determination of the molecule sites where degradation could start [89-95]. Fig.5 contains information about the H-BDE values. According to the results presented in Fig.5, for BBPHD molecule it can be concluded that it is highly stable towards the autoxidation mechanism, since there are no H-BDE values in the region between 70 and 90 kcal/mol [96, 97]. In the same time the lowest BDE value has been calculated for bromine atoms indicating that degradation could start by detaching of these atoms. Sensitivity towards water molecules was investigated by molecular dynamics simulation. The information on the obtained trajectories were used in order to calculate Radial Distribution Functions (RDF) for all atoms of the BBPHD molecule, with the goal to identify atoms with the most important interactions with water. RDFs were calculated with respect to the distance between the observed atom of the BBPHD molecule and oxygen atom of the water molecule. Representative RDFs have been presented in Fig.6. According to the results provided in Fig.6 it can be seen that BBPHD molecule has significant stability in water, as there are no hydrogen atoms with sharp g(r) curves located at distances below 2 Å. The highest g(r) value was calculated for bromine atoms, however their maximal g(r) values are located at distance of around 3.5 Å. On the other side, maximal g(r) values carbon atoms C16 and C35 are located at the distances lower than in case of the bromine atoms, but their maximal g(r) values are much lower. Maximal g(r) values of the carbon atoms C8 and C30 are somewhere between bromine

atoms at carbon atoms C16 and C35, however their peaks are located at high distances of over 4.5 Å.

### 3.12. Molecular docking

Based on the molecular structure, PASS (Prediction of Activity Spectra) [98] online tool for prediction of different types of activities has been applied. According to the results of PASS analysis, which have been summarized in Table 3, the title compound could serve as feruloyl esterase inhibitor, with probability to be active (Pa) value of 0.936. Antioxidants are necessary to control degenerative reactions produced by reactive oxygen and nitrogen species. These species are involved in several ailments including cancer and heart diseases. Several literatures suggest that heptane derivatives show promising antioxidant activities [99, 100]. Ferulic acid is the most abundant hydroxycinnamic acid in the plant world and is one of the most promising sources of antioxidants [101]. Feruloyl esterase is a class of enzymes used in biocatalysis for refinement of hydroxycinnamic acids. These compounds have shown to have antioxidant and antibacterial properties, FAEs and their hydrolytic or transesterification products are of great interest for various biotechnological applications, in particular as modified natural antioxidants or food flavour precursors [102].It prevents low-density lipoprotein from oxidation, exhibits inhibitory effects on tumour promotion [103] and protects against certain chronic diseases such as coronary heart disease and some cancers [104, 105]. Therefore the feruloyl esterase inhibitor is used as a target for docking study. High resolution crystal structure of feruloyl esterase inhibitor was downloaded from the RSCB protein data bank website with PDB ID: 1UWC. All molecular docking calculations were performed on Auto Dock-Vina software [106] and as reported in literature [74, 107]. The ligand binds at the active site of the substrate by weak non-covalent interactions and these interactions are depicted in Fig.S8 (supporting information). Amino acids forms strong hydrophobic interaction with the ligand. The docked ligand forms a stable complex with feruloyl esterase inhibitor (Fig.S9-supporting information) and got a binding affinity value of -5.7 kcal/mol (Table 4). Thus the title compound can be a lead compound for developing new antioxidant drug.

## 4. Conclusion

The title compound, 1,7-bis(4-bromophenyl)heptane-1,7-dione was characterized by single crystal XRD, FT-IR, FT-Raman as well as NMR spectroscopic studies. Within the framework of DFT, the vibrational wavenumbers are theoretically predicted and compared with

experimental wavenumbers. Conformation analysis shows that the two carbonyl groups prefer to point away from the skeleton of the molecule to maintain up to a 6 kcal/mol more stable configuration than when one of them would eclipse any of the $CH_2$ units. MEP plot showed that the negative regions are mainly localized over the oxygen atoms of the carbonyl groups while the maximal positive regions are localized over the hydrogen atom of the aliphatic chain as well as phenyl rings. The first hyperpolarizability of the title compound is 31.98 times that of urea. ALIE surfaces revealed that the near vicinity of bromine atoms could be the most sensitive parts of the BBPHD molecule in terms of electrophilic attacks. Additionally, Fukui functions revealed that the central part of BBPHD molecule could be considered as important reactive center when charge is added or removed. The values of H-BDE indicate that BBPHD molecule is highly stable towards the autoxidation mechanism, while the remaining BDE values indicate that degradation process might start with detaching of bromine atoms. Molecular dynamics study indicated that BBPHD molecule is highly stable in water as well, since there are no hydrogen atoms with significant interactions with water molecules. PASS analysis predicts feruloyl esterase inhibitor activity for the title compound and the docking studies suggest that the title compound can be a lead compound for developing new antioxidant drug.

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**Supplementary Material**

The cif file of the title compound have been assigned CCDC number1577497and can be obtained free of cost on application to CCDC 12 Union Road, Cambridge CB21 EZ, UK. (Fax: (+44) 1223 336-033: e-mail: data_request@ccdc.cam.ac.uk).

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**Figure captions**

Fig.1 Optimized geometry of 1,7-bis(4-bromophenyl)heptane-1,7-dione

Fig.2 MEP plot of 1,7-bis(4-bromophenyl)heptane-1,7-dione

Fig.3 ALIE surface of 1,7-bis(4-bromophenyl)heptane-1,7-dione molecule

Fig.4 Fukui functions of the 1,7-bis(4-bromophenyl)heptane-1,7-dione molecule a) $f^{+}$ and b) $f^{-}$

Fig.5 H-BDE values (blue colour) and BDE values of the remaining single acyclic bonds (red colour)

Fig.6 Significant RDFs of atoms of 1,7-bis(4-bromophenyl)heptane-1,7-dione molecule

ACCEPTED MANUSCRIPT

**Table 1: Crystal data and structure refinement for BBPHD**

| | | |
|---|---|---|
| CCDC Deposit | : | 1577497 |
| Empirical formula | : | $C_{19}H_{18}O_2Br_2$ |
| Formula weight | : | 434.13 |
| Temperature/K | : | 296.15 |
| Crystal system | : | Orthorhombic |
| Space group | : | Abm2 |
| a/Å | : | 7.1227(11) |
| b/Å | : | 42.536(4) |
| c/Å | : | 5.8126(6) |
| α/° | : | 90 |
| β/° | : | 90 |
| γ/° | : | 90 |
| Volume/$Å^3$ | : | 1761.1(4) |
| Z | : | 4 |
| $\rho_{calc}g/cm^3$ | : | 1.653 |
| $\mu/mm^{-1}$ | : | 4.610 |
| F(000) | : | 872.2 |
| Crystal size/$mm^3$ | : | 0.25×0.22×0.18 |
| Radiation | : | Mo Kα (λ = 0.71073) |
| 2Θ range for data collection/° | : | 3.84 to 57.74 |
| Index ranges | : | $-9 \leq h \leq 9$, $-56 \leq k \leq 57$, $-6 \leq l \leq 7$ |
| Reflections collected | : | 12635 |
| Independent reflections | : | 2095 [$R_{int}$ = 0.0808, $R_{sigma}$ = 0.0737] |
| Data/restraints/parameters | : | 2095/1/106 |
| Goodness-of-fit on $F^2$ | : | 1.101 |
| Final R indexes [I>=2σ (I)] | : | $R_1$ = 0.0630, $wR_2$ = 0.1306 |
| Final R indexes [all data] | : | $R_1$ = 0.1174, $wR_2$ = 0.1551 |
| Largest diff. peak/hole/ e $Å^{-3}$ | : | 1.14/-1.15 |
| Flack parameter | : | 0.11(3) |

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Table 2

Calculated scaled wavenumbers, observed IR, Raman bands with assignments

| B3LYP/6-311G++(d,p)(5D, 7F) | | | IR | Raman | Assignments[a] |
|---|---|---|---|---|---|
| υ($cm^{-1}$) | IRI | RA | υ($cm^{-1}$) | υ($cm^{-1}$) | - |
| 3082 | 0.89 | 432.59 | - | - | υCHII(51),υCHI(40) |
| 3082 | 1.48 | 33.26 | - | - | υCHI(51),υCHII(40) |
| 3081 | 2.11 | 8.85 | 3081 | 3079 | υCHII(55),υCHI(43) |
| 3081 | 4.68 | 5.75 | 3081 | 3079 | υCHI(55),υCHII(43) |
| 3069 | 0.41 | 52.50 | - | - | υCHI(66),υCHII(32) |
| 3069 | 0.99 | 34.13 | - | - | υCHII(66),υCHI(32) |
| 3064 | 0.53 | 74.49 | 3062 | 3059 | υCHII(50),υCHI(49) |
| 3064 | 7.37 | 24.17 | 3062 | 3059 | υCHI(50),υCHII(49) |
| 2962 | 66.90 | 25.95 | 2965 | 2965 | $\upsilon CH_2$(88) |
| 2954 | 0.01 | 0.22 | 2952 | - | $\upsilon CH_2$(92) |
| 2925 | 39.15 | 125.82 | - | 2928 | $\upsilon CH_2$(96) |
| 2920 | 2.24 | 0.72 | 2922 | - | $\upsilon CH_2$(98) |
| 2915 | 7.65 | 71.93 | - | - | $\upsilon CH_2$(94) |
| 2914 | 0.01 | 0.43 | - | - | $\upsilon CH_2$(92) |
| 2896 | 19.06 | 74.27 | - | 2897 | $\upsilon CH_2$(91) |
| 2890 | 22.32 | 288.27 | - | - | $\upsilon CH_2$(96) |
| 2890 | 31.55 | 0.65 | - | - | $\upsilon CH_2$(98) |
| 2873 | 16.97 | 81.11 | 2865 | 2877 | $\upsilon CH_2$(96) |
| 1679 | 338.34 | 190.30 | 1668 | 1680 | υC=O(80) |
| 1678 | 18.93 | 73.90 | 1668 | 1680 | υC=O(80) |
| 1558 | 69.35 | 343.39 | 1570 | 1565 | υPhII(26), υPhI(26) |
| 1558 | 176.92 | 213.32 | - | - | υPhI(27), υPhII(26) |
| 1539 | 8.18 | 16.46 | - | - | υPhII(36), υPhI(36) |
| 1539 | 40.30 | 17.65 | 1530 | - | υPhI(36), υPhII(36) |
| 1454 | 3.93 | 7.53 | - | - | υPhII(36), υPhI(36) |
| 1454 | 19.94 | 1.24 | 1450 | - | υPhII(36), υPhI(36) |
| 1453 | 12.69 | 0.75 | 1450 | - | $\delta CH_2$(86) |

| | | | | | |
|---|---|---|---|---|---|
| 1437 | 2.65 | 0.12 | - | 1440 | $\delta CH_2$(92) |
| 1430 | 0.04 | 27.52 | - | - | $\delta CH_2$(95) |
| 1404 | 14.77 | 7.51 | 1410 | - | $\delta CH_2$(88) |
| 1403 | 0.14 | 1.65 | - | - | $\delta CH_2$(88) |
| 1368 | 4.97 | 6.95 | 1374 | - | υPhI(32), υPhII(32), δCHII(11), δCHI(11) |
| 1368 | 73.82 | 3.16 | - | - | υPhI(31), υPhII(31), δCHII(11), δCHI(11) |
| 1351 | 3.25 | 0.59 | - | - | $\delta CH_2$(67), υCC(18) |
| 1345 | 0.01 | 0.64 | 1342 | 1340 | $\delta CH_2$(66) |
| 1320 | 141.41 | 0.85 | - | - | $\delta CH_2$(66), υCC(14) |
| 1284 | 0.06 | 0.16 | 1288 | - | $\delta CH_2$(94) |
| 1281 | 0.01 | 17.04 | 1281 | - | $\delta CH_2$(97) |
| 1280 | 9.05 | 12.74 | 1281 | 1279 | $\delta CH_2$(66) |
| 1276 | 1.64 | 0.01 | - | 1279 | υPhI(11), υPhII(10), δCHI(30), δCHII(30) |
| 1269 | 3.44 | 1.63 | - | - | δCHI(30), δCHII(30), υPhI(11), υPhII(10) |
| 1269 | 0.13 | 0.26 | - | - | υPhI(31), υPhII(31) |
| 1269 | 1.15 | 7.80 | - | - | υPhI(25),υPhII(25), $\delta CH_2$(26) |
| 1260 | 0.01 | 10.11 | 1258 | 1260 | $\delta CH_2$(86) |
| 1220 | 186.53 | 14.42 | 1219 | 1215 | $\delta CH_2$(60), υCC(16) |
| 1202 | 0.04 | 0.22 | - | - | $\delta CH_2$(96) |
| 1173 | 21.27 | 102.83 | 1172 | 1170 | υCC(32), $\delta CH_2$(16) |
| 1162 | 21.38 | 12.12 | 1156 | - | δCHII(44), δCHI(44) |
| 1153 | 13.45 | 88.30 | 1156 | - | δCHI(30), δCHII(31) |
| 1148 | 183.16 | 29.51 | - | 1149 | υCC(18),δCHI(15), δCHII(15) |
| 1095 | 0.01 | 2.44 | - | - | $\delta CH_2$(83) |
| 1087 | 3.80 | 5.47 | 1087 | 1088 | δCHI(25), δCHII(25), |

| | | | | | |
|---|---|---|---|---|---|
| | | | | | υPhI(16), υPhII(16) |
| 1087 | 7.87 | 2.87 | 1087 | 1088 | δCHI(25), δCHII(25), υPhI(15), υPhII(15) |
| 1061 | 0.55 | 58.77 | - | - | υCC(44), $\delta CH_2$(21) |
| 1058 | 0.01 | 0.60 | - | - | $\delta CH_2$(82) |
| 1040 | 78.39 | 8.97 | 1042 | 1042 | υPhI(27), υPhII(27) |
| 1040 | 17.01 | 100.46 | 1042 | 1042 | υPhI(27), υPhII(27) |
| 1028 | 20.51 | 3.71 | 1024 | 1030 | υCC(78) |
| 1008 | 16.55 | 0.09 | - | - | υCC(52) |
| 1000 | 0.17 | 22.49 | - | - | υCC(76) |
| 986 | 11.44 | 6.39 | - | - | δPhI(29),δPhII(29), υPhI(12), υPhII(12) |
| 985 | 92.40 | 0.36 | - | - | δPhI(33), δPhII(33) |
| 965 | 0.01 | 0.10 | - | 968 | γCHI(41), γCHII(41) |
| 964 | 0.81 | 0.06 | 963 | - | γCHII(42), γCHI(42) |
| 953 | 9.04 | 2.68 | - | - | υCC(32), δ(C=O)(14) |
| 937 | 0.00 | 0.29 | - | - | γCHI(32), γCHII(32) |
| 933 | 201.61 | 3.43 | - | - | υCC(46) |
| 932 | 0.03 | 0.19 | - | - | γCHI(38), γCHII(38) |
| 916 | 0.01 | 0.02 | 913 | - | $\delta CH_2$(59) |
| 837 | 14.44 | 0.34 | - | - | $\delta CH_2$(52),γCHI(10), γCHII(10), γ(C=O)(10) |
| 819 | 0.01 | 0.01 | - | 818 | γCHI(43),γCHII(43) |
| 813 | 8.39 | 0.01 | 815 | - | γCHI(44), γCHII(44) |
| 801 | 0.01 | 0.01 | 798 | 798 | γCHI(41), γCHII(41) |
| 788 | 74.69 | 0.03 | - | - | γCHI(33),γCHII(32), $\delta CH_2$(30) |
| 780 | 37.04 | 0.01 | - | - | υCC(32), $\delta CH_2$(12) |
| 759 | 7.71 | 35.99 | 759 | 758 | υCC(32), δPhII(14), δPhI(13) |
| 739 | 0.01 | 0.03 | 737 | 738 | $\delta CH_2$(66) |
| 706 | 12.10 | 0.01 | 706 | 699 | $\delta CH_2$(69) |

| | | | | | |
|---|---|---|---|---|---|
| 688 | 0.01 | 0.63 | - | - | τPhII(34), τPhI(34) |
| 688 | 0.03 | 0.14 | - | - | τPhII(33), τPhI(33) |
| 678 | 0.10 | 0.09 | 679 | - | δPhII(24), δPhI(23), δ(C=O)(38) |
| 668 | 2.62 | 9.28 | 662 | 658 | δ(C=O)(32), δPhII(20), δPhI(19) |
| 616 | 1.94 | 3.94 | 615 | 624 | δPhI(13), δPhII(12) υCBr(36) |
| 616 | 0.68 | 9.73 | 615 | 624 | δPhI(14), δPhII(12) υCBr(37) |
| 553 | 0.01 | 0.02 | - | 551 | γ(C=O)(36), δ$CH_2$(22) |
| 553 | 18.01 | 0.31 | - | 551 | γ(C=O)(37), δ$CH_2$(22), γCC(10) |
| 504 | 3.37 | 0.89 | - | 499 | δ(C=O)(34), δ$CH_2$(12), δCC(12) |
| 483 | 19.50 | 0.72 | - | 479 | δ(C=O)(34), δCC(14), υCBr(10) |
| 456 | 1.77 | 0.60 | - | 456 | δ$CH_2$(34), δ(C=O)(12) |
| 445 | 0.01 | 0.01 | - | - | γCBr(28), τPhI(24), τPhII(22), γCC(12) |
| 444 | 13.25 | 0.21 | - | - | γCBr(28), τPhI(24), τPhII(22), γCC(12) |
| 409 | 17.42 | 0.03 | - | 408 | δ(C=O)(38), δ$CH_2$(30), υCBr(14) |
| 399 | 0.01 | 0.01 | - | - | τPhII(42), τPhI(41) |
| 399 | 0.01 | 0.01 | - | - | τPhII(43), τPhI(39) |
| 372 | 1.92 | 1.14 | - | 369 | δ$CH_2$(28), υCBr(14) |
| 336 | 0.13 | 0.77 | - | 336 | δCC(30), δ$CH_2$(24), δCBr(12) |
| 283 | 11.14 | 0.54 | - | - | δCBr(40), δCC(22) |
| 264 | 0.15 | 2.61 | - | 262 | δCBr(32), δCC(10) |
| 240 | 1.14 | 0.01 | - | - | δCBr(38), δ$CH_2$(24), δ(C=O)(18) |

| | | | | | |
|---|---|---|---|---|---|
| 236 | 0.28 | 0.62 | - | - | γCC(36), γCBr(26), γ(C=O)(12) |
| 236 | 0.01 | 3.68 | - | 234 | γCC(38), γCBr(28), γ(C=O)(12) |
| 215 | 6.95 | 0.44 | - | - | δCBr(32), δPhII(15), δPhI(11) |
| 180 | 9.00 | 0.33 | - | 185 | δCBr(36), δ$CH_2$(32), δCC(18) |
| 144 | 1.72 | 0.01 | - | - | τ$CH_2$(82) |
| 141 | 0.01 | 0.03 | - | - | τ$CH_2$(77), τ(C=O)(13) |
| 134 | 0.01 | 0.97 | - | - | δCC(26), δCBr(24),δ$CH_2$(23) |
| 93 | 0.01 | 0.03 | - | 95 | τ$CH_2$(51), τ(C=O)(13) |
| 91 | 0.12 | 1.31 | - | - | δ(C=O)(22), δ$CH_2$(26) |
| 84 | 0.43 | 0.02 | - | - | τ$CH_2$(41) ,τ(C=O)(27) |
| 69 | 0.01 | 0.01 | - | - | τPhII(12), τCC(12) τ(C=O)(12),τPhI(14), γCC(14) |
| 66 | 3.13 | 0.01 | - | 66 | τPhII(16), τPhI(17), γCC(14) |
| 55 | 0.02 | 0.26 | - | - | δ$CH_2$(46), δ(C=O)(28), δCC(16) |
| 50 | 2.85 | 0.39 | - | - | τ(C=O)(30), τCC(30), τ$CH_2$(12) |
| 28 | 0.01 | 5.22 | - | - | τ(C=O)(34), τCC(29), τ$CH_2$(19) |
| 17 | 1.21 | 4.62 | - | - | τ$CH_2$(45),τ(C=O)(14), τCC(15) |
| 15 | 0.01 | 1.47 | - | - | δ$CH_2$(84), δ(C=O)(10) |
| 12 | 0.01 | 0.60 | - | - | τ$CH_2$(60),τ(C=O)(30) |

[a]υ-stretching; δ-in-plane deformation; γ-out-of-plane deformation; τ-torsion; $IR_I$-IR intensity(KM/Mole) ; $R_A$-Raman activity(Å$^4$/amu); the phenyl rings at C5 and C27 are designated as PhI and PhII.

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Table 3

PASS prediction for the activity spectrum of the1.7-bis(4-bromophenyl)heptane-1.7-dione (Pa represents probability to be active and Pi represents probability to be inactive)

| Pa | Pi | Activity |
|---|---|---|
| 0.936 | 0.003 | Feruloyl esterase inhibitor |
| 0.933 | 0.001 | Alkylglycerone-phosphate synthase inhibitor |
| 0.926 | 0.003 | Prolylaminopeptidase inhibitor |
| 0.918 | 0.005 | Aspulvinonedimethylallyltransferase inhibitor |
| 0.845 | 0.003 | L-glucuronate reductase inhibitor |
| 0.846 | 0.010 | Antineurotic |
| 0.840 | 0.005 | Arginine 2-monooxygenase inhibitor |
| 0.826 | 0.004 | Centromere associated protein inhibitor |
| 0.821 | 0.004 | Fatty-acyl-CoA synthase inhibitor |
| 0.823 | 0.013 | Mucomembranous protector |
| 0.812 | 0.009 | Nicotinic alpha6beta3beta4alpha5 receptor antagonist |
| 0.808 | 0.015 | Sugar-phosphatase inhibitor |
| 0.814 | 0.022 | Testosterone 17beta-dehydrogenase (NADP+) inhibitor |
| 0.782 | 0.007 | Bisphosphoglycerate phosphatase inhibitor |
| 0.776 | 0.005 | Phosphatidylserine decarboxylase inhibitor |
| 0.802 | 0.033 | Phobic disorders treatment |

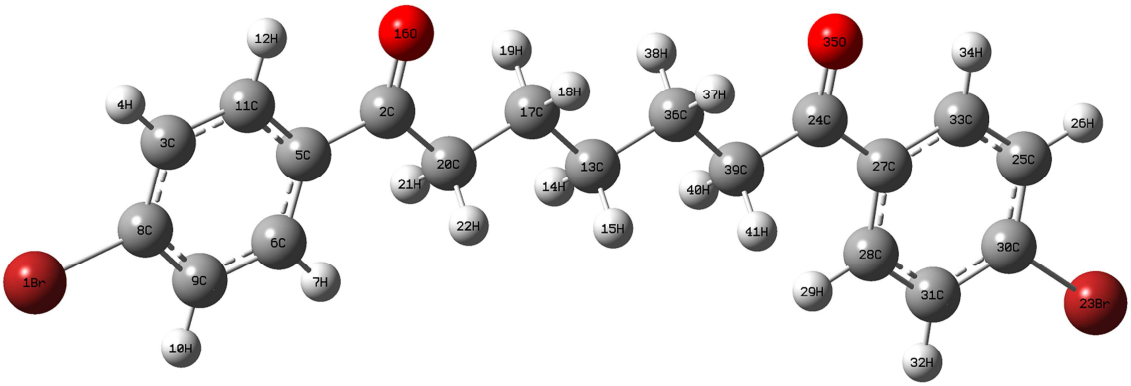
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Table 4

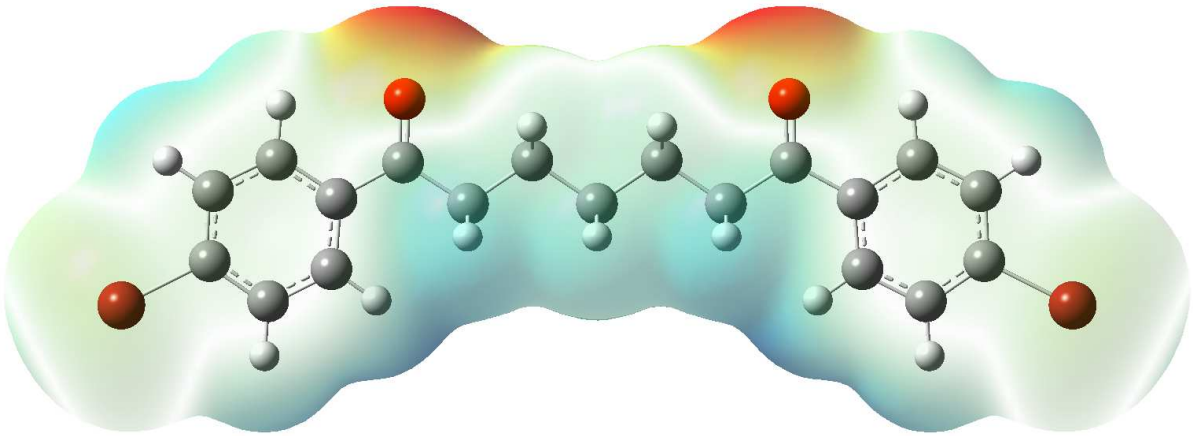
The binding affinity values of different poses of the 1,7-bis(4-bromophenyl)heptane-1,7-dionepredicted by Autodock Vina.

| Mode | Affinity (kcal/mol) | Distance from best mode (Å) | |
|---|---|---|---|
| - | - | RMSD l.b. | RMSD u.b. |
| 1 | -5.7 | 0.000 | 0.000 |
| 2 | -5.5 | 18.856 | 19.653 |
| 3 | -5.5 | 1.347 | 4.716 |
| 4 | -5.5 | 2.621 | 4.743 |
| 5 | -5.5 | 11.763 | 13.521 |
| 6 | -5.4 | 2.282 | 4.146 |
| 7 | -5.4 | 2.929 | 6.059 |
| 8 | -5.3 | 3.144 | 6.394 |
| 9 | -5.3 | 3.368 | 5.280 |

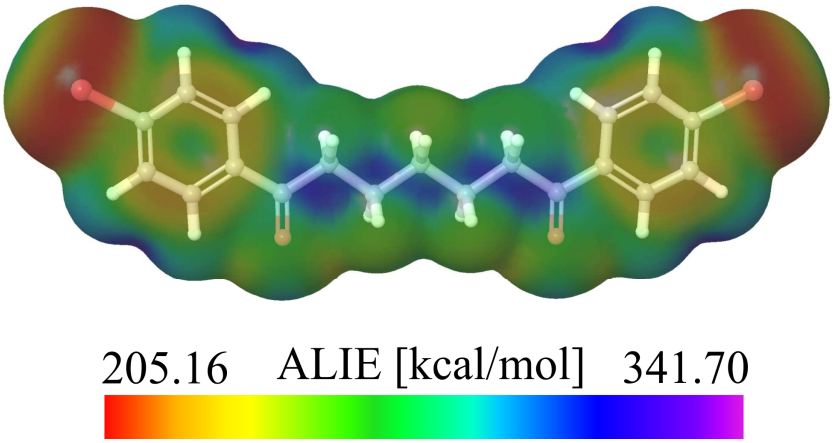
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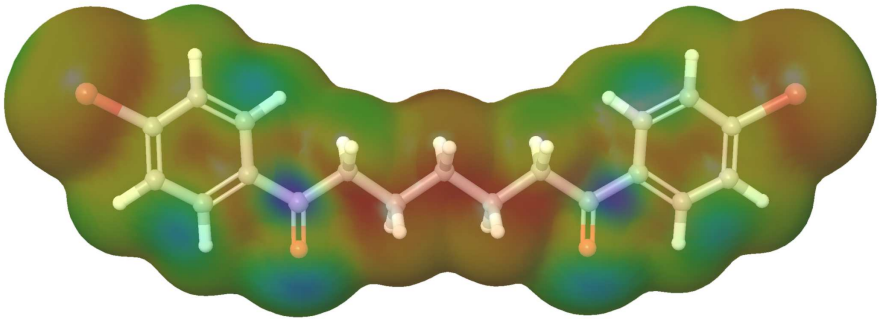


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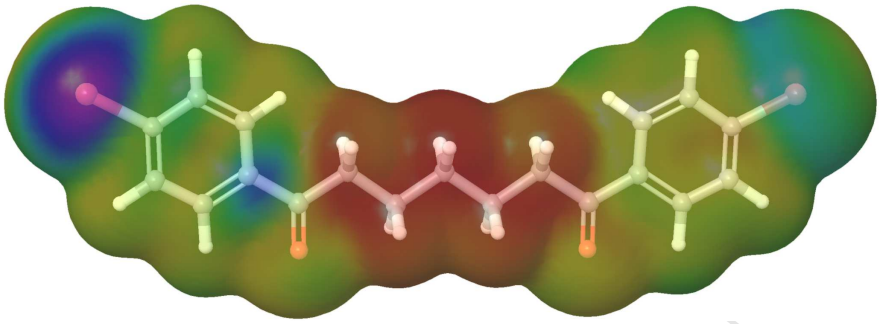



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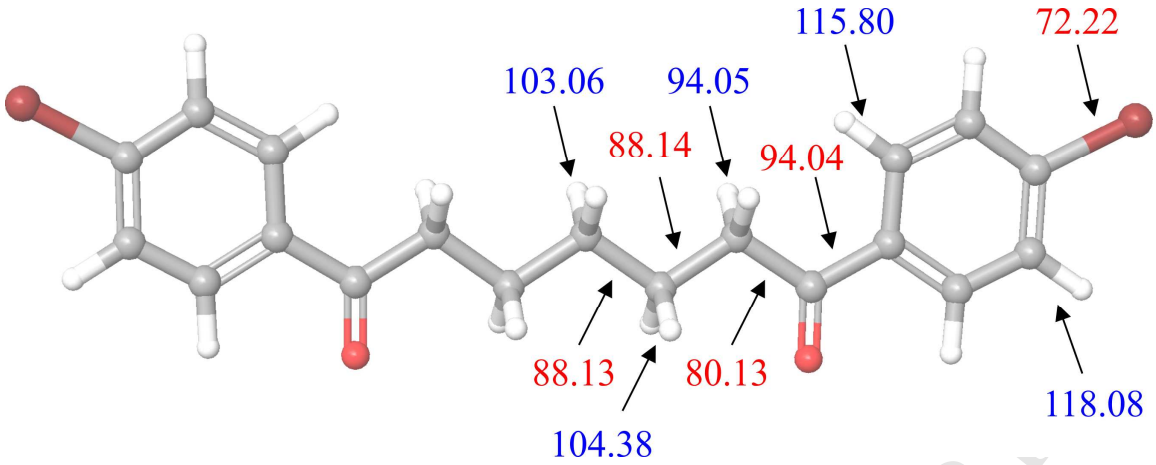
a)



b)

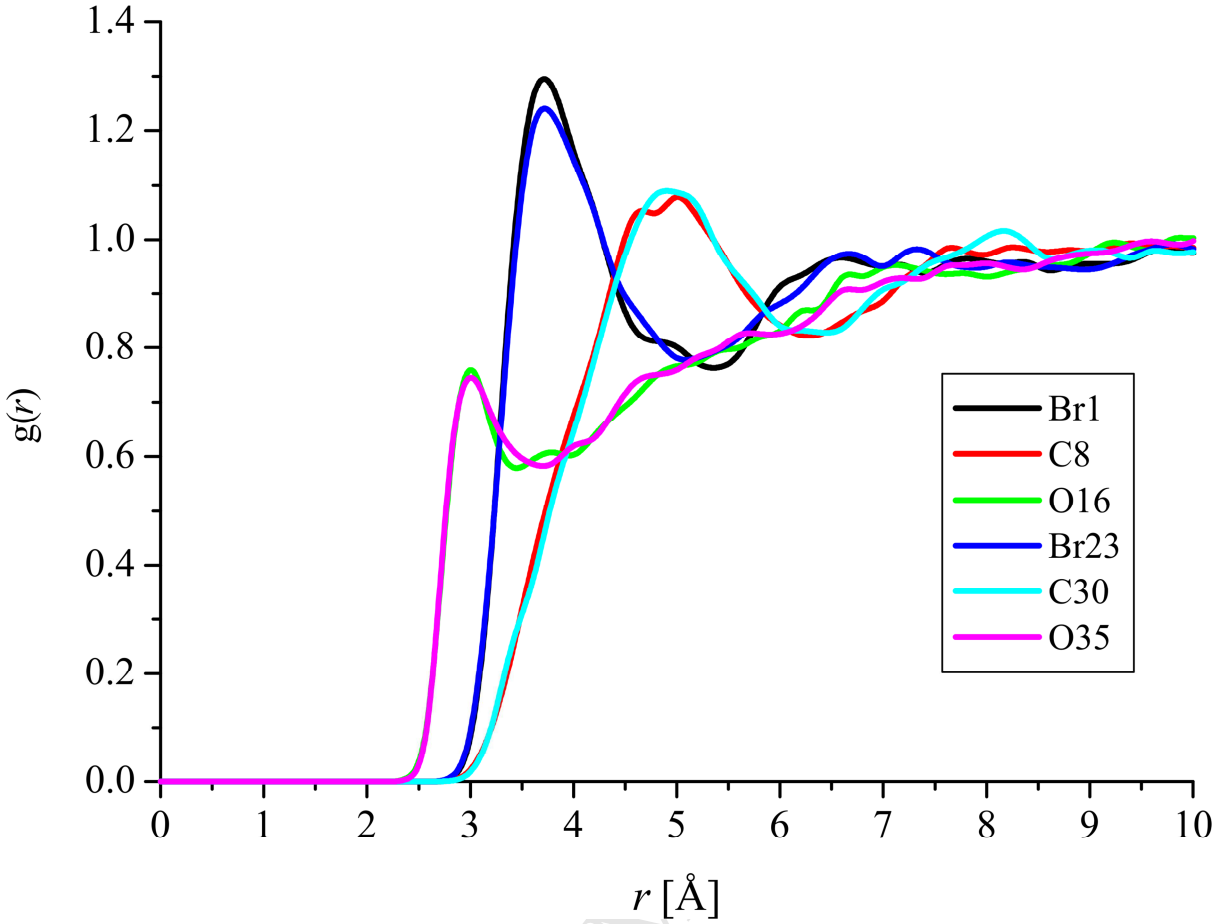


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- Single crystal XRD is reported
- Most reactive sites are identified
- Studied NLO properties, MEP and NBO
- Molecular docking studies have been discussed

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# DISSOLUTION TEST METHOD BY HPLC FOR ROSICILLION 250 MG CAPLETS

**Srinivasa Rao. T*[1], Srinivas rao.Rayapati [2], B.C.K Reddy[3], G.Maniteja[4]**

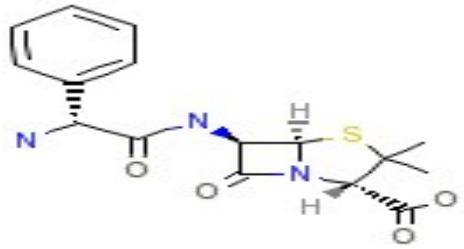
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ABSTRACT: Roscillin is uses full to treat urinary tract, pneumonia, respiratory track infections. It is a Pencillin derivative, used for infections of the stomach or intestines. It is an antibiotic and used to fight bacterial infections. Roscillin 250 MG Capsule is less toxic than other antibiotics. Side effects are rare and hardly occur. They include nausea, vomiting, high level of eosinophils, skin rashes, swelling of tongue and diarrhea. Serious but rare side effects include dark urine, abdominal pain, jaundice, easy bruising or bleeding, persistent sore throat or fever. Dissolution test method by HPLC analysis is proposed for ROSICILLION pharmaceutical dosage forms, maximum absorbance is found at 220 nm, The proposed method is validated according to ICH guidelines, it is very simple and convenient.

Important words: Roscillin API, Antibiotic, Penicillin, urinary tract, HPLC, Absorbance, ICH

INTRODUCTION: Roscillin pharmaceutical dosage form is used to care for a mixture of environment caused by bacterial infections of the body parts, instance lungs, heart, brain and urinary tract. It supposed to be used on vacant stomach for improved absorption. Dissolution test method for Roscilin dosage forms by High performance liquid chromatography is proposed, it's maximum absorbance found to be at 220nm, structure of API and chromatographic conditions as follows

Structure of Roscillin:



Chromatographic conditions: By HPLC

Column: Bond a pack C18

Wave length: 220 nm

Retention time (RT) :4.2 minutes

Injection volume: 20µl

Rate of flow: 2.0 ml/min

Temperature of the Oven: 30 ˚C temp.

Preparation of Mobile Phase:

Preparation of Buffer: 1.36 g of $KH_2PO_4$ and one ml 1N Acetic acid suspended in 1000ml of $H_20$

**Mobile phase:** Buffer and $CH_3CN$ are mixed in the ratio of 92:8 degassed using sonicators

Dissolution: After 45 minutes not less than 70%

Medium: 900 ml, water

Type: USP –I (Basket)

RPM: 100

Temperature: 37±0.5◦C

Preparation of Standard: 50 mg of Roscillin working standard make up to 200ml dilute with water

**Preparation of sample:** Assemble the apparatus. According to individual monograph keep the stated volume of dissolution medium in the vessel of apparatus and maintain the dissolution medium temperature to 37 ±0.5°C, remove the thermometer. Keep the six test sample equivalent to 250mg of Roscillin in the dissolution apparatus, taking care to keep out air bubbles from the surface of dosage-form unit, and instantaneously operate the dissolution equipment at the rate specified in the monograph. within the time period specified, take out a 10ml of sample from a zone middle between the surface of dissolution medium and the top of rotation basket , not less than 1cm from the top of the rotation Basket, not less than 1cm from the vessel wall. Calculate the amount of Roscillin dissolved using the subsequent process.

Process: Separately inject 20µl blank , Mobile phase Five injections, standard preparation and sample preparation in to the chromate graphic system and trace the chromatograms, evaluate the peak responses.

System suitability evolution: Efficiency of the column for the Roscillin is determined from the standard preparation should not less than 2000 theoretical plates and for the same peaks the tailing factor should not be greater than two..

The Relative standard deviation of 5 repeat injections of Roscillin standard preparation should not be greater than 2.0

The Roscillin retention time is 4.2 minutes.

Calculation: Calculate percentage (%) amount of Roscillin released from the caplets at respective time point by using the following formula.

$$\frac{At}{As} \times \frac{WS}{200} \times \frac{900}{Wt} \times \frac{P}{100} \times \frac{100}{lable\ claim} = \text{----------}\%$$

At=Roscillin peak area in the sample solution chromatogram.

AS=Roscillin peak area in the standard solution chromatogram.

WS= Roscillin working standard weight.

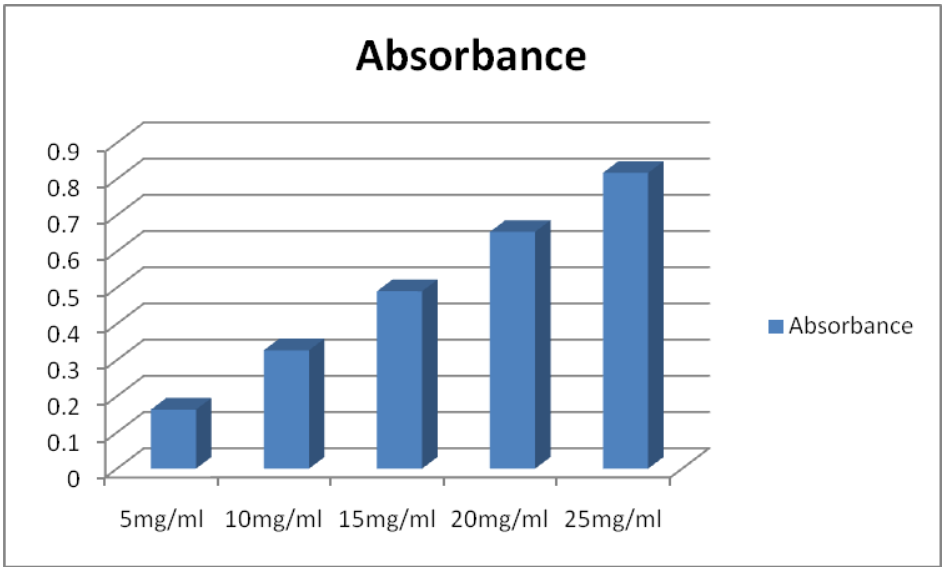
Wt= Roscillin test sample weight.

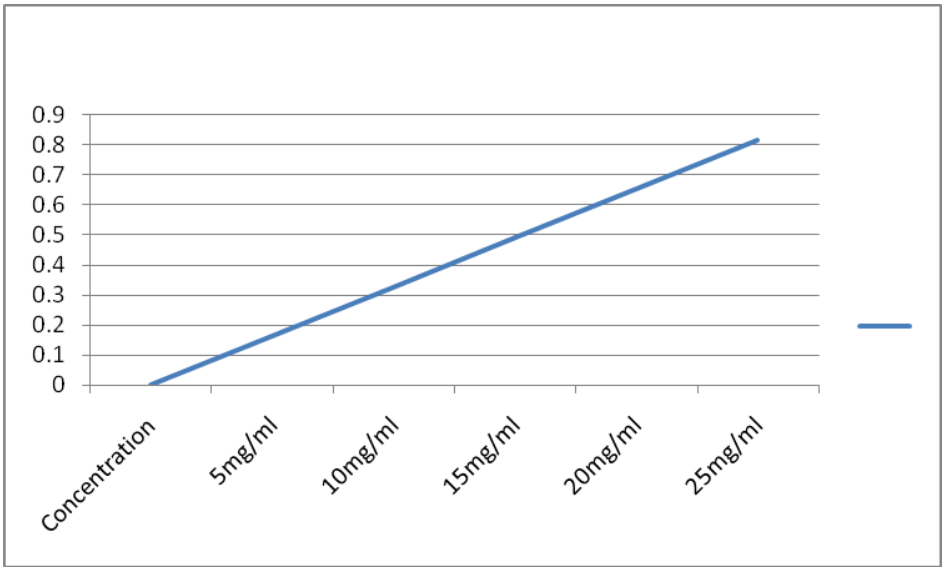
| Formulation | Medium | Bowls NO | Releasing profile | Average | limit | S.D | RSD |
|---|---|---|---|---|---|---|---|
| Capsulate | 900 ml water | 1,2,3,4,5,and 6 | 76.1%,75.9%, 76.3%,76.7%, 76.6%,and 76.5% | 76.35 % | NLT 70% | 0.3082 | 0.403 |

**Revitalization study:** Revitalization experiments were did for to study the linearity, accuracy and precision of proposed method. At two different levels known quantities were added to the sample and analyzed ,the revitalization was estimated to be greater than 99%

Out come and conversation of Linearity: Roscillin linearity is established by scheming a diagram of standard solution absorbance versus concentration. The linearity is found to be between 5-25mg/ml

| S.NO | Concentration of the standard solution | OD values |
|---|---|---|
| 1 | 5mg/ml | 0.163 |
| 2 | 10mg/ml | 0.327 |
| 3. | 15mg/ml | 0.490 |
| 4 | 20mg/ml | 0.654 |
| 5. | 25mg/ml | 0.817 |






The repeatability and consistency of the method has been verified by performing revitalization studies , showed good out put..

Final conclusion: The projected process is free from interference of the additives added in the formulations of Roscillin .It is very easy, fast and no where involves use of complicated sample preparation. High percentage of recovery and validation parameters be evidence for that the method is reliable and acceptable. Therefore the method can be useful in routine quality control analysis.

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:

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# Ethnobotanical Study of Koundinya Wildlife Sanctuary; Andhra Pradesh, India

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## Abstract

Koundinya wild life Sanctuary in Chittoor district, Andhra Pradesh located in the 12° 39'-13° 10' N and 78° 29'-78°.52' E falls in the hill ranges of the Eastern Ghats, a broken and discontinuous line of mountains in peninsular India. Koundinya wildlife Sanctuary is linear in Shape, running ca.70 km north to south. The breath varies from 1 to 15 km. It occupies 357km2.It has a periphery of about 224km with 53 fringe and 8 enclosure villages and is bordered by reserve forest of Andhra Pradesh or Tamil Nadu. The Sanctuary comes under two ranges: Palamaner in the north and Kuppam in the South. Palamaner range has four blocks: Tekumanda, Musalimadugu, Mordana and Nelipatla. The Kuppam range has six blocks: Naikaneri, Peddanaikdurg, Charagallu, Peddur Extension, Peddur and Kangundi. The main water resourses in the Sanctuary consists of the River Palar, its tributaries the Mallatar (or Kaigal) and Koundinya, from which the Sanctuary gets its name. The vegetation comprises predominantly of Southern Tropical Dry Mixed Deciduous (Champion and Seth 1968) with trees of *Hardiwikia binata Chloroxylon swietenia, Albizia amara, Boswellia serrata, Anogeissus latifolia ,Pterocarpus santalinus, Shorea spp, Diospyros spp and Ficus spp.* The vegetation varies widely in different areas as result of terrain soil, impact of graging, fires, woodcutting.

**Keywords**
Nanomedicines · Pharmacokinetics · Delivery · Guidelines

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## INTRODUCTION

The term Protected area is commonly used to describe areas of Ecological and Biological importance. The area which is to be declared as Protected area have the great floral and faunal significance and needs to be conserve an ecological system and needs to be protected. An area which is having some floral or fauna species of great significance must be declared as protected area.

Protected area is classified into four types. These are 1. National Parks, 2. Sanctuaries, 3. Conservation reserves, and 4. Community Reserves. The area, which is having adequate ecological, faunal, floral, Geomorphological, natural, or Zoological significance has described as National Park. The main purpose of the national park is to protect, propagate or develop wildlife and its environment, but the any rights are not allowed inside the living people.

The area which is declared as the sanctuary having ecological, faunal, floral, geo morphological, natural or Zoological significance and to protect, propagate, develop the wild life and its environment but some certain rights were allowed the people living inside the sanctuary.

The areas which links the one protected area to the another is declared as Conservation Reserves. The Conservation Reserves are declared by the State Government. The main purpose of the conservation reserves is to protect landscapes, seascapes, floral and their habitat. The Conservation Reserves are declared by the State Government.

An area where an individual or a community has voluntary conserve the wildlife and its habitat is

declared as community reserves. The main purpose of the community reserves is protecting fauna, flora, and traditional and cultural values. These were also declared by the State Government.

Globally there are more than 161000 protected areas of October 2010 with covering 236 countries and territories throughout the world. (IUCN, World data base on protected areas). The total geographical area of India is 32, 87,590 $km^2$ of which the total forest cover is 6, 97,898 $km^2$ cover 21.23% geographical area of India. There are 17 mega diverse countries in the world of which India is also one among them. India is having only 2.4% of the world's land area, 16.7% human population of the world and 18% livestock.

India harbors a rich wildlife variety and have 730 protected areas of which 103 National Parks, 535 Wildlife sanctuaries, 66 Community reserves,26 conservation reserves covering an area of 160896.51 $Km^2$ covering 4.88 % geographical area of the India. Andhra Pradesh has 1National Park, 13 wildlife sanctuaries and 2 Zoo parks are extended over 9076.82 $Km^2$. (4.57% of the total geographical area). The Eastern Ghats is located between $77^0 22'$ and $85^0$ 20' East longitudes and $11^0 22'$ North latitudes in the tropical region. In Andhra Pradesh, the hilly region in the district of Vizayanagaram, Vishakapatnam, Srikakulam, East Godavari, Krishna, Guntur, Prakasam, Nellore, Kurnool, Anantapuram, Chittor and Kadapa forms the Eastern Ghats. The Northern portion includes the Godavari, Sileru-Machkund Basin and covers the district of Srikakulam, Vijayanagaram, Vishakapatnam, East Godavari and West Godavari. The Southern Eastern Ghats portion covers the districts of Guntur, Prakasam, Nellore, Kurnool, (Veligondas, Palakondas, Nallamalias, Erramalias etc) and extend also into adjoining Kadapa and Chittor districts of Seshachalams. Andhra Pradesh has 1 National Park, 13 wildlife sanctuaries and 2 Zoo parks of which one National Park and Six Wildlife Sanctuaries are in the Eastern Ghats and Four Wildlife Sanctuaries are located along the East Coast. Koundinya wildlife Sanctuary in Chittoor district, Andhra Pradesh is one among the 13 wildlife sanctuaries present in Andhra Pradesh.

## MATERIALS AND METHODS

The study was carried out during July 2019 – March 2020 Plant specimens were collected and identified after studying all characters with the help of standard local flora and the relevant literature available on the internet (www.Googlescholar) the indigenous knowledge of local primitive communities like Yanadies, Yerukula and Loddy etc. The indigenous knowledge of these primitive communities through personal interviews is utilized in the identification of the key flora of the study area. Herbarium was prepared by the standard methods. The entire area of the sacred grove is thoroughly studied by repeated visits in different seasons of the year 2019–2020 covering pre-monsoon, monsoon, and post-monsoon seasons. It helps in observing the different developmental stages of medicinal plant species like vegetative, flowering, and fruiting stages. The plant specimens were collected, identified with the help of Flora of Presidency of Madras Gamble, 1967 and Genera Platarum of Bentham and Hooker 1897. During the field work, the specimens collected for the preparation of herbarium were processed in accordance with the methodology adopted by Jain and Rao 1977. The plant species are given in alphabetical sequence with other details such as botanical name, vernacular name, family, habit in Table 1.

### Identification of plants

The plant species were collected from the forest with the help of practitioners and identified using the Gamble, J.S. 1915-36. Flora of Presidency of Madras, and local floras as well as through comparison with identified specimens deposited in the herbarium of Nedurumalli Bala Krishna Reddy medicinal plant research center Department of Botany Vidyanagar.

## RESULTS AND DISCUSSION

**Table: 1**

| S. No | Scientific Name | Vernacular Name | Family | Habit | Ethnobotanical uses |
|---|---|---|---|---|---|
| 1 | *Abelmoscus esculentus*(L.) | Ladies finger | Lythraceae | Herb | |
| 2 | *Abrus precatorious* L. | Gurivinda | Fabaceae | Climber | Anti inflamatery |
| 3 | *Acacia chundra (*Rothler) | | Mimosaceae | Tree | Piles: |
| 4 | *Acalypha indica* L. | Muripinda | Euphorbiaceae | Herb | Skin diseases |
| 5 | *Accacia catechu* (L.f.) Willd | Sandra | Fabaceae | Tree | |
| 6 | *Accacia leucophloea* (Roxb.) Willd. | Tella thumma | Fabaceae | Tree | Allexiteric (Cold and Bronchites |

| | | | | | |
|---|---|---|---|---|---|
| 7 | *Accacia nilotica* (L.) Willd.ex.Del.ssp.*indica* (Benth.) Brenan. | Nalla Thumma | Fabaceae | Tree | Piles |
| 8 | *Achyranthus aspera* L. | Uttareni | Amaranthaceae | Herb | Wounds |
| 9 | *Actinodaphnae madaraspetana* Bedd.ex.Hook.f. | Kovan Kutti | Lauraceae | Tree | Aphrodisic |
| 10 | *Aegle marmeles* (L.) Correa | Maredu | Rutaceae | Tree | Asthma |
| 11 | *Aerva lanata* (L.) Juss. | Konda pindi | Amaranthaceae | Herb | Kidney diseases |
| 12 | *Alangium salvifolium* (L.f.) | OOduga | Alangiaceae | Tree | Aphrodisiac. |
| 13 | *Albizia amara* (Roxb.) | Chigara | Fabaceae | Tree | Insecticide |
| 14 | *Albizia lebbeck* (L.) Benth | Dirisena | Mimosaceae | Tree | Piles. |
| 15 | *Albizia odoratissima* (L.f.) Benth. | Konda Chigara | Mimosaceae | Tree | Skin diseases |
| 16 | *Allianthus excella* Roxb. | Peddamanu | Simaroubaceae | Tree | Antipyretic |
| 17 | *Anacardium occidentale* L. | Cashenut | Anacardiaceae | Tree | Fruit Edible |
| 18 | *Andrographis Paniculata* (Burm.f.) | Nelavemu | Acanthaceae | Herb | Leucorrhoea |
| 19 | *Annogesus latifolia* (Roxb.ex.Dc.) | Velema | Combretaceae | Tree | Snake bite |
| 20 | *Annona squamosa* L. | Sitapalam | Anonaceae | Tree | Lice |
| 21 | *Aristolochia brachteolata Lam* | Gadida gadapa | Aristolochiaceae | Herb | Snake bite |
| 22 | *Artocarpus integrifolia* L.f. | Panasa | Moraceae | Tree | Fruit edible |
| 23 | *Asperagus racemosus* Willd. | Sathavari | Liliaceae | Shrub | Constipation |
| 24 | *Atlantia monophylla* (L.) Correa | Adavi Nimma | Rutaceae | Tree | Rheumatism |
| 25 | *Azadirachta indica* A.Juss. | Neem | Meliaceae | Tree | Jaundice |
| 26 | *Bauhinia raceosa* Lam | Are | Fabaceae | Tree | Diarrohoea |
| 27 | *Boerhavia diffusa* L. | Aticamamidi | Nyctaginaceae | Herb | Asthma. |
| 28 | *Borassus flabellifera* L. | Tati | Arecaceae | Tree | |
| 29 | *Boswellia serrata* Roxb.ex.Colebr. | Sambrani | Burseraceae | Tree | Skin eruptions |
| 30 | *Bouganvillia glabra* Choisy | Kagitalapulu | Nyctaginaceae | Shrub | Ornamental |
| 31 | *Buchnania axillaris* (Desr.) Raman | Sarapappu | Anacardiaceae | Tree | Diarrohoea |
| 32 | *Buchnania lanzan Spreng.* | Sara | Anacardiaceae | Tree | Glandular swellings. |
| 33 | *Butea monosperma* (Lam.) Taubert | Moduga | Fabaceae | Tree | Gastric troubles. |
| 34 | *Calotropis gigantia* (L.) | Tellagilledu | Asclepiadaceae | Shrub | Tooth ache |
| 35 | *Canthium dicoccum* Gaertn. | Nallabalusu | Rubiaceae | Tree | Fractures. |
| 36 | *Cassia fistula* L. | Rela | Fabaceae | Tree | Rheumatism |
| 37 | *Cassia roxburghii* DC. | Yerra munaga | Fabaceae | Tree | Foot cracks |
| 38 | *Cassine glauca* (Rottb.) | Nerdhi | Caelastraceae | Tree | Cot making |
| 39 | *Chionanthus zeylanica* L. | Punigi | Oleaceae | Tree | Blood dysentery |
| 40 | *Chloroxylon swietinia* DC. | Billudu | Rutaceae | Tree | Antidote. |
| 41 | *Cissus quadrangularis* Linn. | Nalleru | Vitaceae | Shrub | Bone fractures |
| 42 | *Cleisanthus collinus* (Roxb.) | Kodisa | Elaeocarpaceae | Tree | Poultice |
| 43 | *Cleome gynandra* L. | Vaminta | Cleomaceae | Herb | Earache |
| 44 | *Cleome viscosae* L. | Kukkavaminta | Cleomaceae | Herb | Headache |
| 45 | *Cochlospermum religosum* (L.) Alston. | Kondaburuga | Cochlospermaceae | Tree | Ulcers |
| 46 | *Commiphora caudate* (Wight & Arn.) Engler | Kondamamidi | Burseraceae | Tree | Dropsy. |
| 47 | *Cordia monoica* Roxb. | Poda iriki | Boraginaceae | Tree | Excessive Menstruation |
| 48 | *Cordia wallichhi* G.Don. | | Boraginaceae | Tree | Fever |
| 49 | *Cymbopogan citrates* DC | Lemon grass | Poaceae | Herb | Gastric troubles |

| | | | | | |
|---|---|---|---|---|---|
| 50 | *Dalbergia lanceolaria* L.f. | Yerra Pachari | Fabaceae | Tree | Blood dysentery |
| 51 | *Dalbergia latifolia* Roxb. | Jitregi | Fabaceae | Tree | Leucoderma |
| 52 | *Dalbergia paniculata* Roxb. | Pachari | Fabaceae | Tree | Rheumatic swellings. |
| 53 | *Datura metal* L. | Nalla ummetha | Solanaceae | Herb | Bronchial Asthma |
| 54 | *Dendrocalamus strichtus* (Roxb.) | Chinna veduru | Poaceae | Shrub | Wounds |
| 55 | *Dioscorea oppositifolia* L. | Adavidumpa | Dioscoreaceae | Twinning vines | Hydrocele |
| 56 | *Dioscorea pentaphylla* L. | Dukkapendalam | Dioscoreaceae | Tuberous vines | Asthma |
| 57 | *Diospyrus buxifolia* (Blume) Hiern. | Uttipallu | Ebenaceae | Shrub | Urinary disorders |
| 58 | Diospyrus chloroxylon Roxb. | Ullinda | Ebenaceae | Tree | Indigestion |
| 59 | *Diospyrus melanoxylon* Roxb. | Tumki | Ebenaceae | Tree | Urinary disorders |
| 60 | *Diospyrus montana* Roxb. | Jagadagondi | Ebenaceae | Tree | Fever |
| 61 | *Diospyrus peregrina* (Gaertner) | | Ebenaceae | Tree | Dysentery |
| 62 | *Dolichandrone atrovierens* (Heyne ex Roth) | Neerudhi | Bignoniaceae | Tree | improve immunity power in children |
| 63 | *Dolichondrone crispa* Seem | | Bignoniaceae | Tree | Arthritis |
| 64 | *Drypetes sepiaria* (Wight& Arn.) | Manchi beera | Euphorbiaceae | Tree | Cough. |
| 65 | *Ehretia laevis* Roxb. | Pogadi Chettu | Cordiaceae | Tree | Wounds |
| 66 | *Eriolaena hookeriana* Wight & Arn. | Botta | Sterculiaceae | Tree | Cataract |
| 67 | *Erythroxylon indicum* (DC.) | Devadaru | Erythroxylaceae | Tree | Diseases. |
| 68 | *Erythroxylum monogynum* Roxb. | Devadari | Erythroxylaceae | Shrub | Eye Ulcers. |
| 69 | *Euphorbia antiquorum* L. | Pedda jamudu | Euphorbiaceae | Shrub | Ring Worm |
| 70 | *Euphorbia ligularia* Roxb. | Sanna Jamudu | Euphorbiaceae | Shrub | Dog bite |
| 71 | *Euphorbia tirucalli* L. | Kada Jamudu | Euphorbiaceae | Tree | Cough and Cold |
| 72 | *Ficus arnottiana* (Miq.) Miq. | Bandaravi | Moraceae | Tree | Wounds |
| 73 | *Ficus benghalensis* L. | Marri | Moraceae | Tree | Wounds |
| 74 | *Ficus hispida* L.f. | Bramhamedi | Moraceae | Tree | Hydrocele. |
| 75 | *Ficus microcarpa* L.f. | Kondajivvi | Moraceae | Tree | Scabies |
| 76 | *Ficus mollis* Vahl. | Juvvi | Moraceae | Tree | DSiabetes. |
| 77 | *Ficus racemosa* L. | Aathipandu | Moraceae | Tree | Diarrhoea. |
| 78 | *Gardenia gummifera* L.f. | Bikki | Rubiaceae | Tree | Constipation |
| 79 | *Gardenia latifolia* Soland. | Karinga | Rubiaceae | Tree | Edible. |
| 80 | *Gardenia resinifera* Roth. | Errabikki | Rubiaceae | Tree | Curing Worms. |
| 81 | *Gemilina asiatica* L. | Adavigummadi | Verbanaceae | Shrub | Hair falling |
| 82 | *Gloriosa superba* L. | Nabhi | Liliaceae | Climber | Piles. |
| 83 | *Grewia damine* Gaertner | Adavijana | Tiliaceae | Shrub | Snake bite |
| 84 | *Grewia flavescens* A.Juss. | Bankajana | Tiliaceae | Tree | Wounds and Boils. |
| 85 | *Grewia hirsuta* Vahl | Chittijana | Tiliaceae | Tree | Dysentery. |
| 86 | *Gymnema sylvestris* (Retz.) | Podapathri | Asclepiadaceae | Climber | Scorpion sting |
| 87 | *Gyrocarpus americanus* Jacq. | Tellapoliki | Hernandiaceae | Tree | Wounds. |
| 88 | *Hardwikia binata* Roxb. | Api | Fabaceae | Tree | Fibers used for making robes |
| 89 | *Hemidesmus indicus* (L.) | Sugandhipala | Asclepiadaceae | Creeper | Cool drink (Nannari) |
| 90 | *Holoptelia integrifolia* (Roxb,) | Nemalinara | Ulmaceae | Tree | Dysentery |
| 91 | *Hugonia mystax* L. | Kakibeera | Linaceae | Straggling Shrub | Rheumatism. |
| 92 | *Ipomea pes -caprae* | Chevula pilliteega | Convolulaceae | Herb | Body pains. |
| 93 | *Ixora finlaysoniana* Wall.ex.G.Don. | | Rubiaceae | Shrub | Dysentery |

| | | | | | |
|---|---|---|---|---|---|
| 94 | *Ixora pavetta* Andr. | Nooru varahalu | Rubiaceae | Shrub | Constipation |
| 95 | *Jatropha curqas* L. | Adavi amudamu | Euphorbiaceae | Shrub | mouth ulcers |
| 96 | *Jatropha glandulifera* | | Euphorbiaceae | Shrub | Piles |
| 97 | *Lannea coromandelica* (Houtt.)Merr. | Gumphena | Anacardiaceae | Tree | Stomachache |
| 98 | *Lepisanthes tetraphylla* (Vahl) Radlk. | Konda kunkudu | Sapindaceae | Tree | Dysentery |
| 99 | *Leucas aspera* L. | Thummi | Lamiaceae | Herb | Cold |
| 100 | *Leucas indica var nagalapuramina* | Chinna poola thummi | Lamiaceae | Herb | Headache |
| 101 | *Limonia acidissima* L. | Velaga | Rutaceae | Tree | Diarrhoea |
| 102 | *Madhuca indica* J.Gmelin | Ippa | Sapotaceae | Tree | Headache |
| 103 | *Mangifera indica* L. | Mamidi | Anacardiaceae | Tree | Diarrohoea |
| 104 | *Manilkara hexandra* (Roxb.) Dubard | Pala | Sapotaceae | Tree | Agricultural implements. |
| 105 | *Memeselon umbelliatum* Burm.f. | Alli | Lythraceae | Shrub | Astringent. |
| 106 | *Mithrogyna parvifolia* (Roxb.) Korth | Battaganapa | Rubiaceae | Tree | Snake bite |
| 107 | *Morinda pubescens* J.E.Smith | Thogari | Rubiaceae | Tree | Curing mad dog bite |
| 108 | *Naringi crenulata* (Roxb.) | Thorrivelaga | Rutaceae | Tree | Epilepsy. |
| 109 | *Nelumbo nucifera* | Tamara | Nelumbonaceae | Herb | Diarrhoea |
| 110 | *Ochna obtusata* DC | Sonari | Ochnaceae | Tree | Snake bite. |
| 111 | *Phyllanthus amarus* L. | Nela usiri | Euphorbiaceae | Herb | Jaundice |
| 112 | *Phyllanthus emblica* L. | Usiri | Euphorbiaceae | Tree | Diabetes |
| 113 | *Pithecellobium dulce* (Roxb.) | Simachintha | Fabaceae | Tree | Fever. |
| 114 | *Plumaria alba* L. | Deva ganneru | Apocynaceae | Tree | Sprains. |
| 115 | *Polyanthus cerasoides* (Roxb.) | Dudduga | Annonaceae | Tree | Poultice. |
| 116 | *Pongamia pinnata* (L.) Pierre. | Kanuga | Fabaceae | Tree | Boils |
| 117 | *Premna latifolia* Roxb. | Peddanalli | Verbanaceae | Tree | Dropsy |
| 118 | *Premna tomentosa* Willd. | Naguru | Verbanaceae | Tree | Biliousness |
| 119 | *Pterocarpus marsupium* Roxb. | Aegisa | Fabaceae | Tree | Skin diseases. |
| 120 | *Pterocarpus santalinus* | Errachandanam | Fabaceae | Tree | Diabetes |
| 121 | *Pulicaria whitiana* | Adavi chamanthi | Asteraceae | Herb | |
| 122 | *Rhus mysoorensis* | Kadapurugudu | Anacardiaceae | Tree | Piles. |
| 123 | *Santalum album* L. | Chandanam | Santalaceae | Tree | Skin eruptions |
| 124 | *Sapindus emarginatus* Vahl. | Kunkudu | Sapindaceae | Tree | Headache |
| 125 | *Sarcopetalum tomentosum* (Roxb.) | | Annonaceae | Tree | Rheumatism |
| 126 | *Sarcostemma acidum* (Roxb.) | Aakujamudu | Asclepiadaceae | Shrub | Dog bite. |
| 127 | *Semecarpus anacardium* L.f. | Nallajeedi | Anacardiaceae | Tree | Cough. |
| 128 | *Shorea roxburghii* G.Don | Jalari | Dipterocarpaceae | Tree | Asthma. |
| 129 | *Solanum surattense* | Vakudu | Solanaceae | Herb | Cough. |
| 130 | *Soymida febrifuga* (Roxb.) A.Juss. | Somi | Meliaceae | Tree | Fever. |
| 131 | *Sterculia urens* Roxb. | Tapasi | Sapotaceae | Tree | Fever. |
| 132 | *Strychnos nux-vomica* L. | Musti | Loganiaceae | Tree | Leucoderma. |
| 133 | *Strychnos potatorum* L.f. | Chilla | Logaiaceae | Tree | Scorpion sting. |
| 134 | *Syzygium cumini* (L.) Skeels | Neredu | Myrtaceae | Tree | Diabetes. |
| 135 | *Tamarindus indica* L. | Chintha | Fabaceae | Tree | Ascariasis |
| 136 | *Tectona grandis* L.f. | Teak | Verbanaceae | Tree | Furniture |
| 137 | *Terminalia arjuna* Wt.& Arn | Tellamadhi | Combretaceae | Tree | Agricultural implements |

| | | | | | |
|---|---|---|---|---|---|
| 138 | *Terminalia bellerica* (Gaertn.) | Tandra | Combretaceae | Tree | Dropsy. |
| 139 | *Terminalia cuneata* Roth | | Combretaceae | Tree | Diarrhoea. |
| 140 | *Terminalia elliptica* Willd. | | Combretaceae | Tree | Bone fractures. |
| 141 | *Yucca gloriosa* | | Asperagaceae | Shrub | Purgative |
| 142 | *Vanda tessellata* (Roxb.) | Vadanika | Orchidaceae | Herb | Earache. |
| 143 | *Vitex altissima* L.f. | Nemali adugu | Verbanaceae | Tree | Galactogogue. |
| 144 | *Vitex negundo* L. | Vavili | Verbanaceae | Tree | headache |
| 145 | *Vitex pinnata* L. | | Lamiaceae | Tree | Epilepsy. |
| 146 | *Wendlandia tinctoria* DC. | | Rubiaceae | Tree | Syphilis |
| 147 | *Wrightia tinctoria* (Roxb.) R.Br. | Aakupala | Apocynaceae | Tree | Stomachache. |
| 148 | *Ziziphus mauritiana* Lam | Regu | Rhamnaceae | Tree | Snake bite |
| 149 | *Ziziphus xylopyrus* (Retz.) | Gotti | Rhamnaceae | Tree | Wounds. |

## CONCLUSION

Nearly 149 species belonging to 50 families were recorded. Out of 149 plant species herbs 19;Shrubs 19;Trees 104 ;Climbers 04.Fabaceae occupies first place with 18 species; Euphorbiaceous occupies second place with 10 species; Rubiaceae occupies third place with 08 species; Anacardiaceae, Moraceae and Verbanaceae occupies fourth place with 06 species, Rutaceae and Combretaceae occupies fifth place with 05species.

**Figure 1: Dominant families of the Study Area**

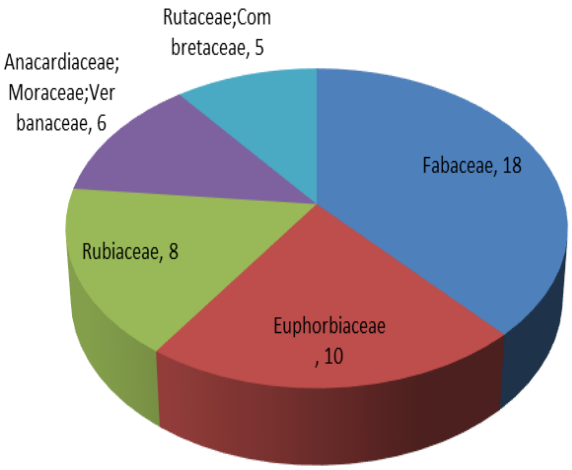
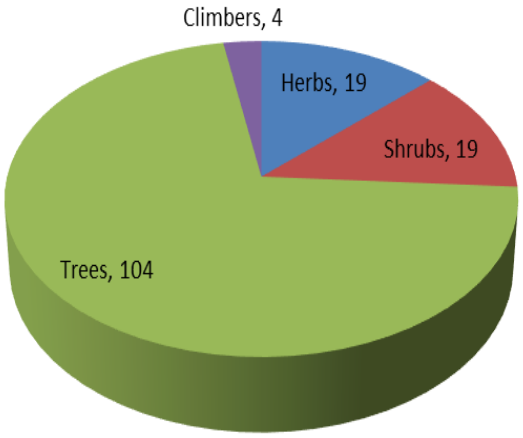



**Figure 2: Habitat analysis of the Study Area**



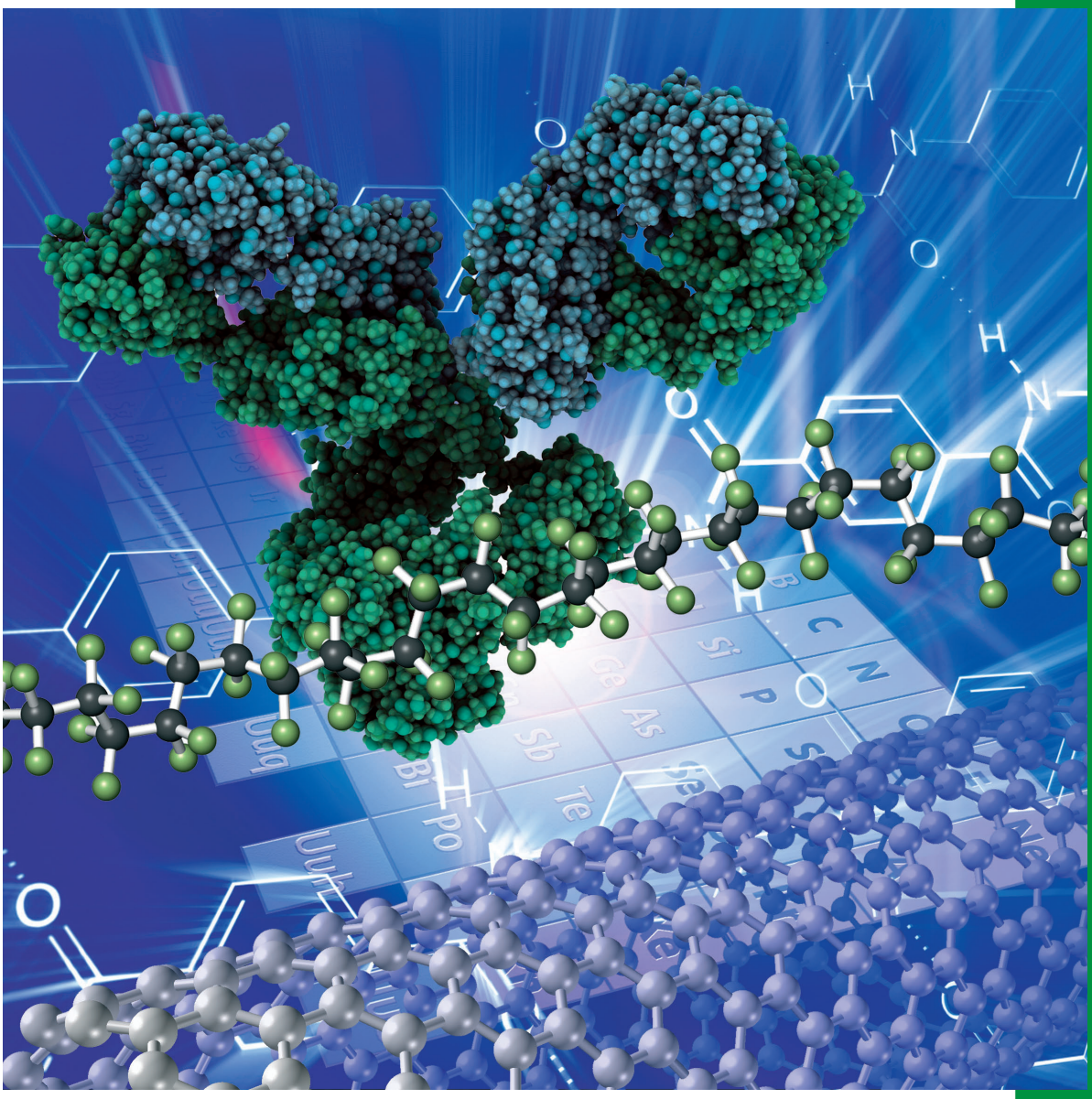
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# A Facile Approach to 3,4-Oxepino-Fused Tricyclic Indoles from MBH-Acetates of Acetylenic Aldehydes *via* Successive Allylic Substitution/Intramolecular [3+2] Annulation†

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Herein, we present our findings on the synthesis of 3,4-oxepino-fused indoles by a two-step reaction sequence involving an initial allylic substitution followed by Rh(III)-catalyzed intramolecular [3+2] annulation *via* C–H activation starting from Morita-Baylis-Hillman (MBH) acetates of acetylenic aldehydes. The strategy is amenable to broad range of MBH acetates providing a facile access to 3,4-oxepino-fused indoles in good yield.

## Introduction

3,4-Fused indole framework is ubiquitous in numerous naturally occurring molecules such as lysergic acid, clavicipitic acid, aurantioclavine, ht-13-A and ht-13-B (Figure 1) that exhibit a wide range of biological and pharmacological activities.[1–3] Among these, 3,4-oxepino-fused indole skeleton is unique and present in ht-13-A and ht-13-B, which were isolated from the *streptomyces sp.* (PA-48561). These two natural products display high affinity towards 5-HT receptors and have prospective application in the treatment of central nervous system (CNS) disorders.[3] Despite of their importance, the synthesis of 3,4-oxepino-fused indoles is under-exploited.[4] They can be readily made by sequential palladium-catalyzed coupling reaction/reductive *N*-hetero annulations,[5] intramolecular Fischer indolization[6] or by Larock indolization from the ortho-halogenated substrates.[7] Recently, 3,4-fused tricyclic indoles were also made by intramolecular amidoarylation or hydroarylation involving transition metal-catalyzed C–H activation strategy.[8] In these efficient methods alkyne-tethered acetanilides were used as the substrates, which were prepared from 3-nitro phenol in three steps. The above observations prompted us to develop an alternative strategy for the synthesis of the functionalized oxepino-fused tricyclic indoles from the readily accessible substrates.

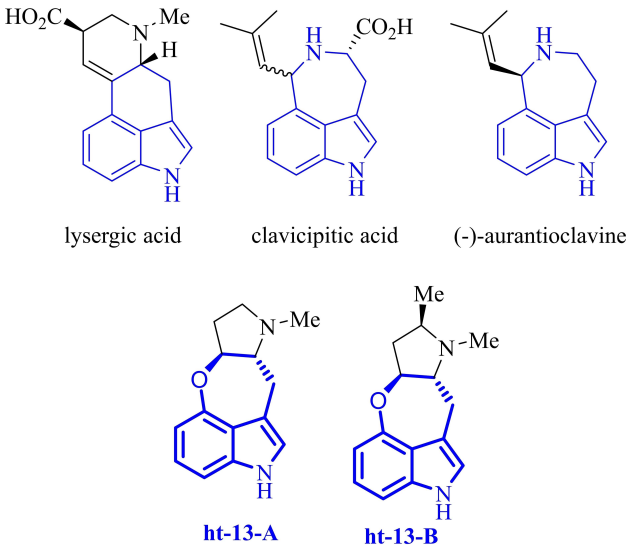



**Figure 1.** Structures of representative 3,4-fused indole alkaloids

Our research group is investigating the annulation reactions using Morita-Baylis-Hillman adducts of acetylenic aldehydes as substrates for the formation of desired alkyne-tethered intermediates, which readily undergo the cyclizations.[9] In continuation, we envisioned that the MBH-acetates (**2**) of acetylenic aldehydes could be handy precursors to obtain the alkyne-tethered acetanilide (**3**) and subsequent intramolecular annulation would provide the oxepino-fused tricyclic indole derivatives (**4**) having conjugated ester functionality. Herein, we report a facile approach to access 3,4-oxepino-fused tricyclic indoles involving the successive allylic substitution/intramolecular [3+2] annulation from the reaction of MBH acetates (**2**) using a new class of nucleophilic reagent (**1**) (Scheme 1).

## Results and Discussion

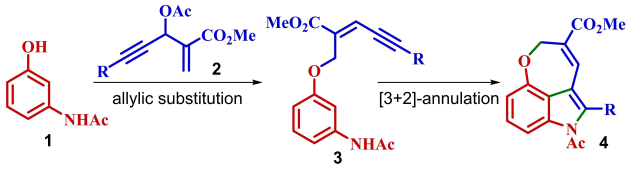
To explore the planned strategy, initially the reaction conditions were optimized by the reaction between 3-acetamido phenol (**1**) and MBH Acetate **2a** (prepared from phenyl acetylene aldehyde). To obtain the desired alkyne-tethered acetamide from the above reaction, $K_2CO_3$ was tested in various

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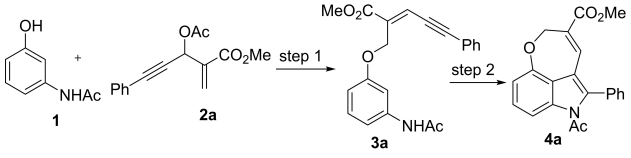

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**Scheme 1.** Proposed strategy to access 3,4-oxepino-fused tricyclic indoles

solvents such as DMF, acetonitrile, *tert*-amyl alcohol (entries 1 to 3, Table 1) and we were pleased to find that potassium

**Table 1.** Optimization of reaction conditions



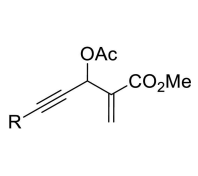
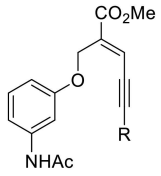
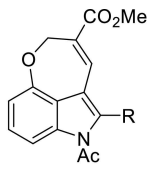

| Entry | Step 1 | Step 2 | Product | Yield (%)[a] |
|---|---|---|---|---|
| 1 | $K_2CO_3$, DMF, 48 h | – | **3a** | 76 |
| 2 | $K_2CO_3$, $^t$AmOH, 48 h | – | **3a** | 91 |
| 3 | $K_2CO_3$, $CH_3CN$, 48 h | – | – | NR |
| 4 | $Cs_2CO_3$, $^t$AmOH, 48 h | – | **3a** | 60 |
| 5[b] | DBU, $^t$AmOH, 40 h | – | – | NR |
| 6[c] | – | A | **4a** | 90 |
| 7[c] | – | B | – | NR |
| 8[c] | – | C | – | NR |
| 9[d] | $K_2CO_3$, $^t$AmOH, 48 h | A | **3a** | 88 |
| 10[e] | $K_2CO_3$, $^t$AmOH, 48 h | A | **4a** | 49 |

[a]Isolated yields; [b]**2a** was decomposed after the addition of DBU; [c]Starting material for the reaction is **3a**; [d]Reaction carried out in one-pot condition; [e]After workup of the step-1, without purifying the intermediate **3a** by silica column, step-2 was carried out; NR = No Reaction; *Condition A*: $[(Cp^*RhCl_2)_2]$, $Cu(OAc)_2{\cdot}H_2O$, $AgSbF_6$, $^t$AmOH, 120 °C, 1 h; *Condition B*: $[Cp^*Rh(MeCN)_3][SbF_6]_2$, $Cu(OAc)_2{\cdot}H_2O$, acetone, rt, 10 h; *Condition C*: $[Ru(p\text{-}cymene)Cl_2)_2]$, $Cu(OAc)_2{\cdot}H_2O$, $AgSbF_6$, $^t$AmOH, 120 °C, 10 h.

carbonate in *tert*-amyl alcohol gave 91% yield of **3a**. Other base $Cs_2CO_3$ gave 60% yield of the product **3a** (entry 4, Table 1), while DBU failed to promote the allylic substitution reaction (entry 5, Table 1). Having the enyne intermediate **3a**, the intramolecular annulation was examined in the presence of the rhodium or ruthenium based catalysts, based on the literature reports.[8] To our delight, the annulation of **3a** was observed in the presence of $[RhCp^*Cl_2]_2/AgSbF_6$ (condition **A**) to provide the corresponding 3,4-oxepino-fused indole **4a** in 90% yield (entry 6, Table 1). In case of other two conditions **B** and **C**, no product formation was observed (entries 7 and 8, Table 1). We tried to perform both the steps in one-pot, wherein only the formation of enyne intermediate (**3a**) was observed (entry 9, Table 1). After typical workup of the step-1 reaction, without purifying the intermediate **3a** subjected to the annulation (step-2), which gave the 3,4-oxepino indole **4a** in 49% yield (entry 10, Table 1). Hence, we have proceeded for further investigation through the purification of intermediate and subsequent Rh-catalyzed C–H activation based annulation to obtain the 3,4-oxepino-fused indoles.

With the optimized conditions in hand, the scope of successive allylic substitution/intramolecular [3 + 2] annulations was studied using various MBH-Acetates of acetylenic aldehydes (Table 2). MBH-acetates bearing electron-rich aryls on

**Table 2.** Synthesis of 3,4-oxepino-fused tricyclic indoles[a]

| Entry | MBH-Acetate | Intermediate Time/ Yield (%)[b] | Product Time/ Yield (%)[b] |
|---|---|---|---|
| 1[c] |  |  |  |
| | R = Ph, **2a** | **3a**, 24 h / 91 | **4a**, 1.0 h / 90 |
| 2 | R = 4-Me–Ph, **2b** | **3b**, 40 h / 85 | **4b**, 1.0 h / 90 |
| 3 | R = 1-Naphthyl, **2c** | **3c**, 40 h / 76 | **4c**, 1.0 h / 72 |
| 4 | R = 4-MeO–Ph, **2d** | **3d**, 48 h / 88 | **4d**, 2.0 h / 89 |
| 5 | R = 3,5-*di*-MeO–Ph, **2e** | **3e**, 48 h / 82 | **4e**, 1.5 h / 80 |
| 6 | R = 4-Cl–Ph, **2f** | **3f**, 32 h / 89 | **4f**, 1.0 h / 88 |
| 7 | R = 2-I–Ph, **2g** | **3g**, 24 h / 85 | **4g**, 1.0 h / 85 |
| 8 | R = 4-$CF_3$-Ph, **2h** | **3h**, 24 h / 92 | **4h**, 1.0 h / 93 |
| 9 | R = 4-$NO_2$-Ph, **2i** | **3i**, 40 h / 90 | **4i**, 1.0 h / 85 |
| 10 | R = 2-Thiophenyl, **2j** | **3j**, 24 h / 90 | **4j**, 1.0 h / 91 |
| 11 | R = 3-(N-*Boc*-indolyl), **2k** | **3k**, 48 h / 85 | **4k**, 1.0 h / 85 |
| 12 | R = *n*-pentyl, **2l** | **3l**, 24 h / 88 | **4l**, 1.5 h / 82 |

[a]Reaction Conditions: (i) **1**, $K_2CO_3$, $^t$AmOH, rt (ii) $[(Cp^*RhCl_2)_2]$, $Cu(OAc)_2{\cdot}H_2O$, $AgSbF_6$, $^t$AmOH, 120 °C; [b]Isolated yields, [c]**4a** was synthesized in 2 g scale

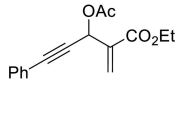
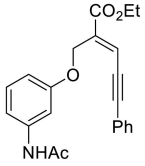
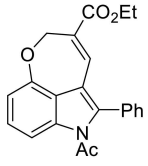
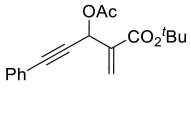
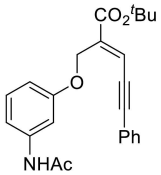
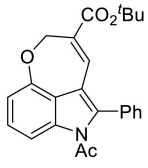
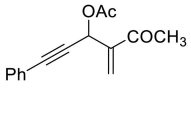
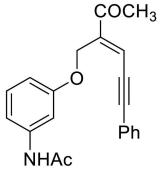
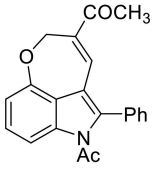
alkyne (**2b** and **2c**) as well as aryl groups on alkyne holding electron-donating (**2d** and **2e**) or electron-withdrawing (**2f** to **2i**) substitution, gave the corresponding 3,4-oxepino-fused indoles **4b** to **4i** *via* enynyl intermediates **3b** to **3i** (entries 2 to 9, Table 2). It is noteworthy to mention chloro, iodo and nitro groups are compatible in the present sequential reactions, which could be further elaborated. MBH substrates having heteroaryls such as 2-thiophenyl (**2j**) and 3-(N-*Boc*)-indolyl (**2k**) on alkyne are also tolerated in allylation to give **3j** (90%) and **3k** (85%) followed by rhodium-catalyzed annulation to offer the desired oxepino indoles **4j** and **4k** in 91% and 85% yields, respectively (entries 10 and 11, Table 2). Next, substrate **2l** with alkyl (*n*-pentyl) substitution on the alkyne was also successfully participated in allylation as well as in subsequent annulation to produce the fused indole **4l** in 82% yield (entry 12, Table 2). To verify the scalability of the described strategy, 3,4-oxepino-fused indole **4a** was prepared in 2 g scale. All the products were fully characterized by IR, mass, $^1$H NMR and $^{13}$C NMR spectral data. In addition, few representative compounds **4b** and **4j** were characterized by HSQC and HMBC NMR experiments (see supporting information).

Further, the reactivity of MBH acetates **5a** and **5b**, derived from different activated alkenes such as ethyl acrylate[10] and *tert*-butyl acrylate, were tested. Pleasingly, sequential allylic


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substitution/intramolecular [3 + 2]-annulation reactions of **5a** and **5b** proceeded well to provide 3,4-oxepino-fused indoles **7a** and **7b** in good yield *via* enynyl intermediates **6a** to **6b** (entry 1 and 2, table 3). To expand the scope, tolerance of other functionalities was verified by the reaction of MBH-acetate **5c** bearing keto group with 3-acetamido phenol (**1**) to get the enyne **6c**, which smoothly underwent [Rh]-catalyzed annulation to give the corresponding 3,4-oxepino indole **7c** in 78% yield (entry 3, Table 3).

**Table 3.** Scope of diverse MBH-acetates **5a** to **5c**[a]

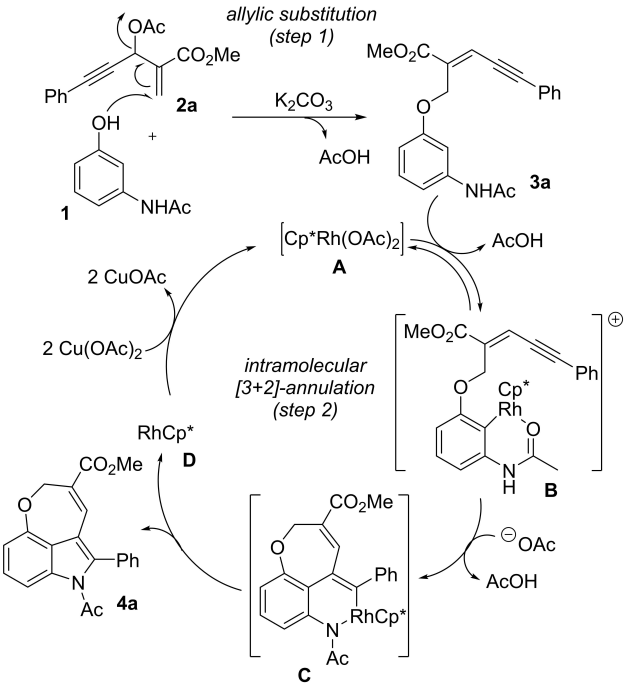
| Entry | MBH-Acetate | Intermediate Time/Yield (%)[b] | Product Time/Yield (%)[b] |
|---|---|---|---|
| 1 |  **5a** |  **6a**, 40 h/84 |  **7a**, 1.5 h/89 |
| 2 |  **5b** |  **6b**, 36 h/82 |  **7b**, 2.0 h/86 |
| 3 |  **5c** |  **6c**, 48 h/71 |  **7c**, 2.0 h/75 |

[a]Reaction Conditions: (i) **1**, $K_2CO_3$, $^t$AmOH, rt (ii) $[(Cp^*RhCl_2)_2]$, $Cu(OAc)_2{\cdot}H_2O$, $AgSbF_6$, $^t$AmOH, 120 °C; [b]Isolated yields.

Based on the results and previous literature,[11] a plausible mechanism for this sequential reactions is proposed in Scheme 2. In the first step, MBH-acetate **2a** will undergo allylic substitution with **1** in the presence of base to provide **3a**. Treatment of **3a** with complex **A** [probably generated from the mixture of $(RhCp^*Cl_2)_2$, $AgSbF_6$, and $Cu(OAc)_2.H_2O$ produces a six-membered rhodium intermediate **B** *via* C–H bond activation involving coordination of amide directing group. Thereafter, insertion of internal alkyne into the Rh – C bond affords rhodacycle **C** through the coordination of alkyne to rhodium. The formation of C–N bond *via* reductive elimination provides the tricyclic indole **4a** and Rh(I) **D**, which reoxidised to Rh(III)-complex A with the copper(II) oxidant.

## Conclusions

In summary, we have developed a convenient approach for the synthesis of 3,4-oxepino-fused indoles starting from readily accessible MBH-acetates of acetylenic aldehydes. The present strategy is based on sequential allylic substitution/ Rh(III)-catalyzed C–H activation based intramolecular [3 + 2] annulations, which enabled the rapid construction of functionalized 3,4-fused indoles.




**Scheme 2.** Proposed mechanism

### Supporting Information Summary

Experimental procedures, characterization data and copies $^1$H and $^{13}$C NMR spectra of all new compounds as well as copies of HSQC and HMBC Spectra of **4b** and **4j** can be found.

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## Conflict of Interest

The authors declare no conflict of interest.

**Keywords:** Fused Indoles · Morita-Baylis-Hillman Acetates · [3 + 2] Annulation · C–H Activation · Allylic Substitution

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# EMERGING TRENDS IN HIGHER EDUCATION, THE ROLE OF – IQAC


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# A CRITICAL STUDY OF THE CHALLENGES FACED BY THE EDUCATION SYSTEM IN INDIA

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## Indian Education System

India is a land of knowledge and history reveals that many people from different countries learnt many things from our motherland. Especially foreign travelers have visited our country for acquiring knowledge and education in the subjects like Astronomy, Mathematics, Physics, Economics, etc. Therefore, the discreet educational system of the time has strong roots in the cultural prosperity of our country. In the 21st century, India has become a super power in education with the standards of world class educational opportunities.India has always been a pioneer of the 'gurukula' system.In this system, the bondage shared by the student and the teacher is unique and special, and this is holistic approach to education in which a comprehensive development of the mind and the soul is observed best. The exact format of the 'gurukula' system is missing in the urban system of the country today.In spite of that, the spirits still remains, and this works to intensify the educational quality and excellence at all levels.In India, the study options are extensively diversified in all fields of education.

One of the best beneficial points of the Indian education system is its inexpensiveness. The teacher-student relationship in India is better than that of the foreign nations.This helps the students to stay motivated while studying andthis can help them to develop in the field of education.Indian institutions provide the students with more ground-work on helping students learn the concept theoretically.Consequently, Indians have generally high intelligence level compared to other countries. Right from our school-days to post graduate level, we have a variety of class tests and semester examsso that the students are able to be in constant touch with their books. This also means that Indians generally will have more scope in scoring in competitive exams not only in India but also in the foreign based standardized tests like GRE, GMAT, etc.

## The Challenges Faced by the Education System in India

The Indian education system is perhaps the second largest in the world, and this system has been struggling for a long time. The current situation of the student mindset compels them to get a good job after their undergraduate course. This makes most of the students drop their interest in theoretical science which kills a lot of dreams. In this connection, the words by Chris Hedges, "The true purpose of education is to make minds, not careers," are apt.The stress is prevalent everywhere in Indian institutions and its systems and we can see and feel it. In India, children are forced to go to schools at the age of four years itself, which reduces the fun that a child deserves to have during their childhood. Moreover, in our country studentsaredifferentiated based on only their marks and most of the people feel thatthe more marks students get, the more intelligent they become. Here, the grading starts right from the beginning of the student's education, and this prohibits the students from taking their own time to understand things which will make them stressful at a much younger age. If we follow Albert Einstein'squotation "everybody is a genius,but if you judge a fish by its capability to climb a tree, it will live its whole life believing that it is stupid," (Matthew Kelly, 2004), our system can be mended up to some extent.

Most importantly, the students should be taught practically, andthis is one of the most important things that our education system doesn't follow. commonsenseand application are not given proper importance. Students are made to mug up information just for the sake of writing in the examinations. In India classes are held almost continuously without any breaks, andabout only an hour in total of all the time they spend in the institutions is utilised for breaks. Many students might not like sitting hours together at the same place and listening to classes which they are not interested in. As rightly remarked by Aristotle, "Educating the mind without educating the heart is no education at all." This reduces the potential of the student in understanding the class.

The education in India is not fully state funded. There is a lot of poverty in India but the government hasn't been able to take up necessary action for free education (for at least the ones who can't afford it). Government institutions aren't being run properly in most of the areas. Though Indian education system is good when it is compared tothe other countries, we are not producing as many scholars as we should be able to produce due to the population and limited resources of our country. That is the reason why we are forced to say that the Indian education system is not up to the mark.

One of the main reasons for our failure in the education system in India is we are forced to follow the same system for all the students and the institutions both in rural and urban areas.The main drawback in India is we are forced to join the students in the institutions to increase the Gross Enrollment Ratio irrespective of the interest of the students, and we are asked to increase pass percentage in the examinations. The students who join with such force or for the sake of some incentive are not at all interested in education, and they attend the institution namesake and expect ultimate pass in the examinations. Consequently, it is leading to deterioration in the standards of our education system. The too much bureaucratic interference in the academic affairs is also one of the drawbacks here. One more hindrance is the work related grading of institutions has become very hectic to the teachers and they are unable to concentrate on the teaching and learning process wholeheartedly.

Now a days, in India the students are highly stressful and they have to face these examinations in order to score as per their parent's expectations. So without getting leisure time, students just prepare for their examinations because those who fail or get fewer marks are not treated well by the teachers, the parents and even by the classmates. Eventually, they lose all the confidence or become trouble makers. Parents pay a lot of fee even for the extra tuition, and expect outcome of their money spent. The system kills creativity and it is not at all helpful not only for students but also for teachers and parents. People talk about great performance by Indian students in the foreign countries, as the system only helps in discrimination between brilliant and dull, and also rich and poor. The people who are doctors or engineers with good salary, lawyers, C.A. or any highly paying job are only getting much respect in society. So it is all about the money in India and so people are crazy about IITs, AIIMS, IISc and so on. It is only helpful for those who run the private institutions as they make a lot of money, and it has become a business.

As rightly said by Jean-Jacques Rousseau, "Plants are shaped by cultivation and humans by education" (Jean-Jacques Rousseau, 1979), unless we shape the students in a proper way, they won't get proper education and develop into good citizens. The present scenario clearly highlights that the Indian education system is not student friendly due to dullness in the classroom, massive syllabus, and more number of examinations. This is happening at every level of education. The most unfortunate thing is that there are high expectations not only from the parents but also from the teachers in case of getting good results. Teachers give a lot of home-work and parents also expect the same. In this situation, the student gets a lot of pressure and stress; consequently the student hardly learns anything but just scores the marks.

We don't need human robots. The world has progressed and now we need people, who think creatively, innovatively, independently with the ability to connect. It is a known fact that no two brains are the same. When it comes to school one teacher stands in front of forty kids with each one having different strength, different needs, different gifts, different dreams and schools teach them at same time in a same way, that's horrific.

If our education system is compared with theeducational system like Finnish, the Indian educational system is not progressingin the right direction.The most important benefit is the freedom and practicality of education withno home work andassignments. Students are not burdened with home works and assignments as they believe that mastery is attained in class. No exams till high school, there iscontinuous andpractical teaching with low teacher-student ratio.Finnish education system is consistently been awarded as the number one education system in the world from many years. Several reports and surveys lay emphasis on the importance of high quality teachers with relevant level of pays.One important factor which needs to be considered here is that Finnish institutions do not charge much tuition fee, and education is sponsored here with the quality of education to all the students from all over the world. Parents do not pressurize their children to study. They learn everything on their own, and the formal education starts here at the age of seven. They are quite relaxed when it comes to educating their children.

The main motto of education system in Finland is 'Education for future, not just the present.' There are no such things called national testing or inspection in schools and colleges. The government looks at the performance of the candidates and recruits them for various posts.Finland has no private schools and they value 'equality over excellence' - equal opportunities for all.Though the Finnish schools have sports, they don't have sports' teams as they don't give importance to competitions.Sahlberg quotes a line from a writer named Samuli Paronen which says that, "Real winners do not compete."( Samuli Paronen,2015). In Finland, their educational system has completely been revolutionized by their intellectual and educational reforms.The Finnish system doesn't encourage forcing or standardized tests, andthere is no grading system at all for teachers. Master's degree is a must to all teachers who wish to enter the teaching profession. Teaching programs are the most rigorous and selective professional schools in the entire country. If a teacher isn't performing well, it is the individual principal's responsibility to do something about it.The educational system in Finland doesn't worry about the merit-based systems. The lists of top performing schools and teachers are not found. The environment of competition is not at all found there, instead cooperation is found.

## Conclusion:

After analyzing the education system in India critically, one can understand that it requires some changes in it in order to make both the teacher and student stress free. After all stress is the root cause for all hindrances to our development in all aspects. That is why our policy makers must go in the direction of making our education system stress-free. In this connection, grading system should be removed both for teachers and institutions as, now a days, we have different kinds of assessment methods. Record work should be minimized to the teachers particularly in the higher education, as the teachers are unable to concentrate on the work what exactly they are supposed to do. Finally, the education system should be helpful to the students in their holistic development, becausenot school but the education system shape the intellect of a student.

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# Information Products and Services in the E-environment

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# Methods Impacts and Challenges of E-Resources in Current Libraries: A Study

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## 1. INTRODUCTION

Electronic resources generally called as E- resources is the order of the day, rise in Information technology, suddenly changed sources man was using once, one of the example is our evolution of e resources. The storage of ideas of the human being from manuscripts to paper and to floppies, cds, DVDs, and hard disks , to the online archives like e resources help the man to access any where 24x7 with a net connections on pc. Gathered, store, organized, accessed, retrieved and consumed information in the form of e resources made a significant impact in science and technology. According to Katz, "the best criteria for evaluating a source are purpose, authority, and scope." (1992, p. 23). It is also important in evaluation of electronic journals to consider format, currency and audience. The wide diversity of materials such as: print, audiovisual, CD-ROM, electronic journals, network databases, and multimedia products are continuously growing. Most libraries are increasing their electronic resources in response to user demand. Consequently, librarians must continually be educated in increasing their skills on automated systems and electronic resources.

## 2. E- REFERENCE SOURCES: AN OVERVIEW

They are plenty of variety of e - reference sources and they are like abbreviations and acronyms, Almanacs, Associations, organizations and conferences, audio/video & Television programs, awards and prizes, biographies, book reviews, book sellers/out of print/rare, calendars and time, career and employment, citations and style guide (MLA&APA), consumer health, consumer information, converters and calculators, country information, Dictionaries and thesauri, Directories, Embassies, Encyclopedia, Government Information, Images, Library home page/ catalogues, Maps, Atlases, & Geo Information, Movies/Films, News and current events, patents and trademarks, Quotations, Scholarships, Statistics, Universities/Colleges, weather and climate.

### *2.1. E- Statistical Sources*

They are many electronic statistical sources and one good example is that the US Census Bureau's internet site devoted exclusive to measuring electronic economy and also provides links like business and industry, 2007 economic census, economic indicators, annual survey of manufactures, annual wholesale trade survey, service annual survey, annual retail trade survey , social science electronic resources : statistics is an electronic eg: economics data, government docume archive, governments on www, international data base, int social sciences statistics and data, nation master, off stat official statistics on web, oxford latin American econo history database, and international organizations, e,g., Eu stat, food and agricultural organizations, international la organizations, international monetary fund, organization f economic cooperation and development, UNESCO, UNIC UNO, united nations high commission for refugees, uni nations populations information network, world bank, wh charity trends, radical statistics group, straight statistics.

### *2.2. Sound Recordings*

Sound recording and reproduction is an electrical mechanical inscription and recreation of sound waves such spoke voice, singing, instrumental music, sound effects two phases in sound recordings are analog and digi recordings. Electronic recording formats starts form magn tapes later tape recorder, later came stereophonic sounds, high fidelity, later transistor radio, and compact cassette , wa introduced commercially in the year 1980s employ las technology to inscribe and read digital information in a wa that avoids actual physical contact between the dises and type of stylus . compact disc technology was super cedded digital versatile disc (DVD) technology with the introduction of DVD- audio format in 1999.Motion picture soundtracks called optical recordings. The sound to be recorded converted in to an electrical signal that is used to modulate intensity of beam light.

### *2.3. Research Guide by Subjects:*

The Research Process will go smoothly if you know what resource to consult and test the genunity. As researcher you should have competency on four factors a) Choosing appropriate resources b) Searching effectively and efficiently c) evaluating resources critically d) citing resources appropriate documentation style know we have different databases which are helpful for our research and it also give authentic sources and peer review Journals and total number of hits to show the popularity of the specific journals. The Indian School of Business Hyderabad, Learning resource centre have collection of nearly 50 databases which give information on Business News, Company information, Management Literature, Marketing research, comes under broad category of databases. These databases useful research guides for the students in their project works.

### *2.4. Indexes*

Database Index helps to speed up retrieval of data and similar to book index. In database index some fields are automatically index, an email address, a user id, a social security number, are automatically indexed and database can quickly check to make sure that you are not going to introduce bad data. The basic idea of index is to limit the findings. Bitmap index, Dense Index, Sparse index, Reverse Index .balanced trees, B+ Trees and Hashes.

### *2.5. Online Databases:*

Database is the collection of file or files brought together as common file and data will be kept in a certain specific and systematic manner without any duplication called database. The databases which are in online available are called online databases. A database management is set of programs that enable storing , modify and extracting information form a database it allow add, delete, access, modify, analyze data stored in one location. They are servers called database servers that hold the actual database and run only the DBMS and related software's we should get the username and passwords to login and browse the IP enabled databases.Types of databases, Navigational DBMS , Relational DBMS, SQL DBMS, Object oriented databases, 21 centaury No SQL database .

### *2.6. E- Thesis*

E-Thesis also called online thesis, electronic thesis which can access in internet at any time ie 24x7 . Electronic thesis and dissertations bibliography includes articles, books, conference papers, technical reports, Un published e prints, and other scholarly textual sources that are useful in understanding electronic thesis and dissertations. This bibliography does not cover digital media works ( MP 3) files, editorials, e-mail messages, interviews, letters to the editors, presentation slides, or transcripts and web blog postings . Example of E - Thesis are Vidyanadhi, Sodhganga, Sodhgangothri. Vidyanidhi (Meaning Treasure of Knowledge In Sanskrit) is Indian premier digital library initiative to facilitate the creation , archiving and accessing of doctorial thesis. Vidyanidhi is an information in fracture a digital library , a portal of resources , tools and facilities for doctoral research in India. Sodhganga at inflibnet centre provides a platform for research students to deposit their Ph.D thesis and make it available to entire scholarly community in open access. The repository has the ability to capture, index, store, disseminate, and preserve ETD,s submitted by researchers. Sodhgangothri under sodhgangothri research scholars / research supervisors in universities are requested to deposit electronic version of approved synopsis submitted by research scholars to the universities for registering themselves for the Ph.D programme it reveals the trends and directions of research being conducted in Indian universities and avoid duplication of research.

### *2.7. Online Student Assessment System (OSAS)*

Inform your data today instruction to multi student achievement goals sadlier's web based online student assessment system (OSAS) is an outstanding tool to increase student learning without a "one size fits all" approach. From creating assignments and test to reporting student results, this secure assessment system makes monitoring student progress easy.

a) preparing students for the online 2014/2015 common core assessments

b) saves teachers time in creating practice worksheets and assessments

c) provides instant feedback with online administration

d) Makes it easy to track student progress and adjust instruction.

e) Is available anytime, anywhere, on any internet - accessible device.

## 3. ADVANTAGES OF E-RESOURCES

- Any where, any time 24x7 access with simple net connection on pc
- Easy in search strategy, for magazines or journals with Vol and Issues exactly with single click.
- Popularity and Value of the articles or books can be known by number of citations it has got.
- Peer reviewed sources can be kept separately for the scholarly community.
- Speed in publication and distribution than in print or any other forms.
- Feed backs, comments, and popularity can be known to the world quickly.
- Well presentations with URL links form topic wise to the another page quickly
- Animated, multimedia, charts, and audio, video can make the stuff attractive and Interesting to the user.
- It is most cost effective compared to print media, print cost, distribution cost, transportation cost can be saved.

## 4. DISADVANTAGES OF E- RESOURCES

a) It is difficult to read in computer screens

b) Lack of peer review of materials

c) Slowness of Internet

d) Power shortage

e) Lack of accessibility of resources that doesn't access the resources.

## 5. CHALLENGES OF E - RESOURCES

- As the consortia acquisition of library resources between libraries made then the role of librarian also will change drastically. Librarian plays key role in providing resources to their users is challenging task know.
- Information pollution as the number of resources on a specific topic has ever increased to choose the specific and a genuine one is very difficult, hear comes the role of librarian, he has to select and send appropriate article or resource with genuinely in time
- Make use of online resources which are available in library properly is one of the main task of the librarians in this electronic world.
- Frequent problems in hard ward and software trouble shooting of the e resources a librarian should knowledge at least and could explain to expert to rectify.
- In the newly changing and challenging trend current librarian should be able to balance both the printed and on line version of resources.
- Classification, cataloging and indexing of E-Resources and keep the site update is one of the key roles of the librarian.
- Librarians has the responsibility to increase the usage of e- resources and also educated the users about the usage and search strategies he has to take frequent orientations to the user community about e- resources of the institution and also he should took feed back regarding the e resources.
- As and when librarian should knew the barriers in usage of e- resources and he has to rectify and solve the problems facing by the users.
- Low band width for internet access
- Lack of sufficient computer systems within the library premises
- Asking Goal Oriented awareness progr Librarian , Librarian make your resear your time.
- We can provide single interface to sea journal platforms.
- Lack of Organizational Information m
- Developing next generation catalogues
- A Librarian should analyze web traff surveys analyze usage statistics and in and feed backs

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## Editors-in-Chief



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**Dr. D. Chandran**, has the distinction of earning two masters degrees in Commerce and Library and Information Science securing gold medals in both for first ranks. The Sri Venkateswara University awarded him doctoral degree in Library and Information Science from Sri Venkateswara University,Tirupati. His publications more than 155. He has been actively involved in organising and participating many national seminars. He has edited 4 books and co-authored one book on 'Information technology' in Telugu language. He has prepared Course materials for the distance education programmes for various universities. He is an examiner and paper setter for more 20 universities and adjudicated more than 100 theses. His research interest include Library automation, database creation, digitization, computer-based information services, on-line search etc.. Under his guidance and supervision, 12 doctoral degrees and twenty M.Phil degrees were awarded. He has delivered guest lectures at a number of workshops in the universities and a resource person in a number of Distance education programmes, Academic Staff Colleges, Departments. He has been closely associated with more than a dozen professional bodies. He served as Joint Secretary for IATLIS and Vice President (south), for ILA. His teaching and research relate mostly to the area of application of Information Technology in Library and Information centers, Library Science education. He served as Chairman, Board of Studies and Head in his own department. Presently he is Chairman, BOS for the DLIS, Sri Krishnadevaraya University, Anantapur. He is a member of BOS of many universities in Andhra Pradesh, Tamilnadu, Karnataka. Currently he is working as Professor in the Dept of Library and Information Science, Sri Venkateswara University, Tirupati.

## Editors



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**Dr. P. Nageswara Rao** possesses triple Masters' degrees in Public Administration, Commerce and Library and Information Science. M.Phil and Ph.D degrees in Library and Information Science. He obtained degrees from the University of Madras and Annamalai University. He served as College Librarian in Tagore College of Arts and Science, Chennai for a period of five years. His experience in the academic libraries has motivated to undertake doctoral study in Autonomous College Libraries, which resulted in the present book form.



**Smt. M. Prasantha Kumari,** presently working as Assistant professor, DLIS, Sri Venkateswara University and joined during the year 2007. Prior to joining in the university, she worked as a librarian and guest lecturer at Anantapur. She cleared her net. Presently she submitted her doctoral degree under the guidance of Prof D Chandran and awaiting for result. She has more 15 research papers published in conference proceedings and journals at national and international level. She participated more than 20 national and international conferences.

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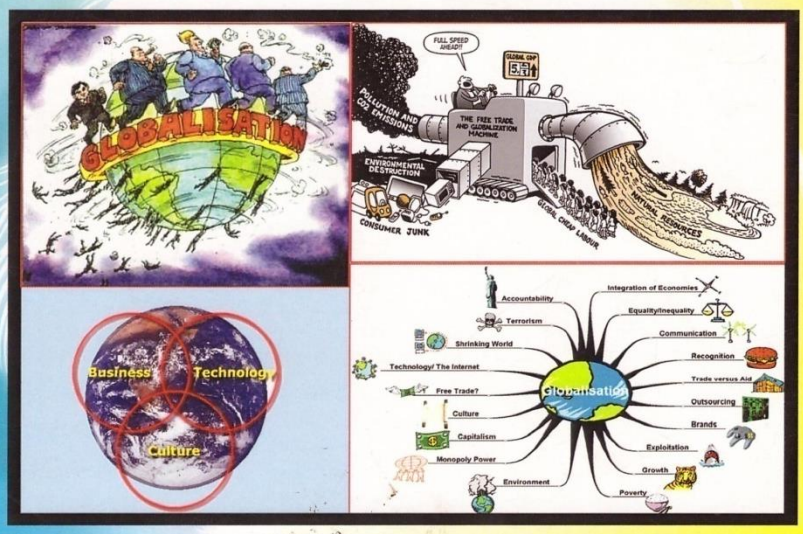
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# GLOBALIZATION AND ITS IMPACT ON ECONOMIC ENVIRONMENT

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**Globalization**

Globalization can be simply defied as the expansion of economic activities across the political boundaries of the native state. In a broader sense it is a process of strengthening economic integration , increasing economic openness and growing economic interdependence between the countries of the world economy.

International Monitory Fund (IMF) defined globalization as the growing economic interdependence of countries worldwide through increasing volume and variety of cross-border transactions in goods and services and of international capital flows and also the more rapid and wide spread diffusion of technology.

**Environment**

Environment is the sum total of what is around something or someone. It includes living things and natural forces. The environment of living things provides conditions for development and growth, as well as of danger and damage. Living things do not simply exist in their environment. They constantly interact with it. Organisms change in response to conditions in their environment. The environment consists of the interactions among plants, animals, soil, water, temperature, light, and other living and non-living things.

Environment can be divided in to four types a) Physical environments b) Economic environments c) Social environment d) Political environment. Generally globalization effects the economic environments either positively or negatively.

**Globalization –Economic Environment**

The term globalization has four important aspects a) Reduction of trade barriers and permit free flow of goods and services between countries b) Creation of environment for the free flow of capital between the countries c) creation of environment for the free flow of technology between countries d) creation of environment for the free flow of labor between countries .

Globalization effects on economic environment assets for example in order to get profit maximization the resources should be utilized more and more than actually needed. During that period income in inequalities and environmental unbalanced activities takes place regularly. To enhance the economic activities forest land may be declined that's why as long as we follow globalization we should check up the steps which are to be implemented without loss of social and economic environment quality.

The aim of globalization is to integrate the countries of the world. If we see the globalization with economic environments it has two main components one is globalization of markets and second is globalization of the product as long as we implement the policy of globalization without the loss of physical environmental quality the developing countries would be able to improve there competitive strength and achieve rapid economic growth. But it is not possible because pollution may arise while producing different goods in such countries.

**Merits of Globalization :** India has skills and investments in several sectors like agro-based industries which make it lowest cost producer and become premier production centre of the world b) India has the potential to be a manufacturing site for many global industries because it has the capabilities to manufacture almost all engineering goods. C) India has certain national advantages in some sectors like knowledge-Led-Services. It can become a multinational abroad and gain world markets d) globalization helps the entrepreneurs to spread there risks of entrepreneurship. It may be better to spread the risks over several markets e) Indian companies

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can tap the huge global capital market and perhaps rise global capital more cheaply f) globalization will enable India to attract foreign investments. As a result of globalization India is getting some benefits .

**Effects of Globalization :** Although globalization policy has some benefits there are some problems the government has to face the policy may not deliver the expected results. The following examples shows demerits or problems of this policy. a) India's share in world export of goods and services not significant.

If we take small scale industries as an example we can analyze the effect of globalization with the below chart.

(Units = Million Nos.)

| Year | Units | % Increase to prev. year | Year | Units | % Increase to prev. year |
|---|---|---|---|---|---|
| 1973-74 | 0.42 | - | 1990-91 | 6.79 | 273.08 |
| 1974-75 | 0.50 | 19.05 | 1991-92 | 7.06 | 3.98 |
| 1975-76 | 0.55 | 10.00 | 1992-93 | 7.35 | 4.11 |
| 1976-77 | 0.59 | 7.27 | 1993-94 | 7.65 | 4.08 |
| 1977-78 | 0.67 | 13.56 | 1994-95 | 7.96 | 4.05 |
| 1978-79 | 0.73 | 8.96 | 1995-96 | 8.28 | 4.02 |
| 1979-80 | 0.81 | 10.96 | 1996-97 | 8.62 | 4.11 |
| 1980-81 | 0.87 | 7.41 | 1997-98 | 8.97 | 4.06 |
| 1981-82 | 0.96 | 10.34 | 1998-99 | 9.34 | 4.12 |
| 1982-83 | 1.06 | 10.42 | 1999-00 | 9.72 | 4.07 |
| 1983-84 | 1.16 | 9.43 | 2000-01 | 10.11 | 4.01 |
| 1984-85 | 1.24 | 6.90 | 2001-02 | 10.52 | 4.06 |
| 1985-86 | 1.35 | 8.87 | 2002-03 | 10.95 | 4.09 |
| 1986-87 | 1.46 | 8.15 | 2003-04 | 11.40 | 4.11 |
| 1987-88 | 1.58 | 8.22 | 2004-05 | 11.86 | 4.04 |
| 1988-89 | 1.71 | 8.23 | 2005-06 | 12.34 | 4.05 |
| 1989-90 | 1.82 | 6.43 | 2006-07 | 12.84 | 4.05 |
| **AAGR** | **9.36** | | **AAGR** | **4.07** | |

Source: Ministry of Micro, Small and Medium Enterprises, GOI.

AAGR= Annual Average Growth Rate or Exponential Growth Rate.

**Analysis:** It is cleared from the above table that the Annual Average Growth Rate of number of units in the pre-liberalisation period, from 1973-74 to 1989-90 was 9.36 percent and in post- liberalisation it was 4.07 percent. In pre- liberalised period, the yearly growth rate was higher than average growth rate in the initial years and from 1984-85 to 1989-90; the yearly

- Foreign investment flows not quit helpful to strengthen Indian economy
- Wide gap between foreign investments approvals and actual flows
- Increase in imports is greater than the increase in exports
- Slow GDP growth rate
- Slowing down the process of poverty alleviation
- Lower employment growth

**Effects on Physical Environments;** Under the part of globalization every country will tries to enhance there business and move forwards to international trade effectively. In this sense some major issues relating to global environment that have attracted the increasing attention of economists , environmentalists ,

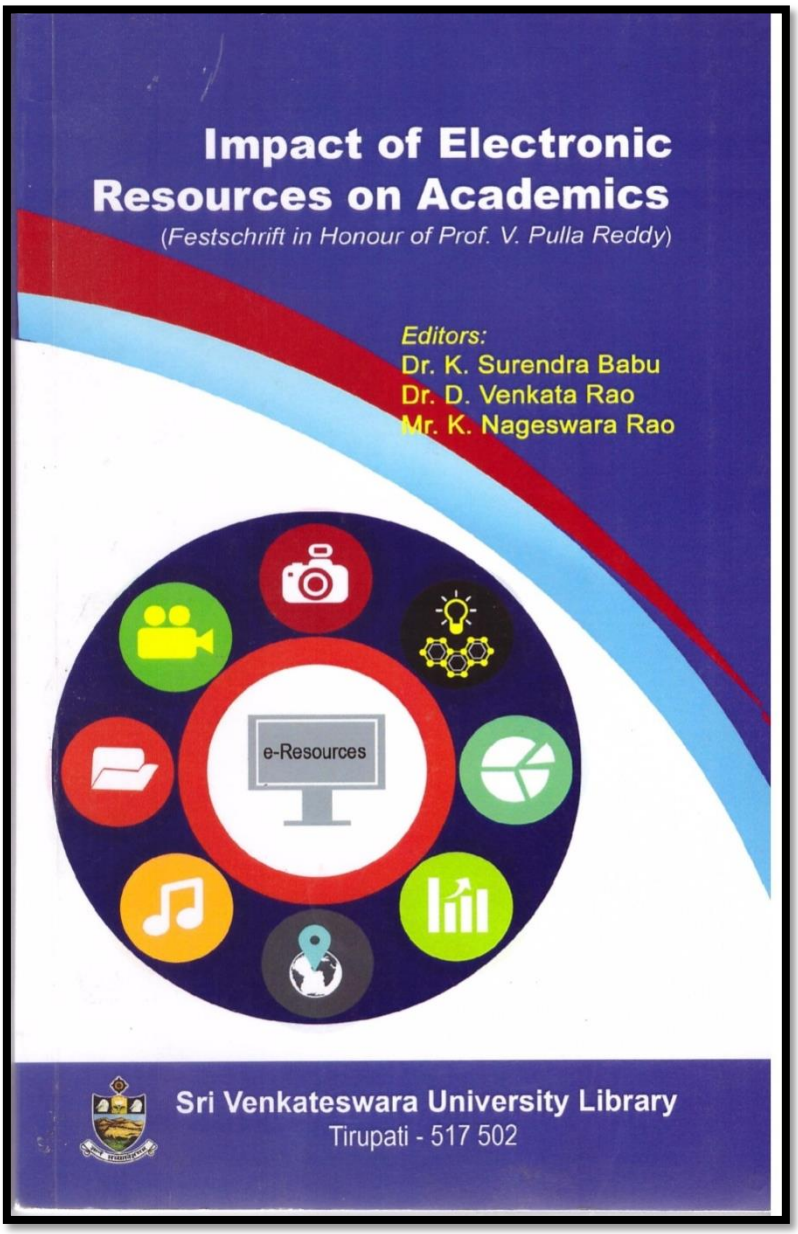
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Impact of Electronic Resources on Academics
(Festschrift in Honour of Prof. V. Pulla Reddy)
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# Use and effectiveness of E-ShodhSindhu in pro of higher education among the research schola faculty members of Dravidian University: A S

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***Abstract*** *- The present study aims to analyse the use and effecti shodhsindhu consortium e-journals in promotion of higher educa the faculty members and research scholars of Dravidian Universit also intends to determine the frequency of use of E-ShodhSindhu, t in E-ShodhSindhu, access place for E-ShodhSindhu, types of e-port ShodhSindhu, effectiveness of E-ShodhSindhu on academic activiti faced and overall satisfaction with E- ShodhSindhu. Questionnaire adopted to elicit data from faculty and research scholars of Dravidia A total 110 respondents participated in the survey from which 6 members and 48 are research scholars. The study reveals that faculty scholars are using E-ShodhSindhu online databases subscribed b University. Majority of faculty and research scholars are using e research purpose and the department is the most preferred location e-journals.*

**Keywords:** E-ShodhSindhu, INFLIBNET, E-journals, e-resou databases, Dravidian University

## Introduction

The recent developments in Information Technology change scenario. Libraries and Information Centres have embrac information technology more profoundly than many othe most of them are currently using electronic products and offers tremendous opportunities to provide solutions to some challenges now libraries are facing. Electronic Publishing or

## Conclusion

The study reveals that the faculty members and research scholars of Dravidian University mostly rely on E-ShodhSindhu e-journals for research purpose and publishing articles. They are using the available e-journals satisfactorily. The library professionals tried their best for promotion, assistance and guidance in accessing e-journals. The increase in e-journals subscription indicates that the library has made drastic changes in E-ShodhSindhu e-journals collection and services. The library has to employ different strategies for effective use of available online resources through E-ShodhSindhu. Central Library has to conduct the orientation programme for the best use of E-ShodhSindhu e-resources.

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# Future Libraries and Future of Libraries

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Dr B Ramesh Babu
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# COMPARATIVE STUDY IN USAGE E-SHODHSINDHU BETWEEN SRI VENKA UNIVERSITY & DRAVADIAN UNIVERSITY

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## INTRODUCTION

The recent developments in Information Technology chan scenario. Libraries and Information Centers have embr information technology more profoundly than many other fi of them are currently using electronic products and serv tremendous opportunities to provide solutions to some of the m now libraries are facing. Based on the recommendation Committee, the MHRD vide their recent note F.No.16-23/20 1st December, 2015 has has formed e-ShodhSindhu merging t initiatives, namely UGC-INFONET Digital Library Consortiu INDEST-AICTE Consortium.The e-ShodhSindhu will contin current as well as archival access to more than 15,000 core and journals and a number of bibliographic, citation and factual different disciplines from a large number of publishers and a its member institutions including centrally-funded technica universities and colleges that are covered under 12(B) and 2 the UGC Act. The main objective of the e-ShodhSindu: Consor Education E-Resources is to provide access to qualitative electr including full-text, bibliographic and factual databases institutions at a lower rates of subscription. Looking towards th of the e-journals, the present study try to analyse the use and ef e-ShodhSindu online journals by the faculty and researc Dravidian University and Sri Venkateswara University to problems and constraints faced by the users for accessing recommendations for its proper use. This study is probably or in both the universities.

satisfactorily. The library professionals tried their best for promotion, assistance and guidance in accessing e-journals. The increase in e-journals subscription indicates that the library has gone drastic changes in E-ShodhSindhu e-journals collection and services. The library has to employ different strategies for effective use of available online resources through E-ShodhSindhu. Central Library has to conduct the orientation programme for the best use of E-ShodhSindhu e-resources.

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30 candidates were awarded Ph. D degree under his guidance. He has published more than 390 research papers in Indian and Foreign journals, Festschrift volumes and National and International seminars/workshops . He has edited about 35 books including conference proceedings and festschrifts. He has organized a number of workshops, seminars and conferences. He is a Resource person in various Distance Education Institutes. He has successfully completed 5 major projects at national and international level. He has been honoured with two festschrifts, He served as the member of Board of studies in about twenty universities, member of Board of Examiner in about 40 universities both in India and abroad. Currently he is the Co-President of the Library and Information Science Society for the Asia and the Pacific (LISSASPAC) now renamed as I-LISS (International Library and Information Science Society).



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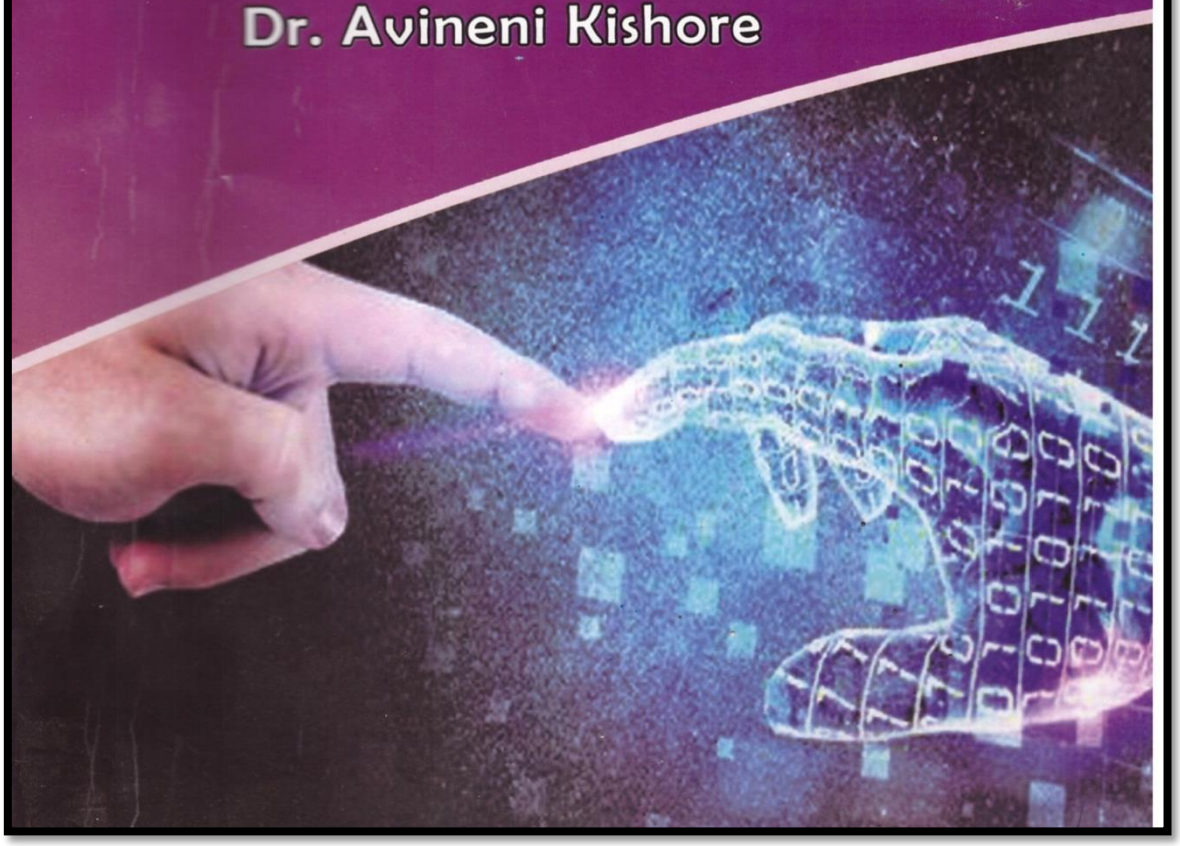


**Dr Raavi Sarada** is the Secretary of Andhra Pradesh Library Association and since 1987 she has been the Principal of Paturi Nagabhushanm School of Library science run by the Association at Vijayawada; editor Granthalaya Sarvaswamu, the first vernacular Journal of India; Jt.Secretary Andhra Pradesh Gandhi Smaraka Nidhi and member of Gandhi hill foundation, Vijayawada.Sheis also Secretary of Sarvottama Granthalayam which works all the 365 days of a year. As a project director Bread Society Chlidren's Libraries, she is instrumental in establishing more than 1200 children's libraries in government and aided schools in all the districts of Andhra Pradesh and Telangana States. She edited good number of Books and Conference volumes She was course writer for some write-ups of Dr Ambedkar Open University Library and information courses. She is the member of many professional Associations of India. She organized many national and regional conferences in Library and Information science. She has been awarded with KALARATNA title by Govt. of Andhra Pradesh in the year 2016.She has been nominated as one of the Directors of Andhra Pradesh Granthalaya Prarishad by the Government of Andhra Pradesh.

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# TRANSITION OF ACADEMIC LIBRARIES BETWEEN PHYSICAL AND DIGITAL CONTEXTS

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Dr. K. Padmini
Dr. Avineni Kishore



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# USE PATTERN OF E-SHODHSINDHU CONSORTIUM BY THE RESEARCH SCHOLARS AND STUDENTS OF SRI VENKATESWARA UNIVERSITY: A STUDY

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**Abstract**

*This paper explains about terms and definitions of Digital libraries, e resources in E-sindhu followed by aims and objectives of E- Resources, Internet, Internet Users. . It explains how remarkable change had occurred with advent of E- shodhsindhu with nce to both print and online e-Journals. It also explains about subscription, usage and of publishing the Journal in terms of Money and Time.*

*Vords : INFLIBNET, consortia, e-Shodhsindhu, repository, networking, digital library, l library consortium,*

**duction**

Role of librarians as custodian, book keeper, changed according to information ist, knowledge manager, information officer with the advent of technological changes refers to e- resources like e-books-Journals, databases, repositories. E-ShodhSindhu: -INFONET Digital Library Consortium recently changed to E -Shodhsindhu consortium igher Education E -resources in order to provide quality e –resources to support learning esearch activities covering full text, bibliographical and factual databases. This has ged as a super gateway for university academic community in India providing access to sive scholarly resources since 2004 at free of cost. The consortium initiated providing s to current and archival 15,000 e- journals and databases extending the benefit to 139 – universities, 40 central universities, 22 – deemed universities, 15 law universities, 6 of of UGC, 72 – AICIT E funded colleges, 4000colleges and IITs, IIMs, IISc etc. able in the E -Shodh Sindhu Collection 135000 E – Books, 40 Resources, 16 databases 6000+ Electronic resources.

**t S.V. University library**

S.V. University library' was established in 1954. It has its own building. It subscribes 0 current periodicals. It has stock of 3, 85,000 includes books and back volumes of dicals. It provides photocopying service, documentation and abstracting service and net services. Its membership is 6000.

**ew of Literature**

**Arora**, Jagdish (2003) found the efforts made by Indian libraries and institutions ds the formation of consortia of libraries for buying access to electronic resources. eration amongst institutions for sharing their library resources has been practiced for les. Consortia- based subscriptions" to journals everywhere in the world, Shared riptions to electronic resources through consortia of libraries is a feasible strategy to

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Solve problems on usage of E ShodhSindhu 25 Respondents say they take help from ibrary staff and 25 say they took help from colleagues and 9 respondents self.

25 Respondents use E ShodhSindhu often and very often for research work and 9 respondents use occasionally.

39 respondents approach E ShodhSindhu to overcome deficiency Journals and 10 consult Librarians and 05 consult publishers and HOD Respectively.

Awareness on E-ShodhSindhu 20 respondents from Lecturers, Seminars, 15 Respondents from Librarian/ Staff, 10 from Internet Websites and 05 from Library website and Books / Journals and 04 from faculty.

20 Respondents use e shodhsindhu for writing papers and 20 for seminars , 05 for Teaching/ Research and knowledge with latest developments and 09 for Project work.

While accessing e shodhsindhu 20 respondents feel lack of speed of Internet 05 respondents say lack of electricity and 05 lack of cooperation from library staff , 05 Lack of sufficient Information and 05 say Unfamiliar with searching strategy 15 respondents say lack of Infrastructure facility, 04 say Difficulty in finding relevant Information.

With help of E-ShodhSindhu 25 Respondents say improved in research quality, 10 respondents say developed technical skills and 10 respondents say improved in searching skills and 09 say improved in academics and 05 say improved in their knowledge.

**estions**

Conducting orientation programme on E-ShodhSindhu

Conducting Workshops

Conducting Seminars

Conducting awareness programmes

Conducting Training Programmes

**rences**

Arora Jagadish et al. (2013). impact of access to e-resources through the UGC-INFONET Digital Library consortium research output of member universities, *Current science*, 104(3)

Kaul, H.K. (1999). Library resource sharing and networks. New Delhi: Virgo Publication

http://www.inflibnet.ac.in















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# Usage of e –Shodh Sindhu in Promition of Research and Academic Knowledge by Scholars and PG Students in Shri Padmavati Mahila Vishvavidyalayam: A Study

**Vijay Mahesh Kumar, P. and Mastanaiah, V.**

*Librarian, PRR & VS GDC, Vidavaluru*

*Librarian, Narayana Engineering College, Nellore.*

**Abstract**

*The aim of this paper is to know about usage of E-shodhsindhu by research scholars and PG Students their awareness, area of specialization, availability, level of satisfaction, and future requirements for their study. It also explains their experience in usage of E-shodhsindhu and productivity.*

***Keywords:*** *E-ShodhSindhu, E-Books, E-Journals, E-Databases, INFLIBNET, Resource Sharing, Sri Padmavati Mahila Vishvavidyalayam.*

## Introduction

Libraries play an important role in vast changing e environment. E resources changed the role of libraries, its scope and users. It also changed its nature of Job what it has done earlier. Modern information and communication technologies had profound influence on its access to various types of online e resources like e journals, databases, e books method of resource sharing and upgrade its resources to attract its users.

## UGC INFONET- Digital Library consortium

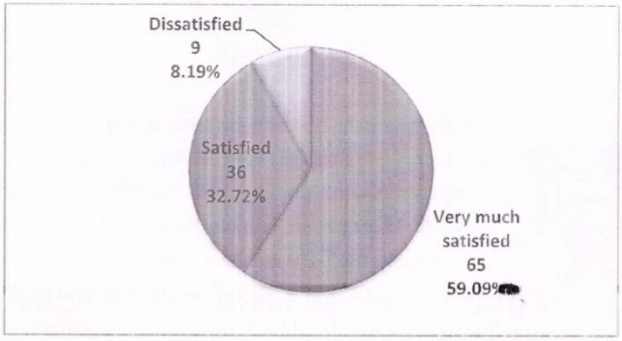
The University Grants Commission (UGC) has initiated a programme to provide e resource over Internet to scholarly literature in all areas of learning to university sector in India. The programme is wholly funded by the UGC. All universities which comes under UGC be the members of this programme and it also be extended to degree colleges also.

## E-ShodhSindhu

Based on the recommendations of an expert committee, the MHRD has formed e-shodhsindhu merging three consortia Initiatives, namely UGC INFONET Digital Library Consortium, NLIST and INDEST-AICTE Consortium. The e-ShodhSindhu will continue to provide current as well as archival access to more than 15,000 core and peer-reviewed journals and a number of bibliographic, citation and factual databases in different disciplines from a large number of publishers and aggregators to its member institutions including centrally-funded technical institutions, universities and colleges that are covered under 12 (B) and 2(f) Sections of the UGC Act.

13) Overall to what extent are you satisfied with E- ShodhSindhu?

(65) Very much satisfied, (36) Satisfied, (09) Dissatisfied




Regarding satisfactory level most of respondents said they are much satisfied while accessing e-shodhsindhu.

**Suggestions and Recommendations**

After analysis and Interpretations of data and looking in to opinion of respondents as given in the questionnaire here are some of suggestions that have been drawn and recommended to solve the problems of Sri Padmathi Mahila Viswavidhalayamu.

- The university library should conduct orientation and training programmes especially for the research scholars for creating awareness and better usage of e shodhsindhu
- The major problem faced by the respondents are Technical problems like in adequate computers and slow speed of Internet connections hence more number of computes be facilitated with increase in bandwidth regarding computers
- A well trained staff who can rectify technical problems on e shodhsindhu , printing, downloading, searching by using various kinds of search strategies

**Conclusion**

The present study exposes about the increased acceptance of electronic journals by the research scholars in the present environment in which the E ShodhSindhu has to play a meaningful role to assist academic and research community. Major problems encountered by the users toward access to e-consortium are lack of training and no proper orientation. Proper response as well as orientation programmes should be conducted from time to time by the university so that the problems encountered must be resolved according to users' requirements. The infrastructure facilities should be enhanced for the better utilization of E ShodhSindhu.

## EDITORS



**Dr. R. Sarangapani,** is working as University Librarian, Bharathiar University, Coimbatore, He finished his PG & Doctorate Degree in LIS at Annamalai University. He has presented 47 papers in various conference and published 15 articles in journals. He also published a book "Information Literacy Expertise". He got Best National Librarian Awards-2017 from MALA, Chennai. He is Resources Person, Invited Speaker, Key Note Speaker, Inaugural Address in various programme. He also Selection Committee Member and External Examiner in various universities in Tamil Nadu. He is a life member of ILA, TLA, ISTE, MALA & SALIS.

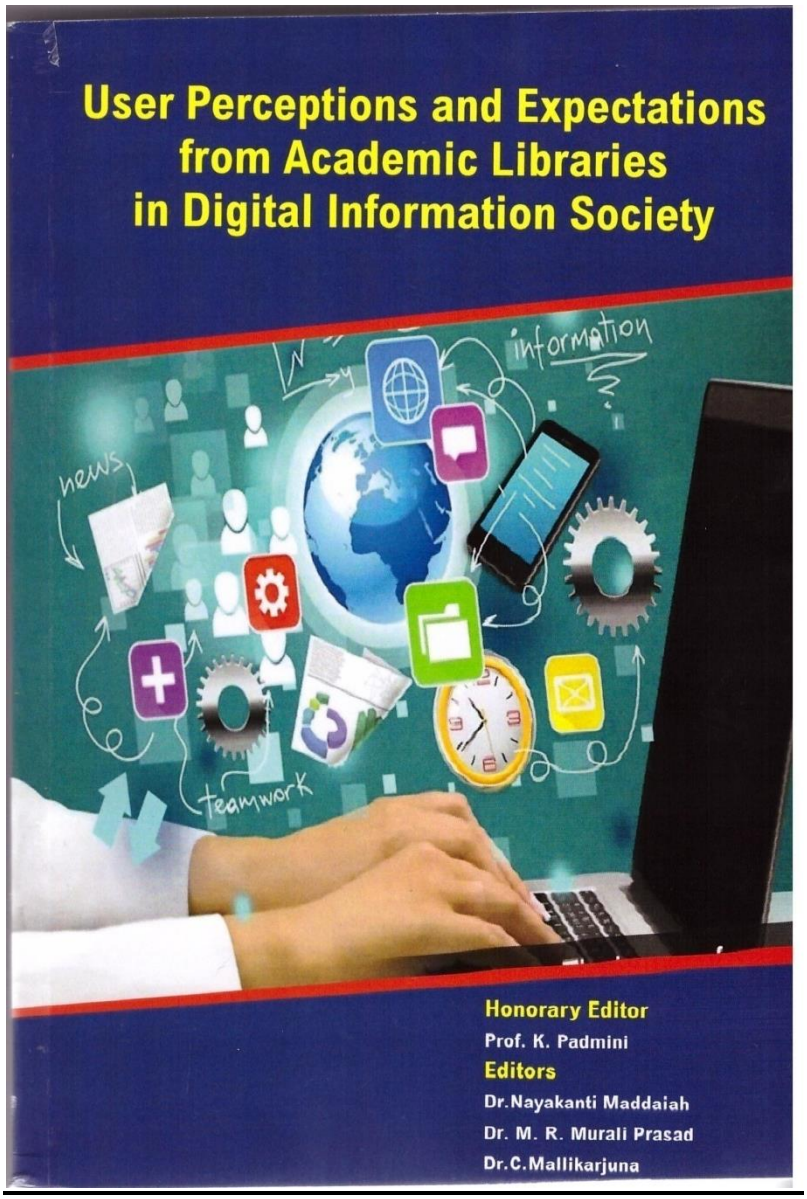


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6. Factors such as internet connectivity, technological infrastructure and government restrictions on the use of Social Media may restrict access.

## 6. Conclusion

His research contributes about various techniques used to improve library services and resources through social media. It has practical implications for how to effectively promote future services and resources and contributes to future researchers wanting to explore library promotional techniques. By using social media libraries can fulfill users need. Study gathers that according to the changing needs of library users, libraries need to be changed correctly. Libraries should be facilitated with internet service and develop their web page and social media page. Social media is used by libraries to supply a merging of user services, news, content etc.

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# User Perceptions and Expectations from Academic Libraries in Digital Information Society

## About the Editors



**Dr. K. Padmini**, is presently working as Principal, S.V.U. College of Arts, S. V. University, Tirupati. She has a rich experience of more than 30 years in teaching and research. She guided 20 Ph.D.s and 7 M.Phils. She participated in good number of national and international conferences and presented papers. She was invited as resource person by many institutions. She is the Principal Investigator for a UGC-Major Research Project. She is a life member in 7 professional associations. She held positions like, Head of the Department, Chair-person BOS, Coordinator- NAAC, Academic Senate Member in S.V. University. Sri Potti Sreeramulu Telugu University honoured her with 'Keerthi Puraskara' in the field of Library and Information Science for the year 2017.



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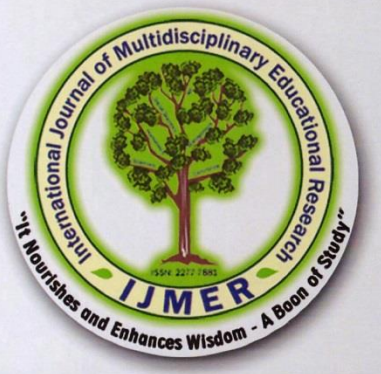
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# USAGE OF E-SHODHSINDHU RESOURCES BY USERS OF SRI PADMAVATHI MAHILA UNIVERSITY: A STUDY

**Vijay Mahesh**
Part Time Research Scholar
Dravadian University, Kuppam, Andhra Pradesh

**Abstract**

Based on the recommendation of an Expert Committee Ministry of Education has formed e-Shodh Sindhu merging three consortia initiatives, namely UGC-INFONET Digital Library Consortium, NLIST and INDEST-AICTE Consortium. The e-Shodh Sindhu will continue to provide current as well as archival access to more than 10,000 core and peer-reviewed journals and a number of bibliographic, citation and factual databases in different disciplines from a large number of publishers and aggregators to its member institutions including centrally-funded technical institutions, universities and colleges that are covered under 12(B) and 2(f) Sections of the UGC Act.

**Keywords:** E-Shodh Sindhu, UGC Infonet, Inflibnet, E-Journals, E-Resources.

## Introduction

Modern libraries provides literature and information through electronic sources and online services to support the academic activity and satisfy the user's information needs, so it is considered as the backbone of any research organization. The development of technology is changing the pattern of library resources and also changing the process of storage and retrieval in the digital environment from the traditional physical environment. Now the modern library is acquiring e-resources through consortia approach. Consortia approach is one of the ways to maintain cooperation, coordination and collaboration between libraries for Resourcessharingandworkasatechnologyforcollectiondevelopmentandminimizethecost.

**Sri Padmavati Mahila Visvavidyalayam** (University for Women)was founded in the year 1983 by Sri N.T.Rama Rao, the then Chief Minister of Andhra Pradesh, with the fervent desire to train women students as better builders of the Nation and to inculcate skills of leadership in all aspects of life. The University was established under the Sri Padmavati Mahila Visvavidyalayam Act of 1983, which has come into force on the 14 of April 1983.It was started with ten faculties and 300 students and twenty staff members. Today the University has a student population nearly 4000 and an academic staff of 105 and 131 academic consultants.

## Objectives of study

1. To look into the information search habits of Faculty Members and Research Scholars and PG Students using ICT facilities.
2. To study the knowledge of Faculty Members, Research Scholars and PG Students

...e of E- Shodh Sindhu Consortium
...To know whether there is essential cooperation in terms of user orientation is ...ible to the faculty members, PG Students and research scholars to use E-Shodh ...dhu Consortium.
...To know regarding frequency of usage of E-Shodh Sindhu
...know the purpose of usage of E-Shodh Sindhu
...know about level of satisfaction in using E-Shodh Sindh
...dentify the problems in facing E-Shodh Sindhu

**...ew of Literature**

Liao1 conducted a study on information seeking behavior of ...cultural researchers as teachers in Taiwan. He investigated that the critical ...s for the teachers to get needed Literature and the use pattern of information ...es is primarily the primary sources of information

Majid2 and Tan investigated the information needs and information seeking ...or of Computer engineering undergraduate students at Nanyang Technological ...ersity (NTU), Singapore. The purpose was to investigate the types of information ...s used by the students, the information formats they preferred, the ...tance of and reasons for using certain Information sources and the use of ...s electronic information sources. A questionnaire was Distributed to 200 ...mly selected students and 102 completed questionnaires were returned. The ...found that printed materials were the most preferred information format among ...tudents. The top five most preferred information sources, in the order of ...nce, were Books, lecturers, the Internet, friends and manuals. Unexpectedly, ...e of databases and Electronic journals were quite low among the computer ...ering students. The study Recommends a promotional campaign for ...ducing electronic information

Sbeba4 discusses agricultural information seeking behavior and use ...s among the African farmers and extension workers. Study suggests for ...shment of agricultural Advisory board comprising both librarians and extension ...rs to make extensive use of Non book material as a means to overcome the ...cap of illiteracy among farmers.

UNESCO (1998) observed that the rapid breakthrough in new ...ation and Communication technologies would further change the way ...dge was developed, acquired and delivered. It was also important to note that ...w technologies have offered opportunities to innovate on course content and ...g methods and to widen access to higher learning.

**...dology and Limitations**

As discussed above, the present study was confined to Sri Padmavathi Mahila ...ity. 2301 post- graduate students, 483 research scholars are studying in the ...ity. Further there are more than 231 Faculty members working in the ...ity. Due to the limited time frame, a sample survey random

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Research Paper

E-ISSN: 2348-4519

# On Lattice Fuzzy Sub Ordered Gamma – Nearrings

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***Abstract:*** In this paper, we introduce and study the concept of L – Fuzzy sub Ordered Γ - Near ring, where L is a complete lattice satisfying infinite meet distributive law. Also, we illustrate the homomorphism of an lattice fuzzy sub Ordered Γ -Near ring and prove some interesting results on it.

***Keywords :*** L – Fuzzy set, L – Fuzzy sub Gamma – Near ring, L – Fuzzy sub Ordered Gamma – Near ring, Normal L – Fuzzy sub Ordered Gamma – Near ring.
***Mathematics Subject Classification :*** *03E72, 16Y30.*

## I. INTRODUCTION

Goguen in [6] generalized the Zadeh [8] definition of a fuzzy subset of X as a mapping of X into the [0,1] into an L – Fuzzy subset, as a mapping from X to a complete lattice L. Fuzzy ideals of rings were introduced by W. Liu and it has studied by several authors. The notion of fuzzy ideals and its properties were applied to various areas like semigroups, semirings, Γ-semirings,.. etc. The concept of ideal theory in Γ - Near ring and fuzzy left (resp. right) ideals in Γ - Near ring were introduced and studied by Bh. Satyanarayana [1] and G.L Booth ([2],[3]), S. Ragamayi[13] introduced the structure of an L – Fuzzy sub Γ - Near ring, its characteristic set and L – Fuzzy ideals of a Γ - Near ring.

Now, we introduce and study the notion of an L – Fuzzy Sub Ordered Γ - Near ring, where L is a complete lattice satisfying infinite meet distributive law. We prove that the homomorphic image and its pre image of an L – Fuzzy sub ordered Γ - Near ring is also a L – Fuzzy sub ordered Γ - Near ring. Moreover we prove that homomorphic image and it's pre image of an L – fuzzy sub ordered Γ - near ring with with Supermum property is also an L – Fuzzy sub ordered Γ - Near ring with supermum property. Further, We prove the intersection of two L – Fuzzy sub ordered Γ - Near rings is also a L – Fuzzy sub ordered Γ - Near ring but the union of two L – Fuzzy sub ordered Γ - Near rings is not an L – Fuzzy sub ordered Γ - Near ring with suitable example.

In this section we recall some of the fundamental definitions, which are necessary for this paper.

## II. PRELIMINARIES

In this section we recall some of the fundamental definitions, which are necessary for this paper.

Definition 2.1 : A zero – Symmetric Γ - Near ring is a tripe (M, +, Γ), where

1. (M, +) is a group

2. "Γ" is a non – empty set of binary operators on M such that for each $\gamma \in \Gamma, (M, +, \gamma)$ is a Near ring

3. $x\gamma(y\beta z) = (x\gamma y)\beta z$, for all $x, y, z \in M$ and $\gamma, \beta \in \Gamma$.

4. $x\gamma 0 = 0$ for every $x \in M, \gamma \in \Gamma$

Definition 2.2 : Let X be a non – empty set. A mapping $\mu : X \to [0,1]$ is called a fuzzy subset of X.

Definition 2.3: Let X be a non – empty set. A mapping $\mu_L : X \to L$ is called a L – Fuzzy subset of X.

Definition 2.5: Let $\mu_L$ be any L – Fuzzy subset of a set M and let $t \in L$. The set $\mu_{Lt} = \{x \in M / \mu_L(x) \geq t\}$ is called a level subset of $\mu_L$.

Definition 2.6: Let M and N be two Γ - -Near rings and $f : M \to N$. Let $\mu_L$ be a L – Fuzzy subset of M. Then the image of $\mu_L, f(\mu_L)$ is the L – Fuzzy subset in N

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defined by

$$f(\mu_L)(y)=\begin{cases}\underset{z\in f^{-1}(y)}{Sub}\ \mu_L(z) & \text{if } f^{-1}(y)f=\varphi\\ O_L & \text{otherwise}\end{cases}$$

For all $y\in N$, where $f^{-1}(y)=\{x/f(x)=y\}$ .Let $\sigma_L$ be a L – Fuzzy subset in N. Then the inverse image $f^{-1}(\sigma_L)$ of $\sigma_L$ is the L – Fuzzy subset in M by $(\sigma_L)(x)=\sigma_L(f(x)),\ \forall x\in M$.

Definition 2.7: A L – Fuzzy subset $\mu_L$ of M is said to have the sup. Property if for any subset A of M, there exists $x_0\in A$ such that $\mu_L(x_0)=\sup_{x\in A}\mu_L(x)$

Definition 2.8: The intersection of two L – Fuzzy subset $\mu_L$ and $\sigma_L$ of a set X, denoted by $\mu_L\cap\sigma_L$, is a L – Fuzzy Subset of "X" is defined by
$(\mu_L\cap\sigma_L)(x)=\mu_L(x)\wedge\sigma_L(x),\ \forall x\in X$

Definition 2.9: Let M be a Γ - Near ring and A be a nonempty subset of M then A is said to be sub Γ - Near ring if 1) $x-y\in A$ 2) $x\gamma y\in A$, for each $\gamma\in\Gamma$ and $x,y\in M$.

Definition 2.10: A Γ-Near ring M is called an ordered Γ - Near ring if it admits a compatible relation "$\leq$":i.e., "$\leq$" is a partial ordering on M satisfies the following conditions.
1) If $x\leq y$ then $x+g\leq y+g,\forall x,y,g\in M$
2) If $x\leq y$ and $c\geq 0$ the $x\gamma c\leq y\gamma c$, and cγx≤ cγy, for all x,y,c Є M.

Definition 2.11: Let M be a partially Order Γ- Near ring, and A be a nonempty subset of M, then A is said to be Sub Ordered Γ- Near ring if
1) $x-y\in A$
2) $x\gamma y\in A$, for each $\gamma\in\Gamma$ and $x,y\in M$
3) $x\leq y$ then $x+g\leq y+g,\forall x,y,g\in M$
4) $x\leq y$ *and* $c\geq 0$ *then* $x\gamma c\leq y\gamma c,\ c\gamma x\leq c\gamma y,\ \forall x,y,c\in M$

Definition 2.12 : Let M be an Ordered Near ring and $\mu$ be a Fuzzy subset of M. We say that $\mu$ is an Fuzzy sub Ordered Near ring of M is

1. $\mu(x-y)\geq\min\{\mu(x),\mu(y)\}$
2. $\mu(x\gamma y)\geq\min\{\mu(x),\mu(y)\}$
3. $x\leq y\Rightarrow\mu(x)\geq\mu(y)$ for all $x,y\in M,\gamma\in\Gamma$

## III. L-FUZZY SUB ORDERED Γ-NEAR RING

In this paper, we introduce and study the concept of L – Fuzzy sub Ordered Γ - Near ring, where L is a complete lattice satisfying infinite meet distributive law. We prove that the homomorphic image and it's pre image of a L – Fuzzy sub Ordered Γ - Near ring is also a L – Fuzzy sub Ordered Γ - Near ring. Moreover we prove that homomorphic image and it's pre image of a L – Fuzzy sub Ordered Γ - Near ring with supermum property is a L – Fuzzy sub Ordered Γ - Near ring with Supermum property. Also, we prove that the intersection of two L – Fuzzy sub Γ - Near rings is also L – Fuzzy sub Γ - Near ring but the union of two L – Fuzzy sub Γ - Near rings is not a L –Fuzzy sub Γ - Near ring with suiable example

Definition 3.1: Let M be an Ordered Γ - Near ring and $\mu_L$ be a L – Fuzzy subset M. We say that $\mu_L$ is an L – Fuzzy sub Ordered Γ - Near ring of M if
1) $\mu_L(p-q)\geq\mu_L(p)\wedge\mu_L(q)$
2) $\mu_L(p\gamma q)\geq\mu_L(p)\wedge\mu_L(y)$
3) $p\leq q\Rightarrow\mu_L(p)\geq\mu_L(q)$ for all $p,q\in M,\gamma\in\Gamma$

Example 3.2 :Consider the additively abelian group $Z_6=\{0,1,2,3,4,5\}$ and $\Gamma=\{0,2,4\}$ Define a mapping from $Z_6\times\Gamma\times Z_6\to Z_6$ by $a\gamma b$ the usual product of $a,\gamma,b,\forall a,b\in M;\gamma\in\Gamma$ Then $Z_6$ is a $\Gamma$-Near ring. And clearly $Z_6$ is admiting a compatible relation "$\leq$" which is partial ordering on M satisfies the following conditions.

If $a\leq b$ *and* $c\leq d$ then
1) $a+c\leq b+d$
2) $a\gamma c\leq b\gamma d$
3). $c\gamma a\leq d\gamma b$;

for all $a,b,c,d\in M;\gamma\in\Gamma$
Hence $Z_6$ is an Ordered Γ- Near ring.
Now, we take a complete distributive lattice, $L=\{1,2,4\}$ with partial order $i\leq j$ define $\mu_6:Z_6\to L$ by

$$\mu(x)=\begin{cases}4 & \text{if } p=0\\ 1 & \text{if } p=0\end{cases}$$ Then $\mu_L$ is an L – Fuzzy sub Ordered Γ - Near ring of $Z_6$.

Theorem 3.3: Let M be an Ordered Γ - Near ring and $\mu_L$ be an L – Fuzzy subset of M. Then $\mu_L$ is an L – Fuzzy sub Ordered Γ - Near ring of M iff its level set $\mu_{L_t}$, $t\in L$ is a sub Ordered Γ- Near ring of M.

Proof : Let M be an Ordered Γ - Near ring and let $\mu_L$ be a L – Fuzzy subset of M, suppose $\mu_L$ is L – Fuzzy sub Ordered Γ - Near ring.

Claim : $\mu_{L_t}=\{p\in M/\mu_L(p)\geq t\}$ is a sub Ordered Γ - Near ring of M. Let $p,q\in\mu_{L_t}$ and $\gamma\in\Gamma$

$$\Rightarrow\mu_L(p)\geq t,\mu_L(q)\geq t$$
$$\mu_L(p-q)\geq\mu_L(p)\wedge\mu_L(q)$$
We have $\geq t$
Therefore $(p-q)\in\mu_{L_t}$

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$\mu_L(p\gamma q) \geq \mu_L(p) \wedge \mu_L(q)$

and $\geq t$

Therefore $p\gamma q \in \mu_{L_t}$

Proof is clear as $\mu_{L_t}$ admits partial Ordering.

Hence, $\mu_{L_t}$ is a sub Ordered $\Gamma$ - Near ring of M.

Conversely suppose $\mu_{L_t}$ is a sub Ordered $\Gamma$ - Near ring of M.

**Claim :** $\mu_L$ is a L – Fuzzy sub Ordered Γ - Near ring of M.

Let $p, q \in M$ *and* $\gamma \in \Gamma$ , put $t = \mu_L(p) \wedge \mu_L(q)$

Then $\mu_L(p) \geq t$ ; $\mu_L(q) \geq t$.

$\Rightarrow p, q \in \mu_{L_t}$

Since $\mu_{L_t}$ is a sub Ordered $\Gamma$ - Near ring of M. we Have $p - q \in \mu_{L_t}$ *and* $p\gamma q \in \mu_{L_t}$.

Now

$p - q \in \mu_{L_t} \Rightarrow \mu_L(p-q) \geq t$

$\Rightarrow \mu_L(p-q) \geq (\mu_L(p) \wedge \mu_L(q))$ *and*

$p\gamma q \in \mu_{L_t} \Rightarrow \mu_L(p\gamma q) \geq t$

$\Rightarrow \mu_L(p\gamma q) \geq (\mu_L(p) \wedge \mu_L(q))$

Let $p \leq q$ .Suppose if possible $\mu_L(p) < \mu_L(q)$

Then there exist $t_1 \in L$ such that $\mu_L(p) < t_1 < \mu_L(q)$

Then $q \in \mu_{L_{t_1}}$ *and* $p \notin \mu_{L_{t_1}}$ which is a contradiction

Therefore $\mu_L(p) \geq \mu_L(q)$

Thus $\mu_L$ is an L-Fuzzy sub Ordered Γ - Near ring of M

Theorem 3.4 : Let M be a Ordered Γ-Near ring. Let $\mu_L$ *and* $\sigma_L$ be two L – Fuzzy sub ordered Γ - Near ring of M. Then $\mu_L \cap \sigma_L$ is also a L – Fuzzy sub Ordered Γ-- Near ring of M.

Proof : Let $p, q \in M; \gamma \in \Gamma$.

1. $(\mu_L \cap \sigma_L)(p-q) = \{\mu_L(p-q) \wedge \sigma_L(p-q)\}$
$\geq \{\mu_L(p) \wedge \mu_L(q)\} \wedge \{\sigma_L(p) \wedge \sigma_L(q)\}$
$= \{\mu_L(p) \wedge \sigma_L(p)\} \wedge \{\mu_L(q) \wedge \sigma_L(q)\}$
$= \{\mu_L \cap \sigma_L\}(p) \wedge \{\mu_L \cap \sigma_L\}(q)$

2. $(\mu_L \cap \sigma_L)(p\gamma q) = \{\mu_L(p\gamma q) \wedge \sigma_L(p\gamma q)\}$
$\geq \{\mu_L(p) \wedge \mu_L(q)\} \wedge \{\sigma_L(p) \wedge \sigma_L(q)\}$
$= \{\mu_L(p) \wedge \sigma_L(p)\} \wedge \{\mu_L(q) \wedge \sigma_L(q)\}$
$= \{\mu_L \cap \sigma_L\}(p) \wedge \{\mu_L \cap \sigma_L\}(q)$

3. *If* $p \leq q$ *then* $\mu_L(p) \geq \mu_L(q)$ *and* $\sigma_L(p) \geq \sigma_L(q)$
$(\mu_L \cap \sigma_L)(p) = \{\mu_L(p) \wedge \sigma_L(p)\}$
$\geq \{\mu_L(q) \wedge \sigma_L(q)\} = (\mu_L \cap \sigma_L)(q)$

Thus $\mu_L \cap \sigma_L$ is a L – Fuzzy sub Ordered Γ- Near ring of M

In general union of two L – Fuzzy sub Ordered Γ-Near rings may not be L – Fuzzy sub Ordered Γ - Near ring

Example 3.5: Consider the additive abelian groups $Z_4 = \{0,1,2,3\}$ *and* $\Gamma = \{0,2\}$

Define $Z_4 \times \Gamma \times Z_4 \to Z_4$ by $a\gamma b$ usual product of $a, \gamma, b$, $\forall a, b \in M; \gamma \in \Gamma$.. Then $Z_4$ is an Ordered Γ-Near ring.

Take $L = [0,1]$ Define

$\mu_L : Z_4 \to [0,1]$ *and* $\sigma_L : Z_4 \to [0,1]$ by

$\mu_L(p) = 0.8$ *if* $p = 0$
$0.6$ *if* $p = 1$
$0.4$ *otherwise*

And

$\sigma_L(p) = 0.6$ *if* $p = 0$
$0.5$ *if* $p = 2$
$0.2$ *otherwise*

Then $\mu_L$ *and* $\sigma_L$ are L – Fuzzy sub Ordered Γ- Near rings of $Z_4$.

But $\mu_L \cup \sigma_L$ is not a L – Fuzzy sub Ordered Γ- Near ring.

In particular we have the following

Theorem 3.6: Let M be an Ordered $\Gamma$ - Near ring. Let $\mu_L$ and $\sigma_L$ be two L – Fuzzy sub Ordered $\Gamma$ - Near rings of M.

Then $\mu_L \cup \sigma_L$ is also a L- Fuzzy sub Ordered $\Gamma$ – Near ring of M if $\mu_L \subseteq \sigma_L$ *or* $\sigma_L \subseteq \mu_L$.

Proof : Let M be a Ordered $\Gamma$ -Near ring .

Let $\mu_L$ *and* $\sigma_L$ be two L – Fuzzy sub Ordered $\Gamma$ - Near rings of M, Suppose $\mu_L \subseteq \sigma_L$

Let $p, q \in M; \gamma \in \Gamma$

1. $(\mu_L \cup \sigma_L)(p-q) = \{\mu_L(p-q) \vee \sigma_L(p-q)\}$
$= \sigma_L(p-q)$
$\geq \{\sigma_L(p) \wedge \sigma_L(q)\}$
$= \{\mu_L(p) \vee \sigma_L(p)\} \wedge \{\mu_L(q) \vee \sigma_L(q)\}$
$= \{\mu_L \cup \sigma_L\}(p) \wedge \{\mu_L \cup \sigma_L\}(q)$

2. $(\mu_L \cup \sigma_L)(p\gamma q) = \{\mu_L(p\gamma q) \vee \sigma_L(p\gamma q)\}$
$= \sigma_L(p\gamma q)$
$\geq \{\sigma_L(p) \wedge \sigma_L(q)\}$
$= \{\mu_L(p) \vee \sigma_L(p)\} \wedge \{\mu_L(q) \vee \sigma_L(q)\}$
$= \{\mu_L \cup \sigma_L\}(p) \wedge \{\mu_L \cup \sigma_L\}(q)$

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3.If $p \le q$ then $\mu_L(p) \ge \mu_L(q)$ and $\sigma_L(p) \ge \sigma_L(q)(\mu_L \cup \sigma_L)(p) = \{\mu_L(p) \vee \sigma_L(p)\}$
$= \{\sigma_L(p) \vee \sigma_L(p)\}$
$= \sigma_L(p) \ge \sigma_L(q) = \{\mu_L(q) \vee \sigma_L(q)\} = (\mu_L \cup \sigma_L)(q)$

Thus $\mu_L \cup \sigma_L$ is a L – Fuzzy sub Ordered $\Gamma$ - Near ring.
Similarly, if $\sigma_L \subseteq \mu_L$, we get $\mu_L \cup \sigma_L$ is a L – Fuzzy sub Ordered $\Gamma$ - Near ring.

Theorem 3.7: Let M be an Ordered $\Gamma$ - Near ring. Let $\mu_L$ be

L – Fuzzy sub Ordered $\Gamma$ - Near ring on M.
Define $\mu_L$ on $M \cup \{0\}$

by $\mu_L = \{p \in M / \mu_L(p) = \mu_L(0)\}$
Then $\mu_L$ is a sub Ordered $\Gamma$ - Near ring on M.

Proof : Let $\mu_L$ be a L – Fuzzy sub Ordered $\Gamma$ - Near ring on

M. Let

$$p, q \in \mu_L \Rightarrow \mu_L(p) = \mu_L(0) \text{ and } \mu_L(q) = \mu_L(0)$$

$$1.\ \mu_L(p-q) \ge \{\mu_L(p) \wedge \mu_L(q)\}$$
$$= \{\mu_L(0) \wedge \mu_L(0)\}$$
$$= \mu_L(0)$$
$$\Rightarrow p - q \in \mu_L$$
$$2.\ \mu_L(p\gamma q) \ge \{\mu_L(p) \wedge \mu_L(q)\}$$
$$= \{\mu_L(0) \wedge \mu_L(0)\}$$
$$= \mu_L(0)$$
$$\Rightarrow p\gamma q \in \mu_L$$

Since $\mu_L$ be an L – Fuzzy sub Ordered $\Gamma$ - Near ring on M,

where M is an ordered $\Gamma$ - Near ring, for every $p, q \in \mu_L, \mu_L$ admits partial ordering. Thus $\mu_L$ is a sub

Ordered $\Gamma$ - Near ring on M.

Theorem 3.8: Let M be an ordered $\Gamma$ - Near ring. If $\mu_L$ is a

L – Fuzzy subset of M then two level subset $\mu_{Ls}$ and $\mu_{Lt}$ with $(s < t \text{ in } L)$ of $\mu_L$ are equal if and only of there is no

$p \in M$ such that $s \le \mu_L(p) \le t$.
Proof: Let $\mu_L$ is an L – Fuzzy subset of M. Suppose there

exists no $p \in M$ such that $s \le \mu_L(p) \le t$

Now, we have to prove that $\mu_{Ls} = \mu_{Lt}$. Assume that $\mu_{Ls} f = \mu_{Lt}$

Let $p \in \mu_{Ls} p \notin \mu_{Lt}$
$\Rightarrow \mu_L(p) \ge s$ and $\mu_L(p) < t$
$\Rightarrow s \le \mu_L(p) < t$

Which is a contradiction to our supposition. Therefore $\mu_{Ls} = \mu_{Lt}$
Conversely suppose $\mu_{Ls} = \mu_{Lt}$
Now we have to prove that there exists no $p \in M$ such that $s \le \mu_L(p) \le t$, Assume that
There exists $p \in M$ such that $s \le \mu_L(p) \le t$
$\Rightarrow \mu_L(p) \ge s$ and $\mu_L(p) \le t$
$\Rightarrow p \in \mu_{Ls}$ and $p \notin \mu_{Lt}$
$\Rightarrow \mu_{Ls} f = \mu_{Lt}$.

Which is a contradiction to our supposition.
Hence there exists no $p \in M$ such that $s \le \mu_L(p) \le t$
Theorem 3.9: An Ordered $\Gamma$ - Near ring homomorphic pre – image of a L – Fuzzy sub Ordered $\Gamma$ - Near ring is a L – Fuzzy sub Ordered $\Gamma$ - Near ring.

Proof : Let $f : M \to N$ be a $\Gamma$ - Near ring homomorphism. Let $\sigma_L$ be a L – Fuzzy sub Ordered $\Gamma$ -

Nearing of N and let $\mu_L$ be the pre – image of $\sigma_L$ under 'f'.

Now, we have to prove that $\mu_L$ is L – Fuzzy sub

Ordered $\Gamma$ - Near ring of M under 'f'. Then,

$$\mu_L(p-q) = \sigma_L(f(p-q))$$
$$= \sigma_L(f(p) - f(q))$$
$$\ge \sigma_L(f(p) \wedge f(q))$$
$$= \sigma_L(f(p)) \wedge \sigma_L(f(q))$$
$$= \mu_L(p) \wedge \mu_L(q)$$

*Therefore* $\mu_L(p-q) \ge \mu_L(p) \wedge \mu_L(q)$ *again,*

$$\mu_L(p\gamma q) = \sigma_L(f(p\gamma q))$$
$$\ge \sigma_L(f(p) \wedge f(q))$$
$$= \sigma_L(f(p)) \wedge \sigma_L(f(q))$$
$$= \mu_L(p) \wedge \mu_L(q)$$

*Therefore* $\mu_L(p\gamma q) \ge \mu_L(p) \wedge \mu_L(q)$ *If* $p \le q$ *then*

$$\mu_L(p) = \sigma_L(f(p)) \ge \sigma_L(f(q))$$
$$= \mu_L(q).$$

Therefore $\mu_L(p) \ge \mu_L(q)$

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# On Homomorphism of Vague Ordered Gamma-Near rings

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**Abstract**

***In this paper, we define Vague homomorpism on Ordered $\Gamma-$ Near ring and prove that homomorphic image and inverse homomorphic image of vague Ordered $\Gamma-$ Nearring is again vague Ordered $\Gamma-$ Nearring.***

***Keywords :*** *Vague set, Vague Ordered $\Gamma-$ Near ring, Vague homomorphism.*
***Mathematics Subject Classification :*** *08A72, 20N25,03E72.*

## 1. Introduction

The theory of fuzzy $\Gamma-$ Near rings has been developed by Bh. Satyanarayana [1] and G.L. Booth. Later W.L.Gau and D.J. Buehrer [19] introduced the theory of vague sets as an improvement of the theory of fuzzy sets in approximating the real life situation. Vague sets are higher order fuzzy sets. According to them a vague set A in the universe of discourse U is a pair $(t_A, f_A)$ , where $t_A$ *and* $f_A$ are fuzzy subsets of U satisfying $t_A(u) + f_A(u) \leq 1, \forall u \in U$ . Later several authors had studied and applied fuzzy sets and vague sets on various algebraic structures like semi rings, semi groups,...etc. Further, by taking, the above as origin S.Ragamayi [ 20] has developed Vague Normal $\Gamma-$ Near rings in her doctorial thesis.

Furthermore K. Balakoteswara rao [2] had introduced and applied the concepts of Fuzzy sets and vague sets on " Ordered $\Gamma-$ Near ring". As a sequel of our work, now we define homomorphism on vague Ordered $\Gamma-$ Near rings. In this article, we prove that homomorphic image and inverse homomorphic image of vague Ordered $\Gamma-$ Nearring is again vague Ordered $\Gamma-$ Nearring. Also, we prove that homomorphic image and inverse homomorphic image of a vague Ordered $\Gamma-$ Nearring possessing supremum property is again vague Ordered $\Gamma-$ Nearring with supremum property .

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## 2. PRELIMINARIES

**Definition 2.1 :** A zero – symmetric $\Gamma$ – Near ring is a trip[le $(M,+,\Gamma)$, where
1. $(M,+)$ is a group
2. $\Gamma$ is a non – empty set of binary operators on M such that for each $\alpha \in \Gamma, (M,+,\alpha)$ is a near ring.
3. $x \in (y\beta z) = (x\alpha y)\beta z$, for all $x,y,z \in M$ and $\alpha,\beta \in \Gamma$.
4. $x\alpha 0 = 0$ for every $x \in M, \alpha \in \Gamma$.

**Definition 2.2 :** Let M be a $\Gamma$ – Near ring and A be a nonempty of M then A is said to be sub $\Gamma$ – Near ring if
1. $x - y \in A$
2. $x\alpha y \in A$, for each $\alpha \in \Gamma$ and $x,y \in M$.

**Definition 2.3 :** Let M be a $\Gamma$ – Near ring and $\mu$ be a Fuzzy subset of M. We say that $\mu$ is a Fuzzy sub $\Gamma$ – Near ring of M If
1. $\mu(x-y) \geq \min\{\mu(x),\mu(y)\}$
2. $\mu(x\alpha y) \geq \min\{\mu(x),\mu(y)\}$ for $x,y \in M, \alpha \in \Gamma$

**Definition 2.4 :** A vague set A in the universe of discourse U is a pair $(t_A, f_A)$, where $t_A : U \to [0,1], f_A : U \to [0,1]$ are mappings such that $t_A(u) + f_A(u) \leq 1, \forall u \in U$ .The functions $t_A$ *and* $f_A$ are called true membership function and false membership function respectively.

**Definition 2.5 :** The interval $[t_A(\mu), 1 - f_A(u)]$ is called the vague value of u in A and it is denoted by $V_A(\mu)$ i.e., $V_A(\mu) = [t_A(u), 1 - f_A(u)]$.

**Definition 2.6 :** A vague sets A is contained order vague set $B, A \subseteq B$ if and only if $V_A(u) \leq V_B(u)$ i.e., $t_A(u) \leq t_B(u)$ and $1 - f_A(u) \leq 1 - f_B(u), \ni u \in U$

**Definition 2.7 :** Two vague sets A and B are equal written as $A = B$. If and only if $A \subseteq B$ and $B \subseteq A$ i.e., $V_A(u) \leq V_B(u)$ and $V_B(u) \leq V_A(u), \forall u \in U$

**Definition 2.8 :** The union of two vague sets A and B with respective truth member ship and false membership function $t_A, f_A : t_B, f_B$ is a vague set S, written as $C = A \cup B$, whose truth membership and false membership functions are related to those of A and B by $t_C = \max\{t_A, t_B\}$ ; $1 - f_C = \max\{1 - f_A, 1 - f_B\} = 1 - \min\{f_A, f_B\}$.

**Definition 2.9 :** The intersection of two vague sets A and B with respective truth membership and false membership functions $t_A, f_A : t_B, f_B$ is a vague set C, written as $C = A \cap B$, whose truth membership and false membership functions are related to those of A and B by $t_C = \min\{t_A, t_B\}$ ; $1 - f_C = \min\{1 - f_A, 1 - f_B\} = 1 - \max\{f_A, f_B\}$

**Definition 2.10 :** The union and intersection of a family $\{A_i / i \in \Delta\}$ of vague sets of a set U are defined by
$V \bigcup_{i \in \Delta} A_i(u) = \sup_{i \in \Delta} V_{A_i}(u), \forall u \in U$
$V \bigcap_{i \in \Delta} A_i(u) = \inf_{i \in \Delta} V_{A_i}(u), \forall u \in U$

**Definition 2.11 :** A vague set A of a set U with $t_A(u) = 0$ and $f_A(u) = 1, \forall u \in U$ is called zero vague set of U.

**Definition 2.12 :** A vague set A of set U with $t_A(u) = 1$ and $f_A(u) = 0, \forall u \in U$ is called unit vague set of U.

**Definition 2.13 :** Let A be a vague set of a universe U with true membership function $t_A$ and false membership function $f_A$. For $\alpha, \beta \in [0.1]$ with $\alpha \leq \beta$, the $(\alpha, \beta)$ cut or vague cut of a vague set A is the crisp subset of U is given by
$A_{(\alpha,\beta)} = \{x \in U / V_A(x) \geq [\alpha, \beta]\}$ i.e., $A_{(\alpha,\beta)} = \{x \in U / t_A(x) \geq \alpha \text{ and } 1 - f_A(x) \geq \beta\}$

**Definition 2.14 :** The $\alpha-$ cut, $A_\alpha$ of the vague set A is the $(\alpha,\alpha)$ - cut of A and hence given by $A_\alpha=\{x\in U / t_A(x)\geq\alpha\}$

**Definition 2.15 :** A vague set $A=(t_A,f_A)$ of M is said to be vague $\Gamma-$ Near ring if $p,q\in M;\ \alpha\in\Gamma$

$V_A(p-q)\geq\min\{V_A(p),V_A(q)\}$ *and*

$V_A(p\alpha q)\geq\min\{V_A(p),V_A(q)\}$

*i.e.,*

$(i).\ t_A(p-q)\geq\min\{t_A(p),t_A(q)\}$

$1-f_A(p-q)\geq\min\{1-f_A(p),1-f_A(q)\}$ *and*

$1-f_A(p\alpha q)\geq\min\{1-f_A(p),f_A(q)\}.$

**Definition 2.16 :** A $\Gamma-$ Near ring M is called an ordered $\Gamma-$ Near ring if it admits a compatible relation "$\leq$ " is a partial ordering on M satisfies the following conditions. If $a\leq b$ and $c\leq d$ then

$(i)\ a+c\leq b+d$

$(ii)\ a\gamma c\leq b\gamma d$

$(iii)\ c\gamma a\leq d\gamma b;$ *for all* $a,b,c,d\in M;\gamma\in\Gamma$

**Definition 2.17 :** Let M be a partially Ordered $\Gamma-$ Near ring and A be a nonempty subset of M then A is said to be sub Ordered $\Gamma-$ Near ring if

*i)* $x-y\in A$

*ii)* $x\gamma y\in A$ *for each* $\gamma\in\Gamma$ *and* $x,y\in M$

*iii)* $x\leq y$ *then* $x+g\leq y+g,\forall x,y,g\in M$

*iv)* $x\leq y$ *and* $c\geq 0$ *then* $y\gamma c$ *and* $c\gamma c$ *and* $c\gamma x\leq c\gamma y,\ \forall x,y,c\in M$

**Definition 2.18 :** Let M be an Ordered Near ring and $\mu$ be a Fuzzy subset of M. We say that $\mu$ is an Fuzzy sub Ordered Near ring Of M if

1) $\mu(x-y)\geq\min\{\mu(x),\mu(y)\}$

2) $\mu(x\gamma y)\geq\min\{\mu(x),\mu(y)\}$

3) $x\leq y\Rightarrow\mu(x)\geq\mu(y)$ *for all* $x,y\in M,\gamma\in\Gamma$

**Notations : Throught out the following section, we use the following notations.**

1. **OGNR** stands for Ordered $\Gamma-$ Near ring.
2. **M** stands for Zero – Symmetric Ordered $\Gamma-$ Near ring.
3. **GNR** stands for $\Gamma-$ Near ring.

## 3. Main Results

Hakimuddin khan, Musheer Ahmad and Rajit Biswas[4] had introduced the concept of vague homomorphism in groups. Taking the above as origin,In this section, we introduce and study the concept of vague homomorphism of a Ordered GNR. We prove that a homomorphic image and an inverse homomorphic image of a vague OGNR of M are also vague OGNRs of M. Also, we define homomorphic image and it's pre-image of a vague OGNR of M possessing supermum property is also a vague OGNR of M possessing supermum property.

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**Definition 3.1 :** Let M and N be two Ordered $\Gamma-$Near rings. Let $f$ be a mapping from a set M into a set N. Let A be a vague set in M with vague value $V_A$. Then the image of A, $f(A)$ is the vague set in N is defined by

$$V_{f(A)(q)} = \begin{cases} \sup\limits_{r\in f^{-1}(q)} V_A(r) & \text{if } f^{-1}(q)\neq\phi \\ [0,0] & \text{otherwise} \end{cases}$$

For all $q\in N$, where $f^{-1}(q)=\{p/f(p)=q\}$

Let B be a vague set in N. Then the image of B, $f^{-1}(B)$ is the vague set in M by
$V_{f^{-1}(B)}(p)=V_B(f(p)),\forall p\in M$

**Definition 3.2 :** A vague set A of an OGNR M is said to have the Sup. Property if for any subset S of M, there exists $p_0\in S$ such that $V_A(p_0)=\sup\limits_{p\in S}V_A(p)$

**Theorem 3.3:** Let $M_1$ be an Ordered $\Gamma-$ Near ring and $M_2$ be an Ordered $\Gamma_2-$ Near ring and let $f$ be a homomorphism of $M_1$ *to* $M_2$. If B is a vague Ordered $\Gamma_2-$Near ring of $M_2$, then the inverse of B, $f^{-1}(B)$ is a vague Ordered $\Gamma_1-$ Near ring of $M_1$

Proof: For all $p,q\in M_1;\gamma_1\in\Gamma$,

1. $$\begin{aligned} V_{f^{-1}(B)}(p-q) &= V_B(f(p-q)) \\ &= V_B(f(p)-f(q)) \\ &\geq \min\{V_B(f(p)),V_B(f(q))\} \\ &= \min\{V_{f^{-1}(B)}(p),V_{f^{-1}(B)}(q)\} \end{aligned}$$

2. $$\begin{aligned} V_{f^{-1}(B)}(p\gamma_1 q) &= V_B(f(p\gamma_1 q)) \\ &= V_B(f(p)g(\gamma_1)f(q)) \\ &\geq \min\{V_B(f(p)),V_B(f(q))\} \\ &= \min\{V_{f^{-1}(B)}(p),V_{f^{-1}(B)}(q)\} \end{aligned}$$

3. *If* $p\leq q$ *then* $$\begin{aligned} V_{f^{-1}(B)}(p) &= V_B(f(p)) \\ &\geq V_B(f(q)) \\ &= V_{f^{-1}(B)}(q) \end{aligned}$$

Hence $f^{-1}(B)$ is a vague Order $\Gamma_1-$ Near ring on $M_1$.

**Theorem 3.4 :** $M_1$ be an Ordered $\Gamma-$ Near ring and $M_2$ be an Ordered $\Gamma_2-$ Near ring and let $f$ be a homomorphism of $M_1$ *onto* $M_2$. If A is a vague Ordered $\Gamma-$ Near ring of $M_1$ with Supermum property, then the homorphic image of A, $f(A)$ is a vague Ordered $\Gamma_2-$ Near ring of $M_2$.

Proof : Let $p,q\in M_2;\gamma_2\in\Gamma_2$

Neither $f^{-1}(p)$ *nor* $f^{-1}(q)$ is empty, since f is onto;

Let $p_0\in f^{-1}(p)$ *and* $q_0\in f^{-1}(q)$ be such that

$V_A(p_0)=SupV_A(\alpha)$ *where* $\alpha\in f^{-1}(p)$

*and* $V_A(q_0)=SupV_A(b)$ *where* $b\in f^{-1}(q)$.

Then

$$1.\ V_{f(A)}(p-q)=\sup_{r\in f^{-1}(p-q)} V_A(r)$$
$$\geq V_A(r), r\in f^{-1}(p-q)$$
$$=V_A(p_0-q_0)$$
$$\geq \min\{V_A(p_0),V_A(q_0)\}$$
$$=\min\{V_{f(A)}(p),V_{f(A)}(q)\}$$

$$2.\ V_{f(A)}(p\gamma_2 q)=\sup_{r\in f^{-1}(p\gamma_2 q)} V_A(r)$$
$$\geq V_A(r), r\in f^{-1}(p\gamma_2 q)$$
$$=V_A(p_0\gamma_1 q_0), \gamma_1\in\Gamma_1$$
$$\geq \min\{V_A(p_0),V_A(q_0)\}$$
$$=\min\{V_{f(A)}(p),V_{f(A)}(q)\}$$

$$3.\ For\ p\leq q\ then\ V_{f(A)}(p)=\sup_{r\in f^{-1}(p)} V_A(r)$$
$$\geq V_A(r), r\in f^{-1}(p)$$
$$=V_A(p_0)$$
$$\geq V_A(q_0)$$
$$=V_{f(A)(q)}.$$

Hence $f(A)$ is a vague Ordered $\Gamma_2$ − Near ring of $M_2$

**Definition 3.5 :** Let $A=(t_A,f_A)$ *and* $B=(t_B,f_B)$ be vague OGNRs of M. If there exists $\phi\in Aut(M)$ such that $V_A(p)=V_B(\phi(p)),\forall p\in M$ *i.e.,* $t_A(p)=t_B(\phi(p))$ *and* $f_A(p)=f_B(\phi(p))$, then we say that A and B are homologous vague OGNRs of M. Clearly, if A and B are homologous, then B and A are also homologous.

**Theorem 3.6 :** Let $B=(t_B,f_B)$ be a vague OGNR of M and $\phi\in Aut(M)$. If $A=(t_A,f_A)$ is a vague set of M such that $V_A(p)=V_B(\phi(p)),\forall p\in M$, then A and B are homologous vague OGNRs of M.

Proof : Let $p,q\in M;\gamma_1\in\Gamma$

$$1.\ V_A(p-q)=V_B(\phi(p-q))$$
$$=V_B(\phi(p)-\phi(q))$$
$$\geq \min\{V_B(\phi(p)),V_B(\phi(q))\}$$
$$=\min\{V_A(p),V_A(q)\}$$

$$2.\ V_A(p\gamma_1 q)=V_B(\phi(p\gamma_1 q))$$
$$=V_B(\phi(p)\gamma_1\phi(q))$$
$$\geq \min\{V_B(\phi(p)),V_B(\phi(q))\}$$
$$=\min\{V_A(p),V_A(q)\}$$

$$3.\ For\ p\leq q\ then\ V_A(p)=V_B(\phi(p))$$
$$\geq V_B(\phi(q))$$
$$=V_A(q)$$

Therefore A is a vague OGNR of M.
Hence A and B are homologous vague OGNR of M.

**Theorem 3.7 :** Let $A=(t_A,f_A)$ be a vague OGNR of M and let $f:M\to M$ be an onto homomorphism. Then the vague set $A^f=(t_{A^f},f_{A^f})$ define by $V_{A^f}(p)=V_A(f(p)),\forall p\in M$ is a vague OGNR of M.

Proof : Let

$$1.\ V_{A^f}(p-q)=V_A(f(p-q))$$
$$=V_A(f(p)-f(q))$$
$$\geq \min\{V_B(f(p)),V_B(f(q))\}$$
$$=\min\{V_{A^f}(p),V_{A^f}(q)\}$$
$$2.V_{A^f}(p\gamma_1 q)=V_B(f(p\gamma_1 q))$$
$$=V_B(f(p)\gamma_1 f(q))$$
$$\geq \min\{V_A(f(p)),V_A(f(q))\}$$
$$=\min\{V_{A^f}(p),V_{A^f}(q)\}$$

3. *For* $p\leq q$ *then* $V_{A^f}(p)=V_B(f(p))$
$$\geq V_A(f(q))$$
$$=V_{A^f}(q)$$

Hence $A^f$ is a vague OGNR of M.

## 4. Conclusions

In this paper, we developed Vague homomorphism on Ordered GNR and proved that the homomorphic image of a Vague Ordered GNR of M is also a Vague Ordered GNR of M. Also, pre- homomorphic image of a Vague Ordered GNR of M is also a Vague Ordered GNR of M.

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# Enhanced red luminescent PBTNAEu glasses for solid state lasers

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ABSTRACT

The luminescence characteristics of $Eu^{3+}$ activated 30 PbO+(50–*x*) $B_2O_3$+5 $TeO_2$+10 NaF+5 $AlF_3$+*x* $EuF_3$ (PBTNAEu) glasses prepared by melt-quenching process were studied for red laser applications. The phonon-side band mechanism of $Eu^{3+}$: $^5D_2$ emission state was discussed with the help of photoluminescence excitation and the Raman spectral features. The Judd-Ofelt intensity parameters that will be used to evaluate various laser characteristic parameters were determined from both the absorption and the emission spectra. The absorption from $^7F_0$ ground and $^7F_1$ first excited states was considered by applying the thermal correction. The emission spectra were used to study the luminescence enhancement and the asymmetric environment around the $Eu^{3+}$ ions. The quantum efficiency of emitted luminescence was determined from the experimental and radiative decay times of $^5D_0$ emission state. From the experimental results, it was suggested that the PBTNAEu glass containing 2.0 mol% of $EuF_3$ has more potentiality for red laser applications.

## 1. Introduction

The oxyfluoride based glasses activated with trivalent rare earth (RE) ions have drawn much attention as optoelectronic devices (such as switching, memory and sensor devices), solid state lasers (like visible and infrared lasers), optical amplifiers (like fiber and waveguide amplifiers), efficient dielectrics and infrared to visible converters owing to their widespread inhomogeneous band-widths, huge quantity of RE ion solubility, high thermal stability, good glass forming tendency and high quantum efficiency compared to other conventional glasses [1,2]. It is clear that the luminescence intensity and its efficiency depend greatly on the ligand environment in the vicinity of RE ions. Thus, the glassy materials with considerably low phonon energy, least $OH^-$ content, relatively high thermal stability and prolonged chemical durability are more favourable to develop potential solid-state lasers to achieve the requirements of present advanced technology in eco-friendly way [3,4].

The studied 30 PbO+50 $B_2O_3$+5 $TeO_2$+10 NaF+5 $AlF_3$ (PBTNA) glass has high-quality glass forming tendency, considerably high thermal stability, relatively large rigidity, low $OH^-$ content and low phonon energy (1005 $cm^{-1}$) [5]. The inclusion of little quantities of impurities for example network modifiers and alkali ions to the network of borate avoid the multi-phase formation by modifying the $BO_3$ units as $BO_4$ units. The absorption spectral profile indicates that they are transparent to UV–Vis–NIR regions. The optical band gap energy of undoped PBTNA glass is found nearly 2.642 eV and it decrease gradually with the addition of RE impurities creating additional quantum states thereby to structural modifications. These key results initiated to search the applicability of $Eu^{3+}$ -doped PBTNAEu glasses as visible and fiber lasers to meet the requirements of industrial, medical, science and engineering applications.

The trivalent europium ($Eu^{3+}$) ions have been used as the best choice to produce intense red emission through $^5D_0 \rightarrow {}^7F_2$ transition as well as a good spectroscopic probe to study the asymmetry of the host environment in its vicinity where it presents [6]. The non-degenerate $^7F_0$ and $^5D_0$ energy states and fairly simple energy level structure of $Eu^{3+}$ ions facilitates to investigate the site to site structural modifications. Particularly, the $Eu^{3+}$ -doped glassy materials find wide range of applications as lasers, display devices and white LEDs [7–9]. The luminescence properties of different concentrations of $Eu^{3+}$ ions in different multi-component host matrices such as $TeO_2{\cdot}WO_3.GeO_2$ [10], $PbF_2{\cdot}TeO_2{\cdot}H_3BO_3$ [11], $PbF_2{\cdot}WO_3{\cdot}TeO_2$ [12], (Li, Na, K) $F{\cdot}PbO{\cdot}TeO_2{\cdot}H_3BO_3$ [13] and $PbO{\cdot}H_3BO_3{\cdot}TiO_2{\cdot}AlF_3$ [14] were reported for visible lasers. The present host glass has been designed with high thermal stability and good glass forming tendency with easy fiber

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drawing compared to our previous work [10–14].

The present research work reports the structural, spectroscopic and optical analysis of various amounts of $EuF_3$ -doped PBTNAEu glasses for red laser applications. The Judd and Ofelt (J-O) model [15,16] was applied to evaluate different radiative and laser characteristic parameters. The phonon side band mechanism, luminescence decay, non-radiative multi-phonon relaxation rates were discussed in detail. The suitability of studied glasses for laser applications was also explored.

## 2. Experimental techniques

The $Eu^{3+}$ -activated lead-borate based oxyfluoride glasses: 30 PbO+ (50–$x$) $B_2O_3$+5 $TeO_2$+10 NaF+5 $AlF_3$+$x$ $EuF_3$ (PBTNAEu), where $x = 0$, 1.0, 2.0 and 5.0 mol%, were prepared through melt quenching method. PbO of assay 98.0% from Himedia, $H_3BO_3$ of assay ≥99.5% from Merk, $TeO_2$ of assay ≥99% from Sigma Aldrich, NaF of assay ≥97% from Merk, $AlF_3$ of assay 97% from Sigma Aldrich and $EuF_3$ of assay ≥99.9% from Alfa aesar were used as starting materials. About 20 g batches of homogeneous powders of starting chemicals were used to prepare the studied glasses and they were named as PBTNAEu0, PBTNAEu1, PBTNAEu2 and PBTNAEu5 glasses for $x = 0$, 1.0, 2.0 and 5.0 mol%, respectively. The prepared glass samples were polished for optical quality with 0.16 ± 0.01 cm thickness and they were used for further characterizations. The details of method of preparation and estimation of significant basic properties were explored in our earlier work [5].

The X-ray diffraction (XRD) profiles were obtained with RIGAKU (Miniflex-600) X-ray diffractometer using $\lambda_{CuK\alpha} = 1.5406$ Å. The KBr technique Fourier transforms infrared (FTIR) spectral patterns were obtained on PerkinElmer Spectrum One: FT-IR Spectrometer. The Raman analysis was carried out on HORIBA LAB-RAM HR MICRO-RAMAN Spectrometer. The scanning electron microscope and energy dispersive X-ray (SEM-EDX) analysis was carried out on VEGA3 TESCAN equipped with BrukerEasy EDS instrument. The optical absorption investigations were done on PerkinElmer Lambda 950 spectrophotometer. The excitation and emission spectral measurements were recorded with Hitachi-F7000 Fluorescence spectrophotometer. The lifetime of $Eu^{3+}$: $^5D_0$ emission state was carried out using JOBIN YVON FLUOROLOG-3 fluorimeter provided with xenon flash lamp and photomultiplier tube (PMT) as a detector. The experimental quantum yield (QY) was measured with Edinburgh FLS 980 spectrometer equipped with an integrating sphere. All the spectral measurements were executed at normal temperature.

## 3. Results and discussion

### 3.1. Basic properties

The doping of different amounts of $EuF_3$ to the PBTNAEu glasses leads considerable changes in some of their physical and optical properties due to the structural modifications around the $Eu^{3+}$ ions and they are evaluated following our previous work [**5**] and summarized in Table 1. The density (ρ), index of refraction (n), average-molecular weight ($\overline{M}$) and molar-volume ($V_m$) increases with increase of $EuF_3$ content as illustrated in Fig. 1. The reflection losses are found to be 5.00 ± 0.02% showing high transparency for the studied glasses.

### 3.2. Structural analysis

The powder XRD and FTIR patterns of PBTNAEu2 glass are presented in Fig. 2. The absence of sharp crystalline peaks and the presence of broad band in the 2θ ranges from 10° to 35° (see Fig. 2a) confirm the glassy nature of studied glasses. The FTIR spectral features shown in Fig. 2b are identical to that of undoped PBTNA glasses [5]. This spectrum reveals the presence of various vibrational modes occurs in PBTNAEu glasses. The assignment of these bands has been done following the literature [ [17–19] and they are summarized in Table 2.

**Table 1**
Comparison of density (ρ±0.01 g/cm$^3$), refractive index (n±0.001), $Eu^{3+}$ ions concentration (N±0.02 × $10^{-20}$ ions/cm$^3$), dielectric constant (K±0.01) reflection losses (R±0.02), average molecular weight ($\overline{M}$± 0.05), molar volume ($V_m$±0.02) and optical band gap energy ($E_g$±0.01) of PBTNAEu glasses.

| Property | PBTNAEu0 | PBTNAEu1 | PBTNAEu2 | PBTNAEu5 |
|---|---|---|---|---|
| ρ | 5.42 | 5.46 | 5.51 | 5.64 |
| n | 1.540 | 1.562 | 1.575 | 1.592 |
| N | – | 2.36 | 4.70 | 11.69 |
| K | 2.37 | 2.44 | 2.48 | 2.53 |
| R (%) | ~5.00 | ~5.00 | ~5.00 | ~5.00 |
| $\overline{M}_{(g)}$ | 118.14 | 119.54 | 120.93 | 125.12 |
| $V_m$ (cm$^3$) | 21.78 | 21.91 | 21.96 | 22.17 |
| $E_g$ (eV) | 2.642 | 2.627 | 2.298 | 2.004 |

The Raman analysis is one of the important spectroscopic tools for identifying the existence of various molecular groups and/or structural modes [20–24]. By knowing the energy corresponding to the different vibrational modes, one can confirm the presence of different boroxol units and B–O & Pb–O bond vibrations. The presence of different functional groups noticed from the FTIR spectra (shown in Fig. 2b) have been confirmed from the Raman analysis. The Raman spectra of PBTNAEu0 and PBTNAEu2 glasses in the Raman shift ranges from 400 cm$^{-1}$ to 1600 cm$^{-1}$ is described in Fig. 3. These spectra reveal an intense Raman band at around 751 cm$^{-1}$ along with other considerably weak bands at around 410, 494, 674, 882, 974, 1079, 1222, 1330, 1425 and 1568 cm$^{-1}$.

The Raman band noticed at around 410 cm$^{-1}$ has been ascribed to the symmetric stretching vibrations of Te–O–Te linkage [20]. The Raman peak located at around 494 cm$^{-1}$ is due to the vibrations of isolated di-borate groups as well as Pb–O bonds [21]. The Raman band observed at around 674 cm$^{-1}$ has been assigned to the presence of ring type *meta*-borate units and in-plane bending modes of $BO_3$ units [22]. The Raman bands positioned at around 751 and 882 cm$^{-1}$ represent the presence of symmetric boroxol rings containing $BO_3$ and mixed $BO_3$–$BO_4$ units, respectively while the bands at around 974 and 1079 cm$^{-1}$ are owing to B–O stretching vibrations in $BO_3$ and $BO_4$ structural units, respectively [23]. The Raman peak noticed at 1222 cm$^{-1}$ is ascribed to the B–O stretching vibrations [21]. The Raman peaks positioned at around at 1330 and 1425 cm$^{-1}$ are attributed to B–O stretching vibrations linked with $BO_2O$ triangles and $BO_4$ units, respectively [22]. The Raman band located at around 1568 cm$^{-1}$ is ascribed to the B–O stretching vibrations involving non-bridging oxygens (NBOs) [24]. The assignment of Raman bands is also summarized in Table 2.

The chemical composition of PBTNAEu0 glass has been confirmed from the SEM-EDX studies and the obtained results are presented in Fig. 4. The EDX spectrum reveals the presence of boron (4.14 atm %), oxygen (53.44 atm%), fluorine (34.29 atm%), sodium (1.70 atm%), aluminum (1.05 atm%), tellurium (0.54 atm%) and lead (4.84 atm%) confirming the composition (PbO–$B_2O_3$–$TeO_2$–NaF–$AlF_3$) of PBTNAEu0 host glass without any impurity elements. The percentage of atomic weight of different elements is also presented in Fig. 4.

### 3.3. Absorption spectral analysis

In order to evaluate some of the significant spectroscopic properties, the room temperature absorption spectra of PBTNAEu glasses have been recorded and analyzed. These spectra consist of a total of five weak bands in visible region and two considerably intense bands in infrared (IR) region. All these bands have been originated from the $^7F_0$ and $^7F_1$ energy lavels to various higher energy levels and they are positioned at around 464 nm ($^7F_0 \rightarrow {}^5D_2$), 525 nm ($^7F_0 \rightarrow {}^5D_1$), 532 nm ($^7F_1 \rightarrow {}^5D_1$), 578 nm ($^7F_0 \rightarrow {}^5D_0$), 585 nm ($^7F_1 \rightarrow {}^5D_0$), 2085 nm $^7F_0 \rightarrow {}^7F_6$) and 2200 nm ($^7F_1 \rightarrow {}^7F_6$). The assignment of absorption transitions has been done following Carnall et al. [**25**]. A representative absorption spectrum of

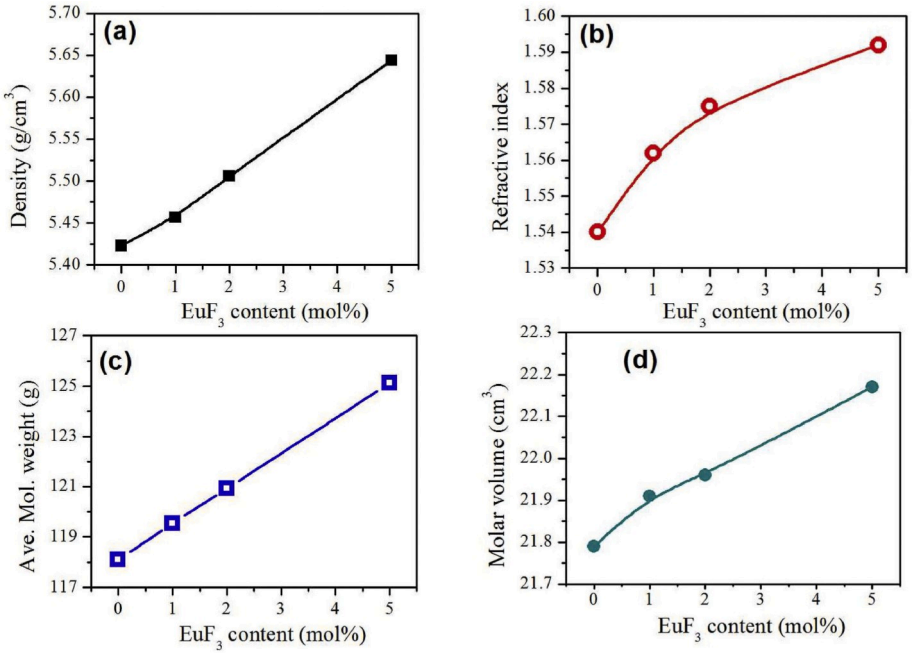



**Fig. 1.** Variation of density (a), refractive index (b), average molecular weight (c) and molar volume (d) as a function of $EuF_3$ content in PBTNAEu glasses.

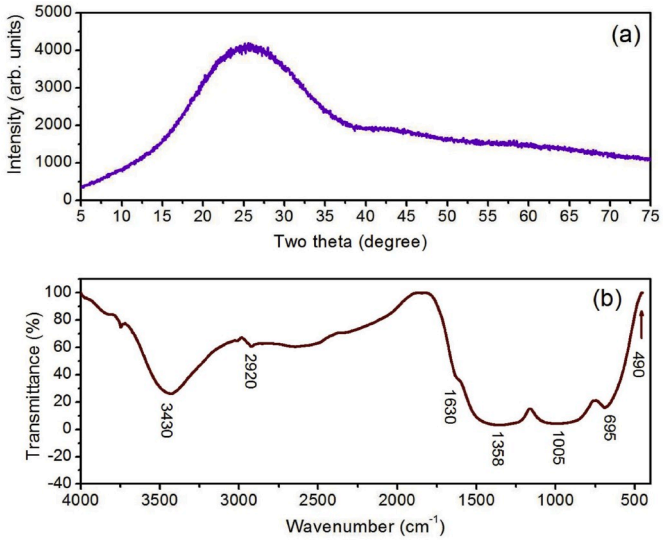



**Fig. 2.** XRD (a) and FTIR (b) patterns of PBTNAEu2 glass.

PBTNAEu2 glass is shown in Fig. 5.

The absorption spectrum of PBTNAEu0 glass in the spectral region from 400 to 2400 nm shown in Fig. 6 consists of a fundamental absorption edge at about 435 nm. Further, the absorption coefficients of different absorption bands increase with increase of $EuF_3$ content but their positions remain unaltered showing the uniform distribution of $Eu^{3+}$ ions in PBTNAEu glasy materials. A representative spectra showing the variation of absorbance of $^7F_0 \rightarrow {}^7F_6$ (2085 nm) and $^7F_1 \rightarrow {}^7F_6$ (2200 nm) transitions with $EuF_3$ content is illustrated as inset of Fig. 6. The covalent or ionic bonding character of $Eu^{3+}$ ions with $O^{2+}/F^{-1}$ has been known by evaluating the bonding parameter, $\delta = \left[\left(1 - \overline{\beta}/\beta\right) \times 100\right]$, here $\overline{\beta}$ represents the mean nephelauxetic ratio. The magnitude of bonding parameter is positive for covalent and negative for ionic bonds [26]. The positions of absorption bands, their nephelauxetic ratios and bonding parameters are presented in Table 3. The average value of δ is found to be +0.0066 indicating covalent character for $Eu^{3+}$ and $O^{2+}/F^{-1}$ bonds in PBTNAEu glasses.

**Table 2**
Assignment of FTIR and Raman band positions ($cm^{-1}$) in PBTNAEu glasses.

| FTIR | Assignment [17–19] | Raman | Assignment [20–24] |
|---|---|---|---|
| 3430 | symmetric stretching vibrations of $OH^-$ group | 1568 | stretching vibrations of B–O bonds involving non-bridging oxygens |
| 2920 | symmetric stretching vibrations of $OH^-$ group | 1425 | stretching vibrations of B–O bonds linked with $BO_4$ units |
| 1630 | asymmetric stretching vibrations of B–O bonds | 1330 | stretching vibrations of B–O bonds linked with $BO_2O$ triangles |
| 1358 | asymmetric stretching vibrations of B–O bonds | 1222 | stretching vibrations of B–O bonds in pyro-borate groups |
| 1005 | stretching vibrations of B–O bonds | 1079 | B–O bond stretching vibrations in $BO_4$ structural units |
| 695 | B–O–B bending vibrations | 974 | B–O bond stretching vibrations in $BO_3$ structural units |
| 490 | O–B–O bending vibrations associated with covalent Pb–O vibrations | 882 | symmetric boroxol rings containing mixed $BO_3$–$BO_4$ structural units |
| | | 751 | symmetric boroxol rings containing pure $BO_3$ units |
| | | 674 | Ring type *meta*-borate units and in-plane bending mode of $BO_3$ units |
| | | 494 | vibrations of isolated di-borate groups as well as Pb–O bonds |
| | | 410 | symmetric stretching vibrations of Te–O–Te linkage |

It is well known that the optical band gap energy ($E_g$) corresponding to the direct allowed transitions is more significant to select a suitable material for efficient optoelectronic and photonic devices. It can be obtained using the relation, $\alpha . (h\nu) = B (h\nu - E_g)^q$, where α represents the coefficient of absorption at the fundamental edge, $h\nu$ represents the energy of photon and B is a constant and it is independent of energy. The factor q = 2, 3, ½ and ⅓ for indirect-allowed, indirect-forbidden, direct-allowed and direct-forbidden transitions, respectively [27]. The

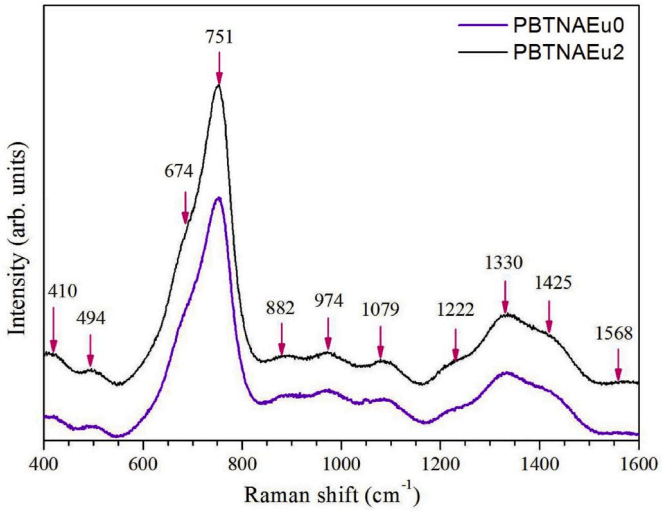



**Fig. 3.** Raman spectra of PBTNAEu glasses.

value of $E_g$ can be obtained by extrapolating the linear part of Tauc's plot (i.e., $(\alpha h\nu)^2$ versus $h\nu$ curve) to meet the $h\nu$ axis at $(\alpha h\nu)^2 = 0$. The Tauc's plots for q = ½ in PBTNAEu glasses are described in Fig. 7. The values of $E_g$ are found to be 2.627, 2.298 and 2.004 eV for PBTNAEu1, PBTNAEu2 and PBTNAEu5 glasses, respectively while for PBTNAEu0 glass, it is found to be 2.642 eV [5]. The gradual decrease of value of $E_g$ with increase of $EuF_3$ content is an indication for the formation of additional quantum level as well as slight structural amendments. The optical band gap energies are comparable to those reported for PTBEu (~2.60 eV) [11] and TBLFE (2.69 eV) [28] glasses.

### 3.4. Thermal correction

In case of $Eu^{3+}$ ion, the $^7F_0$ and the $^7F_1$ energy levels are separated by a small energy difference and it is close to $K_BT$, where $K_B$ is the Boltzmann's constant and T is the absolute temperature. The contributions of population of the $^7F_0$ ground and the $^7F_1$ first quantum states are about 65% and 35%, respectively at room temperature [29,30]. Therefore, the thermal population of $^7F_1$ first quantum state should be taken into account. The fractional thermal population of any excited quantum state ($C_J$) has been determined using the following equation.

$$\frac{C_J}{C_0} = \left(\frac{g_J}{g_0}\right)\exp\left\{-\frac{(E_J - E_0)}{K_B.\,T}\right\} \quad (1)$$

where $C_0$ represents the population of ground state. $E_J$ and $g_J(=2J+1)$ represent the energy and degeneracy of excited state, respectively. In case of PBTNAEu glasses, the thermal correction factors for $^7F_{0,1} \rightarrow {}^{2S+1}L_J$ transitions are estimated to be $C_0 = 0.6506$ and $C_1 = 0.3162$, respectively at T = 300 K.

### 3.5. Excitation spectra and phonon side band

In order to select a suitable radiation to produce strong emission from the studied glasy materials, the photoluminescence excitation spectra ranges from 350 nm to 600 nm were recorded by controlling the emission through $Eu^{3+}$: $^5D_0 \rightarrow {}^7F_2$ (613 nm) transition. These spectra reveal eleven excitation bands originated from the $^7F_0$ and $^7F_1$ energy levels to other higher energy levels. The observed bands have been ascribed to $^7F_0 \rightarrow {}^5D_4$ (363 nm), $^7F_0 \rightarrow {}^5L_7$ (378 nm), $^7F_1 \rightarrow {}^5L_7$ (383 nm), $^7F_0 \rightarrow {}^5L_6$ (395 nm), $^7F_0 \rightarrow {}^5D_3$ (416 nm), $^7F_0 \rightarrow {}^5D_2$ (465 nm), $^7F_1 \rightarrow {}^5D_2$ (526 nm), $^7F_0 \rightarrow {}^5D_1$ (534 nm), $^7F_1 \rightarrow {}^5D_1$ (553 nm), $^7F_0 \rightarrow {}^5D_0$ (579 nm) and $^7F_1 \rightarrow {}^5D_0$ (589 nm) transitions. Among these, the excitation band noticed at ~465 nm ($Eu^{3+}$: $^7F_0 \rightarrow {}^5D_2$) is found to be the prominent one and it could be the best choice to produce intense emission from the PBTNAEu glasses. For reference, the excitation spectrum of PBTNAEu2 glass is presented in Fig. 8. Further, the intensities of these transitions enhances with the activation of $EuF_3$ showing uniform distribution of $Eu^{3+}$ ions in PBTNAEu glasses. The inset of Fig. 8 shows the variation of intensity of $^7F_0 \rightarrow {}^5D_2$ (~465 nm) transition with $EuF_3$ content.

The excitation spectra also reveal phonon-side band (PSB) linked with $Eu^{3+}$: $^7F_0 \rightarrow {}^5D_2$ transition on higher energy region and it is positioned at ~447 nm (PSB–I: ~22,371 $cm^{-1}$) with a sub-peak at ~440 nm (PSB–II: ~22,727 $cm^{-1}$). The $Eu^{3+}$: $^7F_0 \rightarrow {}^5D_2$ transition is purely electronic transition and positioned at ~465 nm (~21,505 $cm^{-1}$) and it is considered to be the zero phonon line (ZPL) as described in Fig. 9. Additionally, the phonon energy related to the vibronic transitions has

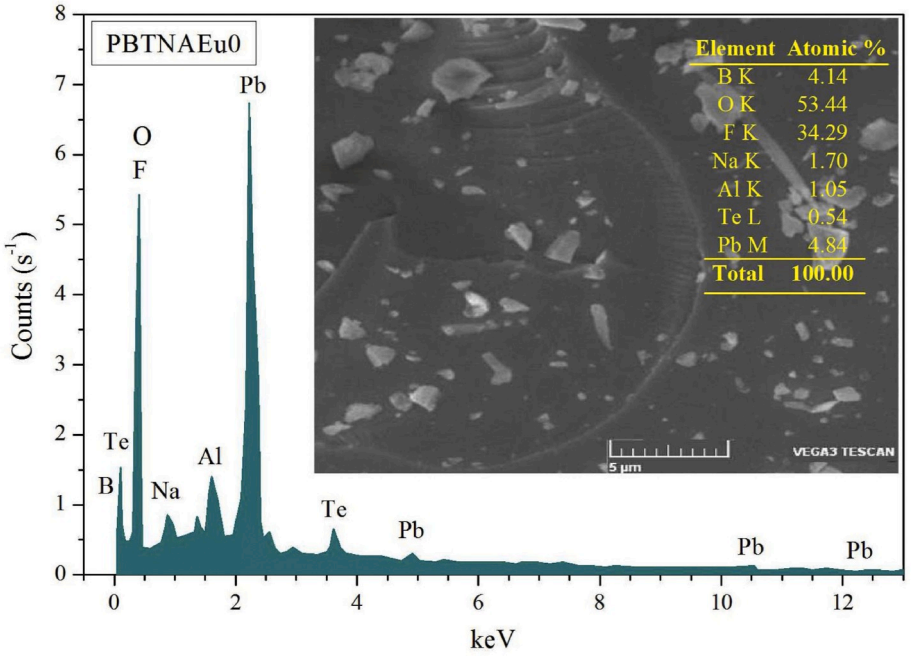



**Fig. 4.** EDX spectrum of PBTNAEu0 glass. Inset show the SEM image of PBTNAEu0 glass.

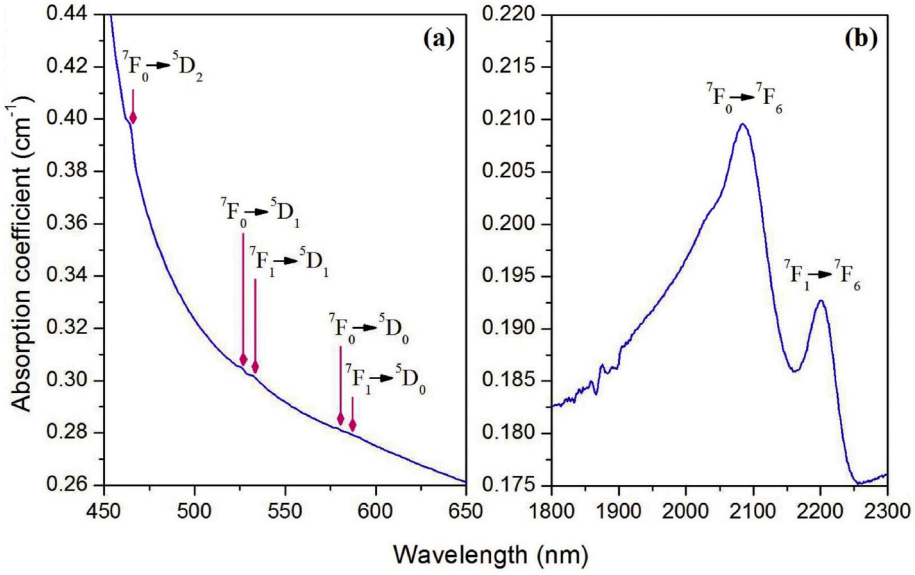



**Fig. 5.** Optical absorption spectra of PBTNAEu2 glass: (a) visible and (b) infrared regions.

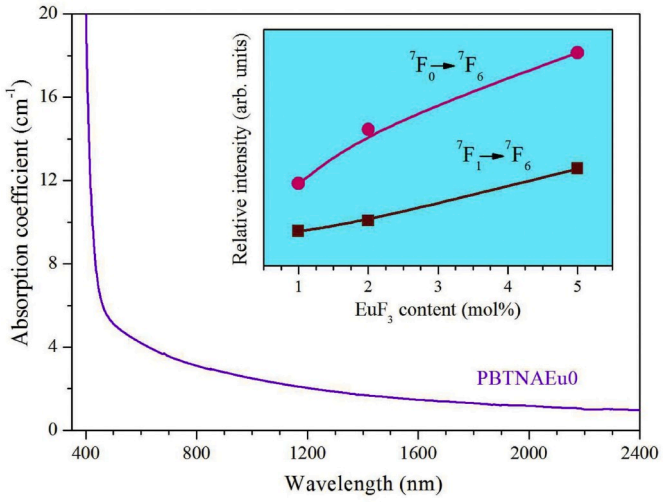



**Fig. 6.** Absorption spectrum of PBTNAEu0 glass. In set is the variation of absorbance of $^7F_0 \rightarrow {}^7F_6$ (2085 nm) and $^7F_1 \rightarrow {}^7F_6$ (2200 nm) transitions as a function of $EuF_3$ content.

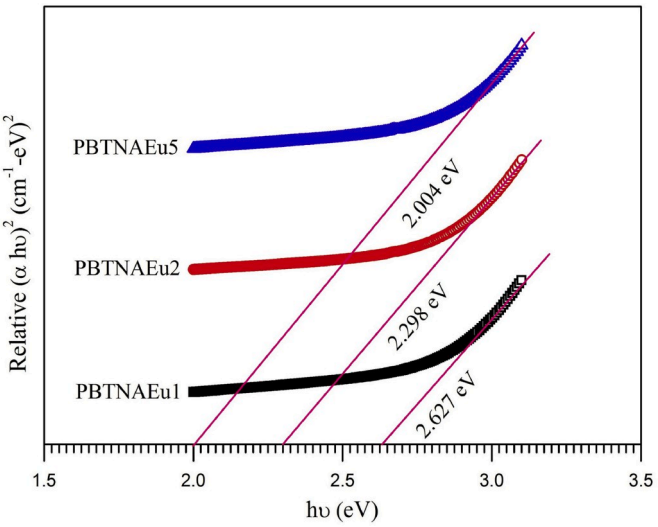



**Fig. 7.** Tauc's plots for direct allowed transitions in PBTNAEu glasses.

**Table 3**
Positions of absorption bands in PBTNAEu glasses ($\bar{\nu}_c$) and in aqua-ion host ($\bar{\nu}_a$), nephelauxetic ratios (β) and bonding parameters (δ).

| Transition | Peak maximum (cm$^{-1}$) | | β | δ |
|---|---|---|---|---|
| | $\bar{\nu}_c$ | $\bar{\nu}_a$ | | |
| $^7F_0 \rightarrow {}^5D_2$ | 21,552 | 21,519 | 1.0015 | 0.0065 |
| $^7F_0 \rightarrow {}^5D_1$ | 19,048 | 19,028 | 1.0011 | 0.0065 |
| $^7F_1 \rightarrow {}^5D_1$ | 18,797 | 18,676 | 1.0065 | 0.0065 |
| $^7F_0 \rightarrow {}^5D_0$ | 17,301 | 17,277 | 1.0014 | 0.0065 |
| $^7F_1 \rightarrow {}^5D_0$ | 17,094 | 16,936 | 1.0093 | 0.0064 |
| $^7F_0 \rightarrow {}^7F_6$ | 4796 | 4980 | 0.9631 | 0.0068 |
| $^7F_1 \rightarrow {}^7F_6$ | 4546 | 4679 | 0.9716 | 0.0067 |
| Average nephelauxetic ratio, $\bar{\beta} = 0.9935$ | | | | |
| Mean bonding parameter, $\delta = +0.0066$ | | | | |

been determined from the shift of the PSB from the pure-electronic-band (PEB). It is well known that the bonding nature of $Eu^{3+}$ ions with surrounding ligand field affects the coupling of vibrational modes to the electronic excited states. The PSBs associated with PEB helps us to recognize the vibrational modes associated with the ligand field around the $Eu^{3+}$ ions.

It is known from the literature [31] that the occurrence of PSB indicates that the incident (excited) radiation coupled not only with the excess energy of vibrational levels in the vicinity of $Eu^{3+}$ ions but also with its electronic states. The phonon side band mechanism at 465 nm excitation is clearly illustrated in Fig. 10. Further, the difference in energies of PEB and PSB represent the phonon energy and it corresponds to maximum energy of the vibrational modes of host matrix surrounding the $Eu^{3+}$ ion. The PSBs noticed at an average energy shift of ~866 and ~1222 cm$^{-1}$ from the ZPL are referred as PSB–I and PSB–II, respectively (see Fig. 9) and they can ascribed to the B–O bond stretching modes in $BO_4$ and pyro-borate groups, respectively. These vibrational modes have been correlated with Raman bands noticed at around 882 and 1222 cm$^{-1}$ (see Fig. 3).

### 3.6. Photoluminescence

Since the excitation band positioned at 465 nm corresponding to the

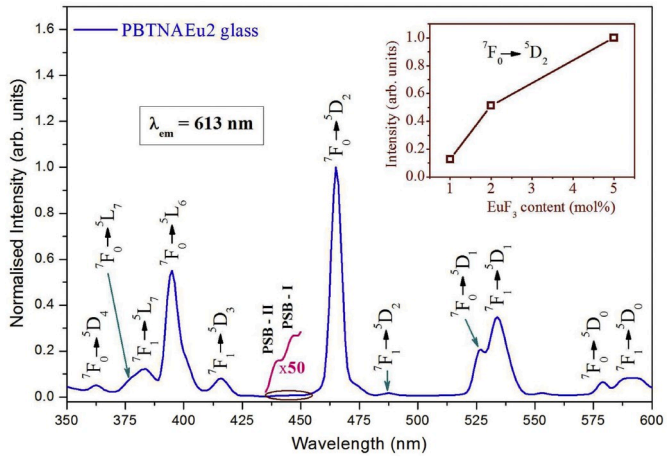



**Fig. 8.** Normalized excitation spectrum ($\lambda_{em}$ = 613 nm) of PBTNAEu2 glass. In set shows the variation of intensity of $^7F_0 \rightarrow {}^5D_2$ (465 nm) excited-state transition as a function of $EuF_3$ content in PBTNAEu glasses.

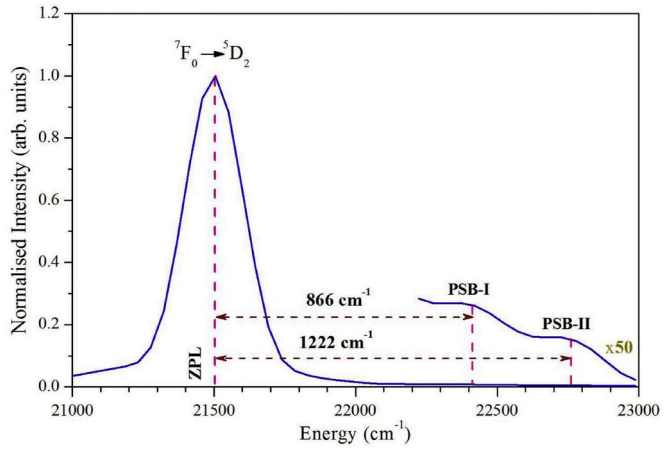



**Fig. 9.** Phonon side band spectrum of PBTNAEu2 glass with $^7F_0 \rightarrow {}^5D_2$ (465 nm) excited-state transition.

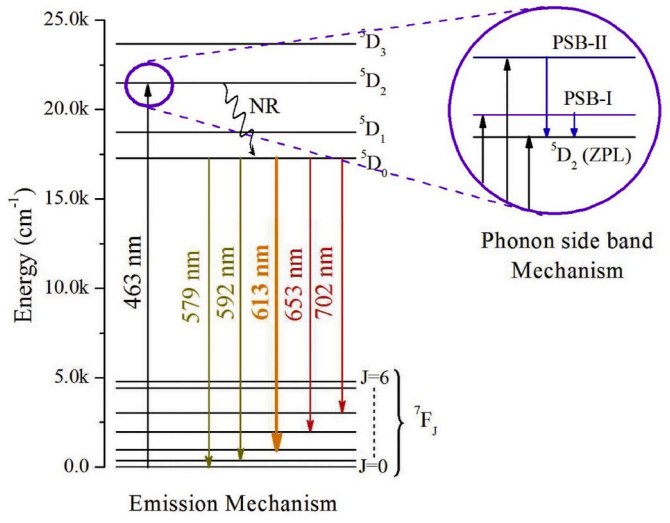



**Fig. 10.** Partial energy level diagram describing the emission and phonon side band mechanisms.

$Eu^{3+}$: $^7F_0 \rightarrow {}^5D_2$ transition has highest intensity compared to others, the emission analysis has been done at 465 nm excitation only. The luminescence spectra of PBTNAEu glasses are depicted in Fig. 11. These spectra reveal five emission bands corresponding to the $^5D_0 \rightarrow {}^7F_0$ (579 nm), $^5D_0 \rightarrow {}^7F_1$ (592 nm), $^5D_0 \rightarrow {}^7F_2$ (613 nm), $^5D_0 \rightarrow {}^7F_3$ (653 nm) and $^5D_0 \rightarrow {}^7F_4$ (702 nm) transitions. Upon 465 nm excitation, the $Eu^{3+}$ ions get excited to $^5D_2$ higher energy state and then de-excite non-radiatively to $^5D_0$ metastable state. Once the condition of population inversion achieved, then lasing action takes place through $^5D_0 \rightarrow {}^7F_2$ transition. The partial energy level structure shown in Fig. 10 describes the emission mechanism of PBTNAEu glasses at 465 nm excitation.

These emission spectra also reveal that the shape of the observed emission bands do not change even the content of $EuF_3$ varied from 1.0 mol% to 5.0 mol% except their intensity which increase with the addition of $EuF_3$ content confirming the absence of luminescence quenching in PBTNAEu glasses in the investigated $EuF_3$ range i.e., $0 \leq x \leq 5.0$ mol %. The in set of Fig. 11 shows the variation of intensity of $^5D_0 \rightarrow {}^7F_2$ transition with $EuF_3$ content in PBTNAEu glasses. These results are similar to TPBFEu [32] and TLKZnFEu [33] glasses. The emission spectral features are identical to our previous reports on $Eu^{3+}$ -doped PTBEu [11], LTTEu [12], RLTB [13] and LBTAF [14] glasses. Among the observed emission transitions, the $^5D_0 \rightarrow {}^7F_2$ (613 nm) transition is found to be the most intense and proficient transition. The emission spectra make known that the studied glasses emit strong, intense and enhanced red luminescence when excited at 465 nm wavelength.

It is well known that the $^5D_0 \rightarrow {}^7F_1$ transition is a magnetic-dipole (M-D) and the $^5D_0 \rightarrow {}^7F_2$ transition is electric-dipole (E-D) in nature obeying the selection rules $\Delta J = 1$ and $\Delta J = 2$, respectively [34]. Further, the transition probability of M-D ($^5D_0 \rightarrow {}^7F_1$) transition is almost insensitive to the host matrix while the transition probability of E-D ($^5D_0 \rightarrow {}^7F_2$) transition is more responsive to the environment surrounding the $Eu^{3+}$ ions. The ratio of intensity of E-D to M-D transitions, called the asymmetric ratio ($R_A$) provides essential information about the symmetry around the $Eu^{3+}$ ions in which it is situated. Therefore,

$$R_A = \frac{\int I_{ED}.d\lambda}{\int I_{MD}.d\lambda} \tag{2}$$

where $\int I_{ED}.\, d\lambda$ and $\int I_{MD}.d\lambda$ are the intensities of $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_1$ transitions, respectively. Thus, the $Eu^{3+}$ ion has been used as a probe to study the site symmetry of any host matrix in which they are present. If the intensity ratio is greater than unity then the $Eu^{3+}$ ions occupy higher symmetry sites in the host matrix resulting intense luminescence through $^5D_0 \rightarrow {}^7F_2$ (E-D) transition than $^5D_0 \rightarrow {}^7F_1$ (M-D) transition and

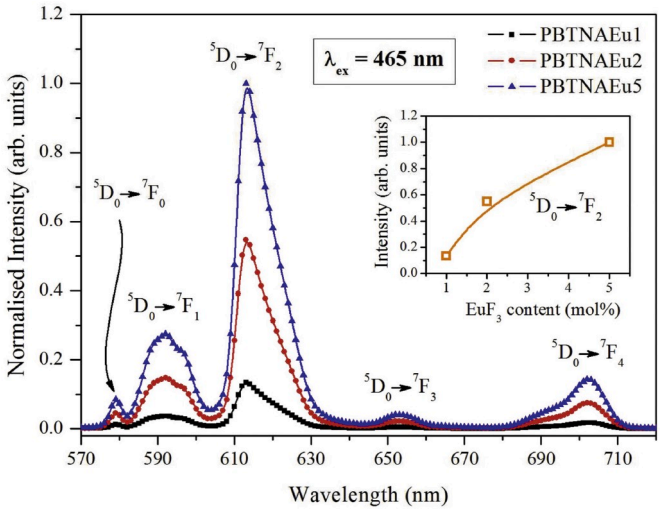



**Fig. 11.** Emission spectra ($\lambda_{ex}$ = 465 nm) of PBTNAEu glasses. In set is the variation of intensity of $^5D_0 \rightarrow {}^7F_2$ transition as a function of $EuF_3$ content.

vice versa. In the present investigation, the values of $R_A$ are found to be 3.61, 3.65 and 3.72 for PBTNAEu1, PBTNAEu2 and PBTNAEu5 glasses, respectively. The increased values of $R_A$ with the addition of $EuF_3$ improves the site symmetry of PBTNAEu host in the vicinity of $Eu^{3+}$ ions promoting enhanced luminescence through $^5D_0 \rightarrow {}^7F_2$ transition with the addition of $EuF_3$ content. The asymmetric ratio of PBTNAEu2 glass is found higher than LTTEu (2.78) [12], TPBFEu (~3) [32], TLKZnFEu10 (2.879) [33] and SB33 (2.53) [35] glasses.

The colour of the emitted light from the PBTNAEu glasses is examined by evaluating the Commission International de I'Eclairage (CIE) colour coordinates using the emission spectra shown in Fig. 11. The evaluated CIE coordinates are found to be (0.570, 0.392), (0.639, 0.355) and (0.648, 0.351) for PBTNAEu1, PBTNAEu2 and PBTNAEu5 glasses, respectively. The location of CIE coordinates shown in Fig. 12 indicates that the colour of emitted luminescence shifts from reddish-orange to pure-red when the $EuF_3$ content changes from 1.0 mol% to 5.0 mol% producing a tunable luminescence at 465 nm excitation. Among the studied glasses, the PBTNAEu2 glass emits enhanced red luminescence when excited at 465 nm wavelength. The CIE coordinates of PBTNAEu2 glass (0.639, 0.355) are comparable to those reported for $PbO–Na_2O–P_2O_5–Eu_2O_3$ (0.634, 0.346) [9], TWGEu05 (0.645, 0.342) [10], TPBFEu (0.639, 0.360) [32] and TLKZnFEu10 (0.638, 0.362) [33] glasses. They are also comparable to commercial red illuminates like $Y_2O_3$: $Eu^{3+}$ (0.64, 0.34) [KX-YOX, Kasei Optonix Ltd., Japan] and (Y,Gd) $BO_3$:$Eu^{3+}$ (0.65, 0.35) [KX-504, Kasei Optonix Ltd., Japan].

### 3.7. Intensity parameters

The quantificational investigation of various spectroscopic and laser characteristic properties of luminescent materials activated with RE ions has been successfully carried out by the use of standard J-O model [15,16]. The probability rates of 4f-4f radiative transitions of RE ions has been represented by means of three phenomenological J-O intensity parameters ($\Omega_{\lambda=2,4,6}$), which can be evaluated by minimizing the difference between the experimental ($f_{exp}$) and theoretical ($f_{cal}$) oscillator strengths by least squares fit approximation. Knowing the $\Omega_\lambda$ parameters, one can find the probability rate of radiative transitions ($A_R$), radiative decay time ($\tau_R$), radiative branching ratio ($\beta_R$) and the stimulated emission cross-section ($\sigma_{emi}$). However, the standard J-O model fails to analyze the luminescence properties of some RE ions, such as $Pr^{3+}$ and $Eu^{3+}$ ions in some host matrices. Thus, the strategy of standard J-O model has been modified accordingly to evaluate the radiative parameters of these ions in different host matrices [36].

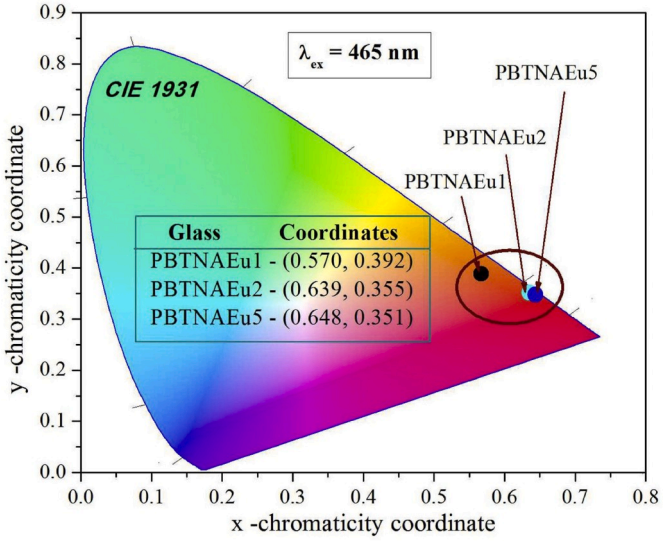



**Fig. 12.** CIE chromaticity coordinate diagram of PBTNAEu glasses.

In case of $Eu^{3+}$ ion, the absorption spectra consists of different transitions originated from both $^7F_0$ and $^7F_1$ energy levels due to considerably small energy gap of the order $K_BT$. Thus, the standard J-O model becomes unwieldy and the corresponding $\Omega_\lambda$ intensity parameters have been obtained by modifying the experimental oscillator strengths with thermal-correction factors to $^7F_0$ and $^7F_1$ state (see section 3.4). Though the thermal-correction has been applied to the oscillator strengths, the least squares fit process becomes invalid to determine the $\Omega_\lambda$ intensity parameters due to zero magnitude of $\|U^4\|^2$ matrix elements. The values of $\|U^\lambda\|^2$ have been collected from Carnall et al. [25] and they are summarized in Table 4. In order to evaluate the $\Omega_\lambda$ intensity parameters of $Eu^{3+}$ ions by overcoming the above discussed difficulties, several efforts have been made for alternate approaches.

In one approach, the $\Omega_\lambda$ parameters have been evaluated by the use of $^7F_0 \rightarrow {}^5D_J$ (J = 0, 2, 4, 6) individual bands from the absorption spectra ignoring thermal correction [29]. This approach has given fever results for radiative parameters of $Eu^{3+}$ ions in some host matrices [14]. Dejneka et al. [30] determined the $\Omega_\lambda$ intensity parameters by adopting thermal correction. Since the $\|U^4\|^2 = 0$ for all the transitions (see Table 4), the magnitude of $\Omega_4$ intensity parameter becomes insignificant in these two approaches. The oscillator strengths for the observed absorption transitions with and without thermal correction are also presented in Table 4. In another approach, the $\Omega_\lambda$ intensity parameters have been evaluated from the $^5D_0 \rightarrow {}^7F_{2,4,6}$ emission transitions [37]. According to standard J-O model, the $\|U^\lambda\|^2$ values for emission transitions originating from $^5D_0$ metastable state becomes zero except for $^5D_0 \rightarrow {}^7F_2$, $^7F_4$, $^7F_6$ transitions. The detailed procedure of evaluating the $\Omega_\lambda$ intensity parameters from the $^5D_0 \rightarrow {}^7F_2$, $^7F_4$, $^7F_6$ emission transitions was explored in our earlier work [38].

Though the PBTNAEu2 and PBTNAEu5 glasses emit enhanced red luminescence at 465 nm excitation, the evaluation of radiative and other optical properties are restricted to PBTNAEu2 glass sample only owing to least consumption of $EuF_3$ thereby reducing the cost and protecting the environment. In the present investigation, the $\Omega_\lambda$ intensity parameters have been determined using both the emission and the room temperature absorption spectra with thermal correction for oscillator strengths. Applying the thermal correction, the $\Omega_\lambda$ parameters are evaluated as $\Omega_2 = 11.49 \times 10^{-20}$ $cm^2$, $\Omega_4 \approx 0$ and $\Omega_6 = 1.91 \times 10^{-20}$ $cm^2$ for PBTNAEu2 glass. A comparison of $\Omega_\lambda$ parameters evaluated from the $^5D_0 \rightarrow {}^7F_{1,2,4,6}$ emission transitions is given in Table 5. Since the emission band corresponding to the $^5D_0 \rightarrow {}^7F_6$ transitions is not located in visible region, the $\Omega_6$ intensity parameter is considered as zero ($\Omega_6 \approx 0$) in evaluating various radiative properties. The $\Omega_\lambda$ intensity parameters of PBTNAEu2 glass obtained from the emission spectral features are very close to other reports [ [13,39–41]]. Table 6 summarizes the $\Omega_\lambda$ parameters for different host glasses.

It is well known that the $\Omega_2$ intensity parameter is a measure of covalency and asymmetry of the host medium in the vicinity of RE ions in which they are present. Higher the magnitude of $\Omega_2$ parameter greater will be the asymmetry and the covalency of metal-ligand bonds [42]. So, the $\Omega_2$ parameter is more sensitive to the host. But the $\Omega_4$ parameter is practically constant and the $\Omega_6$ parameter do not vary appreciably as it depends on the viscosity of the host medium. In the present research work, the considerably higher value of $\Omega_2$ parameter is an indication for the large asymmetric environment around the $Eu^{3+}$ ions. These results are similar to that of the intensity ratio evaluated from the emission spectral profiles. The covalency of $Eu^{3+}$ ions with host ligands is also higher confirming the results obtained from the bonding character (δ) described in see section 3.3.

### 3.8. Radiative parameters

The $\Omega_\lambda$ parameters were used to evaluate the various radiative parameters, such as radiative transition probability rate ($A_{rad}$), radiative lifetime ($\tau_{rad}$) and radiative branching ratio ($\beta_{rad}$). These parameters are further used to obtain significant laser properties like emission cross-

**Table 4**
Oscillator strengths (experimental, $f_{exp}$ and calculated, $f_{cal}$) and squared reduced matrix elements for the observed absorption transitions of $Eu^{3+}$ ions in PBTNAEu2 glass.

| Transition | Peak maximum | | Oscillator strengths ( $\times 10^{-6}$) | | | Squared reduced matrix elements, $\|U^{\lambda}\|^2$ | | |
|---|---|---|---|---|---|---|---|---|
| | λ, nm | ν, $cm^{-1}$ | [a]$f_{exp}$ | [b]$f_{exp}$ | [b]$f_{cal}$ | $\|U^2\|^2$ | $\|U^4\|^2$ | $\|U^6\|^2$ |
| $^7F_0 \rightarrow {}^5D_2$ | 464 | 21,552 | 0.1178 | 0.1811 | 0.3078 | 0.0008 | 0 | 0 |
| $^7F_0 \rightarrow {}^5D_1$ | 525 | 19,048 | 0.0116 | 0.0178 | ~0 | 0 | 0 | 0 |
| $^7F_1 \rightarrow {}^5D_1$ | 532 | 18,797 | 0.0226 | 0.0715 | 0.8727 | 0.0026 | 0 | 0 |
| $^7F_0 \rightarrow {}^5D_0$ | 578 | 17,301 | 0.0036 | 0.0055 | ~0 | 0 | 0 | 0 |
| $^7F_1 \rightarrow {}^5D_0$ | 585 | 17,094 | 0.0856 | 0.2707 | ~0 | 0 | 0 | 0 |
| $^7F_0 \rightarrow {}^7F_6$ | 2085 | 4796 | 0.7881 | 1.2113 | 2.0591 | 0 | 0 | 0.1450 |
| $^7F_1 \rightarrow {}^7F_6$ | 2200 | 4546 | 0.1314 | 0.4156 | 5.0786 | 0 | 0 | 0.3773 |

[a] $f_{exp}$ – As evaluated.
[b] $f_{exp}$ – Thermally corrected.

**Table 5**
Comparison of $\Omega_\lambda$ intensity parameters obtained from the $^5D_0 \rightarrow {}^7F_{J=1,2,4,6}$ emission transitions and radiative parameters of PBTNAEu glasses.

| Parameter | PBTNAEu1 | PBTNAEu2 | PBTNAEu5 |
|---|---|---|---|
| $\Omega_2$ ( $\times 10^{-20}$ $cm^2$) | 12.53 | 12.02 | 11.75 |
| $\Omega_4$ ( $\times 10^{-20}$ $cm^2$) | 4.10 | 4.05 | 3.96 |
| $\Omega_6$ ( $\times 10^{-20}$ $cm^2$) | ~0 | ~0 | ~0 |
| Radiative transition rate, $A_{rad}$ ($s^{-1}$) | 549.04 | 556.41 | 560.38 |
| Radiative branching ratio, $\beta_{rad}$ (%) | 78 | 78 | 77 |
| Radiative lifetime, $\tau_{rad}$ (ms) | 1.82 | 1.80 | 1.78 |
| Experimental lifetime, $\tau_{exp}$ (ms) | 1.11 | 1.09 | 1.07 |
| Quantum efficiency, η (%) | 60.99 | 60.56 | 60.11 |
| Non-radiative losses, $W_{NR}$ ($s^{-1}$) | 351.45 | 361.88 | 372.78 |
| Experimental branching ratio, $\beta_{exp}$ (%) | 68 | 69 | 67 |
| Emission peak position, $\lambda_P$ (nm) | 613 | 613 | 613 |
| Effective band width, $\Delta\lambda_{eff}$ (nm) | 10.72 | 10.89 | 11.16 |
| Stimulated emission cross-section, $\sigma_{emi}$ ( $\times 10^{-21}$ $cm^2$) | 3.93 | 3.87 | 3.71 |
| Gain bandwidth, ($\sigma_{emi} \times \Delta\lambda_{eff}$) ( $\times 10^{-27}$ $cm^3$) | 4.21 | 4.22 | 4.14 |
| Optical gain, ($\sigma_{emi} \times \tau_{exp}$) ( $\times 10^{-24}$ $cm^2$-s) | 7.16 | 6.96 | 6.62 |

**Table 6**
Comparison of $\Omega_\lambda$ intensity parameters for different multi-component glasses.

| Glass | $\Omega_\lambda$ ( $\times 10^{-20}$ $cm^2$) intensity parameters | | | Reference |
|---|---|---|---|---|
| | $\Omega_2$ | $\Omega_4$ | $\Omega_6$ | |
| PBTNAEu2 | 12.02 | 4.05 | ~0 | [This work] |
| PBTNAEu2[a] | 11.49 | ~0 | 1.91 | [This work] |
| Eu: LiLTB | 12.08 | ~0 | 1.35 | [13] |
| Eu: NaLTB | 12.60 | ~0 | 1.41 | [13] |
| Eu/Ag: Tellurite glass | 10.00 | 1.76 | – | [39] |
| 3.0Eu-GICZPS | 11.17 | 5.91 | 1.41 | [40] |
| 5.0Eu-GICZPS | 10.84 | 16.61 | 2.39 | [40] |
| Tellurite glass | 11.06 | 4.58 | 0.96 | [41] |

[a] Evaluated from the thermally corrected absorption transitions.

sections ($\sigma_{emi}$), gain band-widths ($\sigma_{emi} \times \Delta\lambda_{eff}$) and optical gains ($\sigma_{emi} \times \tau_{exp}$) for the potential emission transitions. The $\Omega_\lambda$ parameters obtained from the $^5D_0 \rightarrow {}^7F_{1,2,4,6}$ emission transitions are more reliable than those evaluated from the thermally corrected $^7F_0 \rightarrow {}^5D_J$ absorption transitions. Thus, the $\Omega_\lambda$ parameters evaluated from the emission spectra have been used to determine various radiative and laser properties as the $\Omega_2$ intensity parameter is close to that obtained from thermally corrected absorption transitions (see Table 6). Some of the significant laser characteristic parameters like experimentally measured branching ratios ($\beta_{exp}$) and effective band-widths ($\Delta\lambda_{eff}$) have been obtained using the emission spectral profiles. If the experimentally measured branching ratio ($\beta_{exp}$) for any emission transition is found higher than 50%, then it emits intense luminescence with considerably high quantum efficiency [43]. The magnitude of $\sigma_{emi}$ for $\Psi J \rightarrow \Psi' J'$ emission transition is given as

$$\sigma_{emi}(\Psi J, \Psi' J') = \frac{\lambda_p^{\,4}}{8\,\pi\,c\,n^2\,\Delta\lambda_{eff}} A_{rad}(\Psi J, \Psi' J') \quad (3)$$

where $\lambda_P$ represents the wavelength corresponding to emission peak maximum, $c$ represents the velocity of light, $\Delta\lambda_{eff}$ represents the effective-bandwidth of $\Psi J \rightarrow \Psi' J'$ transition. Table 5 presents the observed laser parameters of PBTNAEu glasses. These values obtained for PBTNAEu2 glass are comparable to LiPbAlB [8], TWGEu05 [10], PTBEu20 [11], TPBFEu16 [32], TLKZnF:$Eu^{3+}$ [33] and TeEu1.5 [44] glasses. Table 7 summarizes the laser parameters of different multi-component glasses.

### 3.9. Luminescence decay, non-radiative losses and quantum efficiency

The lifetime of $Eu^{3+}$: $^5D_0$ emission state of PBTNAEu glasses has been determined from the luminescence decay profiles obtained by monitoring the emission (613 nm) and excitation (465 nm) wavelengths corresponding to $^5D_0 \rightarrow {}^7F_2$ and $^7F_0 \rightarrow {}^5D_2$ transitions, respectively. All these decay profiles are suitably fitted to $I(t) = I(0) \cdot e^{-t/\tau}$, where $I(0)$ represents the intensity at t = 0 and $\tau$ represents the decay time of corresponding emission state. The luminescence decay profiles of PBTNAEu1, PBTNAEu2 and PBTNAEu5 glasses are presented in Fig. 13 (a), (b) and (c), respectively. The experimentally measured lifetime ($\tau_{exp}$) of $Eu^{3+}$: $^5D_0$ emission state is evaluated taking the first e-folding times of the initial intensity. For the studied PBTNAEu1, PBTNAEu2 and PBTNAEu5 glasses, the lifetime values are fund to be 1.11, 1.09 and 1.07 ms, respectively. The accuracy in determining the lifetime is nearly ±0.01 ms. In general, the dependence of lifetime of $Eu^{3+}$: $^5D_0$ emission state is fever on its concentration [45]. In the present investigation, the observed results show a shortening in lifetime with the addition of $EuF_3$. The variation of decay time of $Eu^{3+}$: $^5D_0$ emission state in PBTNAEu glasses with $EuF_3$ content is shown in Fig. 13d.

One of the reasons for shortening in lifetime is the multiphonon-

**Table 7**
Comparison of laser characteristics parameters of $Eu^{3+}$: $^5D_0 \rightarrow {}^7F_2$ (613 nm) transition in different multi-component glasses.

| Glass Host | Laser characteristics parameters | | | | |
|---|---|---|---|---|---|
| | $\Delta\lambda_{eff}$ (nm) | $\beta_{exp}$ (%) | $\sigma_{emi}$ ( $\times 10^{-21}$ $cm^2$) | ($\sigma_{emi} \times \Delta\lambda_{eff}$) ( $\times 10^{-27}$ $cm^3$) | ($\sigma_{emi} \times \tau_{exp}$) ( $\times 10^{-24}$ $cm^2$-s) |
| PBTNAEu2 [Present work] | 10.89 | 69 | 3.87 | 4.22 | 6.96 |
| LiPbAlB [8] | 11.24 | 63 | 0.499 | 0.56 | – |
| TWGEu05 [10] | 12.79 | 58 | 2.712 | 3.468 | 1.51 |
| PTBEu20 [11] | 12.35 | 65 | 0.87 | 1.074 | 4.89 |
| TPBFEu16 [32] | 9.712 | 70.47 | 1.458 | 1.416 | – |
| TLKZnF:$Eu^{3+}$ [33] | 6.3753 | 72.38 | 2.210 | 1.4089 | – |
| TeEu1.5 [44] | 10.44 | 64 | 2.319 | 2.421 | – |

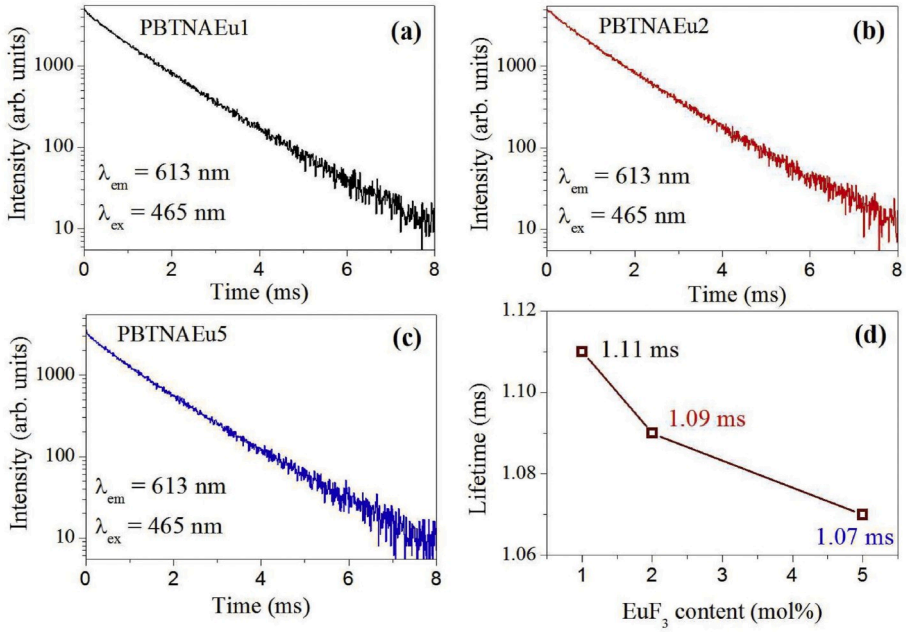



**Fig. 13.** Logarithmic plots of decay profiles of $Eu^{3+}$: $^5D_0$ emission state for PBTNAEu1 (a), PBTNAEu2 (b) and PBTNAEu5 (c) glasses. The variation of lifetime as a function of $EuF_3$ content in PBTNAEu glasses (d).

relaxation rates ($W_{MP}$). The non-radiative decay rates ($W_{NR}$) include the multiphonon-relaxation rates ($W_{MP}$), energy transfer rates ($W_{ET}$), concentration quenching rates ($W_{CQ}$) and the $OH^-$ content rates ($W_{OH}$) and thus, $W_{NR} = W_{MP} + W_{ET} + W_{CQ} + W_{OH}$. In case of PBTNAEu glasses, the $W_{OH}$ becomes insignificant due to small value of $OH^-$ content [**5**]. For the studied concentrations of $EuF_3$ in PBTNAEu glasses, the $W_{ET}$ and $W_{CQ}$ become insignificant due to the absence of luminescence quenching. To bridge the energy gap of ~12,475 $cm^{-1}$ between the $^5D_0$ emission state and its lower lying $^7F_6$ state, the PBTNAEu glasses require nearly 12 phonons owing to its small phonon energy. Therefore, the multiphonon-relaxation rates play a key role in the shortening of decay time. The NR multiphonon-relaxation rates ($W_{MP}$) responsible for shortening in lifetime ($W_{MP} = W_{NR} = \tau_{exp}^{-1} - \tau_{rad}^{-1}$) for PBTNAEu1, PBTNAEu2 and PBTNAEu5 glasses are found nearly 351, 362 and 373 $cm^{-1}$, respectively. These values show that no considerable change takes place when the content of $EuF_3$ is increased from 1.0 mol% to 5.0 mol% in PBTNAEu glasses.

The quantum efficiency (η) of a laser host material is one of the important parameters for its applicability as a practical laser and it has been obtained from the ratio of experimental and radiative lifetimes. Therefore,

$$\eta = \frac{\tau_{exp}}{\tau_R} \quad (4)$$

where $\tau_{exp}$ and $\tau_R$ represents the experimental and radiative lifetimes, respectively. For PBTNAEu1, PBTNAEu2 and PBTNAEu5 glasses, the quantum efficiencies are evaluated to be 60.99%, 60.56% and 60.11%, respectively. These values are found higher than LiPbAlB (58%) [**8**], PTBEu20 (40%) [11], LTTEu20 (53%) [12], TPBFEu16 (53.4%) [32], TLKZnFEu10 (51.6%) [33], Tellurite (57.2%) [39], Borosilicate (33%) [44] and $Eu^{3+}$: B1TMK (56.76%) [46] glasy materials. These results suggest that the studied PBTNAEu glasses show improved quantum efficiencies compared to above mentioned reports. The experimental quantum yield (QY) of PBTNAEu2 glass is found to be 9.52% which is close to $Li_2B_4O_7$:Eu (1.0 mol%) glass (QY = 10.7%) [36]. Based on the evaluated spectroscopic, radiative and laser characteristic properties, it has been suggested that the PBTNAEu2 glass has more potentiality to produce enhanced and rich red luminescence through $^5D_0 \rightarrow {}^7F_2$ (613 nm) transition.

## 4. Conclusions

Optically transparent PBTNAEu glasses containing different amounts of $EuF_3$ ($0 \leq x \leq 5.0$ mol%) were prepared and characterized for red laser applications. The presence of Te–O–Te, Pb–O and O–B–O linkage and $BO_4$ units has been confirmed from the Raman spectra. The SEM-EDX results confirm the intrinsic nature of studied glass composition. Thermal correction factors for $^7F_0$ and $^7F_1$ energy levels are found to be $C_0 = 0.6506$ and $C_1 = 0.3162$, respectively at T = 300 K. The phonon energy corresponding to PSB–I (~866 $cm^{-1}$) and PSB–II (~1222 $cm^{-1}$) has been attributed to the B–O stretching vibrations in $BO_4$ and pyroborate groups, respectively. The $^5D_0 \rightarrow {}^7F_J$ emission spectral profiles have been used to examine the enhanced luminescence and asymmetricity around the $Eu^{3+}$ ions. The $\Omega_\lambda$ parameters obtained from the $^5D_0 \rightarrow {}^7F_1$, $^7F_2$, $^7F_4$, $^7F_6$ emission transitions have been used to evaluate various laser characteristic parameters. The luminescence decay profiles of $Eu^{3+}$: $^5D_0$ emission state have been well fitted to single exponential function. The lifetime shortening of has been assigned to the non-radiative multi-phonon relaxation rates. The luminescence quantum efficiencies are estimated to be around 60%. The observed experimental results suggest that the PBTNAEu2 glass could be the best candidate for rich red laser applications.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## CRediT authorship contribution statement

**B.C. Jamalaiah:** Conceptualization, Methodology, Software, Writing - original draft, Investigation, Supervision, Visualization, Formal analysis, Validation, Writing - review & editing, Project administration, Funding acquisition. **N. Madhu:** Software, Data curation, Resources, Visualization, Writing - review & editing. **K. Venkata Rao:** Software, Data curation, Resources, Visualization, Writing - review

& editing. **G. Viswanadha:** Methodology, Software, Writing - original draft, Investigation, Supervision, Visualization, Formal analysis. **D.V. Raghu Ram:** Software, Data curation, Resources, Visualization, Writing - review & editing.

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## Appendix A. Supplementary data

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# Luminescence properties of $SrAl_2O_4$: $Tb^{3+}$/ $Bi^{3+}$ nanophosphors for photonic applications

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ABSTRACT

The $Tb^{3+}/Bi^{3+}$ co-doped $SrAl_2O_4$ (SAOTB) nanophosphors were synthesized and characterized through X-ray diffraction, Raman, photoluminescence excitation, emission and luminescence decay studies. The studied materials were crystallize into monoclinic phase with lattice parameters a = 8.4419 Å, b = 8.8217 Å, c = 5.1592 Å. The phase of SAOTB nanophosphors was confirmed by the Raman analysis. The morphological study reveals homogeneous distribution of particles of different size. The luminescence of $Tb^{3+}$ ions was enhanced by the effective sensitization of $Bi^{3+}$ ions when excited at 340 nm corresponding to $Bi^{3+}$: $^1S_0 \rightarrow {}^1P_1$ transition. The spectral overlap of $Tb^{3+}$: $^7F_6 \rightarrow {}^5G_6$ and $Bi^{3+}$: $^3P_1 \rightarrow {}^1S_0$ transition reveals the existence of transfer of energy from $Bi^{3+}$ to $Tb^{3+}$ ions. The SAOTB nanophosphors emit strong and enhanced green luminescence through $Tb^{3+}$: $^5D_4 \rightarrow {}^7F_J$ transitions when excited at 340 nm radiation. The colour perception and the luminescence quantum efficiency were investigated using the emission spectral profiles. The luminescence decay time of $Tb^{3+}$: $^5D_4$ emission level in SAOTB nanophosphors was found to be nearly 2.60 ms. The experimental results suggest that the SAOTB nanophosphors were more potential for display applications.

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## 1. Introduction

The mono-phase nanophosphors activated with trivalent rare earth (RE) ions have been the most significant materials in the field of photonics, optoelectronics and display technology. They find wide range of applications as lasers, sensors, surface coatings, energy storage devices etc., owing to their improved tunable emission, high thermal stability, good chemical durability and eco-friendly nature [1–5]. They possess excellent optimistic properties such as compact size, low power consumption, long lifetime, and excellent luminescence efficiency [6,7]. Among the available phosphate, borate, silicate, and molybdate phosphors, the $SrAl_2O_4$ crystallized into monoclinic phase exhibits excellent luminescence properties, good ultraviolet (UV) absorption, high thermal strength, prolonged chemical stability and environmental friendly nature [8–12]. The significance of $SrAl_2O_4$ nanophosphors for various applications were described in our previous work [13,14]. They crystallized into monoclinic structure with lattice parameters a = 8.4419 Å, b = 8.8217 Å, c = 5.1592 Å [15]. The transmission electron microscope (TEM) study confirms the nanophase of $SrAl_2O_4$ phosphors and the Fourier transform infrared (FTIR) investigations validate the presence of Al–O, Sr–O and Sr–O–Al vibrational bands.

From the literature [16–18], it is clear that the $Tb^{3+}$ ions activated nanophosphors are favourable to tune the colour of emitted luminescence from blue to green by the way of controlling $Tb^{3+}$ ions concentration. For <0.5% concentrations, the blue luminescence ($Tb^{3+}$: $^5D_3 \rightarrow {}^7F_J$) become superior while for ≥ 0.5% concentrations, the green luminescence ($Tb^{3+}$: $^5D_4 \rightarrow {}^7F_J$) become superior. The trivalent bismuth ($Bi^{3+}$) with [Xe] $4f^{14}5d^{10}6s^26p^3$ electronic configuration has been identified as an efficient activator to enhance the luminescence of some of the trivalent RE ions due to its electronic transitions between 6s [2] ground and 6s6p excited energy levels. It has been one of the interesting metal-ions for various photonic applications due to its diverse oxidation levels (such as 0, +1, +2, +3 and + 5) and multi-type energy level structure. $Bi^{3+}$ can also be used as probe to investigate the

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luminescence of $RE^{3+}$ active ions due to its host sensitive optical properties associated with 6s [2] lone pair electrons [19–21]. Since the $^1S_0 \rightarrow {}^3P_0$, $^3P_2$ transitions are totally spin forbidden, the $Bi^{3+}$ ions show broad absorption through $^1S_0 \rightarrow {}^3P_1$, $^1P_1$ transitions in any host environment. This broad absorption facilitates to absorb UV light and initiate energy transfer from $Bi^{3+}$ ions to other luminescent centers, like $RE^{3+}$ ions. Thus, the $Bi^{3+}$ could acts as an efficient sensitizer to enhance the luminescence of $RE^{3+}$ ions.

The present work reports the effect of $Bi^{3+}$ on the luminescence of $Tb^{3+}$ ions in $SrAl_2O_4$ nanophosphors. The energy transfer from $Bi^{3+}$ to $Tb^{3+}$ ions under UV excitation, the site-symmetry around $Tb^{3+}$, the colour perception, the lifetime of $Tb^{3+}$: $^5D_4$ emission level and the luminescence quantum efficiency were reported. The structural and morphological investigations together with the applicability of SAOTB nanophosphors for display applications were also discussed.

## 2. Experimental

In order to investigate the effect of $Bi^{3+}$ sensitization on $Tb^{3+}$ luminescence, the $SrAl_2O_4$:$x$$Tb^{3+}$/$y$$Bi^{3+}$ (SAOTB) nanophosphors, where $x = 0$, 5.0 mol% and $0 \leq y \leq 10.0$ mol% were synthesized by solid-state reaction method using $SrCO_3$ (99%-Sigma), $Al_2O_3$ (99.9%-Himedia), $Tb_4O_7$ (99.9%-Alfa Aesar) and $Bi_2O_3$ (99.9%-Merck) as starting materials and $H_3BO_3$ (99.5%-Merck) as a flux. The initial materials were taken in stoichiometric amounts along with 2.0 wt% of $H_3BO_3$ and they were mixed well using acetone to get homogeneous powders. These powders were heat treated at 200 °C for 3 h and then sintered at 1050 °C. The samples were referred as SAOT0B0 for $x = 0$ mol% and $y = 0$ mol%, SAOT0B1 for $x = 0$ mol% and $y = 1.0$ mol% and SAOT5B0, SAOT5B1, SAOT5B3, SAOT5B5, SAOT5B10 for $x = 5.0$ mol% and $y = 0$, 1.0, 3.0, 5.0, 10.0 mol%, respectively.

The crystalline phase of SAOTB nanophosphors was obtained with X' Pert- Pro Materials Research Diffractometer using $\lambda_{CuK\alpha} = 1.5406$ Å. The Raman spectral analysis of SAOT0B0 was carried out with BRUKER RFS27 FT-Raman spectrometer using Nd: YAG laser ($\lambda = 1064$ nm). The morphology of SAOT5B5 nanophosphor was examined with Hitachi SU-70 scanning electron microscope (SEM). The photoluminescence excitation, emission and luminescence decay analysis was carried out using Jobin YVON Fluorolog-3 spectrofluorimeter provided with xenon flash lamp. All the measurements were carried out at room temperature.

## 3. Results and discussion

### 3.1. PXRD, Raman and morphological studies

The powder X-ray diffraction (PXRD) patterns of SAOTB nanophosphors shown in Fig. 1 (a) are well consistent with JCPDS No. 34-0379 and confirm that they crystallized into monoclinic phase. The schematic representation of the unit cell of monoclinic $SrAl_2O_4$ is shown in Fig. 1 (b). From the PXRD patterns one can notice that the intensity of SAOTB nanophosphors decrease with the addition of $Tb^{3+}$ or $Bi^{3+}$ or $Tb^{3+}$/$Bi^{3+}$ ions. When the electron density of the doped atom is different than that of the surrounding atoms, then a change in intensity of PXRD peaks (i.e., some peaks become more intense and other peaks less intense) as well as a shift in peak position takes place. However, the degree of these changes depends on the percentage of addition of impurities. If the electron densities of the doped atom and the surrounding atoms are close, then there is a probability to enhance the intensity of PXRD peaks. On the other hand, if the electron densities are differ then there is a possibility for reduction in intensity of PXRD peaks. In the present work, the effective ionic radius of $Sr^{2+}$ (1.18 Å) is considerably larger than the effective ionic radii of $Tb^{3+}$ (0.92 Å) and $Bi^{3+}$ (1.03 Å). Thus, the $Tb^{3+}$ and $Bi^{3+}$ replace the $Sr^{2+}$ sites rather than the $Al^{3+}$ (0.535 Å) sites without any change in coordination environment of $SrAl_2O_4$ crystal lattice. The increased amounts of $Tb^{3+}$ and $Bi^{3+}$ result a strain in lattice constant by stretching the bonds without any change in the phase of $SrAl_2O_4$ due to the difference in electron density of $Sr^{2+}$ and the impurities ($Tb^{3+}$ and $Bi^{3+}$). Thus, a reduction in intensity of PXRD peaks occurs without a change in their positions confirming the absence of phase modifications. According to the Scherrer's formula, the average size of SAOTB crystallites is estimated to be ~45 nm.

In order to identify the presence of different molecular units and to confirm the monoclinic phase of synthesized samples, the Raman analysis has been carried out for SAOT0B0 and it is presented in Fig. 1 (c). A sharp and intense Raman peak positioned at around 467 $cm^{-1}$ confirms the monoclinic phase of SAOTB nanophosphor. The observed Raman profile is similar to $SrAl_2O_4$ nanosized particles [22]. The Raman band noticed at 467 $cm^{-1}$ has been ascribed to the O–Al–O bending vibrations [23]. According to Raman selection rules, nearly 81 active modes are possible for monoclinic $SrAl_2O_4$ [24]. In the present investigation, nearly ten weak Raman features along with intense band at 467 $cm^{-1}$ have been identified. The observed Raman results support the FTIR results presented in our previous work [13,14].

In order to study the surface morphology, the grain size and the shape of particles, the SEM image of SAOT5B5 was obtained and shown in Fig. 2. The SEM results reveal a grain like morphology with homogeneous distribution of particles of different size. The average size of crystallites is found to be in the order of nanometer scale of the order of ~56 nm, which is close to those obtained from the PXRD studies. The nanophase of $SrAl_2O_4$ has been confirmed by TEM analysis [15]. The homogeneous distribution and the nanoscale crystallites could be responsible for enhanced luminescence from the SAOTB nanophosphors.

### 3.2. Luminescence of $Bi^{3+}$

The photoluminescence excitation and emission spectra of SAOT0B1 nanophosphor are illustrated in Fig. 3. The excitation spectrum reveals an intense band positioned at around 340 nm corresponding to $Bi^{3+}$: $^1S_0 \rightarrow {}^1P_1$ transition and the emission spectrum exhibits a broad band with peak maximum at around 378 nm corresponding to $Bi^{3+}$: $^3P_1 \rightarrow {}^1S_0$ transition. The Stokes shift between the excitation and emission maxima is estimated to be 2956 $cm^{-1}$, which is close to those reported for C-$GdO_3$: $Bi^{3+}$ (2700 $cm^{-1}$), $Y_2O_3$: $Bi^{3+}$ (2400 $cm^{-1}$) [25] and B-$GdO_3$: $Bi^{3+}$ (5700 $cm^{-1}$) [26]. The broad emission band with full width at half maximum (FWHM) of ~113.1 nm reveals that the $Bi^{3+}$ ions can act as good sensitizers to enhance the luminescence of $Tb^{3+}$ ions. The partial energy level diagram shown in Fig. 4 describes the excitation and emission mechanism of $Bi^{3+}$ ions in SAOTB nanophosphors.

### 3.3. Luminescence of $Tb^{3+}$/$Bi^{3+}$

The concentration of $Tb^{3+}$ ions has been optimized as 5.0 mol% for proficient green emission from SAOT nanophosphors [15]. In order to investigate the effect of $Bi^{3+}$ ions sensitization on the luminescence of $Tb^{3+}$ ions, different concentrations of $Bi^{3+}$ ions ($0 \leq y \leq 10.0$ mol%) activated SAOTB nanophosphors have been synthesized and characterized through photoluminescence excitation, emission and luminescence decay. The excitation spectra of SAOTB nanophosphors in the spectral region from 200 nm to 475 nm monitoring the emission at 544 nm corresponding to $Tb^{3+}$: $^5D_4 \rightarrow {}^7F_5$ transition are shown in Fig. 5. The excitation spectra consist of eleven $Tb^{3+}$ excitation bands. The excitation bands due to

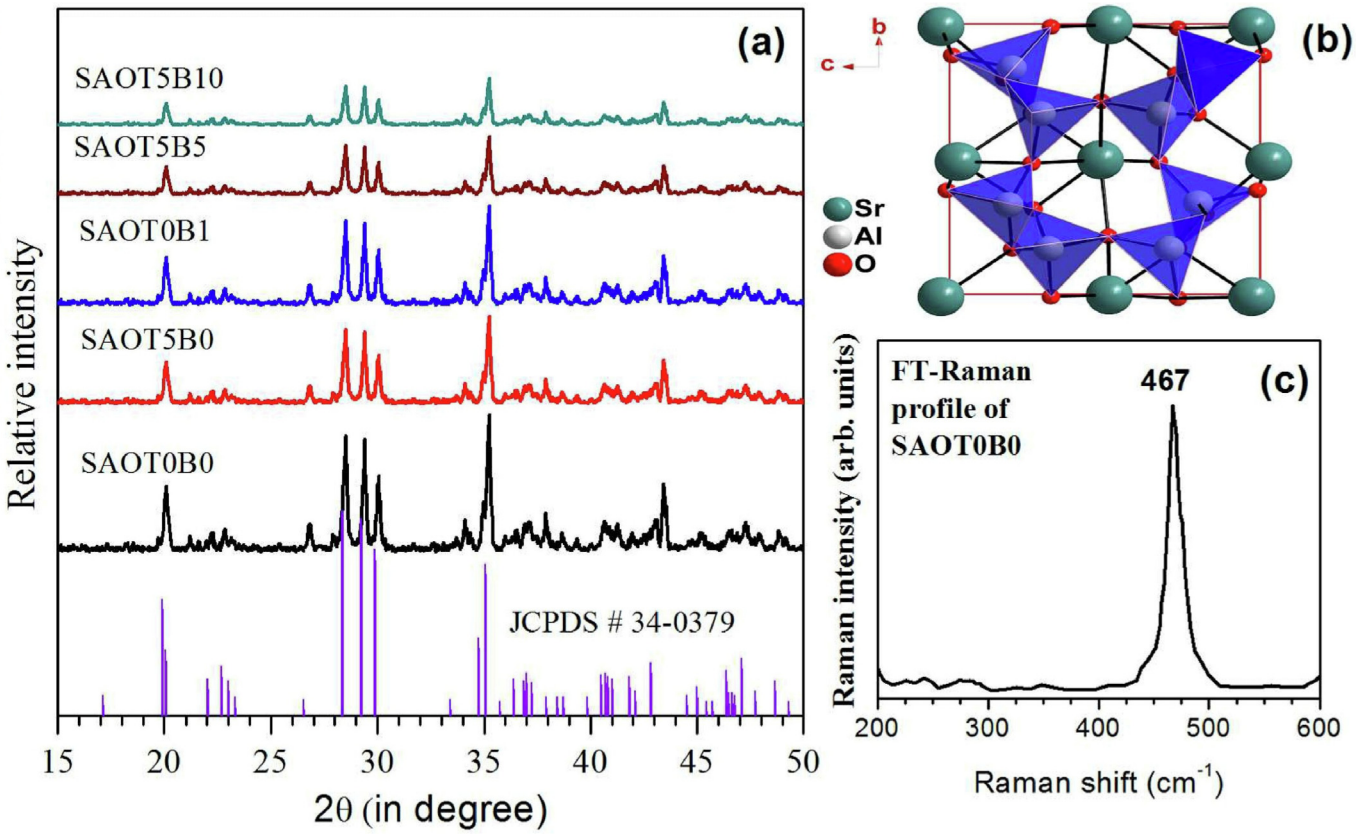



**Fig. 1.** The PXRD profiles of SAOTB nanophosphors (a) and the unit cell of SAOT0B0 (b) and the FT-Raman spectrum of SAOT0B0 (c).

$Tb^{3+}$ ions have been attributed to $^7F_6 \rightarrow {}^5K_7$ (239 nm), $^7F_6 \rightarrow {}^5K_9$ (255 nm), $^7F_6 \rightarrow {}^5F_5$ (286 nm), $^7F_6 \rightarrow {}^5H_6$ (304 nm), $^7F_6 \rightarrow {}^5D_1$ (319 nm), $^7F_6 \rightarrow {}^5L_7$ (339 nm), $^7F_6 \rightarrow {}^5L_9$ (353 nm), $^7F_6 \rightarrow {}^5L_{10}$ (371 nm), $^7F_6 \rightarrow {}^5G_6$ (378 nm), $^7F_6 \rightarrow {}^5D_3$ (390 nm) and $^7F_6 \rightarrow {}^5D_4$ (471 nm) transitions [27]. The excitation band located at around 340 nm has been ascribed to $Bi^{3+}$: $^1S_0 \rightarrow {}^1P_1$ transition.

The excitation spectra reveal an interesting variation in intensity of $Tb^{3+}$ ions with the addition of $Bi^{3+}$ ions. As the concentration of $Bi^{3+}$ ions increases, the intensity of $^7F_6 \rightarrow ({}^5K_7, {}^5K_9, {}^5F_5, {}^5H_6)$ transitions decrease and that of $^7F_6 \rightarrow ({}^5D_1, {}^5L_7, {}^5L_9, {}^5L_{10}, {}^5G_6, {}^5D_3, {}^5D_4)$ transitions increase. Since the excitation band of $Bi^{3+}$ ions occurs at ~340 nm ($Bi^{3+}$: $^1S_0 \rightarrow {}^1P_1$), the $Bi^{3+}$ ions are enable to enhance the intensity of $^7F_6 \rightarrow ({}^5D_1, {}^5L_7, {}^5L_9, {}^5L_{10}, {}^5G_6, {}^5D_3, {}^5D_4)$ transitions. The increased intensity of these transitions represents the uniform distribution of both $Tb^{3+}$ and $Bi^{3+}$ ions in SAOTB nanophosphors. It is well known that if a transfer of energy existed between an activator and sensitizer, there should be a characteristic excitation band of sensitizer in the excitation spectrum of activator obtained by monitoring its emission and there should be an overlap between the emission band of sensitizer and the excitation band of activator [28]. The excitation spectra of SAOTB nanophosphors obtained monitoring the emission through $Tb^{3+}$: $^5D_4 \rightarrow {}^7F_5$ (544 nm) transition (see Fig. 5) consists of $Bi^{3+}$: $^1S_0 \rightarrow {}^1P_1$ transition located at ~340 nm. In the present investigation, an overlapping region of emission band of $Bi^{3+}$ (sensitizer) and the excitation band of $Tb^{3+}$ (activator) has been noticed and it is illustrated in Fig. 6. One can notice from Fig. 6 that the $Tb^{3+}$: $^7F_6 \rightarrow {}^5G_6$ excitation band and the $Bi^{3+}$: $^3P_1 \rightarrow {}^1S_0$ emission band are located at ~378 nm. Since the $Tb^{3+}$: $^5L_7$ (~29498 $cm^{-1}$) and the $Bi^{3+}$: $^1P_1$ (~29412 $cm^{-1}$) energy levels have almost the same energy, the transfer of energy has been initiated from $Bi^{3+}$ to $Tb^{3+}$. These results evidence the existence of energy transfer from $Bi^{3+}$ ions to $Tb^{3+}$ ions. Thus, the luminescence analysis of SAOTB nanophosphors has been carried out by exciting at 340 nm wavelength only.

The emission spectral profiles of SAOT5By ($0 \leq y \leq 10.0$ mol%) nanophosphors excited at 340 nm wavelength in the spectral region from 480 nm to 640 nm are illustrated in Fig. 7. These spectra consist of four emission bands located at around 489, 544, 585 and 623 nm corresponding to $^5D_4 \rightarrow {}^7F_6$, $^5D_4 \rightarrow {}^7F_5$, $^5D_4 \rightarrow {}^7F_4$, $^5D_4 \rightarrow {}^7F_3$ transitions, respectively. Among these, the $^5D_4 \rightarrow {}^7F_5$ transition (544 nm) has maximum intensity exhibiting strong green emission. Additionally, the intensity of $^5D_4 \rightarrow {}^7F_J$ transitions enhances with increase of $Bi^{3+}$ concentration due to the transfer of energy from $Bi^{3+}$ ions to $Tb^{3+}$ ions upon excitation at 340 nm wavelength. The inset of Fig. 7 describes the variation of intensity of $Tb^{3+}$: $^5D_4 \rightarrow {}^7F_5$ (544 nm) transition as a function of $Bi^{3+}$ concentration in SAOT5By nanophosphors.

Upon 340 nm excitation, the population density of $Tb^{3+}$: $^5D_4$ metastable level enhances in three different ways. In the first way, the ground state $Bi^{3+}$ ions absorb the energy of incident photons and jumps to $Bi^{3+}$: $^1P_1$ level and then decays non-radiatively (NR) to $Bi^{3+}$: $^3P_1$ level causing blue emission through $Bi^{3+}$: $^3P_1 \rightarrow {}^1S_0$ (378 nm) transition when excited at 340 nm wavelength. The emitted photons through $Bi^{3+}$: $^3P_1 \rightarrow {}^1S_0$ transition stimulates some of the ground state $Tb^{3+}$ ions to $Tb^{3+}$: $^5G_6$ energy level. These excited $Tb^{3+}$ ions de-populate to $Tb^{3+}$: $^5D_4$ metastable level through a fast non-radiative process resulting to improve its population. In the second way, some of the excited $Bi^{3+}$ ions at $Bi^{3+}$: $^1P_1$ level excites few $Tb^{3+}$ ions to $Tb^{3+}$: $^5L_7$ energy level by energy transfer process. In the third way, some of $Tb^{3+}$ ions absorb the energy of incident photons and get excited to $Tb^{3+}$: $^5L_7$ energy level. These excited $Tb^{3+}$ ions at $Tb^{3+}$: $^5L_7$ energy level de-populate to

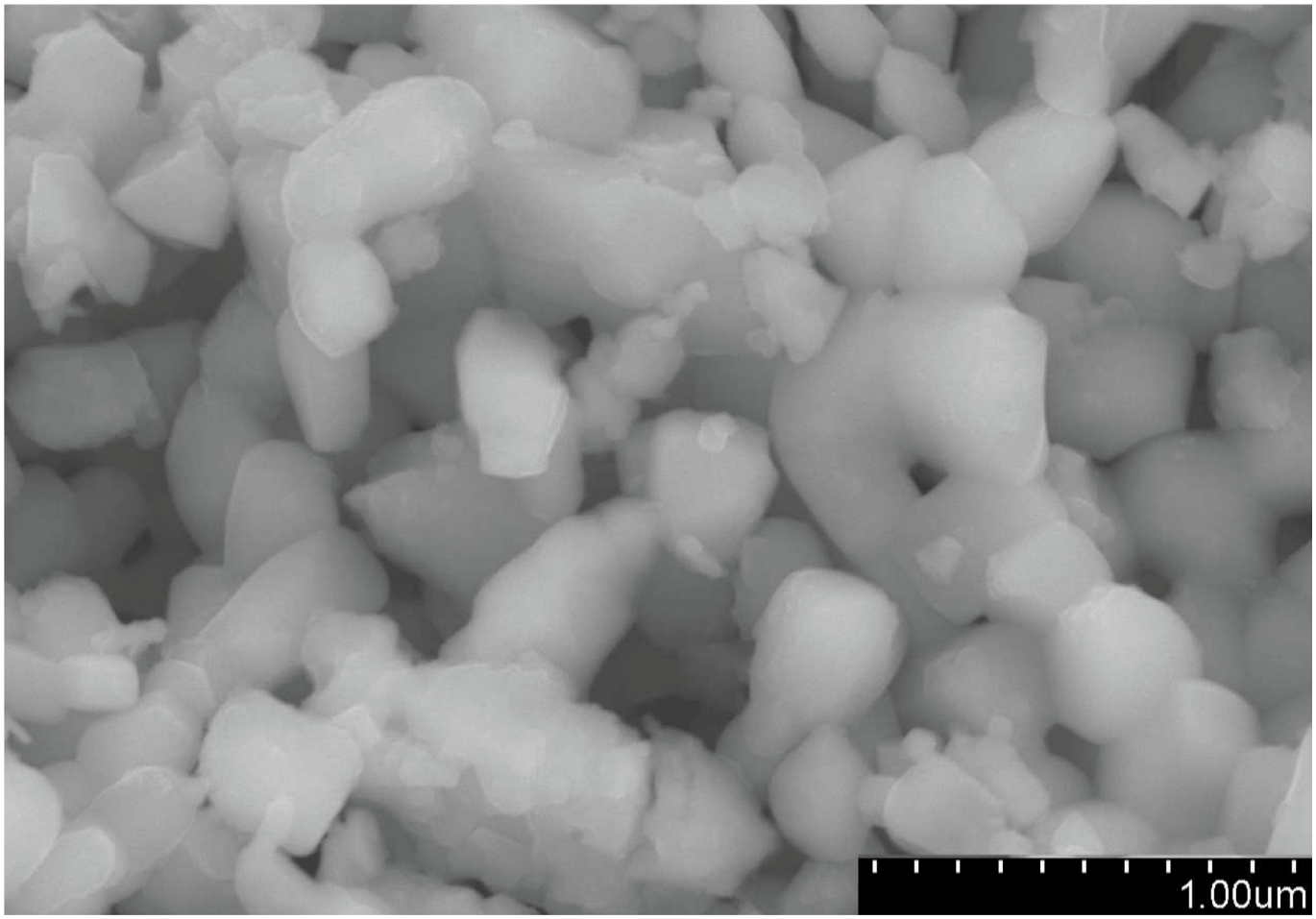



**Fig. 2.** The SEM image of SAOT5B5 nanophosphor.

$Tb^{3+}$: $^5D_4$ metastable level through a fast non-radiative decay resulting to enhance the population density at $Tb^{3+}$: $^5D_4$ metastable level. Once there exists population inversion between the $Tb^{3+}$: $^5D_4$ metastable level and its $Tb^{3+}$: $^7F_J$ lower lying energy levels, a strong and intense luminescence occurs through $Tb^{3+}$: $^5D_4 \rightarrow {}^7F_J$ transitions. The emission and the energy transfer mechanism in SAOTB

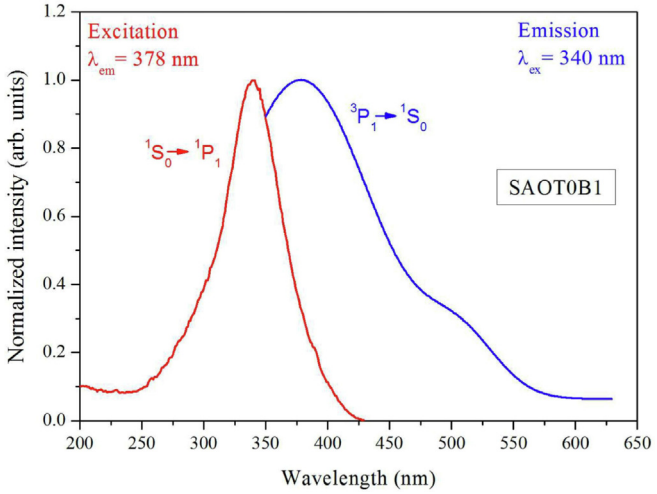



**Fig. 3.** The excitation and the emission spectra of SAOT0B1 nanophosphor.

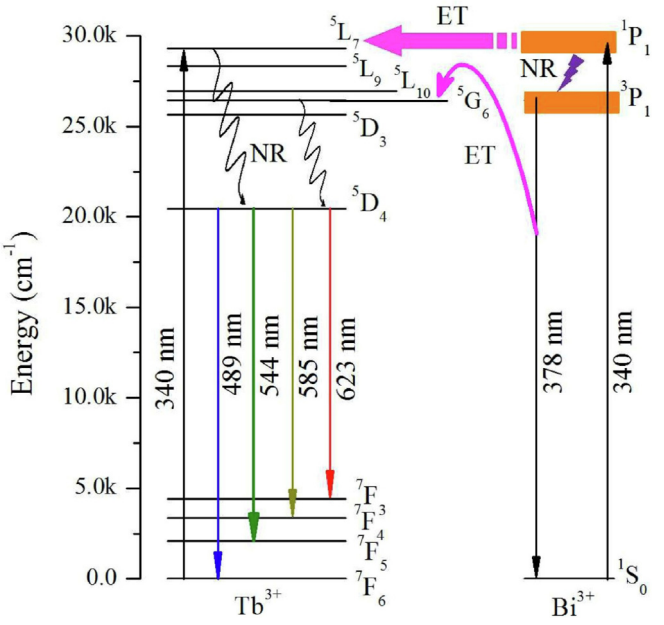



**Fig. 4.** The partial energy-level diagram illustrating the emission of $Tb^{3+}$ and $Bi^{3+}$ ions at 340 nm excitation and the energy transfer mechanism from $Bi^{3+}$ to $Tb^{3+}$ ions in SAOTB nanophosphors.

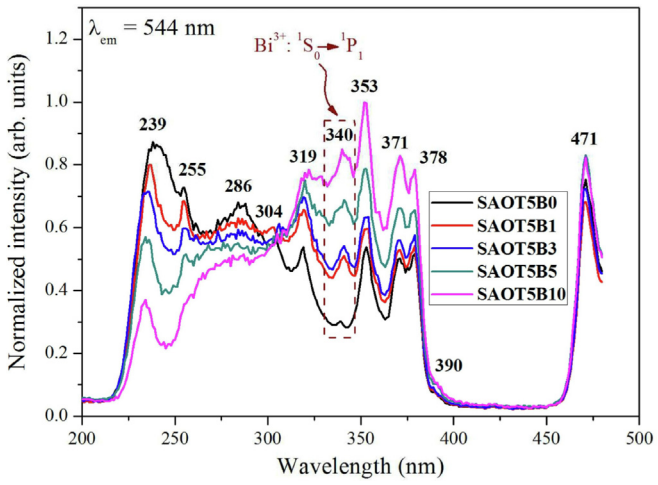



**Fig. 5.** The excitation spectra of SAOTB nanophosphors.

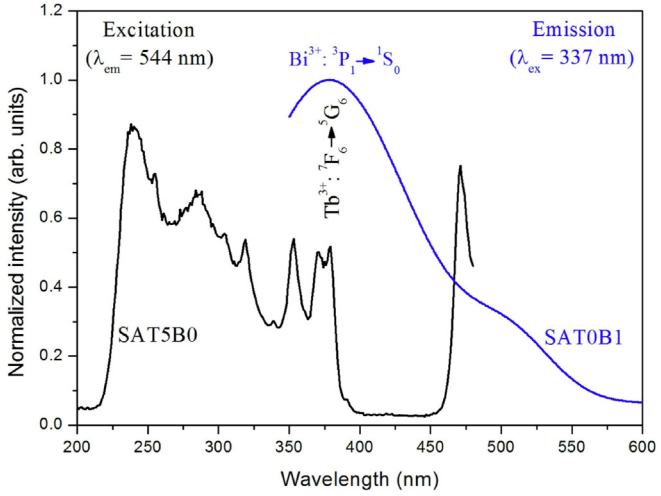



**Fig. 6.** The excitation spectrum of SAOT5B0 and the emission spectrum of SAOT0B1 nanophosphors.

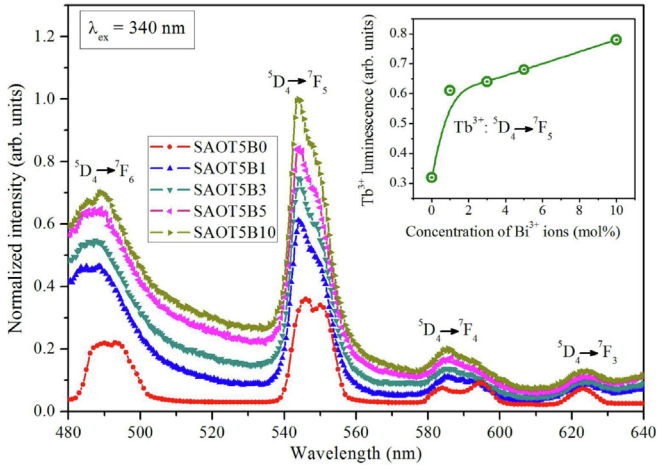



**Fig. 7.** Emission spectra of SAOTB nanophosphors. Inset is the variation of intensity of $Tb^{3+}$: $^5D_4 \rightarrow {}^7F_5$ transition as a function of $Bi^{3+}$ concentration.

nanophosphors at 340 nm excitation is illustrated in partial energy level diagram shown in Fig. 4.

The intensity of a magnetic-dipole transition ($\Delta J = \pm 1$) of $RE^{3+}$ ions becomes proficient when it has a centre of inversion symmetry with its surrounding atoms. On the other hand, the intensity of an electric-dipole transition ($\Delta J = \pm 2$) becomes prominent when it has non-inversion symmetry with its surrounding atoms [29]. In case of $Tb^{3+}$ ions, the $^5D_4 \rightarrow {}^7F_6$ (489 nm) is an electric-dipole transition and the $^5D_4 \rightarrow {}^7F_5$ (544 nm) is a magnetic-dipole transition. The emission spectral profiles shown in Fig. 7 reveal that the intensity of $^5D_4 \rightarrow {}^7F_5$ (544 nm) magnetic-dipole transition dominates the intensity of $^5D_4 \rightarrow {}^7F_6$ (489 nm) electric-dipole transition confirming the centre of inversion symmetry around the $Tb^{3+}$ ions in SAOTB nanophosphors. Furthermore, when the magnitude of intensity ratio of electric-dipole (ED) to magnetic-dipole (MD) transitions ($I_{ED/MD}$) is lower than unity, then the $Tb^{3+}$ ions invariably are present in non-inversion symmetric environment [30]. The values of $I_{ED/MD}$ are found to be 0.69, 0.74, 0.83, 0.94 and 0.85 for SAOT5B0, SAOT5B1, SAOT5B3, SAOT5B5 and SAOT5B10 nanophosphors, respectively. These results show that the $Tb^{3+}$ ions has non-inversion symmetry with its surrounding atoms. In the present investigation, the SAOT5By nanophosphors exhibit enhanced luminescence due to the effective sensitization of $Bi^{3+}$ ions by the process of transfer of energy from $Bi^{3+}$ to $Tb^{3+}$ active centers. Since, the value of $I_{ED/MD}$ increase with increase of $Bi^{3+}$ ions concentration, reaches to maximum at y = 5.0 mol% and then decrease for further rise of its concentration, the optimum concentration of $Bi^{3+}$ ions for effective and enhanced luminescence from the SAOTB nanophosphors become y = 5.0 mol%.

The Commission International de l'Eclairage (CIE) coordinates evaluated from the emission spectra (shown in Fig. 7) have been used to study the colour perception of emitted luminescence of SAOTB nanophosphors. These coordinates are found to be (0.162, 0.185), (0.296, 0.478), (0.267, 0.569), (0.287, 0.607), (0.302, 0.615) and (0.312, 0.605) for SAOT0B1, SAOT5B0, SAOT5B1, SAOT5B3, SAOT5B5 and SAOT5B10 nanophosphors, respectively and they are presented in CIE diagram shown in Fig. 8. From this figure one can notice that the SAOT0B1 nanophosphor emits intense blue luminescence and the SAOT5B0 nanophosphor emits green luminescence at 340 nm excitation. But the luminescence from the $Tb^{3+}$/$Bi^{3+}$ codoped SAOTB nanophosphors varies from bluish-green to intense green to yellowish-green when the concentration of $Bi^{3+}$

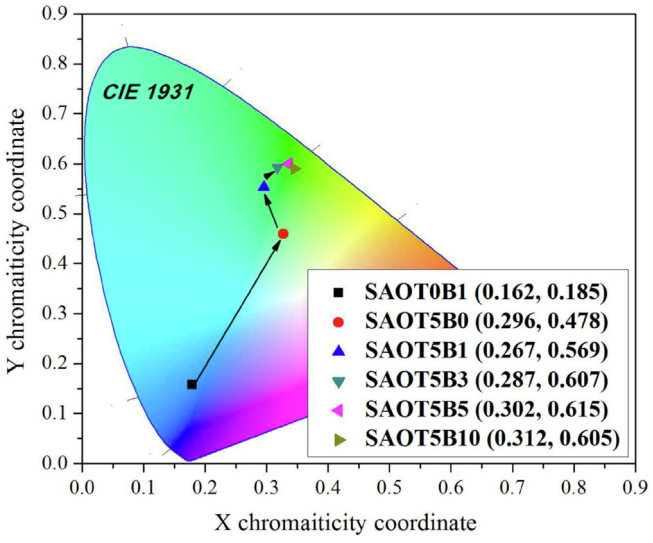



**Fig. 8.** The CIE diagram of SAOTB nanophosphors.

ions changes from 1.0 mol% to 10.0 mol%. The colour coordinates of SAOT5B5 nanophosphor (0.302, 0.615) are well located in the bright and intense green region of CIE diagram and they found close to the ITU-R BT.709-4 standard green (0.300, 0.600) and β-SiAlON:$Eu^{2+}$ (0.31, 0.60) nanophosphor [31].

The luminescence decay of $Tb^{3+}$: $^5D_4$ metastable level has been examined by exciting SAOTB nanophosphors at 340 nm wavelength and controlling the emission at 544 nm corresponding to $Tb^{3+}$: $^5D_4 \rightarrow {}^7F_5$ transition. The decay profiles of studied phosphors are well fitted to $I = I_0\, e^{-t/\tau}$, where $I$ is the intensity at time t, $I_0$ is the initial intensity and $\tau$ is the lifetime of metastable level and it can be estimated taking the first e-folding times the initial intensity of decay profiles. For SAOT5B0 nanophosphor, the lifetime is found to be ~2.53 ms, while for all the SAOT5By ($0 \leq y \leq 10.0$ mol%) nanophosphors, the lifetime is found close to ~2.60 ms, i.e., no considerable variation in lifetime of $Tb^{3+}$: $^5D_4$ metastable level is noticed when the concentration of $Bi^{3+}$ ions varies from 1.0 mol% to 10.0 mol%. However, the addition of $Bi^{3+}$ ions results a slight increase in lifetime (i.e., from 2.53 ms to 2.60 ms) due to energy transfer from $Bi^{3+}$ ions to $Tb^{3+}$ ions. For reference, the logarithmic plots of luminescence decay curves of SAOT5B0 and SAOT5B5 nanophosphors are shown in Fig. 9.

In order to know the applicability of studied phosphors for display applications, it is essential to know its luminescence quantum efficiency (η) that can be evaluated using the formula, $\eta = \frac{1}{\tau} \int I(t)\,.\,dt$, where $I(t)$ and τ represents the maximum luminescence intensity and the lifetime, respectively. For SAOT5By ($0 \leq y \leq 10.0$ mol%) nanophosphors, the value of η is found to be 0.78. The experimental results show that the luminescence intensity of $Tb^{3+}$ ions enhanced by constructive sensitization of $Bi^{3+}$ ions in SAOTB nanophosphors with no considerable variation in their quantum efficiency. Among the studied materials, the SAOT5B5 nanophosphor could be the best candidate to produce strong and intense green luminescence in a eco-friendly manner.

## 4. Conclusions

The SAOTB nanophosphors have been synthesized and characterized for various display applications. The studied materials crystallize into nanoscale monoclinic phase and the crystallites have been distributed homogeneously causing enhanced luminescence. Upon 340 nm excitation, the emitted luminescence has been tuned from bluish-green to intense green to yellowish-green when the concentration of $Bi^{3+}$ ions varies from 1.0 mol% to 5.0 mol % to 10.0 mol%. The $Bi^{3+}$ ions effectively sensitize the luminescence of $Tb^{3+}$ ions in SAOTB nanophosphors by transferring their energy to $Tb^{3+}$ ions. The SAOTB nanophosphors emit enhanced green luminescence due to non-inversion symmetric environment around the $Tb^{3+}$ ions. The observed results confirm that the SAOT5B5 nanophosphor has the highest potentiality to design new display devices operating at 544 nm green luminescence.

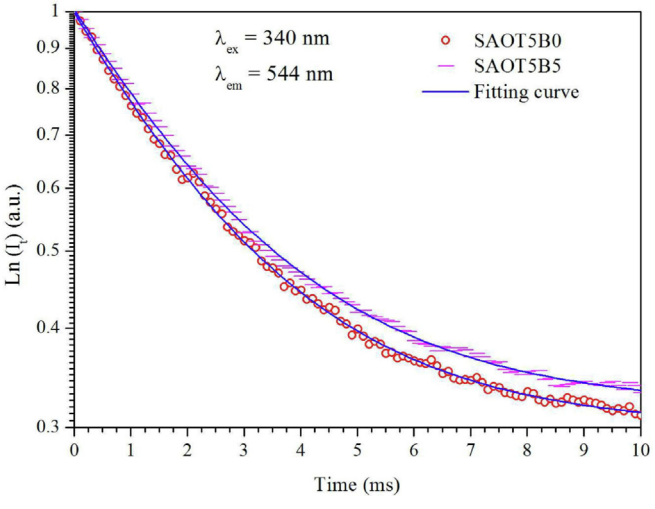



**Fig. 9.** Logarithmic plots of luminescence decay of SAOTB0 and SAOTB5 nanophosphors.

## Credit author statement

**B.C. Jamalaiah:** Conceptualization, Methodology, Software, Writing- Original draft preparation, Investigation, Supervision, Visualization, Formal analysis, Validation, Writing- Reviewing and Editing, Project administration, Funding acquisition. **N. Madhu:** Software, Data curation, Resources, Visualization, Writing-Reviewing and Editing, Funding acquisition.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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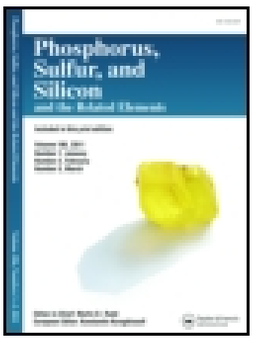
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# Synthesis and anti-diabetic activity evaluation of phosphonates containing thiazolidinedione moiety

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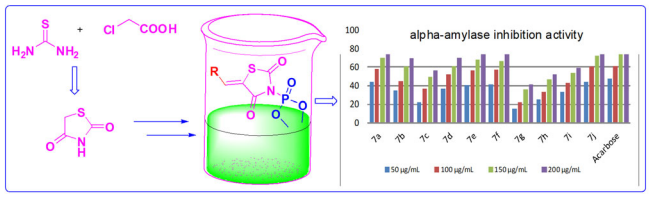
**ABSTRACT**

A sequence of substituted phosphonates containing the thiazolidinedione moiety was synthesized with good yields. The structures of all the synthesized compounds were confirmed by NMR ($^{31}$P, $^{1}$H and $^{13}$C) and IR spectroscopy, mass spectrometry and C, H, N elemental analyses. In silico molecular docking study was also carried out to evaluate their interaction and binding modes on ligands against human PPAR $\gamma$ protein for their anti-diabetic activity. From the docking results, it was determined that the compounds (Z)-dimethyl 5-(3-nitrobenzylidene)−2,4-dioxothiazolidin-3-ylphosphonate (7a), (Z)-dimethyl 5-(3-chloro-4-fluorobenzylidene)−2,4-dioxothiazolidin-3-ylphosphonate (7f), (Z)-dimethyl 5-(2,4-dichlorobenzylidene)−2,4-dioxothiazolidin-3-ylphosphonate (7e) and (Z)-dimethyl 5-((5-methoxypyridin-2-yl)methylene)−2,4-dioxothiazolidin-3-ylphosphonate (7j) have shown better binding energies (**−7.8**, **−7.6**, **−7.5** and **−7.6** Kcal/mol) with the target gene, PPAR $\gamma$ than the reference drug, Rosiglitazone (**−7.4** Kcal/mol). In vitro anti-diabetic activity of the title compounds was also screened by standard $\alpha$-amylase inhibition assay. Some of the tested compounds proved to possess promising activity when compared with the reference drug.

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Phosphonates; thiazolidinedione; molecular docking study; $\alpha$-amylase inhibition assay

**GRAPHICAL ABSTRACT**




## Introduction

A global status report on non- communicable diseases[1] revealed that Type 2 diabetes mellitus (T2DM), is a quickly progressing disease worldwide. Greenfield and Chisholm[2] reported that thiazolidinediones (TZDs) are oral anti-diabetic drugs that control Type 2 diabetes via enhancement of insulin sensitivity.[3] Pioglitazone 1, Rosiglitazone 2 and Lobeglitazone 3 (Figure 1) are examples of drugs belonging to TZD category. They act as PPAR$\gamma$ agonists and showing their effectiveness in controlling T2DM. However they are effective in controlling T2DM, hepatotoxicity is certainly one of their severe side effects. Consequently, researchers are searching out higher options in novel drug improvement for T2DM.

Literature[4a–f] reported that in organic synthesis and biochemistry, the phosphonate moiety is a key functional group. Phosphonates are structurally related to phosphorous acid as reported by Savignac and Iorga.[5] In the literature,[6–11] it is reported that phosphonates have found extensive applications in agriculture and as pharmaceuticals. They have been reported to show a wide range of biological activities with use herbicides, pesticides, detergentsv and with antibacterial, anti-diabetic, antiviral and antitumor properties. Numerous biomolecules which might be inhibitors of a few biosynthetic pathways carry a phosphonate motif. Resistance to biodegradation makes organophosphorus of interest for designing novel drugs as reported by Kononova and Nesmeyanova.[12] Recent investigations by Pettersen *et al.*[13] demonstrated the use of organophosphorus compounds in diabetic treatment. Several patents have been filed and granted on various P containing compounds as potential anti-diabetic agents. These results encouraged the author to synthesize some new organophosphorus compounds with potent anti-diabetic activity.

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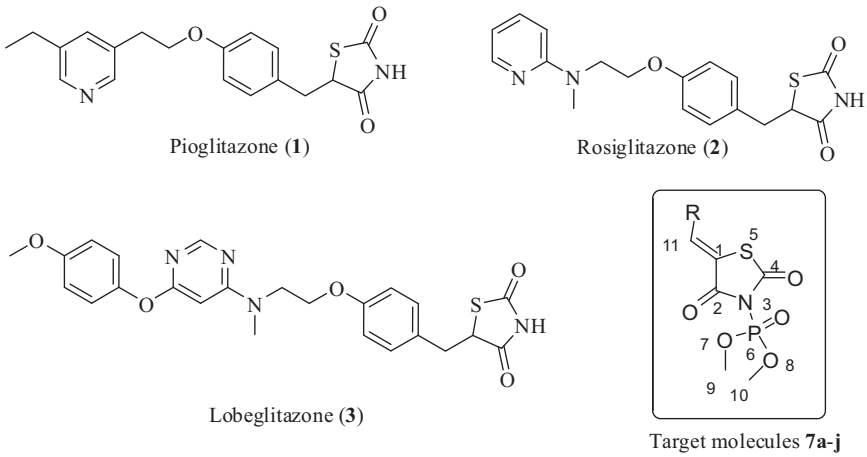
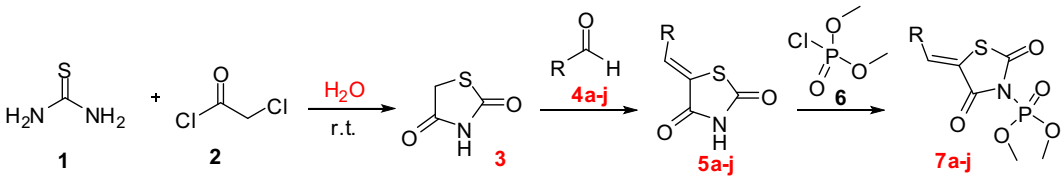
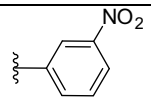
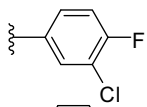
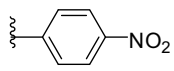
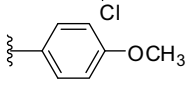
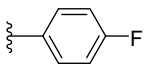
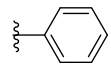
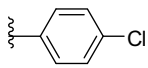
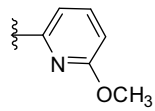
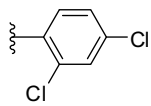
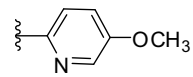



Figure 1. Biologically active anti-diabetic drugs.




| Compd | R | Compd | R |
|---|---|---|---|
| 7a |  | 7f |  |
| 7b |  | 7g |  |
| 7c |  | 7h |  |
| 7d |  | 7i |  |
| 7e |  | 7j |  |

Scheme 1. Synthesis of Phosphonates 7a–j.

On the premise of preceding reviews and continuing interest in the synthesis of phosphonates containing TZD moiety and in the extension of our studies to broaden new anti-diabetic agents, we targeted the synthesis of some new phosphonates containing TZD moiety. Molecular docking studies were also carried out to assess their interaction and binding modes with the target receptor.

## Results and discussion

### Chemistry

In the present work, we have synthesized a series of phosphonates containing TZD moiety from 2,4-thiazolidinedione in high yields with simple chemistry. The synthetic route was shown in (Scheme 1).

IR, $^{1}$H, $^{13}$C, $^{31}$P NMR, mass spectral data and elemental analyses were carried out to characterize 7a–j which are described in the Experimental. IR absorptions in the range 1729–1720 and 1218–1210 cm$^{-1}$ were assigned to C = O and P = O stretching vibrations respectively for 7a–j. In $^{1}$H NMR spectra, signals due to Ar-H were observed as in the range of $\delta$ 8.31–7.65 ppm. The singlets at $\delta$ 3.72 and $\delta$ 8.02 were due to methyl protons of P-O-CH$_3$ and = C-H protons respectively for 7a–j. $^{13}$C NMR chemical shift for = C-H carbon and methyl carbons of P-O-CH$_3$ were observed at 142.8 and 51.5 ppm respectively. $^{31}$P NMR spectra showed signals for 7a–j in the range 22.8–15.6 ppm. $M^{+\cdot}$ ions were found in the predictable m/z values in mass spectra. The representative spectra ($^{1}$H, $^{31}$P and IR) of new compounds 7a–j are available in the Supplemental Materials (Figures S 1-S 19).

### Pharmacology

From the docking results, it is observed that the compounds **7a**, **7f, 7h, 7e** and **7j** formed higher binding energies (**−7.8**, **−7.6**, **−7.4, −7.5** and **−7.6** *Kcal/mol*) with the target gene, PPAR $\gamma$ than the reference compound (**−7.4** *Kcal/mol*). Although the binding energies of the rest of the compounds were close to the reference compound, they were fitted in the active site of the target gene properly. Binding energies and bonding pose of ligands with target protein were mentioned in detail in Table S 1 and Figure S 20. (See Supplemental Materials). Out of the all title compounds, **7c**, **7d** and **7e** have formed hydrophobic interactions with the target protein (Figure S 21). The present investigation demonstrates that the synthesized compounds will be possible promising anti-diabetic drugs, which can be effectively used in the treatment of manifestation of diabetic complications.

Molecular docking results motivated us to screen the title compounds for their *in vitro* anti-diabetic activity by α-amylase inhibition activity method at four concentrations of 50, 100, 150 and 200 µg/mL. The screening results (See Supplemental Materials for Table S 2) of 7a–j showed that most of the derivatives exhibit good α-amylase inhibition activity when compared with the standard drug, Acarbose. Especially compound 7j bearing a 5-methoxypyridin-2-yl moiety (44.3–82.2 µg/mL), 7a bearing a 3-nitrobenzylidene motif (43.9–79.6 µg/mL), 7f incorporating a 3-chloro-4-fluorobenzylidene motif (41.4–76.5 µg/mL) and 7e bearing a 2,4-dichlorobenzylidene moiety (40.9–75.4 µg/mL) exhibited good inhibition when compared with the standard drug, Acarbose (47.8–85.9 µg/mL).

## Conclusion

The present study reports the successful synthesis of phosphonates in high yield with simple chemistry. *In silico* molecular docking study was performed for the ligands against human PPAR$\gamma$ protein for their anti-diabetic activity. The study showed that 7a (3-$NO_2$), 7f (3-Cl, 4-F), 7 h (-H), 7e (2,4-di-Cl) and 7j (4-$OCH_3$) were formed higher binding energies (−7.8, −7.6, −7.4, −7.5 and −7.6 *Kcal/mol*) with the target gene, PPAR$\gamma$ than the reference drug, Rosiglitazone (−7.4 *Kcal/mol*) which demonstrate that the synthesized compounds may become the promising next generation of anti-diabetic agents. *In vitro* anti-diabetic activity was also performed by α-amylase inhibition activity method. The screening results of 7a–j showed that most of the derivatives exhibit good α-amylase inhibition activity when compared with the standard drug, Acarbose. Especially the compounds 7j, 7a, 7f and 7e exhibited good inhibition when compared with the standard drug.

## Experimental

### Materials and characterization techniques

The chemical compounds were purchased from Sd. Fine Chem. Ltd., India; Qualigens, Mumbai and some of them have been purified the usage of popular processes. The purity of the compounds was checked by TLC chromatography on Al sheet of silica gel. *J* (coupling constants) and $\delta$ (chemical shift) values have been said in Hz and ppm, respectively. Bruker AMX spectrometer became used to record $^{31}$P (161.9 MHz), $^{1}$H (400 MHz) and $^{13}$C (100 MHz) NMR spectra. The symbols 's' for singlet, 'd' for doublet, 't' for triplet and 'm' for multiplet have been used to represent peaks in NMR spectra. LC-MS were recorded on SHIMADZU 2010 A. Thermo Finnigan Flash 1112 apparatus was used for CHN evaluation. Bruker IFS 55 (Equinox) FTIR spectrometer in KBr was used to report IR spectra. The Supplemental Materials contains sample $^{1}$H, $^{13}$C and $^{31}$P NMR spectra for products 7 (Figures S 1 – S 19).

### Procedures

#### Synthesis of 2,4-thiazolidinedione[2,14]

A solution containing of chloroacetic acid (0.5 mol) in water (50 mL) and of thiourea (0.5 mol) in water (50 mL) were mixed in a round bottomed flask and stirred for 15 min to obtain a white ppt on cooling. Concentrated HCl (50 mL) was added slowly using a dropping funnel and refluxed for 10–15 h at around 105 °C. On cooling, the contents of the flask solidified to a cluster of white needles shaped compound. Traces of HCl removed by using washing with water after which dried. The pure compound became obtained by recrystallization from ethyl alcohol. m.p. 122–124 °C.

#### Synthesis of 5-substituted-2,4-thiazolidinedione (5a–j)[15–17]

Substituted benzaldehyde (0.1 mol) [3a–j] was added to 2,4-thiazolidinedione (0.1 mol) in toluene in the presence of piperidine and refluxed at 110 °C for 6–7 h and then cooled to room temperature to precipitate out the corresponding TZD derivatives (5a–j). TLC (ethylacetate: *n*-hexane, 6:4) was used for verifying the improvement of the process.

#### Synthesis of phosphonates (7a–j)

The compound **5a** (0.01 mol) in THF:Pyridine (20 mL, 1:2 ratio) and sodium hydride (0.01 mol) were mixed at 0 °C and stirred for 1 h at 15 °C to offer the sodium salt of **5a**. Afterward, dimethyl phosphorochloridate (0.01 mol)[6] in dry THF (10 mL) was added and the reaction mixture was kept at 10oC and then stirred for 4 h at 40 °C. After completion of the reaction checked by TLC, the reaction mixture was filtered to remove salt (NaCl) and leaving the filtrate. The crude product was obtained from the filtrate using a rotary evaporator. The pure compound (Z)-dimethyl-5-(3-nitrobenzylidene)−2,4-dioxothiazolidin-3-yl phosphonate was obtained by column chromatography using ethyl acetate: *n*-hexane (3:2) as eluent. The same experimental protocol was used to synthesize the remaining title compounds 7b–j.

### Characterization of title compounds (7a–j)

*(Z)-dimethyl 5-(3-nitrobenzylidene)-2,4-dioxothiazolidin-3-ylphosphonate (7a).* Yield: 85%; Solid. mp: 234–236 °C; $^{1}$H NMR (DMSO-$d_6$) 8.43 (s, 1H, Ar-H), 8.12 (d, $J$ = 8.4 Hz, 1H, Ar-H), 7.73 (s, 1H, =C-H), 7.49 (d, $J$ = 8.4 Hz, 1H, Ar-H), 6.67 (t, $J$ = 8.0 Hz, 1H, Ar-H), 3.64 (s, 6H, O-$CH_3$); $^{13}$C NMR (DMSO-$d_6$) 118.2 (C-1), 165.4 (C-2), 164.1 (C-4), 51.5 (C-9, C-10), 142.8 (C-11), 135.5 (C-12), 133.8 (C-13), 128.7 (C-14), 123.8 (C-15), 145.9 (C-16), 123.4 (C-17); $^{31}$P NMR (DMSO-$d_6$) 22.4 ppm; IR (KBr) ($\nu_{max}$ cm$^{-1}$): 2922 (=C-H), 1743 (C = O), 1228 (P = O), 1017 (P-O-$C_{alip}$); LCMS (m/z, %): 359 (M + H$^+$, 100); For $C_{12}H_{11}N_2O_7PS$; calcd: C, 40.23; H, 3.09; N, 7.82; found: C, 40.29; H, 3.03; N, 7.89%.

*(Z)-dimethyl 5-(4-nitrobenzylidene)-2,4-dioxothiazolidin-3-ylphosphonate (7b).* Yield: 88%; Solid. mp: 212–214 °C; $^{1}$H NMR (DMSO-$d_6$) 8.14 (d, $J$ = 8.4 Hz, 2H, Ar-H), 8.01 (d, $J$ = 8.4 Hz, 2H, Ar-H), 7.73 (s, 1H, =C-H), 3.64 (s, 6H, O-$CH_3$); $^{13}$C NMR (DMSO-$d_6$) 118.2 (C-1), 165.4 (C-2), 164.1 (C-4), 51.5 (C-9, C-10), 142.8 (C-11), 140.5 (C-12), 129.5 (C-13, C-17), 124.3 (C-14, C-16), 145.6 (C-15); $^{31}$P NMR (DMSO-$d_6$) 22.0 ppm; IR (KBr) ($\nu_{max}$ cm$^{-1}$): 2922 (=C-H), 1741 (C = O), 1226 (P = O), 1016 (P-O-$C_{alip}$); LCMS (m/z, %): 359 (M + H$^+$, 100); For $C_{12}H_{11}N_2O_7PS$; calcd: C, 40.23; H, 3.09; N, 7.82; found: C, 40.32; H, 3.05; N, 7.90%.

*(Z)-dimethyl 5-(4-fluorobenzylidene)-2,4-dioxothiazolidin-3-ylphosphonate (7c).* Yield: 81%; Solid. mp: 203–204 °C; $^{1}$H NMR (DMSO-$d_6$) 7.87–7.25 (m, 4H, Ar-H), 7.73 (s, 1H, =C-H), 3.64 (s, 6H, O-$CH_3$); $^{13}$C NMR (DMSO-$d_6$) 118.2 (C-1), 165.4 (C-2), 164.1 (C-4), 51.5 (C-9, C-10), 142.8 (C-11), 131.2 (C-12), 131.7 (C-13, C-17), 116.6 (C-14, C-16), 161.4 (C-15); $^{31}$P NMR (DMSO-$d_6$) 21.2 ppm; IR (KBr) ($\nu_{max}$ cm$^{-1}$): 2918 (=C-H), 1727 (C = O), 1215 (P = O), 1015 (P-O-$C_{alip}$); LCMS (m/z, %): 332 (M + H$^+$, 100); For $C_{12}H_{11}FNO_5PS$; calcd: C, 43.51; H, 3.35; N, 4.23; found: 43.58; H, 3.29; N, 4.28%.

*(Z)-dimethyl 5-(4-chlorobenzylidene)-2,4-dioxothiazolidin-3-ylphosphonate (7d).* Yield: 87%; Solid. mp: 238–240 °C; $^{1}$H NMR (DMSO-$d_6$) 7.76–7.52 (m, 4H, Ar-H), 7.73 (s, 1H, =C-H), 3.64 (s, 6H, O-$CH_3$); $^{13}$C NMR (DMSO-$d_6$) 118.2 (C-1), 165.4 (C-2), 164.1 (C-4), 51.5 (C-9, C-10), 142.8 (C-11), 134.5 (C-12), 129.5 (C-13, C-17), 127.3 (C-14, C-16), 132.6 (C-15); $^{31}$P NMR (DMSO-$d_6$) 19.7 ppm; IR (KBr) ($\nu_{max}$ cm$^{-1}$): 2912 (=C-H), 1722 (C = O), 1211 (P = O), 1010 (P-O-$C_{alip}$); LCMS (m/z, %): 348 (M + H$^+$, 100); For $C_{12}H_{11}ClNO_5PS$; calcd: C, 41.45; H, 3.19; N, 4.03; found: C, 41.52; H, 3.13; N, 4.10%.

*(Z)-dimethyl 5-(2,4-dichlorobenzylidene)-2,4-dioxothiazolidin-3-ylphosphonate (7e).* Yield: 90%; Solid. mp: 246–248 °C; $^{1}$H NMR (DMSO-$d_6$) 7.73 (s, 1H, =C-H), 7.71 (d, $J$ = 8.0 Hz, 1H, Ar-H), 7.49 (s, 1H, Ar-H), 7.32 (d, $J$ = 7.6 Hz, 1H, Ar-H), 3.64 (s, 6H, O-$CH_3$); $^{13}$C NMR (DMSO-$d_6$) 118.2 (C-1), 165.4 (C-2), 164.1 (C-4), 51.5 (C-9, C-10), 142.8 (C-11), 132.4 (C-12), 131.7 (C-13), 127.9 (C-14), 126.7 (C-15), 129.3 (C-16), 135.3 (C-17); $^{31}$P NMR (DMSO-$d_6$) 20.5 ppm; IR (KBr) ($\nu_{max}$ cm$^{-1}$): 2915 (=C-H), 1726 (C = O), 1213 (P = O), 1016 (P-O-$C_{alip}$); LCMS (m/z, %): 382 (M + H$^+$, 100); For $C_{12}H_{10}Cl_2NO_5PS$; calcd: C, 37.71; H, 2.64; N, 3.67; found: C, 37.78; H, 2.60; N, 3.72%.

*(Z)-dimethyl 5-(3-chloro-4-fluorobenzylidene)-2,4-dioxothiazolidin-3-ylphosphonate (7f).* Yield: 92%; Solid. mp: 241–243 °C; $^{1}$H NMR (DMSO-$d_6$) 7.73 (s, 1H, =C-H), 7.71 (d, $J$ = 8.0 Hz, 1H, Ar-H), 7.45 (s, 1H, Ar-H), 7.25 (d, $J$ = 7.6 Hz, 1H, Ar-H), 3.64 (s, 6H, O-$CH_3$); $^{13}$C NMR (DMSO-$d_6$) 118.2 (C-1), 165.4 (C-2), 164.1 (C-4), 51.5 (C-9, C-10), 142.8 (C-11), 133.4 (C-12), 129.1 (C-13), 122.3 (C-14), 157.4 (C-15), 117.6 (C-16), 129.2 (C-17); $^{31}$P NMR (DMSO-$d_6$) 21.3 ppm; IR (KBr) ($\nu_{max}$ cm$^{-1}$): 2916 (=C-H), 1727 (C = O), 1216 (P = O), 1015 (P-O-$C_{alip}$); LCMS (m/z, %): 366 (M + H$^+$, 100); For $C_{12}H_{10}ClFNO_5PS$; calcd: C, 39.41; H, 2.76; N, 3.83; found: C, 39.47; H, 2.70; N, 3.89%.

*(Z)-dimethyl 5-(4-methoxybenzylidene)-2,4-dioxothiazolidin-3-ylphosphonate (7g).* Yield: 91%; Solid. mp: 228–230 °C; $^{1}$H NMR (DMSO-$d_6$) 7.73 (s, 1H, =C-H), 7.49 (d, $J$ = 8.0 Hz, 2H, Ar-H), 6.67 (d, $J$ = 8.0 Hz, 2H, Ar-H), 3.90 (s, 3H, O-$CH_3$), 3.64 (s, 6H, O-$CH_3$); $^{13}$C NMR (DMSO-$d_6$) 118.2 (C-1), 165.4 (C-2), 164.1 (C-4), 51.5 (C-9, C-10), 142.8 (C-11), 126.8 (C-12), 131.4 (C-13, C-17), 116.2 (C-14, C-16), 157.9 (C-15), 54.6 (C-18); $^{31}$P NMR (DMSO-$d_6$) 16.8 ppm; IR (KBr) ($\nu_{max}$ cm$^{-1}$): 2881 (=C-H), 1721 (C = O), 1226 (P = O), 1008 (P-O-$C_{alip}$); LCMS (m/z, %): 344 (M + H$^+$, 100); For $C_{13}H_{14}NO_6PS$; calcd: C, 45.48; H, 4.11; N, 4.08; found: C, 45.54; H, 4.05; N, 4.14%.

*(Z)-dimethyl 5-benzylidene-2,4-dioxothiazolidin-3-ylphosphonate (7h).* Yield: 85%; Solid. mp: 207–209 °C; $^{1}$H NMR (DMSO-$d_6$) 7.78–7.29 (m, 5H, Ar-H), 7.73 (s, 1H, =C-H), 3.64 (s, 6H, O-$CH_3$); $^{13}$C NMR (DMSO-$d_6$) 118.2 (C-1), 165.4 (C-2), 164.1 (C-4), 51.5 (C-9, C-10), 142.8 (C-11), 134.7 (C-12), 129.3 (C-13, C-17), 127.8 (C-14, C-16), 126.6 (C-15); $^{31}$P NMR (DMSO-$d_6$) 17.5 ppm; IR (KBr) ($\nu_{max}$ cm$^{-1}$): 2903 (=C-H), 1727 (C = O), 1210 (P = O), 1012 (P-O-$C_{alip}$); LCMS (m/z, %): 314 (M + H$^+$, 100); For $C_{12}H_{12}NO_5PS$; calcd: C, 46.01; H, 3.86; N, 4.47; found: C, 46.07; H, 3.80; N, 4.52%.

*(Z)-dimethyl 5-((6-methoxypyridin-2-yl)methylene)-2,4-dioxothiazolidin-3-ylphosphonate (7i).* Yield: 84%; Solid. mp: 253–255 °C; $^{1}$H NMR (DMSO-$d_6$) 7.73 (s, 1H, =C-H), 7.67 (t, $J$ = 7.6 Hz, 1H, Ar-H), 6.54 (d, $J$ = 7.6 Hz, 2H, Ar-H), 3.93 (s, 3H, O-$CH_3$), 3.64 (s, 6H, O-$CH_3$); $^{13}$C NMR (DMSO-$d_6$) 118.2 (C-1), 165.4 (C-2), 164.1 (C-4), 51.5 (C-9, C-10), 142.8 (C-11), 150.7 (C-12), 161.5 (C-14), 107.4 (C-15), 137.8 (C-16), 112.4 (C-17), 53.5 (C-18); $^{31}$P NMR (DMSO-$d_6$) 18.6 ppm; IR (KBr) ($\nu_{max}$ cm$^{-1}$): 2912 (=C-H), 1729 (C = O), 1218 (P = O), 1016 (P-O-$C_{alip}$); LCMS (m/z, %): 345 (M + H$^+$, 100); For $C_{12}H_{13}N_2O_6PS$; calcd: C, 41.86; H, 3.81; N, 8.14; found: C, 41.92; H, 3.75; N, 8.19%.

*(Z)-dimethyl 5-((5-methoxypyridin-2-yl)methylene)-2,4-dioxothiazolidin-3-ylphosphonate (7j).* Yield: 80%; Solid. mp:

221–223 °C; $^{1}$H NMR (DMSO-$d_6$) 8.17 (s, 1H, Ar-H), 7.73 (s, 1H, =C-H), 7.49 (d, $J$ = 8.4 Hz, 1H, Ar-H), 7.13 (d, $J$ = 8.4 Hz, 1H, Ar-H), 3.93 (s, 3H, O-$\underline{CH_3}$), 3.64 (s, 6H, O-$\underline{CH_3}$); $^{13}$C NMR (DMSO-$d_6$) 118.2 (C-1), 165.4 (C-2), 164.1 (C-4), 51.5 (C-9, C-10), 142.8 (C-11), 144.6 (C-12), 128.5 (C-14), 153.3 (C-15), 121.4 (C-16), 122.3 (C-17), 54.7 (C-18); $^{31}$P NMR (DMSO-$d_6$) 18.8 ppm; IR (KBr) ($\nu_{max}$ cm$^{-1}$): 2814 (=C-H), 1722 (C = O), 1222 (P = O), 1019 (P-O-C$_{alip}$); LCMS (m/z, %): 345 (M + H$^+$, 100); For $C_{12}H_{13}N_2O_6PS$; calcd: C, 41.86; H, 3.81; N, 8.14; found: C, 41.93; H, 3.77; N, 8.21%.

### *In silico molecular docking studies*

The structure of PPAR $\gamma$ (PDB: 5YCP) and the reference drug, Rosiglitazone (Pub Chem ID 77999) (Figure S14) was downloaded from the RCSB protein Data Bank and Pub Chem Database. The water molecules and hetero atoms were removed from the structures and were loaded into MOE working environment followed by protonation and energy minimization using MMFF94x force field at a cut off value of 0.05. Chem sketch Module has been used for structure drawing of the compounds; energy minimized was done with universal force field (UFF) and converted into pdb format as required for docking. Alpha triangle placement methodology was used for effective docking of all the title compounds and the poses are generated by superposition of triplets of receptor site points and ligand atom triplets. For each compound, 10 conformations were generated and they were refined and rescored. Interactions of the ligands with target protein were analyzed using PyMol Visualizer.[18]

### *α-Amylase inhibitory activity*

The α-amylase inhibitory activity had been executed employing standard procedure according to B. Nickavar and G. Amin (2011)[19] which was at first proposed by Patil *et al* with slight modifications.[20] (See Supplemental Materials for detailed procedure).

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# Plant Compounds for the Treatment of Diabetes, a Metabolic Disorder: NF-κB as a Therapeutic Target

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## Abstract

**Background:** The prevalence of diabetes in the world population hás reached 8.8 % and is expected to rise to 10.4% by 2040. Hence, there is an urgent need for the discovery of drugs against therapeutic targets to sojourn its prevalence. Previous studies proved that NF-κB serves as a central agent in the development of diabetic complications.

**Objectives:** This review intended to list the natural plant compounds that would act as inhibitors of NF-κB signalling in different organs under the diabetic condition with their possible mechanism of action.

**Methods:** Information on NF-κB, diabetes, natural products, and relation in between them, was gathered from scientific literature databases such as Pubmed, Medline, Google scholar, Science Direct, Springer, Wiley online library.

**Results and conclusion:** NF-κB plays a crucial role in the development of diabetic complications because of its link in the expression of genes that are responsible for organs damage such as kidney, brain, eye, liver, heart, muscle, endothelium, adipose tissue and pancreas by inflammation, apoptosis and oxidative stress. Activation of PPAR-α, SIRT3/1, and FXR through many cascades by plant compounds such as terpenoids, iridoids, flavonoids, alkaloids, phenols, tannins, carbohydrates, and phytocannabinoids recovers diabetic complications. These compounds also exhibit the prevention of NF-κB translocation into the nucleus by inhibiting NF-κB activators, such as VEGFR, RAGE and TLR4 receptors, which in turn, prevent the activation of many genes involved in tissue damage. Current knowledge on the treatment of diabetes by targeting NF-κB is limited, so future studies would enlighten accordingly.

**Keywords:** Diabetes; NF-κB; diabetic complications; hyperglycemia; inflammatory mediators; insulin resistance; natural products.

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# Non-differentiable multi objective fractional minimax programming problem under $[F, \alpha, \rho, d]$-convex functions

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**Abstract**
In this paper, we derive some theorems and duality theorems on non-differentiable Multiobject Fractional Minimax Programming Under $[F, \alpha, \rho, d]$ convex function.

**Keywords:** $[F, \alpha, \rho, d]$ convex function and Duality

## 1. Introduction

Minimax fractional problems appear in the formulation of discrete and continous rational approximation problems with respect to the Chebyshev Norm [3], in continuous rational games [12], in multiobjective programming [15], in engineering design as well as in some portfolio selection problems discussed by Bajona-Xandri and Martinez legaz [2].

Minimax mathematical programming has been of much interest in the recent past [1, 4, 5, 11, 13, 17, 18, 19]. Schmitendorf [11] established necessary and sufficient optimality conditions for minimax problem. Tanimoto [14] applied these optimality conditions to define a dual problem and derived duality theorms, which were extended for the fractional analogue of generalized minimax problem by Yadav and Mukherjee [18].

Motivated by various concepts of generalized convexity, Liang *et al*. [8, 9] introduced a unified formulation of generalized convexity, which was called $[F, \alpha, \rho, d]$- convexity and obtained some corresponding optimality conditions and duality results for the single objective practional problems and multiobjective problems. Recently, Liang and Shi [10] obtained sufficient conditions and duality theorems for minimax fractional problem under $[F, \alpha, \rho, d]$-convexity. Lia *et al*. [7] derived necessary and sufficient conditions for nondifferentiable minimax fractional problem with generalized convexity and applied these optimality conditions to construct one parametric dual model and also discussed duality theorems, Lai and Lee [6] obtained duality theorems for two parametric-free dual models of non-differentiable minimax fractional problem involving generalized convexity assumptions. Recently, Mishra *et al*. [12] established duality results for one parametric and two parametric-free dual models of nondifferentiable minimax fractional programming problem under generalized univexity.

But no serious attempt in utilizing multiobjective fractional minimiax under $[F, \alpha, \rho, d]$-convexity. Hence in this Paper an attempt is made to fill the gap in the aim of research by developing some theorems based on $[F, \alpha, \rho, d]$ convex function.

## 2. Formulation

We now consider the following non-differentiable minimax fractional programming problem.

### 2.1. Primal Problem

$$(FP)\quad \min_{x \in R^n} \sup_{y \in Y} \frac{f_i(x, y) + (x^t, Bx)^{\frac{1}{2}}}{h_i(x, y) - (x^t, Dx)^{\frac{1}{2}}},$$

$$\text{Subject to } g_j(x) \leq 0,\ x \in X,$$

Where Y is a compact subset of $R^m, f_i, h_i : R^n \times R^m \to R$ are $C^1$ on $R^n \times R^m$ and $g_j : R^n \to R^p$ is $C^1$ on $R^n$. B and D are nxn positive semidefinite matrices.

Let $S = \{x \in X : g(x) \leq 0\}$ denote the set of all feasible solutions of $(FP)$. For each $(x, y) \in R^n \times R^m$, we define

$$\phi(x, y) = \frac{f_i(x, y) + (x^t, Bx)^{\frac{1}{2}}}{h_i(x, y) - (x^t, Dx)^{\frac{1}{2}}},$$

Such that for each $(x, y) \in s \times Y, f_i(x, y) + (x^t, Bx)^{\frac{1}{2}} \geq 0$ and $h_i(x, y) - (x^t, Dx)^{\frac{1}{2}} > 0$. For each $x \in s,$ we define

$$J(x) = \left\{ j \in J \quad g_j(x) = 0 \right\}. \text{ where } J = \{1, 2, ..... p\}$$

$$Y(x) = \left\{ y \in Y : \frac{f_i(x, y) + (x^t, Bx)^{\frac{1}{2}}}{h_i(x, y) - (x^t, Dx)^{\frac{1}{2}}} = \sup_{z \in Y} \frac{f_i(x, z) + (x^t, Bx)^{\frac{1}{2}}}{h_i(x, z) - (x^t, Dx)^{\frac{1}{2}}} \right\},$$

$$k(x) = \left(s, t_i, \bar{y}\right) \in N \times R_+^s \times R^{ms} : 1 \leq s \leq n+1, t = (t_1, t_2 ..... t_s) \in R_+^s$$

$$\text{with } \sum_{i=1}^{s} t_i = 1, \ \bar{y} = (\bar{y}_1, \bar{y}_2 ..... \bar{y}_s) \text{ with } \bar{y}_i \in Y(x) \ (i = 1, 2, .... s)$$

Since f and h are continuously differentiable and Y is compact in $R^m$, it follows that for each $x^* \in s, y(x^*) \neq \phi$, and for any $\bar{y}_i \in Y(x^*)$, we have a positive constant

$$k_0 = \phi(x^*, \bar{y}_i) = \frac{f_i(x^*, \bar{y}_i) + (x^{*t}, Bx^*)^{\frac{1}{2}}}{h_i(x^*, \bar{y}_i) - (x^{*t}, Dx^*)^{\frac{1}{2}}}$$

We shall need the following generalized Schwartz inequality.
Let B be a positive semidefinite matrix of order n. Then for all $x, w \in R^n,$

$$x^t Bw \leq (x^t Bx)^{\frac{1}{2}} (w^t Bw)^{\frac{1}{2}} \tag{21.1.1}$$

We observe that equality holds if $Bx = \lambda Bw$ for some $\lambda \geq 0$. Evidently, if $(w^t Bw)^{\frac{1}{2}} \leq 1,$ we have $x^t Bw \leq \left(x^t Bw\right)^{\frac{1}{2}}$.

If the functions $f_i$, $g_i$ and $h_i$ in problem $(FP)$ are continuously differentiable with respect to $x \in R^n$.

**2.2. Dual Formulation**

$$(D) \qquad \max_{(s, t^*, \bar{y}) \in K(z)} \ \sup_{(z, \mu, v, w) \in H(s, t_i^*, \bar{y})} \frac{\sum_{i=1}^{s} t_i^* \left\{ f_i(z, \bar{y}_i) + z^t Bw \right\} + \sum_{j=1}^{p} \mu_j g_j(z)}{\sum_{i=1}^{s} t_i^* \left\{ h_i(z, \bar{y}_i) - z^t DV \right\}}$$

Where $H(s, t_i^*, \bar{y})$ denote the set of all $(z, \mu, v, w) \in R^n \times R_+^p \times R^n \times R^n$
Satisfying

$$\nabla \left( \frac{\sum_{i=1}^{s} t_i^* \left\{ f_i(z, \bar{y}_i) + z^t Bw \right\} + \sum_{j=1}^{p} \mu_j g_j(z)}{\sum_{i=1}^{s} t_i^* \left\{ h_i(z, \bar{y}_i) - z^t DV \right\}} \right) = 0$$

$$\begin{cases} w^t\, Bw \le 1, \quad (z^t\, Bz)^{\frac{1}{2}} = z^t\, Bw, \\ v^t\, Dv \le 1, \quad (z^t\, Dz)^{\frac{1}{2}} = z^t\, Dv \end{cases}$$

If the set $H(s, t^*, \bar{y})$ is empty, we define supremum over it to be $-\infty$. For convenience, we use the notation:

$$\psi(\square) = \left[\sum_{i=1}^{s} t_i^* \left\{h_i(z, \bar{y}_i) - z^t Dv\right\}\right]\left[\sum_{i=1}^{s} t_i^* \left\{f_i(\cdot, \bar{Y}_i) + (\cdot)^t, Bw\right\} + \sum_{j=1}^{p} \mu_j g_j(\cdot)\right]$$

$$-\left[\sum_{i=1}^{s} t_i^* \left\{f_i(z, \bar{y}_i) + z^t, Bw)\right\} + \sum_{j=1}^{p} \mu_j g_j(z)\right]\left[\sum_{i=1}^{s} t_i^* \left\{h_i(\cdot, \bar{Y}_i) - (\cdot)^t\, Dv\right\}\right]$$

Suppose that

$$\sum_{i=1}^{s} t_i^* \left\{f_i(z, \bar{y}_i) + z^t Bw\right\} + \sum_{j=1}^{p} \mu_j g_j(z) \ge 0 \quad \text{and} \quad \sum_{i=1}^{s} t_i^* \left\{h_i(z, \bar{y}_i) - z^t Dv\right\} > 0, \quad \text{For all } (s, t^*, \bar{y}) \in k(z),$$

$(z, \mu, w, v) \in H(s, t^*, \bar{y})$.

**3. Definition**

Let $R^n$ be the n-dimensional Euclidean space and X and open set in $R^n$.

**Definition (3.1):** A functional $F: X \times X \times R^n \to R$ is said to be sublinear if $\forall x, \bar{x} \in X$

(i) $F(x, \bar{x}; a_1 + a_2) \le F(x, \bar{x}; a_1) + F(x, \bar{x}; a_2)\ \forall\, a_1, a_2 \in R^n$

(ii) $F(x, \bar{x}; \beta a) = \beta F(x, \bar{x}; a)\ \forall \beta \in R_+$ And $\forall a \in R^n$.

By (ii) it is clear that $F(x, \bar{x}, 0) = 0$.

**Definition (3.2)**

[8, 9] given an open set $x \subset R^n$, a number $\rho \in R$, and two functions $\alpha: X \times X \times \to R_+ \setminus \{0\}$ and $d\left(\cdot, \cdot\right) X \times X \to R$, a differentiable function $\zeta$ over x is said to be $(F, \alpha, \rho, d)$ - convex at $\bar{x}$, if for any $x \in X$, $F: X \times X \times \to R^n \to R$ is sublinear, and $\zeta$ (x) satisfies the following condition.

$$\zeta(x) - \zeta(\bar{x}) \ge F\left(x, \bar{x}; \alpha(x, \bar{x}) \nabla \zeta(\bar{x})\right) + \rho d^2(x, \bar{x})$$

**Definition (3.3)**

Given an open set $x \subset R^n$, a number $\rho \in R$, and two functions $\alpha: X \times X \times \to R_+ \setminus \{0\}$ and $d\left(\cdot, \cdot\right) X \times X \to R$, a differentiable function $\zeta$ over x is said to be $(F, \alpha, \rho, d)$ -Pseudo convex at $\bar{x}$, if for any $x \in X$, there exists a sublinear functional $F: X \times X \times R^n \to R$ such that $\mu(x) < \mu(\bar{x}) \Rightarrow F\left(x, \bar{x}; \alpha(x, \bar{x}) \nabla G(\bar{x})\right) - \rho^2 d^2(x, \bar{x})$

Further $\mu$ is said to be strictly $F(\alpha, \rho, d)$ -Pseudo convext at $\bar{x}$ if for any $x \in X$, there exists a sublinear functional $FiX \times X \times R^n \to R$

Such that

$F\left(x, \bar{x}; \alpha(x, \bar{x}) \nabla \zeta(\bar{x})\right) \ge -\rho d^2(x, \bar{x}) \Rightarrow \zeta(x) > \zeta(\bar{x})$.

**4. Necessary optimality condition**

If $x^*$ is a solution of problem $(FP)$. Assuming $z_{\bar{y}}(x^*)$ to be empty, there exist $(s, t^*, \bar{y}) \in k(x^*)$, $w, v \in R^n$ and $\mu^* \in R_+^p$ satisfying

$$\nabla\left(\frac{\sum_{i=1}^{s} t_i^*\left\{f(x^*, \bar{y}_i)+x^{*t}Bw\right\}+\sum_{j=1}^{p}\mu_j^* g_j(x^*)}{\sum_{i=1}^{s} t_i^*\left\{h(x^*, \bar{y}_i)-x^{*t}DV\right\}}\right)=0$$

$$\sum_{j=1}^{p}\mu_j^* g_j(x^*)=0$$

$$t_i^* \in R_+^s \ (i=1, 2, ..... s), \ \sum_{i=1}^{s} t_i^* = 1$$

$$w^t\ Bw \le 1, \quad (x^{*t}\ Bx^*)^{\frac{1}{2}} = x^{*t}\ Bw,$$

$$v^t\ Dv \le 1, \quad (x^{*t}\ Dx^*)^{\frac{1}{2}} = x^{*t}\ Dv$$

**5. Duality Theorems**

**5.1. Theorem (Weak Duality):** Suppose that x and $(z, \mu, v, w, s, t, \bar{y})$ are respectively the feasible solution for $(FP)$ and (D). Also assume that $\psi(\square)$ is $[F, \alpha, \rho, d]$-Pseudo Convex at z and the inequality $\frac{\rho}{\alpha(x, z)} \ge 0$. Holds, then

$$\sup_{y\in Y} \frac{f_i\ (x, y)+(x^t, Bx)^{\frac{1}{2}}}{h_i\ (x, y_i)-(x^*, Dx)^{\frac{1}{2}}} \ge \frac{\sum_{i=1}^{s} t_i^*\left\{f_i\ (z, \bar{y}_i)+z^tBw\right\}+\sum_{j=1}^{p}\mu_j g_j(z)}{\sum_{i=1}^{s} t_i^*\left\{h_i\ (z, \bar{y}_i)-z^tDV\right\}}$$

**Proof:** By means of a contradiction, suppose that

$$\sup_{y\in Y} \frac{f_i\ (x, y)+(x^t\ Bx)^{\frac{1}{2}}}{h_i\ (x, y)-(x^t\ Dx)^{\frac{1}{2}}} < \frac{\sum_{i=1}^{s} t_i\left\{f_i\ (z, \bar{y}_i)+z^tBw\right\}+\sum_{j=1}^{p}\mu_j g_j(z)}{\sum_{i=1}^{s} t_i\left\{h_i\ (z, \bar{y}_i)-z^tDv\right\}}$$

For $y \in Y$. If we replace y by $\bar{y}_i$ in the above in equality and sum up after multiplying by $t_i$, then we have

$$\left[\sum_{i=1}^{s} t_i\left\{f_i\ (x, \bar{y}_i)+(x^t\ Bx)^{\frac{1}{2}}\right\}\right]\left[\sum_{i=1}^{s} t_i\left\{h_i\ (z, \bar{y}_i)-z^tDv\right\}\right]$$

$$<\left[\sum_{i=1}^{s} t_i\left\{f_i\ (z, \bar{y}_i)+z^tBw\right\}+\sum_{j=1}^{p}\mu_j g_i(z)\right]\left[\sum_{i=1}^{s} t_i\left\{h_i\ (x, \bar{y}_i)-(x^t\ Dx)^{\frac{1}{2}}\right\}\right]$$

Using the generalized Schwartz inequality and (2.2.2) we get

$$\phi(x) \le \left[\sum_{i=1}^{s} t_i\left\{h_i\ (z, \bar{y}_i)-z^tDv\right\}\right]\left[\sum_{i=1}^{s} t_i\left\{f_i\ (x, \bar{y}_i)+(x^t\ Bx)^{\frac{1}{2}}+\sum_{j=1}^{p}\mu_j g_j(x)\right\}\right]$$

$$-\left[\sum_{i=1}^{s} t_i\left\{f_i\ (z, \bar{y}_i)+z^tBw\right\}+\sum_{j=1}^{p}\mu_j g_j(x)\right]\left[\sum_{i=1}^{s} t_i\left\{h_i\ (x, \bar{y}_i)-(x^t\ Dx)^{\frac{1}{2}}\right\}\right]$$

$$<\sum_{j=1}^{p}\mu_j g_j(x)\sum_{i=1}^{s} t_i\left\{h_i\ (z, \bar{y}_i)-z^tDv\right\}$$

Since $\sum_{i=1}^{s} t_i \left\{ h_i(z, \bar{y}_i) - z^t Dv \right\} > 0 \ \sum_{j=1}^{p} \mu_j g_j(x) \le 0,$

It follows that $\psi(x) < 0 = \psi(z)$

As $\psi$ (.) is $(F, \alpha, \rho, d)$ - Pseudo Convex at z. Therefore $F\left(x, z; \alpha(x, z)\nabla\psi(z)\right) < -\rho d^2(x, z),$ that is

$$F(x, z; \alpha(x, z)\left[\sum_{i=1}^{s} t_i \left\{ h_i(z, \bar{y}_i) - z^t Dv \right\}\right] \nabla \left[\sum_{i=1}^{s} t_i \left\{ f_i(z, \bar{y}_i) + z^t Bw + \sum_{j=1}^{p} \mu_j g_j(z) \right\}\right]$$

$$-\left[\sum_{i=1}^{s} t_i \left\{ f_i(z, \bar{y}_i) \times z^t Bw \right\} + \sum_{j=1}^{p} \mu_j g_j(z)\right] \nabla \left[\sum_{i=1}^{s} t_i \left\{ h_i(z, \bar{y}_i) - z^t Dv \right\}\right] < -\rho d^2(x, z)$$

On multiplying the above inequality by

$$\frac{1}{\alpha(x, z)\left[\sum_{i=1}^{s} t_i \left\{ h_i(z, \bar{y}_i) - z^t\, Dv \right\}\right]^2}$$ and using the sublinearity of F, we have

$$F(x, z; \nabla \left( \frac{\sum_{i=1}^{s} t_i \left\{ f_i(z, \bar{y}_i) + z^t\, Bw \right\} + \sum_{j=1}^{p} \mu_j g_j(z)}{\sum_{i=1}^{s} t_i \left\{ h_i(z, \bar{y}_i) - z^t\, Dv \right\}} \right) < \frac{-\rho d^2(x, z)}{\alpha(x, z)\left[\sum_{i=1}^{s} t_i \left\{ h_i(z, \bar{y}_i) - z^t\, Dv \right\}\right]^2}$$

Using the fact that $\frac{\rho}{\alpha(x, z)} \ge 0,$

We have

$$F\left( x, z; \nabla \left( \frac{\sum_{i=1}^{s} t_i \left\{ f_i(z, \bar{y}_i) + z^t\, Bw \right\} + \sum_{j=1}^{p} \mu_j g_j(z)}{\sum_{i=1}^{s} t_i \left\{ h_i(z, \bar{y}_i) - z^t\, Dv \right\}} \right) \right) < 0 \qquad (5.1.1)$$

In the right of (2.2.1) in equality (5.1.1) contradicts F(x, z; 0) =0.

**Theorem (5.2) (Strong Duality)**

Suppose that $\bar{x}$ is optimal for $(FP)$ and $\nabla g_j(\bar{x}),\ j \in J(\bar{x})$ is linearly independent. Then there exist $(\bar{s}, \bar{t}, \bar{y}^*) \in k(\bar{x})$ and $(\bar{x}, \bar{\mu}, \bar{v}, \bar{w}) \in H(\bar{s}, \bar{t}, \bar{y}^*)$ such that $(\bar{x}, \bar{\mu}, \bar{v}, \bar{w}, \bar{s}, \bar{t}, \bar{y}^*)$ is feasible for (D).

Further, if the weak duality (theorem 5.1) holds for all feasible $(z, \mu, v, w, s, t, \bar{y})$ of (D), then $(\bar{x}, \bar{\mu}, \bar{v}, \bar{w}, \bar{s}, \bar{t}, \bar{y}^*)$ is optimal for (D) and the two objectives have the same extreme values.

**Proof:** Since $\bar{x}$ is optimal for $(FP)$ and $\nabla g_j(\bar{x}),\ j \in J(\bar{x})$ is linearly independent. Then by necessary condition there exist $(\bar{s}, \bar{t}, \bar{y}^*) \in k(\bar{x})$ and $(\bar{x}, \bar{\mu}, \bar{v}, \bar{w}) \in H(\bar{s}, \bar{t}, \bar{y}^*)$ such that $(\bar{x}, \bar{\mu}, \bar{v}, \bar{w}, \bar{s}, \bar{t}, \bar{y}^*)$ is feasible for (D) and the two objective values are equal. The optimality of $(\bar{x}, \bar{\mu}, \bar{v}, \bar{w}, \bar{s}, \bar{t}, \bar{y}^*)$ for $(FP)$ thus follows from weak duality (Theorem 5.1).

**Theorem (5.3) (Strict Converse Duality)**

Let $\bar{x}$ and $(\bar{z}, \bar{\mu}, \bar{v}, \bar{w}, \bar{s}, \bar{t}, \bar{y}^*)$ be optimal solutions for $(FP)$ and (D) respectively. Also suppose that $\psi$ (.) is strictly $[F, \alpha, \rho, d]$-Pseudo Convex at $\sum$, for all $(\bar{s}, \bar{t}, \bar{y}^*) \in k(\bar{x})$, $(\bar{z}, \bar{\mu}, \bar{w}, \bar{v}) \in H(\bar{s}, \bar{t}, \bar{y}^*)$, and the inequality $\frac{\rho}{\alpha(x, z)} \ge 0$ holds, and $\nabla g_j(\bar{x}),\ j \in J(\bar{x})$ is linearly independent. Then $\bar{z} = \bar{x};$ that is, $\bar{z}$ is optimal for $(FP)$.

**Proof:** We shall assume that $\bar{z} \neq \bar{x};$ and exhibit a contradiction. Since $(\bar{z}, \bar{\mu}, \bar{v}, \bar{w}, \bar{s}, \bar{t}, \bar{y}^*)$ is feasible for (D), it follows that

$$\nabla\left(\frac{\sum_{i=1}^{\bar{s}} \bar{t}_i \left\{f_i(\bar{z}, \bar{y}_i^*) + \bar{z}^t B\bar{w}\right\} + \sum_{j=1}^{p} \bar{\mu}_j g_j(\bar{z})}{\sum_{i=1}^{s} \bar{t}_i \left\{h_i(\bar{z}, \bar{y}_i^*) - \bar{z}^t D\bar{v}\right\}}\right) = 0$$

The above inequality along with the sublinearity of F and $\frac{\rho}{\alpha(\bar{x}, \bar{z})} \geq 0$

$$F(\bar{x}, \bar{z}; \nabla\left[\frac{\sum_{i=1}^{\bar{s}} \bar{t}_i \left\{f_i(\bar{z}, \bar{y}_i^*) + \bar{z}^t B\bar{w}\right\} + \sum_{j=1}^{p} \bar{\mu}_j g_j(\bar{z})}{\sum_{i=1}^{\bar{s}} \bar{t}_i \left\{h_i(\bar{z}, \bar{y}_i^*) - \bar{z}^t D\bar{v}\right\}}\right] = 0$$

$$\geq \frac{-\rho d^2(\bar{x}, \bar{z})}{\alpha(\bar{x}, \bar{z})}$$

Which together with the sublinearity of F and $\alpha(\bar{x}, \bar{z}) > 0$ yields

$$F\left(\bar{x}, \bar{z}; \alpha(\bar{x}, \bar{z})\right) \nabla \left[\frac{\sum_{i=1}^{\bar{s}} \bar{t}_i \left\{f_i(\bar{z}, \bar{y}_i^*) + \bar{z}^t B\bar{w}\right\} + \sum_{j=1}^{p} \bar{\mu}_j g_j(\bar{z})}{\sum_{i=1}^{\bar{s}} \bar{t}_i \left\{h_i(\bar{z}, \bar{y}_i^*) - \bar{z}^t D\bar{v}\right\}}\right] \geq -\rho d^2(\bar{x}, \bar{z})$$

Using strict $[F, \alpha, \rho, d]$- Pseudo convexity of $\psi(.)$, we obtain $\psi(\bar{x}) > \psi(\bar{z})$

Since $\psi(\bar{z})$ =0, then we have $\psi(\bar{x}) > 0,$ that is

$$\left[\sum_{i=1}^{\bar{s}} \bar{t}_i \left\{h_i(\bar{z}, \bar{y}_i^*) - \bar{z}^t D\bar{v}\right\}\right] \left[\sum_{i=1}^{\bar{s}} \bar{t}_i \left\{f_i(\bar{x}, \bar{y}_i^*) + (\bar{x}^t B\bar{w})\right\} + \sum_{j=1}^{p} \bar{\mu}_j g_j(\bar{x})\right]$$

$$> \left[\sum_{i=1}^{\bar{s}} \bar{t}_i \left\{f_i(\bar{z}, \bar{y}_i^*) + \bar{z}^t B\bar{w}\right\} + \sum_{j=1}^{p} \bar{\mu}_j g_j(\bar{z})\right] \left[\sum_{i=1}^{\bar{s}} \bar{t}_i \left\{f_i(\bar{z}, \bar{y}_i^*) + (\bar{z}^t B\bar{w})\right\} + \sum_{j=1}^{p} \bar{\mu}_j g_j(\bar{z})\right]$$

$$\left[\sum_{i=1}^{\bar{s}} \bar{t}_i \left\{h_i(\bar{x}, \bar{y}_i^*) - (\bar{x}^t D\bar{v})\right\}\right] \qquad (5.3.1)$$

The relations (2.1), (2.2.2), (5.3.1) and

$\sum_{j=1}^{p} \bar{\mu}_j g_j(\bar{x}) \leq 0$ Imply

$$\sup_{y \in Y} \frac{f_i(\bar{x}, y) + (\bar{x}^t \bar{B}x)^{\frac{1}{2}}}{h_i(\bar{x}, y) - (\bar{x}^t D\bar{x})^{\frac{1}{2}}} > \frac{\sum_{i=1}^{\bar{s}} \bar{t}_i \left\{f_i(\bar{z}, \bar{y}_i^*) + \bar{z}^t B\bar{w}\right\} + \sum_{j=1}^{p} \mu_j g_j(\bar{z})}{\sum_{i=1}^{s} \bar{t}_i \left\{h_i(\bar{z}, \bar{y}_i^*) - \bar{z}^t D\bar{v}\right\}} \qquad (5.3.2)$$

Since $\bar{x}$ is optimal for $(FP)$ and $g_j(\bar{x}), j \in J(\bar{x})$ is linearly independent, by strong duality (Theorem 5.2), there exist $(\bar{s}, \bar{t}, \bar{y}^*) \in k(\bar{x})$ and $(\bar{x}, \bar{\mu}, \bar{v}, \bar{w}) \in H(\bar{s}, \bar{t}, \bar{y}^*)$ such that $(\bar{x}, \bar{\mu}, \bar{v}, \bar{w}, \bar{s}, \bar{t}, \bar{y}^*)$ turns to be an optimal solution of (D) and

$$\sup_{y\in Y} \frac{f_i(\bar{x}, y) + (\bar{x}^t \bar{B}x)^{\frac{1}{2}}}{h_i(\bar{x}, y) - (\bar{x}^t D\bar{x})^{\frac{1}{2}}} = \frac{\sum_{i=1}^{\bar{s}} \bar{t}_i \left\{f_i(\bar{z}, \bar{y}_i^*) + \bar{z}^t B\bar{w}\right\} + \sum_{j=1}^{p} \bar{\mu}_j g_j(\bar{z})}{\sum_{i=1}^{\bar{s}} \bar{t}_i \left\{h_i(\bar{z}, \bar{y}_i^*) - \bar{z}^t D\bar{v}\right\}}$$

Which contradicts the fact of (5.3.2). Hence $\bar{x} = \bar{z}$.

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# Vector convex functions for differentiable multiobjective fractional programming problem

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**Abstract**
The concept of Differentiable multiobjective fractional programming problem under V-convex functions and some other classes of non linear Composite problems as a special case.

**Keywords:** V-convex functions, multiobjective fractional programming

## 1. Introduction

In the differentiable case, Jeyakumar and Mond [6] defined a vector invexity that avoids the major difficulty of verifying that the inequality holds for the same function $\eta$ for invex functions Jeyakumar and Mond [6] established sufficient optimality criteria under V-pseudo invexity and obtained duality results under these assumptions. Egudo & Hanson [3] used the concept of Zhao [7] to generalize, the concept of V-invexity of Jeyakumar and Mond [6] to the non smooth case by replacing the gradients with gradients of Clarke [2] V. Jeyakumar and Mond [6] defined on generalized convex mathematical programming. But they not consider this in multiobjective fractional programming problem. Hence, in this paper an attempt is mode to fill the gap in the aim of research we extended the concept of Differentiable multiobjective fractional programming problem under Vector convex functions and some other classes of non linear Composite problems as a special case.

## 2. Notations & Preliminaries

Consider constrained multiobjective fractional optimization problem.

$$\text{(VFP) V- Minimize } \left[\frac{f_i(x)}{g_i(x)},---,\frac{f_p(x)}{g_p(x)}\right]$$

Subject to $h_j(x) \le 0,\ j = 1,2.....,m$

Where $\frac{f_i}{g_i}: X_\circ \to R.$ and $h_j : X_\circ \to R^m$ are differential functions and $X_\circ$ is an open set in $R^n$. Here the symbol V-minimize stands for vector minimization. This is the problem of finding the set of weak minimum for points (VFP). When P=1, the problem (VPF) reduces to a Scalar optimization problem and it is denoted by (FP). Convexity of the Scalar problem (FP) is characterized by the inequalities.

$$\frac{f_i(x)}{g_i(x)} - \frac{f_i(a)}{g_i(a)} - \frac{f_i^{\,1}(a)}{g_i^{\,1}(a)}(x-a) \ge 0$$

$$h_j(x) - h_j(a) - h_j^{\,1}(x)(x-a) \ge 0 \forall x, a \in x_\circ.$$

The functional form $(x-a)$ here plays no role in establishing the following two well-known properties in scalar convex programming:
(s). Every feasible Kuhn - Tucker point is a global minimum
(w) weak duality holds between (FP) and its associated dual problem. Having this in mind, considered problem (FP) for which there exists a function $\eta : X_\circ * X_\circ \to R^n$ such that

$$\text{(I) } \frac{f_i(x)}{g_i(x)} - \frac{f_i(a)}{g_i(a)} - \frac{f_i^{\,1}(a)}{g_i^{\,1}(a)}\eta(x,a) \ge 0$$

$$h_j(x) - h_j(a) - h_j^{\,1}(a)\mu(x,a) \ge 0, \forall x, a \in x_\circ.$$

and showed that such problems (known now as invex problem) also. Possess properties (s) and (w). Since then, various generalization of conditions ( I ) to multiobjective problems and many properties of functions that satisfy ( I ) have been established in the literature. However, the major difficulty is that the invex problems require the same function $\eta(x,a)$ for the objective function and the constraints. This requirement turns out to be a severe restriction in applications. Because of this restriction, pseudo liner multiobjective, problems and certain non-linear multiobjective fractional programming problems require separate treatment as far as optimality and duality properties are concerned. In this chapter we show how this situation can be improved and how the properties (s) and (w) can be extended to hold for generalized convex multiobjective problems and certain multi- objective fraction problems. To this, we modify the condition (I) in the next section as follows:

## 3. New classes & generalized convex vector functions

A vector function $\frac{f_i}{g_i}: X_\circ \to R^p$ is said to be V-Convex if there exist functions $\mu : X_\circ * X_\circ \to R^p$ and $\alpha_i : X_\circ * X_\circ \to R_+ \setminus \{0\}$ such that for each $x, a \in X_\circ$, and for i=1,2,……,p,

$$\frac{f_i(x)}{g_i(x)}-\frac{f_i(a)}{g_i(a)}-\alpha(x,a)\frac{f_i^{1}(a)}{g_i^{1}(a)}(x-a)\geq 0,$$

When p=1, the definition of Vector Convexity reduces to the notion of convexity. The problem of (VPF) is said to be V-Convex if the vector function

$$\left(\frac{f_1}{g_2},\frac{f_2}{g_2}.....\frac{f_p}{g_p}\right)\&(h_1,h_2,.....,h_m)$$

is V- convex. Equivalently, Vector Convexity of (VFP) means that there exists function $\mu: X_\circ * X_\circ \to R^n$ and $\alpha_i,\beta_j: X_\circ * X_\circ \to R_+ \setminus\{0\},\quad i=1,2,...,p,\ j=1,2,..m$ such that

$$(VI)x,a\in X_\circ \Rightarrow \begin{cases}\dfrac{f_i(x)}{g_i(x)}-\dfrac{f_i(a)}{g_i(a)}-\alpha_i(x,a)\dfrac{f_i'(a)}{g_i'(a)}(x-a)\\ h_j(x)-h_j(a)-\beta_j(x,a)h_j'(a)(x-a)\end{cases}$$

Let $\alpha_i(x,a)=1=\beta_j(x,a),\ for\ i=1,2,...p,\ j=1,2,...,m$ and p=1, the scalar problem (FP) becomes the strongly pseudo convex programming problem.

**Example 2.2.1**

Consider the function $Z: R^n \to R^p$ defined by

$$Z(x)=\left(\frac{f_1}{g_1}(\varphi\varphi(x)),...,\frac{f_p}{g_p}(\varphi\varphi(x)\right)$$

where $\frac{f_i}{g_i}: R^n \to R, i=1,2,...,p$ are strongly pseudo-convex functions with real positive functions $\alpha_i(x,a),\varphi: R^n \to R^n$ is subjective with $\phi'(a)$ onto for each $a\in R^n$. Then, the function Z is V-convex. To see this, Let $x,a\in R^n$

$u=\phi(x), v=\phi(a),$ Then, by strong pseudo convexity,

$$\frac{f_i(\varphi\varphi(x)}{g_i(\varphi\varphi(x)}-\frac{f_i(\varphi\varphi(a)}{g_i(\varphi\varphi(a)}=\frac{f_i(u)}{g_i(u)}-\frac{f_i(v)}{g_i(v)}\geq\alpha_i(u,v)\frac{f_i'(u)}{g_i'(v)}(u-v)$$

Since $\phi'(a)$ is onto $(u-v)=\varphi'(a)(x-a)$ is solvable for some $(x-a)\in R^n$

Hence

$$\frac{f_i(\varphi\varphi(x)}{g_i(\varphi\varphi(x)}-\frac{f_i(\varphi\varphi(a)}{g_i(\varphi\varphi(a)}\geq\alpha_i(u,v)\frac{f_i'(v)}{g_i'(v)}\varphi(a)(x-a)$$

$$=\overline{\alpha_i}(x,a)(f_i.\phi)'(a)(x-a),$$

Where $\overline{\alpha_i}(x,a)=\alpha_i(\phi(x),\phi(a))>0.$

**Example 2.2**

Consider the composite vector function $Z(X)=\left(\frac{f_i(F_1(x)}{g_i(G_1(x)},...,\frac{f_p(F_p(x)}{g_p(G_p(x)}\right),$ where for each i=1,2,…,p. $\frac{F_i}{G_i}: X_\circ \to R$ is continuously differentiable and pseudo linear with the possible proportional function $\alpha_i(.,.)$ and $\frac{f_i}{g_i}: R\to R$ is convex. The Z is V- Convex with this follows from the following convex inequality and pseudo linear equality conditions.

$$f_i\left(\frac{F_i(x)}{G_i(x)}\right)-f_i\left(\frac{F_i(a)}{G_i(a)}\right)\geq f_i'\left(\frac{F_i(a)}{G_i(a)}\right)\left(\frac{F_i(x)}{G_i(x)}-\frac{F_i(a)}{G_i(a)}\right)$$

$$=f_i'\left(\frac{F_i(a)}{G_i(a)}\right)\alpha_i(x,a)\frac{F_i'(a)}{G_i'(a)}(x-a)\quad \text{for a simple}$$

numerical example of a composite vector function, consider

$$Z(x_1,x_2)=\left(e^{x_1/x_2},\frac{x_1-x_2}{x_1+x_2}\right),\text{Where}$$

$$X_\circ=\{(x_1,x_2)\in R^2/x_1\geq 1,x_2\geq 1\}.$$

We now show that the Vector Convexity is preserved under smooth convex transformation.

**4. Necessary Theorem**

**Theorem**: Let $\psi: R\to R$ be differentiable and convex with positive derivative everywhere. Let $P: X_\circ \to R^p$ be V-convex. Then, the function

$P_\psi(x)=(\psi(p,(x)),..\psi(h_p(x)),x\in X_\circ$ is V-Convex

**Proof:** Let $x,a\in X_\circ$, Then from the monotonicity of $\psi$ and Vector Convexity of P, we get

$$\psi(P_i(x))\geq\psi(P_i(a))+\alpha_i(x,a)P_i'(a)(x-a))\geq\psi(P_i(a))+\psi'(P_i(a))\alpha_i(x,a)P'(a)(x-a)$$

$$=\psi(P_i(a))+\alpha_i(x,a)(\psi.P_i)'(a)(x-a)$$

Thus, $P.\psi(x)$ is V-Convex the notations of pseudo-convexity and quasi-convexity for a scalar function can now be extended to a vector function. A vector function $\frac{f_i}{g_i}: X_\circ \to R^p$ is said to be V-pseudo convex if there exists functions $\mu: X_\circ * X_\circ \to R^p$ and $\beta_i: X_\circ * X_\circ$ such that for each $x,a\in X_\circ$,

$$\sum_{i=1}^{p}\frac{fi'(a)}{gi'(a)}(x-a)\geq 0\Rightarrow\sum_{i=1}^{p}\beta_i(x,a)\frac{f_i(x)}{g_i(x)}\geq\sum_{i=1}^{p}\beta_i(x,a)\frac{f_i(a)}{g_i(a)}$$

The vector function $\frac{f_i}{g_i}$ is said to be V-quasi-convex if there exists functions $\mu : X_\circ * X_\circ \to R^p$ and $\bar{r_i} : X_\circ * X_\circ \to R_+ \setminus \{0\}$ such that for each $x, a \in X_\circ$, $\sum_{i=1}^{p} \bar{r}_i(x,a)\frac{f_i(x)}{g_i(x)} \le \sum_{i=1}^{p} \bar{r}_i(x,a)\frac{f_i(a)}{g_i(a)}$ is inconsistent. Assume that $\sum_{i=1}^{p} \tau_i \frac{f_i'(a)}{g_i'(a)} = 0$, for some $0 \neq \tau \in R^p, \tau_i \ge 0$. Suppose that $a$ is not a weak minimum for $\frac{f_i}{g_i}$. Then there exists $x_\circ \in R^n$ such that $\frac{f_i(x_\circ)}{g_i(x_\circ)} \le \frac{f_i(a)}{g_i(a)}$, i=1, 2,…,p. Since $\frac{f_i}{g_i}$ is V-convex, there exist $\alpha_i(x_\circ, a), i = 1,2,..,p$

$$\frac{1}{\alpha_i(x_\circ, a)}\left(\frac{f_i(x_\circ)}{g_i(x_\circ)} - \frac{f_i(a)}{g_i(a)}\right) \ge \frac{f_i'(a)}{g_i'(a)}(x_\circ - a).$$

So, $\sum_{i=1}^{p}\left(\frac{\tau_i}{\alpha_i(x_\circ,a)}\right)\frac{f_i(x_\circ)}{g_i(x_\circ)} - \frac{f_i(a)}{g_i(a)} < 0$,

and hence $\sum_{i=1}^{p} \tau_i \frac{f_i'(a)}{g_i'(a)}(x_\circ - a) < 0.$ This is a contradiction.

## 5. Sufficiency theorem

Consider the multiobjective fractional problem (VFP). Suppose that the Lagrange multiplier conditions that $\sum_{i=1}^{p}\tau_i \frac{f_i'(a)}{g_i'(a)} + \sum_{j=1}^{m}\lambda_j h_j'(a) = 0, \lambda_j h_j(a) = 0, \tau \in R^p, \tau \neq 0, \tau \ge 0, \tau \in R^m, \lambda \ge 0$, hold at a feasible point $a \in X_\circ$. If $\left(\tau_1\frac{f_1}{g_1}, \tau_2\frac{f_2}{g_2}, ..., \tau_p\frac{f_p}{g_p}\right)$ is V-pseudo convex with respect to $\mu$ and $(\lambda_1 h_1, ....., \lambda_m h_m)$ is V-quasi convex with respect to $\mu$ then $a$ is a global weak minimum point for (VFP).

**Proof:-** Suppose that $a$ is not a global minimum point. Then there exists feasible $x_\circ \in X_\circ$ such that $\frac{f_i(x_\circ)}{g_i(x_\circ)} < \frac{f_i(a)}{g_i(a)}$, i=1, 2,.., p. So, $\sum_{i=1}^{p}\beta_i(x_\circ,a)\tau_i\frac{f_i(x_\circ)}{g_i(x_\circ)} < \sum_{i=1}^{p}\beta_i(x_\circ,a)\tau_i\frac{f_i(a)}{g_i(a)}$. Now by the V-pseudo convexity condition, we get $\sum_{i=1}^{p}\tau_i\frac{f_i'(a)}{g_i'(a)}\mu(x_\circ,a) < 0$. Since the Lagrangian condition holds at $a$, $\sum_{j=1}^{m}\lambda_j h_j'(a)\mu(x_\circ,a) > 0$ From the V-quasi-convexity condition, we get $\sum_{j=1}^{m}\bar{r_j}(x_\circ,a)\lambda_j h_j(x_\circ) > \sum_{j=1}^{m}\bar{r_j}(x_\circ,a)\lambda_j$ this is a contradiction, since $\lambda_j h_j(x_\circ) \le 0, \lambda_j h_j(a) = 0, and \bar{r_j}(x_\circ, a) > 0, \ for j = 1,2,...,m$

## 6. Duality

### Dual Formulation

V-maximize $\left(\frac{f_1}{g_1}(\xi), ....., \frac{f_p}{g_p}(\xi)\right)$,

(VFD) Subject to

$$\sum_{i=1}^{p}\tau_i\frac{f_i'}{g_i'}(\xi) + \sum_{j=1}^{m}\lambda_j h_j'(\xi) \ge 0, \lambda_j \ge 0, \tau_i \ge 0, \tau e = 1, \lambda_j h_j(\xi) \ge 0, \ j = 1,2,..,m.$$

Where e= (1, 1… 1). Note that the Lagrangian conditions in sufficiency theorem hold for (VFP) at a weak minimum point $a$ under a constraint qualification and they can equivalently be written as

$$\sum_{i=1}^{p}\tau_i\frac{f_i'(a)}{g_i'(a)} + \sum_{j=1}^{m}\lambda_j h_j'(a) = 0, \lambda \ \ge 0, \tau \ \ge 0, \tau e = 1, \lambda_j h_j(a) = 0, \ j = 1,2,.., \ m.$$

**Weak Duality Theorem:** Consider the multiobjective fractional problem (VFP) and (VFD). Let $x$ feasible for (VFP) and $(\xi, \tau, \lambda)$ be feasible for (VFD). If $\left(\tau_1\frac{f_1}{g_1}, \tau_2\frac{f_2}{g_2}, ..., \tau_p\frac{f_p}{g_p}\right)$ is V-pseudo convex and $(\lambda_1 h_1, ....., \lambda_m h_m)$ is V-quasi convex with respect to the same $\mu$, then

$$\left(\frac{f_1(x)}{g_1(x)}, ...., \frac{f_p(x)}{g_p(x)}\right)^T - \left(\frac{f_1(\xi\xi}{g_1(\xi\xi}, ...., \frac{f_p(\xi\xi}{g_p(\xi\xi}\right)^T \notin in + R^p{}_+ .$$

**Proof:** from the feasibility conditions, $\lambda_j h_j(x) - h_j h_j(\xi\xi \le 0$, for each j=1,2,..,m. Since $\bar{r_j}(x,\xi)$ is positive $\sum_{j=1}^{m}\bar{r}_j(x,\xi)[h_j(x) - h_j(\xi\xi] \le 0$. Hence, $\sum_{j=1}^{m}\lambda_j h_j'(\xi\xi\mu(x,\xi) \le 0,$ and so, $\sum_{i=1}^{p}\tau_i\frac{f_i'(\xi\xi}{g_i'(\xi\xi}\mu(x,\xi) \ge 0,$ the conclusion now follows from the V-pseudo convexity condition since $\tau e = 1$ and $\beta_i(x,\xi) > 0$.

### Theorem: Strong Duality Theorem

Assume that $a$ is a weak minimum of (VFP) and that a suitable constraint qualification is satisfied at $a$. Then there exist $(\tau, \lambda)$ such that $(a, \tau, \lambda)$ is a feasible for (FVD).

**Proof:** since $a$ is a weak minimum for (FVP) and a constraint qualification is satisfied at $a$, from the Lagrangian conditions, there exists $(\tau, \lambda)$ such that $(a, \tau, \lambda)$ is a feasible for (VFD). Clearly the values of (VFP) and (VFD) are equal at $a$, since the objective function for both problems are the same. By the generalized Vector Convexity hypothesis, weak duality holds, hence if $(a, \tau, \lambda)$ is not a weak optimum for

(VFD), there must exist $(\xi, \tau^*, \lambda^*)$ feasible for (VFD), $\xi \neq a$ such that

$$\left(\frac{f_1(\xi)}{g_1(\xi)},....,\frac{f_p(\xi)}{g_p(\xi)}\right)^T - \left(\frac{f_1(a)}{g_1(a)},....,\frac{f_p(a)}{g_p(a)}\right)^T \in in + R^p_+$$

Contradicting weak duality.

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# చారిత్రక, వేద పురాణాల్లో చేనేత మూలాలు

- డా॥ గోపవరం పద్మప్రియ, ఆంధ్రోపన్యాసకురాలు, డి.కె.ప్రభుత్వ మహిళా డిగ్రీ కళాశాల, నెల్లూరు.

పడుగు, పేకల అల్లికల నైపుణ్యాలతో, అగ్గిపెట్టెలో పట్టే చీరలతో, 30 గజాల నేతతో ప్రపంచపటం మీద చేసిన కీర్తి సంతకం భారతదేశ చేనేత పరిశ్రమది. భారత దేశానికి వ్యవసాయం, చేనేతలు రెండు కళ్లు. ప్రపంచ చేనేత భాగస్వామ్యతలో 85 శాతం మనదే. 30 మిలియన్ల ప్రజలకు జీవనభృతి కల్పిస్తూ, భారతదేశపు వెన్నెముకగా చేనేత పరిశ్రమ గణతికెక్కినది. భారతదేశపు స్వాతంత్ర్య సంగ్రామపు రెపరెపల్లో మన రాట్నం విజయకేతనం ఎగ రేసింది. ఆ రాట్నాన్ని అశోక చక్రం కనుమరుగు చేసినట్లు, నేడు మరయంత్రపు చక్రాలు చేనేత కళను మసక బారుస్తు న్నాయి. దాన్ని ప్రాణప్రదంగా కాపాడుకుంటూ వస్తున్న నేతన్న బతుకు మాత్రం కొడగట్టి పోతున్న దీపమైనది. పడుగు, పేకలపై నాడి, కండెల్లా అల్లాడి పోతూ నేతను బతికించాలని చూసే నేతన్న చేనేత చరిత్ర ఈనాటిది కాదు. సహస్ర శతాబ్ధాల నాటిది. ఆ చరిత్ర పుటల్లో వేద పురాణాల్లో దాగిన ఆ చరిత్రను తెలుసుకోవడం మన బాధ్యత.

## చారిత్రక ఆధారాలు :

క్రీ.పూ. 5500 సం॥ పూర్వమే వస్త్రం కలదని, ప్రత్తి - నూలు - మగ్గం అనే వాటిని భారతదేశంలోకి వచ్చిన రెండవ తరంవారైన ఆస్ట్రిక్ జాతి వారు ప్రవేశ పెట్టినట్లు సునీల్ చటర్జీ (1953 అక్టోబర్‌లో అహమ్మదాబాద్‌లో జరిగిన ఆల్ ఇండియా ఓరియంటల్ కాన్ఫెరెన్స్) అభి ప్రాయపడ్డారు. వేదం కాలంలో మగ్గం పుట్టిందనే కొందరి విశ్వాసాన్ని 1921 సం॥ నాటి మొహంజదారో త్రవ్వకాలు తోసిపుచ్చాయి. ఇండియా ప్రభుత్వం ప్రకటించిన గ్రంధం "Mohanjedaro between 1927-31" లో

1) 431 పేజిలో పనిముట్ల వర్గంలో 55 నెం॥ గల ఎముకలలో చేయబడిన వస్తువును ఒక నేత పలకగా నిర్ధారణ చేశారు.
2) 1928 సం॥లో ప్రచురించిన టెక్నలాజికల్ బులెటన్ 3వ నెంబరు, సిరిస్ 'బి' ప్రకారం కొన్ని వెండి, రాగి వస్తువుల మడతల మధ్యనున్న నునిని గుడ్డ ముక్కగా ఇండియన్ సెంట్రల్ కమిటీ తేల్చింది.
3) దొరికిన నూలు ముక్కల్లో ఒకటి 34 నెంబరుదని, ఇంచికి 60 పోగులు పడుగు, 20 పోగులు పేకలు కలవని, కొన్ని జములు పోగులు కనిపించాయని వివరించింది.

## వస్త్రం - నేత :

వస్త్రం ముందా? నేతముందా? అంటే నేత భావనే ముందనేది పరిశోధకుల అభిప్రాయం. "క్షేత్ర గణితం" ఆధారంగా బుట్టలల్లిక ప్రారంభమై క్రమంగా ఆ అల్లిక వస్త్రంలోకి ప్రవేశించింది. వస్త్రం కంటే ముందే నేత కలదన డానికి ఆధారాలున్నాయి

1) బోర్నియా అడవుల్లో కోయవారు నార గుడ్డలు అల్లి వస్త్రాలు కట్టుకునేవారు.
2) అలాగే ఉత్తర కెనడాలో ఇండియనులనబడేవారు కుందేటి వెంట్రుకలతో చారల కంబళ్లు నేటికి చేస్తున్నారు.
3) మెడిటేరియన్స్ రంగు నార ప్రాంతంలో నారపోగు పడుగును పై నుండి క్రిందకి రాళ్లతో వ్రేలాడగట్టి పేక పోగులను నేస్తారు. ప్రతి శిల్కు లభించే ప్రాంతాల్లో పడుగును నేల మీద పరచి నేస్తారు. ఈ విధానమే మగ్గాల ఉత్పత్తికి పునాదైనది.

చేనేత పరిశ్రమ ప్రాచీనతను తెలిపే ఆధారాలు చరిత్రలోనే కాదు మనకు సాహిత్యంలోను కన్పిస్తాయి.

## సాహిత్యాధారాలు :

సాహిత్యం నాగరిక సామాజిక, సాంస్కృతిక లక్షణం. సమాజ దర్పణం, సమాజ లక్షణాల్ని పొందు పరచడం



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దాని లక్షణం. చేనేత, మూలపురుషుడు మొ॥ అంశాలు ప్రథమ సాహిత్యం నుంచి మనకు కన్పిస్తూనే ఉన్నాయి.

**ఋగ్వేదం :**

గుణత్రయాత్మకం యజ్ఞసూత్రం బ్రాహ్మణ్య హేతుకం
దేవలేన పురాదత్తం దేవతాభ్యశ్చవాజ్ఞయా॥

(త్రిగుణ స్వరూపమైన యజ్ఞోపవీతము బ్రాహ్మణ్యానికి కారణభూతమైనది. పూర్వం పరమశివుని ఆజ్ఞానుసారం దేవలుని చేత అవి దేవతలకు ఈయబడ్డది)

**సామవేదం :**

మనసా వాచా వదంతి సత్యం దేవాంగం దేవతా యజ్ఞా భుజం, యజ్ఞకర్తారం, యజ్ఞరూపం, విశ్వస్పభర్తారం గోప్పారం, హర్తారం తస్యరూపమే వైతత్సర్యం సూత్ర కర్తార మహు ప్రజా పతిస్తప సాతప్త్యా దేవాంగ మబ్రువత్.

(దేవతలందరు దేవాంగుని గురించి మనస్సులోను, తమ మాటల్లోను యజ్ఞభోక్త, యజ్ఞ స్వరూపులు, యజ్ఞాధికారం, సమస్త విశ్వానికి అధినాధులు, రక్షకుడు, లయకర్త ఈ సమస్తము దేవల రూపమేననే సత్యాన్ని చెప్పున్నారు. ఇతడే యజ్ఞసూత్రకర్తని చెప్పున్నారు. దేవలుడు గూర్చి తపస్సు చేసి ఈ లోకాన్ని ఎలా సృష్టించాలో బ్రహ్మదేవుడు ప్రార్థించెను)

**యజుర్వేదం :**

సర్వేషాం మానరక్షార్థం, వస్త్రం కర్తుం తథాపరా నిర్గుణో నిరహంకారో, నిర్వికల్పావ్యవహం శకాగుణత్రయేణ సంయుక్తావ్యాభకం దేహ సంయుత: తతో దేవాంగ నామ్నాహం ప్రసిద్ధి మ భజం పురాసత్యాం రేన మయా సృష్టా మద్యం శియా మహోయెశా: తదా ప్రభృతి దేవాంగ బ్రాహ్మణ ఇత భూతరే ప్రతీతిం ప్రాప్య వర్తంతి వస్త్ర సూత్ర ప్రహేతవ: అప్రాకృత ద్విజా ఏతే సర్వలోక ప్రపూజితా:

(ప్రపంచ ఉత్పత్తికి పూర్వమే నేను నిర్గుణుడను, నిర్వికల్పుడను, నిరహంకారుడును. లోక సృష్టి జరిగిన పిమ్మట భూమి యందలి ప్రాకృత బ్రాహ్మణులకు, క్షత్రియులకు, వైశ్యులకు నియమితమైన వైదిక కర్మల యందు అధికార సిద్ధి కల్గిజాలిన యజ్ఞోపవీతమును నిర్మించుట కొరకు)

ఋగ్వేద కాలంలో దేవతలకు యజ్ఞోపవీతం నిర్మించిన దేవలుడు, యజుర్వేద కాలం నాటికి దేవతలతో పాటు భూమిపై గల బ్రాహ్మణ, క్షత్రియ, వైశ్యులకు యజ్ఞోపవీత నిర్మాణానికి ఉద్భవించినట్లు చెప్పబడినది.

**బ్రహ్మాండ పురాణం :**

దేవౌ ధాతృవిధారతౌ భృగో: ఖ్యాతి రసూయత।
శ్రియంచ దేవదేవస్య పత్నీర్నాయణస్య యా॥ అయతిర్ని
యతిశ్చైవ మేరో: కన్యామహాత్మన:। భార్యే ధాతృవిధాత్రో
స్తేతయో ర్జాతౌ సుతా పుభౌ॥ ప్రాణుశ్చైవ మృకండు శ్చ
వియమహమహాయశా:। మనస్విన్యా మహం తస్మా త్పుత్రో
వేదశిరా మయ॥ ధూమ్రవత్యాం సమభవత్ ప్రాణ స్యావి
నిబోధ మే। ప్రాణస్య ద్యుతిమాన్ పుత్ర స్తూత్పన్నస్య
నిజాత్మజ:। అజరా శ్చ తయో: పౌత్రాశ్చ బహవో భవన్॥

(భృగుమహర్షికి ఖ్యాతి యను భార్యయందు నారాయణుని పత్నియగు శ్రీయును, ధాత విధాతలును జన్మించిరి. ఆ ధాతవిధాతలు మేరుపుత్రిక లగు ఆయతిని, యతిని బెండ్లి యాడిరి. విధాతకు ప్రాణుడును. ధాతకు మృకండుడును, వానికి మనస్విని (మరుద్వతి) యందు నేనును (మార్కండేయుడు), నాకు ధూమ్రవతియందు వేదశిరుడును (భావనముని) ఇట్లు వారికి పుత్రులు, పౌత్రులు పలువురు గలిగిరి) (అనుషంగ పాదము 11వ అధ్యాయము)

ప్రాణు శ్చైవ మృకండుశ్చ బ్రహ్మకోశో సనాతన:।
మనస్విన్యా మృకండన్య మార్కండేయా భభూవహ॥ సుతో
వేదశిరా స్తస్య ధూమ్రవత్యా మజాయత। పీవర్యాం
వేదశిరస: పుత్రా వంశకరా శ్శతం॥ మార్కండేయ సమా
ఖ్యాత ఋషయో వేదపారగా:॥

(భృగువంశజుం దగు ప్రాణుని తమ్ముడు మృకండునకు మనస్విని యందు మార్కండేయుడు జనించెను. అతనికి పీవరి (భద్రావతి) యందు వేదపారంగతులగు మార్కండేయులను (పద్మశాలి) పేరుగల నూర్వురు కుమారులు గలిగిరి)



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**భారత, భాగవతాలు :**

భారత, భాగవతాల్లో దేవాంగ కుల మూల పురుషుడైన దేవలుని ప్రస్తావన అనేక సంచర్భాల్లో కన్పిస్తుంది.

1. సర్పయాగక్రతువు కోసం వివిధ విధులు నిర్వహించడానికి నియమించబడిన ఋత్విజులలో 'దేవలుడు' ఒకడు (ఆ.ప. ద్వి.ఆ. 208), 2. సత్యవతిని, అసితవంశానికి చెందిన వాడుగా దేవలుని ప్రస్తావన కలదు. (ఆ.ప.ద్వి.ఆ.వ. 208)
2. అష్టసుడు గంధర్వుడిలో ఏ వ్యక్తిని పురోహితునిగా స్వీకరించాలో చెప్పమనగా దేవలుని తోబుట్టువైన ధౌమ్యుడని పురోహితునిగా స్వీకరించమని వివరించెను (ఆ.ప., స.ఆ.ఏ. 158).
3. భాగవత చతుర్థస్కంధము, ప్రథమ అధ్యాయం, విష్ణు పురాణాలు ప్రథమాంశంలో 10వ అధ్యాయంలో మార్కండేయ పురణాం వివరించబడింది.

**కుల పురాణాలు :**

ప్రతికులానికి చరిత్ర ఉన్నట్లే చేనేతనాశ్రయించిన దేవాంగ, పద్మశాలీల చరిత్రను తెలిపే కుల పురాణాలు లభ్యమవుతున్నాయి. చేనేత మూల పురుషుడుగా దేవాంగ పురాణం, దేవల మనుబ్రహ్మగాను, పద్మశాలీ పురాణం భావన మహర్షిని చేనేత ప్రతిపాదించాయి.

**దేవాగం పురాణం :**

వ్యాస మహర్షి రచించిన బ్రహ్మాండ పురాణంలో బ్రహ్మ నారద సంవాదాత్మకమైన 29 అధ్యాయాల వృత్తాంతం చేనేతకుల మూల పురుషుడికి సంబంధించినది. అది అనంతర కాలంలో మృగమై పోయింది. కర్ణాటక లిపిలో బాదరాయణము నుండి గ్రహించిన దేవల చరిత్రను 1914లో పింజల సోమశేఖర శర్మ దేవాంగ పురాణంగా రచించారు. తర్వాత ఇది అనేక ప్రక్రియల్లో, అనేక రూపాలలో వివిధ రచయితలచే రచించబడింది.

**సారాంశం :**

బ్రహ్మ స్థావర, జంగమాత్మకాలైన 14 లోకాల సృష్టి అనంతరం స్త్రీ, పురుషుల మానరక్షణావశ్యకతలో బ్రహ్మ తన అశక్యతను గుర్తించి శివుడని ఆశ్రయించెను. శాశ్వతానందంలో ఉన్న పూర్వకల్ప వస్త్రప్రదాతైన మనువును తన ఫాలనేత్రమునించి సృష్టించెను. తన జన్మ కారణాన్ని కోరగా విష్ణువు సహాయంతో దేవ, మానవ, రాక్షస దేహ రక్షణకై వస్త్ర సృష్టి కావించమనెను. వస్త్ర నిర్మాణానికి భూమండంలోని ఆమోద పట్టణాన్ని అనువైనదిగా గుర్తించి తన కార్యక్రమం నిర్విఘ్నంగా సాగుటకై పార్వతీ దేవిని ప్రార్థించగా ఆమె నుంచి చక్రాన్ని, అనుగ్రహాన్ని పొంది, సువార్ణశ్రమం చేసి విష్ణువుకై తపస్సు చేరి విష్ణువు నాభి నుంచి అక్షయం కాని తంతువులను పొందెను. తనకు పొంచి వున్న ఆపదను గుర్తించి విష్ణువు తన చక్రము నుంచి మరొక చక్రాన్ని సృష్టించి ఇచ్చెను.

దేవలుడు సువర్ణాశ్రమమును వీడి లవణ సముద్ర తీర ప్రాంతంలోని మాయాశ్రమంలో కపటముని వద్ద విశ్రమించెను. వారిని మాయా రాక్షసులుగా గుర్తించి వారిపై విష్ణు చక్రాన్ని ప్రయోగించి రాక్షస సంహారం చేసెను. కాని ఆ సైన్యంలో 1) వజ్రముష్టి, 2) ద్రుమాక్షి, 3) ద్రుమాన్త, 4) చిత్రసేన, 5) వంచ సేనలు మాకుమ్మడిగా దాడిచేసారు. పార్వతి దేవిని ప్రార్థించగా ఆమె చౌడీశ్వరీ దేవిగా అవతరించి వారిని అంతమొందించెను. ఆ జగన్మాత ఆదేశాను సారం అసిత, శ్రోణిత, హరిత, నీల, పేత వర్ణాలలో ఉన్న ఆ రాక్షసుల రక్తంలో దేవలుడు తంతువులను ముంచెను అని చిత్ర వర్ణాలలో మారి పోయాయి. దేవలుడు ఆమోద పట్టణం చేరి ఆ తంతువు సహాయంతో దేవ మానవులను నస్త్ర సృష్టించగా వించెను.

**పద్మశాలి పురాణం :**

పద్మపురాణము సృష్టిఖండము 33 అధ్యాయము. స్కాందపురాణము నాగరఖండము 21వ అధ్యాయము, చతురశీతిలింగమహత్వఖండము 36వ అధ్యాయము, బ్రహ్మవైవర్తపురాణము ప్రకృతిఖండము 154వ అధ్యాయము, మత్స్య పురాణము 166వ అధ్యాయము, నారదీయపురాణము, 4, 5 అధ్యాయములు, భాగవత పురాణము, ద్వాదశస్కంధము 8వ అధ్యాయములలో



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మార్కండేయ పురాణము కొద్ది భేదాలతో వర్ణింపబడి యున్నది.

పద్మశాలీ వంశస్తుల మూల పురుషుడు భావనా మహర్షి - మార్కండేయుని కుమారుడు. మార్కండేయుని యజ్ఞము నుంచి పంచవటి, భావన ఋషి జన్మించారు. వీరిని భావనారాయణుడు, పద్మశాలి అని దేవతలు ధీవించారు. పంచవటి, భావనారాయణులను విద్యాభ్యాసం కొరకు నారదుని వెంట మార్కండేయ దంపతులు పంపించారు. వీరు మహావిష్ణువును దర్శించుకోగా, జనులందరు అర్ధనగ్నులుగా తిరుగుతున్నారని వారి మాన రక్షణకు వస్త్రాలు తయారుచేయమని విష్ణుమూర్తి తన నాభి కమలం నుండి సన్నని తంతువులను ఇచ్చి వాటితో పట్టునూలు తయారుచేసి పడుగు, పేకలను ఏర్పరచి సమస్త లోక జనులకు మానరక్షకుడివై వుండి, "నా అంశవైన ఓ! పద్మశాలి నీ కీర్తి ఆచంద్రార్కము నిలిచి వుంటుందని", శ్రీ మహావిష్ణువు దీవించాడు. పంచవటి తపస్సు కొరకై వెళ్ళిపోగా భావనా మహర్షి వాటిని తీసుకొని వస్త్ర నిర్మాణ విద్యను శివుడు వద్ద నేర్చుకొని భూలోకానికి బయలుదేరాడు. భావనాఋషి తెచ్చే పద్మ తంతువులను నాశనం చేయమని కాలువాసురడు మూలకాసురుడ్ని పంపిస్తాడు. భావనఋషిని అడ్డగించి అతనిపై యుద్ధం చేసి పద్మ తంతువులను మింగివేస్తాడు. వాటిని మింగి వేయగానే భావనాఋషి రుద్రరూపుడై మూలకాసురుడి సైన్యాన్ని ఓడించి మూలకాసురుడి ఉదరము చీల్చి పద్మ తంతువులను బయటకు తీస్తాడు. ఆ పద్మ తంతువులు పంచవర్ణములుగా బయట పడినవి. ఆ కారణంగా నేడు ఇన్ని రంగులుగా వస్త్రములు ఉండుటకు కారణం అదియే. భావనాఋషి మూలకాసురుని శల్యాన్ని మగ్గంగా, వాని వెన్నుపూసను 'దోనె'గా, రెండు కొమ్ములను 'నాడెలుగా", నరాలను తాళ్ళుగా చేసుకొని వస్త్ర నిర్మాణానికి కావలసిన పనిముట్లను తయారు చేసుకొన్నాడు.

వీటి సహాయంతో వస్త్ర నిర్మాణం చేసి తన తల్లిదండ్రులైన మార్కండేయునికి, దాక్షవతికి ఇవ్వగా పద్మతంతువులు ఇచ్చిన శ్రీ మహావిష్ణువుకి ప్రసాదించమని తల్లిదండ్రులుసలహా ఇస్తారు. వారి సలహా మేరకు శ్రీ మహా విష్ణువునికి పీతాంబరాలు బహుకరించగా, వాటిలో పసుపు వర్ణం కలిగిన వాటిని తీసుకొని ప్రేమతో ధరించాడు. శ్రీమహాలక్ష్మికి పుష్పములు గులాబి వర్ణం కలిగిన పట్టు వస్త్రాలను ఇచ్చాడు. అప్పుడుఆమె ఓ మహర్షి నీ కళా కౌశలం అద్భుతం నీ ఆడపడుచుగా నాకు ఆయనం లభించింది కాబట్టి ఈ రోజు నుండి మీరు పద్మశాలీలుగా పేరు పొందుతారని దీవించింది. భావనాఋషి సూర్యుడి కుమార్తె ఆయన బద్రావతిని వివాహం చేసుకొని కాలువాసురిడిని చంపి ఆ రాజ్యన్నికైవసం చేసుకొని, అందులో పద్మ భీజములను భూమిపై చల్లి వాటి నుంచి ప్రకాశవంతమైన పత్తిని ఉత్పత్తి చేసి దానిని దారాలుగా చేసి రకరకాలరంగులతో వస్త్రోత్పత్తి చేస్తు 101 మంది పుత్రులతో జీవించసాగారు. ఇలా మార్కండేయ గోత్ర నామంతో, యజుశాఖతో, భృగు సూత్రముతో పద్మశాలీ వంశం వర్ధిల్లినది.

## చేనేతకుల తెగలు :

భారతదేశంలో దాదాపు 29 చేనేత కుల తెగలు కలవు. 1)పద్మశాలి 2)దేవాంగ 3)జాండ్ర 4)పట్టుశాలి 5)సాలి 6)స్వకులశాలి 7)కురిమిసెట్టిశాలి 8)సేనాపతులు 9)కైకాల 10)కర్ణభక్తులు 11)తొగటశాలీలు 12)తొగట వీరక్షత్రియ 13)కరికాల భక్తులు 14)సాధనాశూరులు 15)అచ్చుకట్లవాళ్లు 16)దూదేకుల 17)కురి 18)ఖత్రి 19)నీలి 20)నీలకంఠ 21)కోష్టి 22)నక్కల 23)పట్కార్ 24)కైకోలన్ 25)సెంగుండు 26)సెంగుతర్ 27)సాలివన్ 28)సెస్సి మొదలైన చేనేత ఉపకులాలుగా భారతదేశా అంతటా వ్యాపించి యుండగా ఇందులో మొదటి 18 దక్షిణ భారతదేశంలో ఉన్నాయని గుర్తించడమైనది.

ఇందులో ప్రధానంగా దేవాంగ, పద్మశాలీలు విశిష్టులుగా చెప్పుకుంటారు. ఒకరికంటె ఒకరు గొప్ప అనేభావన ఆయా కులాలను కదిలించి సంభాషించినప్పుడు తెలుస్తుంది. సాహిత్యపరమైన ఆదారాలు, ఈ రెండు కూలాలకే కన్పిస్తాయి. దేవాంగులైతే రాజ్యపాలనలోను భాగ స్వామ్యత వహించినట్లు ఆనవాళ్లు కలవు. వీరిజాతి



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జనకుడైన దేవల మహర్షి సంప్రదాయాన్ని అనుసరిస్తూ వస్త్ర, గాయత్రీ, సూత్రోద్యోగాలు కావిస్తూ రాచరిక మర్యాదలను పాటించే వారని, తమిళనాట వడవీటిని పాలించే వారని భద్రగవి, లింగకవులు తమ ద్విపద పురాణంలో రాశారు. హరిహరరాయలు, బుక్క రాయలు, శ్రీ కృష్ణ దేవరాయల కాలంలో వీరు సామంతులుగా ఉన్నారని, దానికి నిదర్శనంగా ప్రతి సంవత్సరం ఆషాడ అమావాస్య నాడు చూడాంబికకు షోడషోపచారాలు నిర్వహించి చౌడేశ్వరీ దేవి జ్యోతిర్మహోత్సవం జరుపుతారు. వీర సైనిక లక్షణానికి గుర్తుగా నేటికి ఖడ్గసాధన, రక్తతర్పణ చేయడం జరుగుతోంది. పద్మశాలి కుల పురాణం ప్రసిద్ధి కెక్కింది.

## ఉపయుక్త గ్రంధసూచి :

1. ఆంధ్ర మహా భారతం - కవిత్రయ విరచితం, టి.టి.డి. ప్రచురణ
2. ఆంధ్ర మహాభాగవతం - పోతన విరచితం, టి.టి.డి. ప్రచురణ
3. చేనేత దర్పణం - శ్రీ వుత్పల సత్యనారాయణ - విశాలాంధ్ర ప్రచురణ
4. దేవాంగ పురాణం - పింజల సోమశేఖరశర్మ
5. వస్త్ర నిర్మాత దేవాంగ - డా॥ దంతం వెంకట సుబ్బారావు, సంపాదకులు - సంచిక , అర్ధవార్షిక సంచిక సెప్టెంబర్ 2015
6. భృగ్వాదుల ప్రభావం - గుంటక నరసయ్య పంతులు - సంఘమిత్ర పబ్లికేషన్స్ (2015)
7. శ్రీ భావనాఋషి మహాత్మ్యమ్ - కీ.శే. బ్రహ్మశ్రీ జనమంచి శేషాద్రిశర్మ (పరిష్కర్త) ప్రచురణ: శ్రీ కార్యంపూడి రామకృష్ణారావు (ద్వి.ము.)

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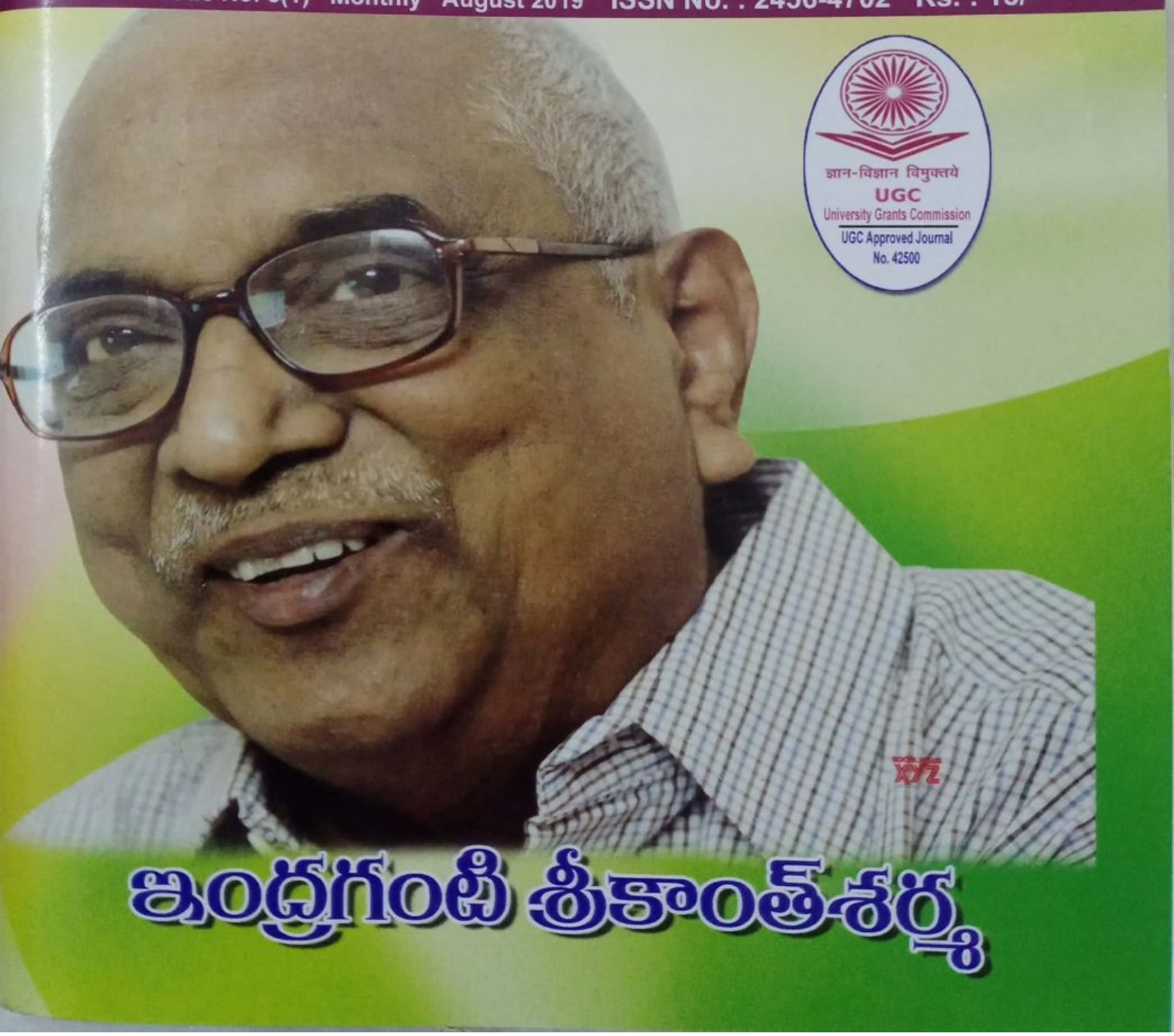
# భావ వీణ

తెలుగు సాహిత్య సాంస్కృతిక భాషాధ్యయన పత్రిక

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## ఇంద్రగంటి శ్రీకాంతశర్మ

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# దేవాంగుల వరప్రదాయని - చౌడేశ్వరీ దేవి

- డా॥ గోపవరం పద్మప్రియ, శాఖాధిపతి, తెలుగు విభాగం, డి.కె.ప్రభుత్వ మహిళా డిగ్రీ కళాశాల, నెల్లూరు.

"ఆర్యావర్త : పుణ్యభూమిర్మధ్యం విన్ధహిమగయో: నీ వృజ్జన పదౌ దేశ విషయౌ తూపవర్తనమ్" అని అమరం. జనపద సంబంధమైనది జానపదం. జానపదమంటే పల్లెటూరు. పల్లె, దేశం, రాజ్యం, చోటు అనేవి నైఘంటి కార్థాలు. జానపదాల్లో ఉండేవారు జానపదులు. కొన్ని సమాన లక్షణాలు గల జన సముదాయమూ జానపదమే. ఆధునిక జానపద విజ్ఞాన శాస్త్రవేత్తలు జానపదానికి నూతన దృక్పథాన్ని ప్రతిపాదించారు. నివాస స్థలాలు అప్రధానమై సంస్కృతి ప్రధాన భూమిక వహించింది. ప్రపంచమంతా 'సంస్కృతి' మూలాంశంగా జానపద విజ్ఞానం బయలుదేరింది. సాహిత్యం, సంస్కృతి, ఆచార సంప్రదాయాలు, కళలు, చేతివృత్తులు మొదలయినవి ఇందులో భాగమయ్యాయి.

ఈ విశాలమయిన జానపద విజ్ఞానంలో చేనేతవృత్తికి ప్రాచీనమైన, ప్రధానమైన భాగస్వామ్యం కలదు. భారత దేశంలో వ్యవసాయం తరువాత అతిపెద్ద వృత్తి చేనేత. దీని ఔన్నత్యాన్ని తెలిపే సామెతలూ జనవ్యవహారంలో కలవు.

"కదురు, కవ్వంబులు గలయాడునింట కరువు కాట కములు కలికాన లేవు"

"అందచందములేని ఆడకూతురుకు అందమేరు పరచు ఆ పత్తిచెట్టు"

ఇలా చేనేత ప్రాధాన్యత విస్తారమైనది. దీనిని ఆశ్ర యించి దాదాపు 29 తెగలవాళ్ళు జీవిస్తున్నారు వారిలో ప్రముఖమైన కులం దేవాంగ పద్మశాలి.

దేవాంగ పురాణంలో చేనేతకుల ఆవిర్భావం, వారు కొలిచే చౌడేశ్వరి దేవి మహాత్మ్యము వర్ణించబడింది. ఈ సృష్టి ఏర్పడిన ప్రారంభ దినాల్లో దేవతలు, మానవాది సమస్తదేవతలు తమ మానములకు ఎలాంటి ఆచ్ఛాదన లేకపోవుటచే సిగ్గుచెంది ఆకులు, చెట్టుబెరడులు, జంతు చర్మాలతో కప్పుకొనుచుండిరి. వీటితో విసుగు చెందిన వారు బ్రహ్మదగ్గరకు వెళ్లి తమ దీనావస్థను విన్నవించు కున్నారు. తమ మానములను కాపాడుకొనుటకు వస్త్రకారుని సృష్టించమని బ్రహ్మదేవుడిని వేడుకున్నారు. అప్పుడు బ్రహ్మదేవుడు వీరితో కైలాసానికి వెళ్ళి ఓ సదా శివా! నీ ఆజ్ఞ ప్రకారము నాకు ఇచ్చిన శక్తి సామర్థ్యముల మేర జగత్‌సృష్టిని గావించాను. కాని వస్త్రము సృష్టిచేయు శక్తి సామర్థ్యాలు తమరు నాకు ఇవ్వలేదు. పూర్వ కల్పమందు వస్త్ర నిర్మాత నీయందు సాయుజ్యమై వున్నాడు, అతడిని తిరిగి సృష్టించమని ప్రార్థించగా, అప్పుడు సదాశివుడు కొద్దిసేపు ధ్యాననిమగ్నుడైనాడు. అప్పుడు ఆ సదాశివుని సద్యోజాత ముఖమునందలి ఫాల నేత్రము నుండి ఒక దివ్యతేజస్సు వెలుపలికి వచ్చి ఒక పురుషాకారముగా ఆవిర్భవించింది. ఆ దేవతల సమక్షంలో వారికి 'దేవల' అని నామకరణం చేశాడు. అనగా దేవతలచే లాలింపబడినవడా! అని ; దేవాంగ: అంటే దేవతల యొక్క అంగవస్త్రములు చేసినవాడు అగుట వలన దేవాంగుడుగా, నా మానసపుత్రుడుగా ప్రసిద్ధి చెందుతాడు అని ఆశీర్వదించాడు.

### పరమేశ్వరుడు వస్త్రములు నిర్మించి అందరికి ప్రదానము చేయమని దేవల మను బ్రహ్మను ఆజ్ఞా పించుట :

శివుడు దేవల మునితో క్షీరసాగరమునకు వెళ్ళి అచ్చటవున్న శ్రీమన్నారాయణుడిని దర్శించి తంతువులను గ్రహించి శీఘ్రముగా ఆమోద పట్టణానికి వెళ్ళి ఆ పట్టణానికి పాలకుడిగా వుంటూ వస్త్రాలు నిర్మించి సకల దేవతలకు, సకల జాతుల వారికి వస్త్రములు ఇచ్చి పది దిక్కుల యందు నీ కీర్తిని వ్యాపింపచేయి. నీకు జన్మించిన నీ వంశమువారు ఉత్తములు, సంస్కారవంతులు, దైవ బ్రాహ్మణ భక్తిగలవారు, యుక్తాయుక్త విచక్షణ జ్ఞానము



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కలవాయగా ప్రసిద్ధికెక్కుతారని దీవించాడు. దేవలుడు అచిరిధంగా ఆమోద పట్టణానికి బయలుదేరాడు.

**పంచరాక్షసులు దేవలుడిని మోసగించి చంప బూనుట :**

తంతువులను తీసుకొని ఆమోద పట్టణానికి బయలు దేరగా ఈ విషయం తెలుసుకున్న కొందరు రాక్షసులు ఆ తంతువులను దొంగలించి వస్త్ర నిర్మాణం ఆపుటకు తంతువులను దొంగలించుటకు మాయా మునీశ్వరుడి వేషం ధరించి మాయా ఆశ్రమాన్ని సృష్టించి దేవలుడిని ఆకర్షించేటట్లు చేశారు. ఆ మాయా ఆశ్రమాన్ని చూసి ముగ్ధుడై లోపలికి ప్రవేశించాడు. అక్కడ కపటమంత్రాలు జపిస్తున్న ఒక వృద్ధ మునీశ్వరుడు కనిపించాడు. దేవలుడి పట్ల వినయ విధేయతలు చూపిస్తూ అతిథిగా ఆనాటి రాత్రి అక్కడే బస చేయమని వేడుకున్నారు. వారి మాటలు నమ్మి అక్కడే నిద్రించాడు. హఠాత్తుగా అర్ధరాత్రి వారి వేషాలు తొలగించి వజ్రముష్టి, ధూమవ్యక్తులు, ధూమ్రాస్యుడు, చిత్రసేనుడు, పంచసేనుడు అను వీరు తమ నిజరూపాలలో దేవలుడిని చంపడానికి ప్రయత్నిస్తారు. దేవలుడు విష్ణువు నుండి పొందిన సుదర్శన చక్రాన్ని ప్రయోగిస్తాడు. అది ఆ అయిదుగురిని తప్ప మిగతా వారిని చంపుతుంది. ఆ రాక్షసులలో పెనుగులాడి ఏమీ చేయలేక మహాదేవిని స్మరించాడు.

**మహాదేవి ఆవిర్భావము :**



అప్పుడు శివుని పత్ని అర్ధనారీశ్వరి యగు దుర్గా దేవిని - జగజ్జనని, త్రిలోక మాతవు, దుర్గవు, చండివి, ... ఇలా స్తుతిస్తూ కాపాడమని ప్రార్థించాడు. ఆయన ప్రార్థనను మన్నించి నాయనా దేవలా! భయపడకుము ఒక ముహూర్తము (24 నిమిషాలు) లోపల నా బలము నీవు తెలుసుకోగలము నా శూలంచే వారిని సంహరిస్తాను, వారి రక్తం త్రాగుతాను అని అభయమిచ్చింది. ఆషాడమాస అమావాస్య అర్ధరాత్రి అంత్య సమయంలో ఆవిర్భవించింది.

**మహాదేవి పంచ రాక్షసులలో యుద్ధం చేయుట:**

నాలుగు భుజములు కలిగి అతిపెద్దదైన నాలుకను చాచి కన్నులు అగ్నిగుండం వలె ఎరుపెక్కినవై మహాబలం గల ఆ మహాదేవి అట్టహాసం చేస్తూ శూలమును, చక్రమును, కత్తిని, గదను చేతబట్టి భయంకరమైన ఆయుధాలు కల్గి, కాటుకవలె నల్లగా మెరిసిపోవుచు కోటి సూర్య వెలుగులు గల ఒక శక్తివంతమైన కిరీటాన్ని శిరస్సుపై ధరించి మిక్కిలి బలవంతురాలై శూలాన్ని త్రిప్పుచూ వారితో పోరుకు సిద్ధమైనది. రాక్షసులు ఆయుధాలు సమకూర్చుకున్నారు. కాని ఆ తల్లి హూంకారానికి రాక్షసులంతా మూర్చిల్లినారు. ఆమె శూలాన్ని గిరగిరా త్రిప్పుతూ గదా, ఖడ్గ, చక్రములనే నాలుగాయుధాలలో పెక్కుమంది రాక్షసులను చంపింది. తనచేతి శూలముతో పంచరాక్షసులను చంపింది.

ఆ పంచ రాక్షసుల రక్తం ఎరుపు, తెలుపు, నలుపు, పసుపు పచ్చరంగుల్లో ప్రవహించింది. వెంటనే దేవలుడు తన వద్దనున్న ఒక్కొక్క తంతువులను ఒక్కొక్క రంగు రక్తంలో తడిపి తన వద్దనున్న తంతువులు పంచ వర్ణాలయ్యేటట్లు చేసుకున్నాడు.

**పంచరాక్షసుల రక్తము ఐదురంగుల్లో ప్రవహించుటకు కారణం :**

ఒకానొకప్పుడు 5గురు రాక్షసులు శుక్రాచార్యుని వద్దకు విద్యనిమిత్తమై వచ్చారు. వారు దేవయాని అందానికి ముగ్ధులై ఆమె వద్దకు వెళ్లి మా ఐదుగురి వివాహ మాడమని కోరారు. ఆమె మిక్కిలి వ్యధ చెంది గురుపుత్రి సోదరితో సమానం ఆడదంటే మీ దృష్టిలో అంతచులకనా? మీరు ఏదో ఒక సందర్భంలో ఆడదానిచేతిలో మరణిస్తారని శపించి అక్కడనుంచి వెళ్ళిపోయింది. వారు ఈ శాప నివృత్తి కొరకు బలపరాక్రమాల కొరకు శివునిపై తపస్సు



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చేశారు. పరమేశ్వరుడు ప్రత్యక్షమై వరం కోరు కోమనగా మా రక్తాన్ని ప్రజలు ధరించాలని పరమేశ్వరుడు కోరారు. తథాస్తు అని వరమిచ్చాడు. అందువల్లనే వారి రక్తాలు వివిధ రంగుల్లో ప్రవహించాయి. వాటిల్లో దేవ లుడు తంతువులు ముంచి ఆ దారాలతో నేసిన వస్త్రాలు ప్రజలు ధరిస్తున్నారు.





## మహాదేవికి చౌడేశ్వరి అనునామం ఏర్పడడం :

పంచరాక్షసులలో యుద్ధం చేయడానికి వచ్చిన ఆ మహాదేవి కిరీటం కోటిసూర్యుల ప్రకాశంతో వెదజల్లినది. ఆ కిరీట కాంతులకు వెలుగులకు రాక్షసరాజులు స్తంభించిపోయారు. అటువంటి శక్తివంతమైన చూడ మును ధరించుట వలన చూడేశ్వరి, చూడాంబా అని పిలువబడింది కాలక్రమంలో అది చౌడేశ్వరి అయింది. దేవలుడు అతని సంతతి వారైన దేవాంగ వంశీయు లందరు తమ కులదేవతగా చౌడేశ్వరీదేవిని కొలుస్తూ వస్తున్నారు.

## చౌడేశ్వరీ పూజావిధానం :

చౌడేశ్వరీ దేవికి దేవాంగులు దసరా పండుగ దినాల్లో ఆమెను ఒక శక్తి స్వరూపిణిగా భావించి పూజిస్తారు. ఆ దేవతా ప్రతిమను చేసి రోజుకో అలంకారంతో అలంకరించి ప్రతిపూట నైవేద్యం సమర్పిస్తారు. దసరా రోజున కత్తి వేయడం కూడా ఈ కులములో ఆచారంగా కన్పిస్తుంది. పులివాహనం బొమ్మగీసి దానిపై అన్నపురాసి పోసి రక్త తర్పణ గావించి కత్తిపట్టుకొని ఆమెను దండకాలతో స్తుతిస్తారు. ఆ తరువాత కత్తివేసుకొని ఆ ప్రతిమను ఊరంతా ఊరేగిస్తారు. ప్రతినిత్యం ఆ పండుగదినాల్లో కత్తిపట్టుకొని, దండకంతో స్తుతిస్తూ నైవేద్యం సమర్పిస్తారు. దాన్నే 'తళియ' అంటారు. ఆ నైవేధ్యాన్ని ప్రతి దేవాంగుల ఇంటికి పంచుతారు. ఇలా చౌడేశ్వరీ దేవి దేవాంగుకుల రక్షకురాలిగా, వరాలమూటగా ప్రసిద్ధికెక్కినది.



## ఉపయుక్త గ్రంథసూచి :

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# వ్యవహారిక భాషోద్యమ ఊతం - గిడుగు 'బాలకవి శరణ్యం'

డా. గోపవరం పద్మప్రియ
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మహిళా కళాశాల, నెల్లూరు

ఈనాడు మనం అనుభవిస్తున్నసాంఘీక, సాహిత్య స్వేచ్ఛ వెనుక మనమూహించలేనంత ఉద్యమ నేపధ్యం కన్పిస్తుంది .సాంఘీక దురాచారాల నిర్మూలనకు ,స్త్రీవికాసం కొరకు రాజా రామ్మోహన్ రాయ్, కందుకూరి వీరేశలింగం లాంటివారు ఎంత పోరాటం చేయవలసి వచ్చిందో ,అంతే పోరాటాన్ని మాట్లాడే భాష ,రాసే భాష ఒకే విధంగా ఉండడానికీ చేయాల్సి వచ్చింది .ఈనాడు వ్యవహారిక భాషోద్యమం గురించి ప్రస్తావిస్తే నేటి తరానికి హాస్యాస్పదంగానే ఉంటుంది . కాలమిచ్చిన తీర్పు వల్ల నేడు కొన్ని వందల పేజీలు మనం మాట్లాడే భాషలోనే అచ్చవుతు ప్రజల మధ్యకు వస్తున్నాయి .

కాని పూర్వం మాట్లాడే భాష వేరుగా , రాసే భాష వేరుగా చెలామణి అవుతూ వచ్చింది.అయితే ఈ భేదం పట్ల పూర్వం మనకంత నిరసన భావం కూడా లేదు .భారతదేశం లో సార్వత్రిక విద్యా విధానం అమలు లోకి వచ్చిన తర్వాత పరిస్థితుల్లో మార్పులొచ్చాయి .1852సంII లో మద్రాసు ,బొంబాయి, కలకత్తాల్లో విశ్వ విద్యాలయాలు ఏర్పాటు చేశారు.వాటిలో చదువుకొన్నవారు దేశంలో విద్యావ్యాప్తికి కృషి చేస్తారని తలచారు. అయితే ఆంగ్లం లో చదువుకోవడం వల్ల దేసబాషల అభివృద్ధికి వీరు తగిననత కృషి చేయలేదనే చెప్పవచ్చు.1901లోగవర్నర్ జనరల్ గా ఉన్న లార్డ్ కర్జన్ సిమ్లాలో ఒక సమావేశం ఏర్పాటు చేసి ప్రాథమిక స్థాయి నుంచి విశ్వవిద్యాలయ స్థాయి వరకు పరిష్కరించవలసిన సమస్యల గురించి చర్చించి 150 తీర్మానాలను చేశారు. దానిలో భాగంగా మాతృభాషలో వ్యాసరచనలను నిర్బంధపాఠ్యాంశంగా ప్రవేశపెట్టాలని అలాగే ఇంగ్లీషు లోని పుస్తకాలను ప్రాంతీయ బాషల్లోకి అనువదించేటప్పుడు వారికి శిక్షణ కల్పించాలనినిర్ణయించారు ఇలాంటి తరుణంలో1906 సంవత్సరంలో J.A ఏట్స్ గంజాం ,విశాఖ ,గోదావరి జిల్లాలకు పరీక్షా అధికారిగా నియమించబడ్డాడు ఇతనికి తెలుగు బాగా ఒంట బట్టింది .ఆయన మన పుస్తకాల్లో ఉన్న తెలుగుకి, ఆ పుస్తకాలను బోధించే అధ్యాపకులు మాట్లాడే తెలుగు మధ్య భేదాన్ని గుర్తించి ఆయన ఆశ్చర్యపోయారు.ఈ విషయం గురించి కళాశాల అధ్యక్షులైన టి. శ్రీనివాస అయ్యంగారు ని ఈ విషయమై ప్రస్తావించగా విజయనగరం లో ఉన్న గురజాడ వెంకటమిడి లోని గిడుగు రామ్మూర్తి పంతులు తనకంటే బాగా చెప్పగలరని సూచించాడు. ఏట్స్ వాళ్ళిద్దరిని సంప్రదించి చర్చించి ఈ వ్యవహారిక,గ్రాంధిక బాషా బేధాల వ్యత్యాసాన్ని తగ్గించడానికి ఉపాధ్యాయ వార్షిక సమావేశాలు ఏర్పాటు చేసి గిడుగు చేత ఉపన్యాసాలిప్పించాడు. ఇది పండితులందరికి కంట్లో కారం అయింది. ఈ సమయంలోనే స్కూల్ ఫైనల్ పరీక్ష F.A స్థానంలో ఇంటర్మీడియట్ వచ్చింది. అప్పుడు విద్యార్థులు ఎంచుకోవలసిన అనువాద అంశాలు,



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వ్యాసాలకు పరిచయించి దగడ పెంచుతుంది. ఈ సందర్భంలో V.I లెనిన్‌గారు Language like as Deathఅని వ్యాఖ్యాన్ని ప్రచురించారు. ఈ విధమైన పరిణామాలు వెలిసి ఉద్యమంలో వ్యవహారిక భాష నిరంతరంగా ఒక ఉద్యమాన్ని లేవదీశారు.

ఈ గడిచిదను గమనించి మద్రాసులోనిహైకోర్టులు 1911లో పెద్దలను ఒక ఒక సంఘాన్నిఏర్పాటు చేసింది.ఇందులో 9 మందిసభ్యులు ఉన్నారు. ఇందులో ఆరుగురు ఆంగ్లేయులు కాగా మిగతా వారులు, నలుగురు వ్యవహారిక భాష వాదులు ఒకరు గ్రాంథిక వాదులు వీరు అనేక చర్చలు సమావేశాలు జరిపిన తరువాత గిడుగు రామ్మూర్తి పంతులుని Memorandum of Modern Telugu గురజాడ Deccan పుణ్యాన శిష్ట వ్యవహారిక భాషలోనే రచనలు సాగించాలని సిద్ధపరిచి ఇచ్చారు. కాని గ్రాంథిక వాదులు వ్యవహారిక వాదాన్ని ఎదుర్కోడానికి ఆంధ్ర సాహిత్య పరిషత్తు ఏర్పాటు చేశారు. శిష్ట వ్యవహారాన్ని గ్రామ్యమని ఊరూరాసభలు జరిపి సంతకాలు సేకరిస్తూ వచ్చారు. మొత్తమ్మీదను చీరాలలోనే గ్రాంథిక ఏలుబడి చెల్లుతూ వచ్చింది. క్రమంగా ఉత్తరోత్తరా వచన రచనల్లో వ్యవహారిక భాష ప్రాధాన్యం పెరుగుతూ వచ్చింది .క్రమక్రమంగా కాల ప్రవాహంలోఅన్ని రంగాల్లోనూ వ్యవహారిక భాష పేరొందుకుంది దీనికి ప్రధాన కారకులు గిడుగు, గురజాడలు. గిడుగు సిద్ధాంతవాది అయితే గురజాడ అచరణ వాది. గిడుగు భాషా సంస్కరణకు, కందుకూరి సంఘ సంస్కరణకు తన సాహిత్యం లో ప్రతిపాదిక చేసి అడుగడుగు ప్రోత్సాహకుడు అయ్యాడు. గురజాడ సహాయంతో సహాయంతో గిడుగురామ్మూర్తి పంతులు భాషా సంస్కరణకు తన జీవితాన్ని ధారపోసాడు.పూర్వరచనలన్నీ శిష్టవ్యవహారికం లోనికిపోగినాయని, మధ్యలోనే భాష కృతకంగా మారిపోయిందని భావించిన గిడుగు రామ్మూర్తి పంతులు ఆ విషయాన్ని నిరూపించడానికి వ్యవహారిక భాషను పూర్ణ ప్రాచ్య చేయడానికి కినాలుగు మార్గాలను అనుసరించారు.

1. భాషా తత్వాన్నివివరిస్తూ ప్రపంచంలోని ఇతర భాషావాఙ్మయమంతాలౌకిక భాషలోనే పొందని అలాగే తెలుగు భాషలో కూడా ఆయాకవులు ఆనాటి శిష్టవ్యవహారికాన్ని కావ్యాల్లో ప్రయోగిస్తూ వచ్చారని కాల పరిణామంలో మధ్యలో తెలుగు పరిస్థితి మారిందని ఇతని అభిప్రాయం. ఆ విషయాన్ని ఉదాహరణ పూర్వకంగా నిరూపించారు

2. తాళపత్ర గ్రంథాల్లోనూ, గ్రంథ పరిష్కారాల్లోనూ లౌకికభాష స్థానంలో గ్రాంథిక భాషను వచ్చారని భావించి లక్ష్య సహితంగా నిరూపించారు.

3. గ్రాంథిక భాషను నిర్వచించడం, స్వరూపాన్ని నిరూపించడం కష్టమని తేల్చి చెప్పాడు. భాషా స్వరూపాన్ని వర్ణించే వ్యాకరణ గ్రంథాలే పరస్పర విరుద్ధ భావాల్ని వ్యక్తం చేస్తున్నాయి. ఒక వ్యాకరణం ఒక పదాన్ని గ్రామ్యంగా పేర్కొంటే మరొక వ్యాకర్త దాన్ని గ్రామ్యం కాదంటారు. వారికి వారే ఏది తప్పో ఏది ఒప్పో సమగ్రంగా చెప్పలేకపోతున్నారు. గ్రాంథిక భాషలో మాత్రమే రాసిన గ్రంథం మన్యుకి ఒక్కటి కూడాఉండదని గిడుగు అభిప్రాయం ఇది ఇతని మూడో మార్గం.

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4. ప్రాచీన కవులు అన్నికావ్యాల్ని సమగ్రంగా పరిశీలించక పోవడం వల్ల వ్యాకరణ కర్తలు,నిఘంటు కారులు ,పండితులు తప్పుగా భావించి లక్షణ విరుద్ధమని,గ్రామ్యాలని నిందించిన రూపాలు వందలకొద్ది కావ్యాల్లో కలవని నిరూపిందారు . వ్యాకరణం ప్రయోగ మూలం కావడంవల్ల కవి ప్రయోగం లక్షణం కంటే బలవత్తర మైనది. కవులు ప్రయోగించిన రూపాలు ఆ లక్షణంతో సమన్వయం కాకపోతే ఆ లక్షణమే అసమగ్రమవుతుంది ,అంతే కాని ఆ కవి ప్రయోగాలు నిందాలు, గ్రామ్యాలు కావని అలాంటి ప్రయోగాలు వందల కొద్ది కావ్యాల్లో కలవని చూపించడం నాలుగోమార్గం. అందుకే "ఆర్యవ్యవహారంబుల దృష్టంబు గ్రాహ్యంబు" (బా.వ్యా-సం.ప 23) అంటారు బాలవ్యాకరణం లో చినయసూరి.

ఈనాలుగు మార్గాలను ఉదాహరణ సహితంగా నిరూపించడానికి గిడుగు రామ్మూర్తిపంతులుగారు 4 గ్రంథాలు రాశారు.

1.వ్యాసావళి

2.గద్యచింతామణి

3.ఆంధ్రపండిత భిషక్కుల భాషాభేషజం

4.బాలకవిశరణ్యం

ప్రస్తుత వ్యాసం నాలుగో మార్గాన్ని నిరూపించే బాలకవిశరణ్యాన్నిచర్చించడం ప్రధాన లక్ష్యం వ్యాకరణాల్లో ఇలాంటి పరిస్థితి సెలకొనడానికి ప్రధాన కారణం ఆ మూలాగ్రం వాఙ్మయాన్ని చదవక పోవడమే కారణం అంటాడు. ప్రధానంగా ఈ గ్రంథంలోబాల వ్యాకరణ సూత్రాలు చెప్పిన రూపాలను తీసుకొని వాటిని ని సాధు నిరూపణ చేయడానికి పూనుకున్నాడు .సాహిత్యంలో ఉపయోగించిన శబ్దాలను అసాధువులని చెప్పడం తప్పని ఇతని అభిప్రాయం. జనవ్యవహారంలో లేని దానిని కవి ప్రయోగించడు కొన్ని గ్రంథాలను ప్రమాణాలుగా తీసుకుని ఇవి సాధువులు , అసాధువులని, నిందాలని పేర్కొనడం తగదని ఇతని అభిప్రాయం.

వాఙ్మయమంటెల్లజుచినవారలెవరు?
బాస యెల్లను బండితల్బాపుకొనిరి?
సాహసముగాది పెద్దల సభ్యభాష
తప్పుతప్పనిదూరుట?తగనికవులు
పల్కులును దప్పులంటయు వాసిగనుక—

అని నిరసనవ్యక్తంచేశాడు.అలాగే .....

లోకయాత్ర కొరకు లౌకికభాషలు
పుట్టి ప్రజలనోట నొందియుండు
జీవలోకమందు జీవంబభాషలు



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జనుల తలపుదెలుపు సాధనములు

లోక వ్యవహారంలో ప్రజల భావాల్ని తెలిపేది భాషని ,కాళ్లు చేతులు అవి ఎలా తమ పనులు చేస్తాయో అలాగే భాష ఉచ్వాస ,నిశ్వాస కరణ ప్రయత్నాల ద్వారా తన విధిని నిర్వర్తిస్తుందని ,ఈ శబ్ద సిద్ధిని తెలపడానికి శాస్త్రాలు సరిపోవని అభిప్రాయపడుతూ ,పరిమితమైన శబ్ద జాలానికి కాక లోక భాషకు ప్రక్రియను ఏర్పరచినవారే గొప్పవారని వివరించారు.

లోకమందుభాషలలోన నున్న
సిద్ధి శబ్దాల పరిపాటి చిత్తగించి
మేరమీరక ప్రక్రియలేరుపరచి
వ్యాకృతికి ద్రోవచూపినవారి గనుడు

దీన్నిబట్టి చూస్తే అసలు భాషకు వ్యాకరణం ఏర్పరచడం కష్టమనే అభిప్రాయం మనకు కలుగుతుంది. వ్యాకరణ పేత్తలు చెప్పిందే వేదం కాదనేది గిడుగు అభిప్రాయం .ఇక్కడ ఒక ఉదాహరణను పరిశీలిద్దాం.
"కూతు శబ్దముప్రాథమైక వచనంబునకు రువర్ణంబగు"(బా.వ్యా-ఆ.ప 8) "కూతురు-కూతులు – కూతురులు – కూతుళ్ళు-కూతురిని ఇత్యాది రూపంబులు గ్రామ్యంబులని యేరుంగునది " అనే సూత్రం ప్రకారం కూతురు మాత్రమే సరి అయిన రూపమని,గ్రాహ్యమని అర్థం . మరి శిష్టవ్యవహారంలో ఉన్న కూతురిని– కూతురికి – కూతుళ్ళూ మొదలైన రూపాలన్నీ గ్రామ్యాలైయిపోయాయని, అవి రాయడానికి తగినవి కాదని పండితులు వాటిని బహిష్కరించారు. అందువల్ల పూర్వపు గ్రంధాలను అచ్చు వేసేటప్పుడు, పరిష్కరించేటప్పుడు ఆ వ్యవహారిక భాషా పదాల స్థానంలోఈ రూపాన్ని చేర్చారు. వ్యాఖ్యానాల్లో, టీకల్లో కూతురు ,కూతురిని అని ఉన్న చోట్ల అంతా ఆ కవులకు అపఖ్యాతి కలుగుతుందని లేక గ్రామ్యాలనే వాటిని దిద్ది వేశారు. అయితే జీవాద్భాష ఒకరు దిద్దితే అక్కడే ఆగేది కాదు. సాక్షాత్తు చిన్నయ్యసూరే తాను రాసిన హిందూ ధర్మ శాస్త్ర గ్రంథం లో కూతుండ్రు అని రాశాడు. ఇది తప్పని గాని ఒప్పని గాని తన లక్షణగ్రంథంలో చెప్పలేదు. తను రాసినశబ్దాన్నే తాను గ్రహించలేదు కాబట్టి ఏది తప్పు, ఏది ఒప్పని మనంనిర్ణయించలేమంటాడు.

ఇక్కడ మనం చెప్పదలచేదేమిటంటే ఏవ్యాకరణమూ ప్రమాణమూకాదు అలాగనీ నిరాదరణీయమూ కాదు. పాణిని అష్టాధ్యాయిలోనే కాత్యాయనుడు 10 పేలకుపైగా తప్పులుదిద్దాడు. అలాగే బహుజనపల్లి సీతారామాచార్యులు మొ. వారు బాలవ్యాకరణం లో వదిలిన అనేక విషయాల్ని ప్రస్తావించారు. ఇక్కడ మనం చిన్నయ సూరిని తప్పుపట్టలేము, ఆయన గ్రందమే వేదమని చెప్పలేదు. శిస్తుల ప్రయోగాల నుండి శేషమును తెలుసుకోవాలని చెప్పాడు. అంతేగాక లక్షణ విరుద్ధమైన దానిని పెద్దలు వాడితే దానిని యదా ప్రకారంగానే గ్రహించాలన్నాడు. ఇది తెలియని మనము ఇవి మాత్రమే ప్రయోగార్హాలని , ఇవి గ్రామ్యాలని, నింద్యాలని చెప్పడం , అవి ప్రయోగానికి అనర్హాలని చెప్పుకోవడం మన పండితుల తప్పని నిరూపించాడు. ఈ



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అంతరం వల్లనే శిష్ట వ్యవహారిక భాషని, గ్రాంధికభాషని రెండు విభాగాలైంది. ఒకప్పటి శిష్టవ్యవహారికమే నేడు గ్రాంధికమని మన గిడుగు వారల అభిప్రాయం.

నన్నయ్య 'ప్రవాహినీ దేశ్య' అన్నారు.భాష నిరంతరం మారుతూ ఉంటుంది. ప్రాచీనులు వాడిన ఆనాటి వ్యవహారిక భాషను ఆ ప్రక్రియలతో సహా అనుసరించడం సరికాదంటాడు.

ఏరు పారునట్లు పారుచునుండును
దేశ భాష తెరుగు తెలియుటరది
మారుచుండు గాని మారుపు గనరాదు
లోటు చూచి కనుడు లోని గుట్టు
మనమే కానలేము మనము మారెడుచొప్పు
భాసయొక్కటే కాదు బ్రహ్మాండ
మెల్ల మారుచుండు తెరున్గా లొక్కో
ఎప్పుదేద్ది కలదో యప్పతికడే నిత్య
మదియ మనకు సేవ్యమగుట యొప్పు.

భాషకేకాదు బ్రహ్మాండానికీ మార్పు సహజమనీ ఎప్పుడు దేనిని వ్యవహరిస్తామో అదే నిత్యమని దానినే మనం అనుసరించాలని చెప్పి వ్యవహారిక భాషోద్యమాన్ని నడిపిన కారణాన ఈనాడు మనం ఆ ఫలాలను అనుభవిస్తున్నాము. ప్రతీ రంగంలోనూ వ్యవహారిక భాష మాత్రమే ప్రయోగించ బడుతుంది. ఇంకా సాహిత్యమైతే ప్రాంతీయతనూ ఆదరిస్తుంది. మాండలిక సాహిత్య సృష్టికి ఊపిరి వ్యవహారిక భాషోద్యమమని చెప్పవచ్చు. ఈనాడు వ్యవహారక భాష ప్రయోగం కోసం కూడా ఇంత ఉద్యమం జరిగిందా అన్న స్థాయిలో వ్యవహారిక భాష వేయిచెరుగులా తెలుగు నేల నలుమూలలా విస్తరించింది. దీనికి కారణమైన గిడుగు రామ్మూర్తి పంతులు గారికి , గురజాడ గారికి ఆంధ్రజాతి ఋణపడ్డది. ఈ ఘనులను ఇలా స్మరించుకోవడం చంద్రునికో నూలుపోగులాంటిది.

ఆధార గ్రంధాలు :

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# చేనేత సాహిత్యంలో స్త్రీ

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సామాజిక చిత్రణ సాహిత్యం పని. ఈ పని ప్రక్రియా రూపాల నుంచి ఇజాలవైపు కొనసాగింది. సమాజంలోని ప్రతి చిన్న అంశాన్ని అక్షరబద్ధం చేస్తూ కాలం, దేశం, సమాజం, సంస్కృతుల్లో వచ్చే మార్పుల్ని పొందుపరుస్తూ పురాణం, ఇతిహాసం, కావ్యం, ప్రబంధం, గేయం, కథ, వచన, కవిత్వం ఇలా సాహిత్యం సమాజంతో పాటూ తాను పరిణామం చెందుతూ వచ్చింది. ఈ సమాజం గురించి చెప్పడం మాత్రమే సాహిత్యం యొక్క పని కాదు. అంతకంటే మెరుగైన సమాజ నిర్మాణమూ సాధ్యమవుతుందని బోధించడం వాని బాధ్యత. రచయితా అస్పృహను కలిగే రచనలు చేస్తాడు. ఇందులో భాగంగానే వస్తు పరిణామం జరిగింది. వైదికమత పునరుద్ధరణ కోసం నరేంద్రుడి ప్రేరణలో నన్నయ్య భారతాన్ని తెలుగులోకి అనువదించాడు. తిక్కన శైవ – వైష్ణవ సామరస్యం కోసం హరిహరాద్వితాన్ని స్థాపించాడు. శతక రచక నాటి సంఘంలో ఉండే లోటుపాట్లను విప్పి చూపి సంస్కరణలకు దారితీసింది. ప్రబంధ సాహిత్యం ఆనాటి భోగలాలసతను వ్యక్తపరుస్తుంది.

ఆధునిక సాహిత్యంలో సామాజిక తపన, మానవతాకాంక్ష సమతాభావన ప్రతిఫలిస్తాయి. శ్రీశ్రీ యుగంలో అభ్యుదయం వైపు సాగిన సాహిత్యం శాఖోపశాఖలుగా విస్తరించి ఈ అభ్యుదయం, విప్లవ పంథా అణచివేయబడ్డ ప్రతి సమూహం వైపు పయనించి స్త్రీ, దళిత, మైనారిటీ వాదాల రూపంలో వర్గసాహిత్యంగా రూపుదాల్చింది.

సమాజంలో సగం మంది స్త్రీలు..... సాంఘికంగా స్త్రీ సమాజంలో మోసగింపబడుతుంది. కేవలం ఒక పనిముట్టుగా మాడబడుతోంది. ఆర్థిక స్వేచ్ఛ లేమి, పురుషాధిక్యత ఈ పరిస్థితుల మధ్య సాంఘిక న్యాయంకోసం సాహితీ రూప ఉద్యమమూ ఊపందుకుంది. అది 80వ దశకం నుంచి ప్రారంభమై నేటిదాకా కొనసాగుతూనే వుంది. అయితే స్త్రీ తన హక్కుల కోసం, సామాజిక న్యాయం కోసం తన అస్థిత్వపు పోరాటం సాహిత్యంలో ప్రథమం నుంచి కన్పిస్తూనే ఉన్నాయి. సీత తన అస్థిత్వం కోసం భూగర్భంలో కలిసిపోయింది. ద్రౌపది నిండు సభలో తన స్థానాన్ని నిర్ణయించమని ప్రశ్నించింది. ఇలాంటి ఉదాహరణలు సాహిత్యంలో కోకొల్లలు. చేనేత సాహిత్యంలో నా వెతుకులాటలో స్త్రీ అస్తిత్వపు పోరాట ధోరణులూ అక్కడక్కడా కన్పిస్తున్నాయి. చేనేత సాహిత్యం అనగానే భారతదేశ చరిత్రలో చేనేత నిర్వహించిన పాత్ర, ప్రస్తుత సంక్షోభం, ప్రభుత్వచర్యలు – వైష్యాలు, దానికి కారణాలు, చేంత వృత్తిలోని శ్రమ, దానిలోని కళావిలువలు ఇవే కన్పిస్తాయి. కాని వీటితోపాటు స్త్రీ జీవన చిత్రణ, స్త్రీ హింస, అస్థిత్వపు పోరాటం అటు జానపద సాహిత్యంలోను, ఇటు శిష్ట సాహిత్యంలోను కన్పిస్తుంది.



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జానపద పాటలాట్లు :-

పిల్లలపాట పల్లెల పదుగులలో దొరికే ఓ చక్కని జానపద పాటలాట. అందులో ఒక రకం జానపదగీతం పాటలాట్లు. అందులో ఒక పల్లెకి చెందిన స్త్రీలందరూ పాటలు. అది చూసేవాళ్ళు గుర్తించక, గుంపులుగా పాటలాడ తీరాల్సిన అవసరం వారి అవసరాల కోసం ప్రకృతిదేవుడే ఒకొక్కరికి ఒకొక్కటిని చేసిపెట్టాడు. తేనెటీగకి అదనపుపని అవసరమైనట్లు పెట్టాడు. వారిలో ఒకరి చేతిలో చాకలి పనిలాంటి మంచినీటి ఊట ప్రవహిస్తుంది. బట్టలు, కుటుంబ సభ్యులూ చనిపోతే చనిపోయే చిన్న ఉయ్యాలుంటుంది. ఇంట్లో స్త్రీలు చూపులు చదవడం / రాళ్ళాటలో కుదిరలు చూడడం, పిల్లల్లో ఫిరంగులు పదుగుపెట్టడంలో స్త్రీలు వారికి గంత పెట్టడం వారి చదువు చేస్తుంటారు. ఈ క్రమంలో రాళ్ళు తిప్పుతూ స్త్రీ పాడే పాటలు, మర్రం ఆడిస్తూ మూళ్ళు తీసే కూనిరాగాలు జానపద గీతాలుగా కూడుకున్నవున్నాయి. వీటి ఎప్ చాలా చదవ అంతరించిపోయాయి. ఇందులోని రాళ్ళు పాటలు స్త్రీ మానసిక చిత్రణ, వారి అభిరుచిని తెలియచేస్తుంది.

స్త్రీలు ఇంట్లో కూర్చుని చేసే చదువే రాళ్ళు తిప్పడం ఒకటి. బట్టలు చేసేవరిలో కీలకమైంది ఈ రాళ్ళు. చదువరి అన్ని రాయి కట్టలను రాళ్ళాటకి చుట్టి రాళ్ళపై చుట్టాన్ని తిప్పి చిన్న చిన్న కుదుపులు చుట్టించడమే ఈ రాళ్ళాట్లను ఉపయోగిస్తారు. రాళ్ళాట్లు తిప్పుతూ పాడే పాటల్నే రాళ్ళు పాటలంటారు. ఇవి అజ్ఞాతకవు రోదసిలో పాగుతాయి. ఈ పాటలు చదువుతూ స్త్రీ పడ్డింది. తల్లిదండ్రులను సోదరులను తలచుకుంటూ – పడ్డింటిపై తనకు గల మమకారం ప్రదర్శిస్తోంది.

చదువు చదువు చదవవే చిలకా
అమ్మకి కుతలాలు చెప్పవే చిలకా
పాలూరు నీళ్ళకు ఇచ్చిరా చిలకా
పడ్డింటి అన్నల్ని చూసిరా చిలకా
పొందూరు పంచెలా ఇచ్చిరా చిలకా
కడ దాటి రాద ఆగవే చిలకా
కడ దిండా చీళ్ళు తెచ్చియ్యి చిలకా

స్త్రీ పడ్డింటి వారిని తలచుకుంటూ వారి రాకకోసం ఎదురుచూస్తూ వారు వచ్చేటట్లు కాకిని కూడుచుంటుంది.

కాకమ్మ నీ కాల కట్టేము గట్టి, రన్నమ్మ మా వార్ని రాగయ్యి కాకి
కాకమ్మ కూతలు కర్ణలు కావు, కన్నవారొచ్చేటి వేళలు కావు
నీరేడు మందుంది అన్న వాదున్న నీడు వస్తారని నెలకన్నారాడు
అారు దున్నారని కమ్మోళ్ళే పంపు, వినోయి పెద్దన్న ఎన్నటికి రావ
ఏటేటా పెద్దమ్మ కుప్పనూర్చుతు, ఎదలేదు పెద్దిలా నిను చూడారు



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ఈ అంశాన్ని చర్చించిన విశ్వనాథ మరికొన్ని చోట్ల కూడా ఈ విషయాన్ని ప్రస్తావించారు. ఆయన అభిప్రాయంలో స్త్రీ తన భర్తలోని బాధ్యతలను కూడా తీసుకోవాలి అని వివరించారు.

ఒక స్త్రీ తన భర్తకున్న ఈ విధంగా ఎందుకుంటుంది? ఏమంటుంది? అన్నది ప్రస్తుతం పాడుతోంది.

కాలుకి దుమ్ము కొట్టి కడుగా పోదు
పొరుగు రాసిన రాలు తుడిచా పోదు
అన్న వెంగలు పెట్టి అడిగా పోదు
పైరు వెంగలు పెట్టి పుటిమా పోదు

కాబట్టి గానుగు తీసే ఈ రాట్నం పాటలో దున్నపోతు ఎలా ఉండవద్దు. ఒక ఇల్లాలు

మొగుడెందుకే వారీ మొగుడెందుకే –
అరటి మొగుడెందుకే వారి మొగుడెందుకే
రాట్నం వల్లంగుంటి దున్నపోతు గోల్కొండ
మొగుడెందుకే వారీ మొగుడెందుకే

మొగుడు చేతుల్లో బాధపడేకంటే తన స్వంత కాళ్లమీద నిలబడితే వచ్చే భర్తం నుండి దూరమై పోవడం సులభమని స్త్రీ కావాల్సిన ఆర్థిక స్వావలంబన గురించి చెప్పి తన ఆత్మ విశ్వాసాన్ని ప్రకటిస్తుంది.

ఈ జానపద సాహిత్యంలో పుట్టింటి కోసం ఆరాటపడే అతివలు, తల్లిదండ్రులకు దూరంచే అంశాలు, ఆత్మవిశ్వాసంతో నిలబడే సంఘటనలూ కనిపిస్తున్నాయి.

**చిత్ర సాహిత్యం :-**

ఆధునిక కాలంలో పారిశ్రామికీకరణ, గ్లోబలైజేషన్ చేనేత రంగాన్ని అభద్రతాభావానికి గురిచేసిన విధానం దీని ద్వారా మగ్గం గుంతలో కాళ్లుపెట్టి తొక్కుడి బెక్కల్ని లయబద్ధంగా కొడుతూ కుదిపేస్తే కూర్చుని లాగుతూ, ఇంకో చేత్తో పలకను ఆడిస్తూ ఈవారకు, అవారకు పదుగులు చేసే కొమ్ము చుట్టుకి అనుగుణంగా తలను కనుపుతూ జీవనయానం చేసే నేతన్న దుఃఖమయ జీవితాన్ని కవిత్వ కెమెరాతో చిత్రించారు. ఈ చిత్రీకరణలో అక్కడక్కడ స్త్రీ వేదనా భరితమైన జీవితం, వారి అస్తిత్వపు పోరాటాలు కెమెరా స్టైలో అక్కడక్కడ తళుక్కుమంటున్నాయి.

2004, 2005 సంలో చిమ్ సాహిత్యంలో చేనేత కథనాలపై చర్చోపపులు నిర్వహించి ఆ సాహిత్యాన్ని చేనేత గుంటకోత పేరుతో ప్రచురించారు. విరసం కూడా ఈ బాటలో మగ్గం ముక్కులవుతుంటే కవితా సంపుటిని ప్రచురించింది. ఈ సాహిత్య సంపుటులలో 'చేనేత చెల్లి' కవిత స్థలమేదైనా, రంగు ఏదైనా స్త్రీ పరిస్థితిలో మార్పు లేదనే విషాన్ని ధృవీకరిస్తుంది. స్త్రీ అందరినీ చేనేత వృత్తి సాగు చేసే వృత్తిలో స్త్రీ సంపాదాగం. అటు ఇంటి పనిలోను, ఇటు వృత్తిలోను తన పాత్రను అద్భుతంగా నిర్వహించారు.



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పొంచెక్కుల తాడు కాలికి కట్టుకున్నట్లు
పనికి పనికి నేస్తున్నట్లు ఒక్కటే పరుగు
చీపిరిలా సంజకసువూ, చీకటి చిమ్ముతూనే
చిర చిర్లాడుతూ మగడు కేకేస్తే చాలు
నాదలా గుంట దిక్కు వురుకు తావు
ఇంటిపని, పిల్లల పనీ చూస్తూనే
చిక్కుపడన పోగు సరిచూస్తావు

ఉదయం నుంచి పొయ్యిలా మండి మోసిన బరువు
ప్రతికంచానికి రుచులతో నింపి
ప్లేట్లూ, గ్లాసులూ, గిన్నెలు, కంచాలు కడిగి
అట్టనడుమెత్త మధ్యాహ్నం ఆగిన మగ్గాన్ని, కునికీ

భర్తని కుంటుతున్న ఆదాయాన్ని చూచి
తిండి అటుపు తీరకుండానే బాదు బరువు తొక్కడానికి
మగ్గం మీదికెక్కుతావు

సంసారాన్ని, భర్త బరువును తన భుజాలకెత్తుకుని మోస్తున్న ఆ ఇల్లాలి కష్టాల్ని, ప్రాధాన్యతను గుర్తించే వారు లేరు ఈ విషయాన్ని ఇక్కడ 'నోట్' చేయడం జరిగింది.

మెలకువెప్పుడొస్తే అప్పుడు రాత్రి మగ్గమై ఆడినా
మెప్పులేదు, గుర్తింపు లేదు, అయ్యో పాపమన్న ఆర్ద్రత లేదు

స్త్రీలకు భర్త రూపంలో ఎదురయ్యే మరో సమస్య భర్తల చెడు అలవాట్లు. సంసారాన్ని మోయాల్సిన భర్త అలవాట్లకు బానిసలై ఆ సంసారం పట్ల స్త్రీ పడే వేదన ఇలా వుంటుంది.

ఏ తాగుడు, పేకాటకు బానిసయ్యాడో
ఏ అరుగు ముచ్చట్లకతుక్కు పొయ్యాడో
ఏటెక్కు సినిమా ట్రిక్కులకు చిక్కుకు పొయ్యాడో ఆరాతెల్సి
ఎంత గుబ గుబలాడి పొయ్యాడో
కొట్టుకు లాడిన కండెకు తెల్సు
కదిలిన గుడ్డకు తెల్సు
గుడ్డమీది బొమ్మకు తెల్సు
ఒంటరి నీ వూర్చుకు తెల్సు
అన్నీ చూసిన అర్ధరాత్రి అశ్రు పాతానికి అంతా తెల్సు.



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భర్త వ్యసనాలను ఎవరికి చెప్పుకోలేక, బాధను దిగమ్రింగలేక ఆ స్త్రీ పడే మనోవేదనను పై కవిత స్పష్టం చేస్తుంది. వ్యసనాలతోటి, వృత్తిని నిర్లక్ష్యం చేస్తూ, ఆర్థిక దుస్థితి దిగజార్చితే దీనికి కారణం ఏమిటని ప్రశ్నిస్తే తప్పు తాను చేసినా, ఇంటి భారాన్ని మోస్తున్న ఆ తల్లికి ప్రశ్నించే హక్కు లేదని, భావ ప్రకటనా స్వాతంత్ర్యపు హక్కును కాలరాస్తూ పురుషాధిక్యతను హింసతో చాటుతాడు.

దిన దినం సేదదీరని ఇబ్బందులు పోల్చుకొని
ఎంటీల తాకట్టుకూ, చీట్లపాటకూ, పెరిగినప్పులకు కారణమడిగితే
పట్టిచ్చెలా చూసుకుంటాడును కున్న పెనిమిటి
చిరుత పులిలా దూకి తన్నులు, గుద్దులతో నిన్ను హింసిస్తాడు
తెగిన నక్కలా నిన్ను తోసేస్తాడు

పట్టుదారంలా సుతిమెత్తగా చూసుకుంటాడనుకున్నా పెనిమిటే చిరుతపులిలా రక్కుతున్నాడు. ప్రశ్నించే హక్కు లేమితో పాటు బానిసత్వపు సంకెళ్ళు నిన్ను వెంటాడుతాయి.

తాను టిపినికి, టీ నీళ్లకు పోయి
గంటలూ వృధా కొట్టినా పర్వాలేదు గాని
నీ వల్ల ఏ క్షణ అవసరానికి ఆలస్యం జరిగినా
పురుష పెత్తనం చిందులు నిలదిస్తాయి
ప్రశ్నల గద్దింపులు నిన్ను చుట్టుముట్టాయి

భర్తకు అన్నం వడ్డించడంలో గాని, అవసరాలను అందించడంలో గాని, ఆలస్యం చేస్తే ఏమి పనిచేయని దానిలాగా స్త్రీని జమకడతారు. ఇంట్లో పనిబాట లేకుండా కూర్చొని ఏం ఉద్దరిస్తున్నావని' గద్దిస్తాడు. అరుగుల మీద, టీ కొట్టు దగ్గర అతను చేసిన పని గుర్తురాదు. ఇంట్లో నీశ్రమా గుర్తుకు రాదు. ఎడతెగని సమస్యలను ఈదలేక, ఎవ్వడో పోయించిన సారాలో తేలి తాళికట్టిన వాడు దుమ్ములో దేకుతుంటే ఎన్నిసార్లు వీధులు వెదికి నడిపించు వచ్చావు. అయినా స్త్రీ కష్టాన్ని, ఇష్టాన్ని గుర్తించేవారు లేరు. అందరూ ఆఓను పనిముట్టుగా చూసేవారే. భర్త అవసరాలు తీర్చే యంత్రం, ఇంటి భారాన్నే మోసే జంత్రం. స్త్రీ ఏ వృత్తిలో ఉన్న, ఏ ఇంటిలో వున్న ఆమె ఒక జీవమ్ము పనిముట్టుగానే మా సమాజం నిర్ధారిస్తుంది.

ఈ దేశం ఏం మిగిల్చిందీ
ఆకలి చీకటీ, ఆందోళన, అభద్రత తప్ప
మెట్టినింట్లో, పుట్టినింట్లో
నాల్గు గోడల కటకటాల గుడిసెల పంజరాల లోలోపల
గిజ గిజలాడిన ప్రాణమున్న పనిముట్టు జీవితమేగా నీది!

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ఇక్కడ వరకు స్త్రీ దైన్యపు జీవితాన్ని చిత్రిస్తూ, అందులో నుంచి నిర్గమించి చైతన్యంతో అడుగులు వేస్తే జీవితం చిక్కబడుతుందని చైతన్య పరుస్తుంది క్రింది కవి.

నిరాశ వురవడికి కొట్టుకు పోకు
నువ్వూ నిప్పుల వంతెనగా వుద్యమించు
నీ మగని మత్తు పారిపోతుంది
నీ కలత దిబ్బ కరిగిపోతుంది

అని తిరగబడక పోతే నీ స్వేచ్ఛ, స్వాతంత్ర్యాలు నీకు రావని, వ్యసనాలబారిన బడ్డ మగడిని వారిని తెచ్చుకోవడానికి ముందు మనలో మార్పురావాలని ఉద్యమించాలని సూచిస్తున్నారు.

సాహిత్యమేదైనా స్త్రీ వేదనలో మార్పు లేదు. ఆ మార్పుకు శ్రీకారము స్త్రీయే చుట్టాలి.

ఏ సాహిత్యంలోనైనా స్త్రీ వేదన, అస్పృశ్యపు పోరాటాలు కన్పిస్తూనే ఉన్నాయనడం వ్యాస సారాంశం.

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ORIGINAL ARTICLE

# Bioactive Compound of *Ocimum sanctum* Carvacrol Supplementation Attenuates Fluoride Toxicity in Sodium Fluoride Intoxicated Rats: A Study with Respect to Clinical Aspect

**Kondeti Ramudu Shanmugam[1], Mavulapati Siva[1,2], Sahukari Ravi[2], Bhasha Shanmugam[2], Kesireddy Sathyavelu Reddy[2]**

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## ABSTRACT

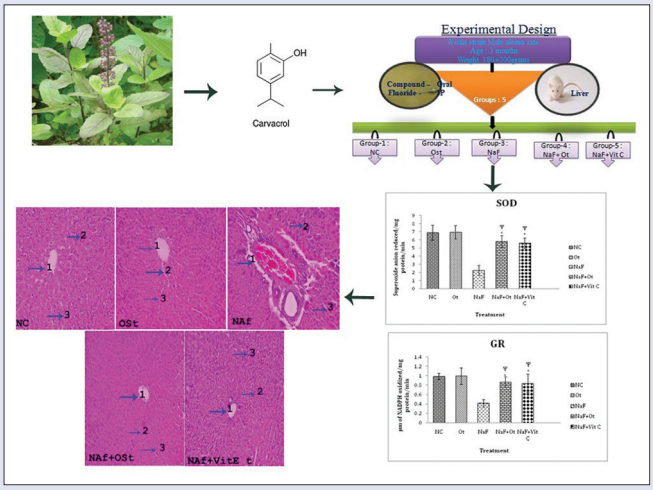
**Background:** *Ocimum sanctum* (OS) Linn. commonly known as Holy Basil or Tulsi is an Ayurvedic herb of India. The culinary, medicinal, and industrial importance of this plant led to explore its chemical and pharmacological properties. **Objective:** The present study was carried out to know the anti-oxidant activity of carvacrol bioactive compound of OS in sodium fluoride (NaF) rats and free-radical scavenging activities of OS. **Materials and Methods:** Superoxide dismutase (SOD), catalase (CAT), glutathione peroxidase (GPx), glutathione reductase (GR), glutathione (GSH), GSH-s-transferase (GST), malonaldehyde (MDA), alanine aminotransferase (AAT), aspartate aminotransferase (AST), alkaline phosphatase (ALKP), calcium (Ca), and phosphorus ($P_4$) levels are estimated in all experimental groups. 2,2-Diphenyl-1-picrylhydrazyl (DPPH), hydrogen peroxide ($H_2O_2$), and hydroxyl radical activities are analyzed in the ethanolic extract of OS. **Results:** SOD, CAT, GPx, GR, GSH, activities, and Ca levels depleted and GST, MDA, AAT, AST, ALKP, and $P_4$ levels elevated in NaF intoxicated rats. Whereas carvacrol supplementation normalized all the antioxidant enzymes and hepatic markers in NaF toxicity rats. DPPH, $H_2O_2$, and hydroxyl radical of OS showed potent free-radical scavenging activities. In addition, histopathological studies also prove that carvacrol protected the liver tissue from fluoride toxicity in rats. **Conclusion:** The present study revealed that carvacrol of OS modulated the antioxidant enzymes and hepatic stress markers in NaF rats. Our research study will be helpful in the development of new active principle and nutraceuticals in the area of drug resistance and therapeutic compounds against disease vectors.

**Key words:** Antioxidant enzymes, carvacrol, free radical scavenging activity, *Ocimum sanctum*, rats

## SUMMARY

- To summarize, the current investigation clearly confirmed that carvacrol bioactive compound of *Ocimum sanctum* protects the hepatic tissue from sodium fluoride toxicity.

**Abbreviations used:** OS: *Ocimum sanctum*; NaF: Sodium fluoride; SOD: Superoxide dismutase; CAT: Catalase; GPx: Glutathione peroxidase; GR: Glutathionereductase; GSH: Glutathione; GST: Glutathione-s-transferase; MDA: Malonaldehyde; AAT: Alanine aminotransferase; AST: Aspartate aminotransferase; ALKP: Alkaline phosphatase; Ca: Calcium; $P_4$: Phosphorus; DPPH: 2,2-Diphenyl-1-picrylhydrazyl; $H_2O_2$: Hydrogen peroxide; TLC: Thin-layer chromatography; HPLC: High-performance liquid chromatography; EDTA: Ethylenediaminetetra acetic acid; $FeCl_3$: Ferric chloride; TCA: Trichloroacetic acid; TBA: Tert-Butyl alcohol; NaOH: Sodium hydroxide; BHA: Butylated hydroxyanisole; SPSS: Statistical package for the social sciences; GC-MS: Gas chromatography–Mass spectrometry; TBARS: Thiobarbituric acid-reactive substances.




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## INTRODUCTION

Medicinal plants play a central role in traditional medicines and are precursors for the modern pharmaceuticals and allopathic medicines.[1] The scientific studies available on a good number of medicinal plants indicate that promising phytochemicals can be developed for many human health problems, including diabetes, cancer, and infectious diseases.[2,3] The medicinal value of plants lies in the bioactive compounds such as alkaloids, flavonoids, tannins, and phenolic compounds that produce a definite physiological action against diseases.

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*Ocimum sanctum* (OS) is known as Holy Basil in English or Tulasi in Hindi, belongs to the family Lamiaceae and is considered as a sacred plant in Hindu culture.[4] OS Linn. has been widely known for its medicinal value for thousands of years.[5] Folklore claims that OS have antiseptic, antimicrobial, anti-bactericidal, anti-inflammatory, anti-oxidative, antiulcer, antidiarrheal, and chemopreventive properties.[6,7]

Carvacrol ($C_6H_3[OH][C_3H_7]$) is a natural component found in OS. Carvacrol, is a monoterpenoid phenol. It has antimicrobial, antitumor, antimutagenic, antigenotoxic, analgesic, antispasmodic, anti-inflammatory, angiogenic, and antiparasitic properties.

Fluorosis is a global disease. Humans take fluoride from water, food, and air, which can develop into dental, skeletal, and nonskeletal fluorosis. The clinical manifestations of fluorosis are mainly teeth and bone damage, but organs and soft tissues such as the liver, kidney, nervous system, reproductive system, blood vessels, and muscles may also be damaged by this disease.

The objective of this study was to investigate the antioxidant, hepatoprotective activity, of carvacrol in NaF intoxicated rats. This is the first report on the effect of carvacrol of OS in fluorosis rats.

## MATERIALS AND METHODS

### Selection and collection of plant material

Leaves of OS were collected from Tirupati, Andhra Pradesh, India and identified by the Dr. Madhav Chetty, Department of Botany, S. V. University, Tirupati. Voucher specimen of OS No 1183 was deposited in the Botany department.

### Extraction of bioactive compound

The bioactive compound carvacrol of OS was extracted by different methods. OS was grinded and add ethanol. Filter the mixture and dry it, by using a rotoevaporator, the mixture is then washed with hexane. This, in turn, gets washed again, with ethyl acetate. At this point, the mixture is dried again, this time using a rotoevaporator and freeze-drying to ensure complete dryness. Once the mixture is completely dry, the mixture is again treated with hexane and ethyl acetate. At this point, thin-layer chromatography (TLC) is performed. After the TLC, the compound is dissolved in 99% ethanol and is further purified using TLC.

The compound is soaked in ethyl acetate, once more. After filtering and drying, it is subjected to high-performance liquid chromatography (HPLC). It is this last process, HPLC that enables the identification of many compounds. Of which, carvacrol is isolated, but check the carvacrol compound with standard compound and used for the study [Figure 1].

### Chemicals and reagents

All chemicals used were of analytical grade and were purchased from Sigma–Aldrich, Merck and all chemicals and reagents were used without further purification.

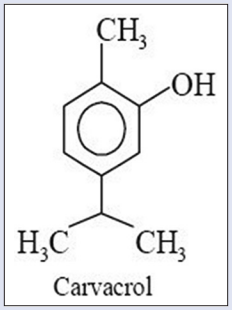



**Figure 1:** Structure of Carvacrol bioactive compound of *Ocimum sanctum*

### Preparation of extracts

Leaves of the plant were air-dried for several days. The dried plant materials were ground to a coarse powder using a dry mill. For the extraction procedure, 500–800 g of powdered plant material was soaked in 95% ethanol for 72 h. The solvent was then removed by rotary evaporation. The dried extract was used for the study of free radical scavenging activities.

#### *Grouping of animals*

The rats were divided into five groups of six rats in each group and treated as follows:

- Group I – Normal Control (NC): Six rats were received saline through orogastric tube for 60 days
- Group II – Ocimum Bioactive compound (Carvacrol) Control (OSt): Six rats received OS bioactive compound Carvacrol (25 mg/kgBW) for 60 days
- Group III – NaF treatment (Na F t): Six rats received the sodium fluoride (NaF) (10 mg/kgBW) dissolved in drinking water for 60 days
- Group IV – NaF + Ocimum Bioactive compound (Carvacrol) treatment (NaF + OSt): Six rats received NaF (10 mg/kgBW) dissolved in drinking water and ocimum bioactive compound carvacrol (25 mg/kgBW) for 60 days
- Group V – Na F + Vitamin C treatment (NaF + Vitamin C): six rats received NaF and Vitamin C for 60 days.

After completion of 60 days treatment and after 24 h of the last treatment the animals were sacrificed by cervical dislocation and the liver tissue was excised at 4°C. The tissues are washed with ice cold saline and immediately stored in a deep freezer at −80°C for further biochemical analysis. Blood samples are also collected, serum was separated and stored for biochemical estimations.

### Biochemical estimations

The selected antioxidant enzymes such as superoxide dismutase (SOD), catalase (CAT), glutathione peroxidase (GPx), glutathione reductase (GR), glutathione (GSH), GSH–s– transferase (GST), and malonaldehyde (MDA), levels were monitored by the methods of Misra and Fridovich,[8] Aebi,[9] Flohe and Gunzler,[10] Carlberg and Mannervik,[11] Akerboom and Sies,[12] Habig *et al.*,[13] and Ohkawa *et al.*,[14] respectively. Alanine aminotransferase (AAT), aspartate aminotransferase (AST) and alkaline phosphatase (ALKP) activities and Calcium (Ca), phosphorus ($P_4$) levels are measured using standard kits.

The experiments were carried out in accordance with guidelines Approved by the institutional Animal Ethics Committee (ResolutionNo. 10/08/a/CPCSCA/IAEC/SVU/09-10/ZOOL/KRS/Dt. 25.09.2009) in its resolution number (9/IAEC/SVU/2001/dt. 4.03.2002).

### Estimation of free radical scavenging activity

The hydroxyl radical scavenging activity of OS was determined by the method of Halliwell *et al.*[15] The reaction mixture consisted of 1 mM Ethylenediaminetetra acetic acid (EDTA), 10 mM Ferric chloride, 10 mM $H_2O_2$, 10 mM deoxyribose, 1 ml of different dilutions of the extract (100–500 µg/ml), 50 mM phosphate buffer (pH 7.4), and 0.1 ml of ascorbic acid in sequence. The mixture was incubated at 37°C for 1 h. A volume of 1 ml portion of the incubated mixture was mixed with 1 ml of 10% Trichloroacetic acid and 1 ml of 0.5% Tert-Butyl alcohol (TBA) (in 0.025 M Sodium hydroxide containing 0.025% butylated hydroxyanisole) to develop the pink chromogen measured at 532 nm.

The ability of OS to scavenge hydrogen peroxide ($H_2O_2$) was determined according to the method of Ruch *et al.*[16] A solution of $H_2O_2$ (2 mM) was prepared in phosphate buffer (0.1 mM, pH 7.4) at 20°C. An aliquot of the extracts was dissolved in phosphate buffer (1 ml; 0.1 mM, pH 7.4) at

various concentrations (100–500 µg/ml) and mixed with 600 µl of $H_2O_2$. Ascorbic acid was used as the reference standard. The concentration of $H_2O_2$ was measured by reading the absorbance at 230 nm after 10 min against a blank solution containing phosphate buffer without $H_2O_2$. The extracts were capable of scavenging $H_2O_2$ in a concentration-dependent manner.

The stable 1,1-diphenyl-2-picrylhydrazyl radical (DPPH) was used for the determination of free radical-scavenging activity of OS. Different concentrations of each ethanolic extract were added and an equal volume of DPPH (100 µM). After 15 min at room temperature, the absorbance was recorded at 517 nm.[17]

## Statistical analysis

The data are expressed as mean values with their standard deviation Readings of the five different groups were compared using one-way ANOVA analysis with Dunnett's multiple comparison test. Statistical analysis was performed using the Statistical package for the social sciences (SPSS) (Version 13.5; SPSS Inc., Chicago, IL, USA). Using M. S. Office, excel software the data have been analyzed for the significance of the main effects (factors), and treatments along with their interactions. Differences were considered statistically significant at $P < 0.001$.

# RESULTS

## Free radical scavenging effect

In DPPH test, the ability of a compound to act as a donor for hydrogen atoms or electrons was measured spectrophotometrically. The scavenging activities of DPPH exerted by OS ethanolic extract and each extract as well as ascorbic acid are summarized in Figure 2. The ethanolic extract at the concentration of 100, 200, 300, 400, and 500 µg/mL exhibited 54.2%, 65.5%, 72.4%, 76.58%, and 86.9% inhibition, respectively, where standard drug ascorbic acid at the same concentration exhibited 63.07%, 68.37%, 78.46,% 87.73%, and 90.89% inhibition, respectively. In the present investigation, OS at different doses demonstrated significant DPPH scavenging activity indicating their abilities to act as radical scavengers.

The deoxyribose method is a simple assay to determine the rate constants for reactions of hydroxyl radicals. Ferric-EDTA was incubated with $H_2O_2$ and ascorbic acid at pH 7.4. Hydroxyl radicals were formed in free solution and were detected by their ability to degrade 2-deoxy-2-ribose into fragments that on heating with TBA at low pH form a pink chromogen. Any hydroxyl radical scavenger added to the reaction would compete with deoxyribose for the availability of hydroxyl radicals, thus reducing the amount of MDA formation. We herein tested the scavenging activity of each extract along with positive control ascorbic acid. OS at concentration 100, 200, 300, 400, and 500 µg/mL inhibited the production of hydroxyl radicals by 40.2%, 62.19%, 70.46%, 81.24%, and 83.68%, while at same concentration, ascorbic acid showed 57.47%, 63.02%, 71.53%, 89.71%, and 83.23%, respectively [Figure 2]. In the current study, OS at different doses demonstrated significant hydroxyl radical scavenging activity.

The ethanolic extract at the concentration of 100, 200, 300, 400, and 500 µg/mL exhibited 31.2%, 52.46%, 62.84%, 71.4% and 82.6% inhibition, respectively, where standard drug α-tocopherol at the same concentration exhibited 23.07%, 68.37%, 72.46%, 76.73%, and 90.89% of $H_2O_2$ inhibition, respectively. The composition of $H_2O_2$ into water may occur according to the antioxidant compounds as the antioxidant component present in the extract are good electron donors, they may accelerate the conversion of $H_2O_2$ to $H_2O$. Our results showed that the $H_2O_2$ scavenging activity of OS decreases than that of α-tocopherol.

## Effect of carvacrol on hepatic antioxidant enzymes in fluorosis rats

In the present investigation, SOD, CAT, GPx, GR, activities, GSH levels are depleted in fluoride intoxicated rats. However, with carvacrol supplementation in NaF rats, we observed the significant elevation of these anti-oxidant enzymes. However, GST, MDA levels significantly increased in fluoride intoxicated rats, but carvacrol treatment decreased GST and MDA levels in NaF rats [Figure 3].

## Effect of carvacrol of on serum markers and fluorosis markers in fluorosis rats

In the current study, we observed that AAT, AST, ALKP activities, and $P_4$ levels are elevated and Ca levels depleted in NaF intoxicated rats. This

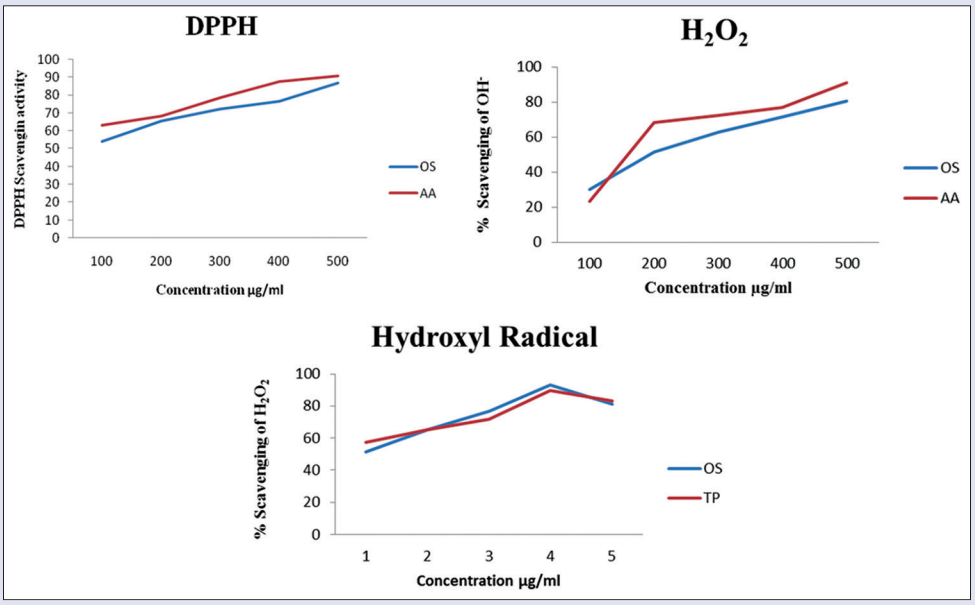



**Figure 2:** Free radical scavenging activity (Hydrogen peroxide, Hydroxy Radicals and 2,2-Diphenyl-1-picrylhydrazyl) of ethanolic extract of *Ocimum sanctum* with ascorbic acid and α tocopherol as standards

indicates severe liver damage in fluorosis condition. Carvacrol treatment for 60 days significantly modulated all the liver markers in fluorosis rats [Table 1].

## Effect of carvacrol on liver tissue in fluorosis rats

In the current study, we observed the degeneration of central vein, hepatocytes, sinusoids, and blood coagulation in NaF intoxicated rats. However, with carvacrol treatment regeneration of central vein, hepatocytes, and sinusoids are observed in NaF rats. Thus, carvacrol supplementation protects the liver tissue from NaF toxicity in rats [Figure 4].

# DISCUSSION

The present study was carried out to know the free radical scavenging effect of OS and antioxidant activity of the bioactive compound of OS Carvacrol in NaF intoxicated rats.

DPPH assay method is based on the ability of 1,1-diphenyl-2-picrylhydrazyl, a stable free radical, to decolorize in the presence of antioxidants.[18] DPPH has characteristic absorbance maximal at 517 nm, which decreases with the scavenging of the proton radical. Antioxidants react with DPPH and convert it to 1-1-diphenyl-2-picrylhydrazine. The degree of discoloration indicates the scavenging potential of OS. This property has been widely used to evaluate the free radical scavenging effect of natural antioxidants.[19] The study reported the free-radical scavenging activity of ethanolic extract of OS.[20] The standard antioxidant ascorbic acid has showed rich DPPH radical scavenging activity at lesser concentrations than the ethanolic extract of OS [Figure 2].

$H_2O_2$ is endogenously produced in the cell, regulates various important physiological processes.[21] Nevertheless, it is overabundance in a cell causes cellular damage because of its interaction with cellular metal ions generates highly reactive hydroxyl radicals. $H_2O_2$ changed into the water in the presence of electron donor by cellular enzymes and external antioxidants. The ethanolic extract of OS converted the $H_2O_2$ into the water on concentration-dependent manner. The increased concentrations of the extract have shown an increase in $H_2O_2$ scavenging activity [Figure 2].

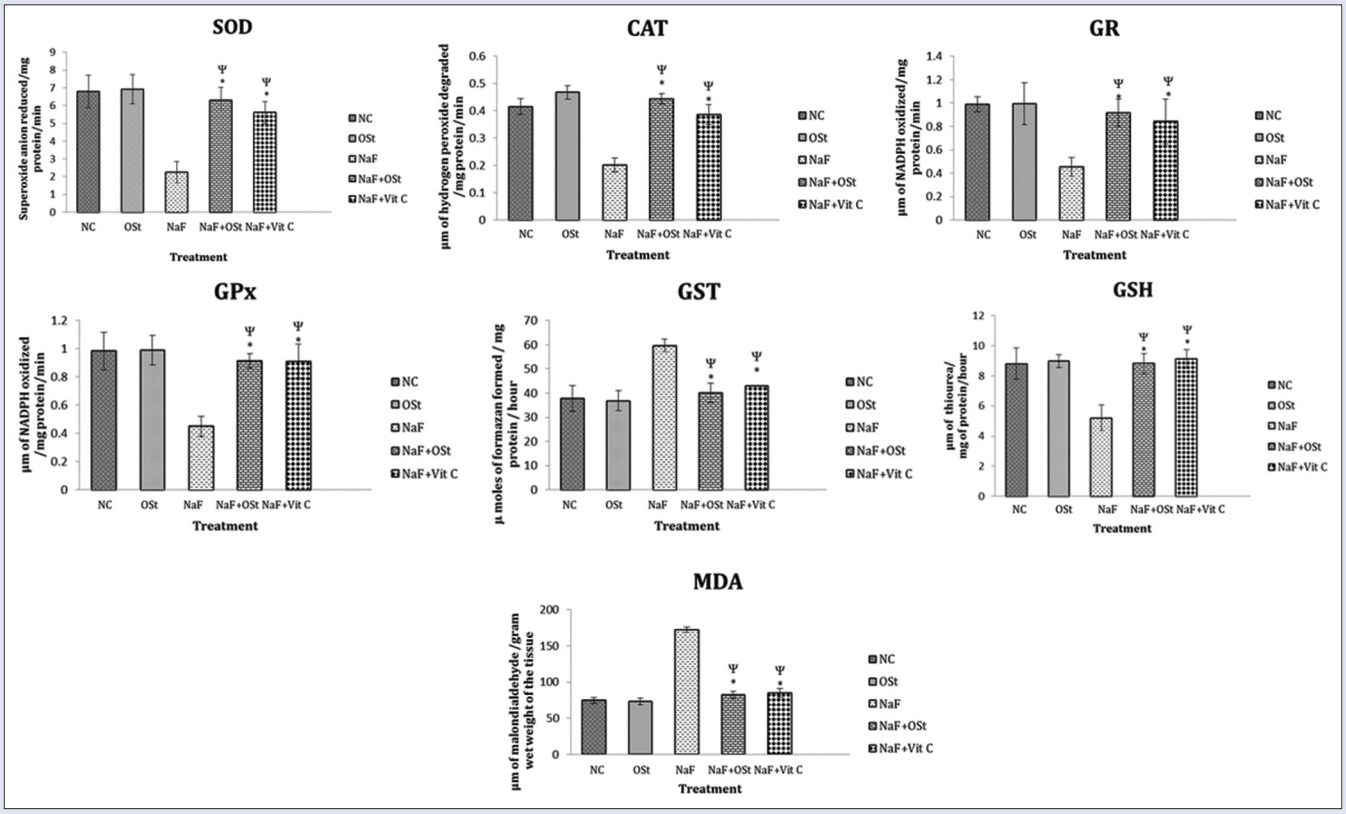



**Figure 3:** Effect of Carvacrol on superoxide dismutase, catalase, glutathione reductase, glutathione peroxidase, glutathione-s-transferase, glutathione and malonaldehyde levels in the liver tissues of Normal and Fluorosis rats. Data are expressed as means ± standard deviation ($n = 6$). *The values are significant compared to the following: control (*$P < 0.001$), Fluorosis (*$P < 0.01$) (Dunnett's multiple comparison tests)

**Table 1:** Effect of carvocral on liver markers and fluorosis markers in sodium fluoride rats

| Groups | AST (IU/L) | ALT (IU/L) | ALP (IU/L) | Ca (mg/dL) | PP (mg/dL) |
|---|---|---|---|---|---|
| Group I (NC) | 586.82 (±12.48) | 94.12 (±1.68) | 414 (±8.26) | 11.31 (±0.62) | 14.24 (±0.24) |
| Group II (OSt) | 545 (±11.26) | 117.535 (±2.14) | 385 (±10.24) | 11.46 (±0.22) | 12.46 (±0.16) |
| Group III (NaFt) | 606.442* (±6.48) | 101.62* (±8.68) | 614* (±11.268) | 8.2* (±0.0.72) | 16.82* (±0.036) |
| Group IV (NaF + Ot) | 572.267* (±4.62) | 87.48* (±4.52) | 380* (±8.42) | 10.84* (±0.082) | 13.14* (±0.032) |
| Group V (NaF+Vitamin C) | 66.731* (±3.14) | 84.189* (±4.12) | 151* (±08.14) | 11.22* (±0.12) | 13.86* (±0.064) |

All the values are means±SD of six individual observations. *Significant at $P<0.001$ with respect to normal control. AST: Aspartate aminotransferase; ALT: Alanine aminotransferase; ALP: Alkaline phosphatase; Ca: Calcium; PP: Phosphorus; SD: Standard deviation

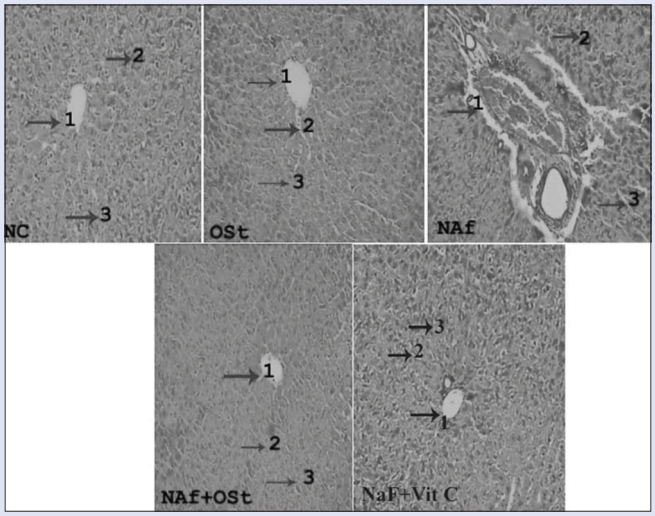



**Figure 4:** Effect of Carvacrol on Liver tissue in Fluorosis rats. (1) Normal Control (Nc). (i) Normal central vein, (ii) Normal hepatocytes, (iii) Normal sinusoids. (2) Carvocral treatment (OSt): (i) Nomal cenntral vein, (ii) Normal hepatocytes, (iii) Normal sinusoids. (3) Sodium fluoride (i) Degeneration of central vein, (ii) Degeneration of hepatocytes, (iii) Degeneration of sinusoids. (4) Sodium fluoride + Carvocral treatment (sodium fluoride + OSt) showed (i) Regeneration of central vein, (ii) Regeneration of hepatocytes, (iii) Regeneration of sinusoids. (5) Sodium fluoride + Vitamin C treatment (sodium fluoride + Vitamin C) (i) Regeneration of central vein, (ii) Regeneration of hepatocytes, (iii) Regeneration of sinusoids

Overall comparison of radical scavenging properties of ethanolic extract with standard ascorbic acid and α tocopherol showed that the OS has shown lower activity than standard, though it has a huge number of antioxidant compounds (found in GC–MS analysis). This difference could be due to the presence of individual antioxidant compounds in the extract which are lower at given concentrations, whereas ascorbic acid and α-tocopherol as standard and completely individual compound; hence, it ultimately showed rich antioxidant activity at tested concentrations than ethanolic extract.

The antioxidant property of active compounds in the ethanolic extract of OS was confirmed by DPPH radical, Hydroxyl, and $H_2O_2$ assays. The importance of these tests is likely to evaluate the antioxidant activity of OS.[22]

In the present investigation, the antioxidant enzymes SOD, CAT, GPx, GR, and GSH are depleted in NaF intoxicated rats. This shows that NaF supplementation for 60 days causes depletion of these antioxidant enzymes. This may be due to the oxidative stress and free radical production in NaF rats. However with Carvacrol of Ocimum treatment in NaF rats for 60 days reversed these antioxidant enzymes. Carvacrol may be responsible for the upregulation of antioxidant enzymes in NaF rats. Carvacrol treatment significantly recuperated the activities of antioxidant enzymes in NaF intoxicated rats [Figure 3].

Carvacrol supplementation may decrease the production of free radicals in fluorosis rats; this may cause up-regulation of antioxidant enzymes. Carvacrol treatment also decreased oxidative damage in NaF intoxicated rats. Hence, all the hepatic antioxidant enzymes are normalized with carvacrol treatment in NaF rats.

Oxidative stress is recognized to be associated with more than 100 diseases such as diabetes, hepatitis, and other diseases. There is a strong correlation between TBARS as a marker of lipid peroxidation and products that reflect oxidative damage to DNA. MDA and GST levels elevated in NAF rats. Oxidative stress in fluorosis rats may be responsible for upregulation of MDA and GST. However, carvacrol treatment, MDA and GST levels depleted in NaF rats [Figure 3].

Liver damage induced by NaF generally reflects disturbances of liver cell metabolism which lead to changes in the activities of many enzymes. AAT, AST, and ALKP are sensitive markers of liver toxicity and their elevated levels are indicative of cellular leakages and loss of functional integrity of cell membrane in the liver. In the current study, we reported significant elevation in AAT, AST, and ALKP activities in NaF intoxicated rats. This shows that during fluorosis condition hepatic cellular dysfunction may result in the upregulation of the liver markers. Whereas carvacrol supplementation depleted serum markers in NaF rats. This show the hepatoprotective activity of carvacrol. Carvacrol could minimize the production of toxic free radicals and enhance the activities of their scavengers, diminishing hepatocellular injury in NaF rats [Table 1].

Ca and $P_4$ are fluorosis markers. In our study, we reported that Ca levels decreased and $P_4$ levels increased in NaF intoxicated rats. This may be due to alterations in the metabolism of Ca and $P_4$. Whereas carvacrol treatment for 60 days, these fluorosis markers are came back to near to normal levels.

In the present study, we reported that fluorosis rat liver showed the degeneration of central vein, hepatocytes, sinusoids, and blood coagulation. However with carvacrol treatment regeneration of central vein, hepatocytes, and sinusoids are observed in NaF rats. This shows the hepatoprotective effect of carvacrol [Figure 4].

The antioxidant and free radical scavenging activities of OS might be due to the presence of phenolic compounds in extracts which is confirmed by phytochemical analysis. Furthermore, it can be concluded that the antioxidant activity of plant extracts is not limited to phenolics. Activity may also due to other antioxidant secondary metabolites, such as volatile oils, carotenoids, and vitamins.[23]

To summarize, the current investigation clearly confirmed that carvacrol bioactive compound of OS protects the hepatic tissue from NaF toxicity. In this study, we reported that antioxidant enzymes and liver markers are modulated with carvacrol treatment in NaF-induced fluorosis rats. This may be due to the free radical scavenging activity of Ocimum. Our gas chromatography–mass spectrometry analysis also confirmed the presence of many bioactive compounds in Ocimum and these compounds may have pharmacological activities. To the best of our knowledge, this study is the first report on the effect of Carvacrol of Ocimum in fluorosis rats.

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## Financial support and sponsorship

Nil.

## Conflicts of interest

There are no conflicts of interest.

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**REVIEW ARTICLE**

# Plant Compounds for the Treatment of Diabetes, a Metabolic Disorder: NF-κB as a Therapeutic Target

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**Abstract:** ***Background:*** The prevalence of diabetes in the world population hás reached 8.8 % and is expected to rise to 10.4% by 2040. Hence, there is an urgent need for the discovery of drugs against therapeutic targets to sojourn its prevalence. Previous studies proved that NF-κB serves as a central agent in the development of diabetic complications.

***Objectives*:** This review intended to list the natural plant compounds that would act as inhibitors of NF-κB signalling in different organs under the diabetic condition with their possible mechanism of action.

***Methods*:** Information on NF-κB, diabetes, natural products, and relation in between them, was gathered from scientific literature databases such as Pubmed, Medline, Google scholar, Science Direct, Springer, Wiley online library.

***Results and Conclusion*:** NF-κB plays a crucial role in the development of diabetic complications because of its link in the expression of genes that are responsible for organs damage such as kidney, brain, eye, liver, heart, muscle, endothelium, adipose tissue and pancreas by inflammation, apoptosis and oxidative stress. Activation of PPAR-α, SIRT3/1, and FXR through many cascades by plant compounds such as terpenoids, iridoids, flavonoids, alkaloids, phenols, tannins, carbohydrates, and phytocannabinoids recovers diabetic complications. These compounds also exhibit the prevention of NF-κB translocation into the nucleus by inhibiting NF-κB activators, such as VEGFR, RAGE and TLR4 receptors, which in turn, prevent the activation of many genes involved in tissue damage. Current knowledge on the treatment of diabetes by targeting NF-κB is limited, so future studies would enlighten accordingly.

**Keywords:** Diabetes, Insulin resistance, Hyperglycemia, NF-κB, Inflammatory mediators, Diabetic complications, Natural products.

## 1. INTRODUCTION

Plants are naturally available resources in discovering drugs for the treatment of many diseases. From past decades, pharmaceutical and chemical industries are looking towards plant compounds and their derivatives because of their potential action with safe and least side effects [1]. Plants produce secondary metabolites, such as phenols, flavonoids, terpenoids, alkaloids, tannins, iridoids, and others, to overcome their stress. However, humans found such metabolites as a good choice to treat many deadly diseases. Plant compounds with different chemical composition determine their interaction with disease-sensitive therapeutic target proteins where interaction causes structural changes in proteins leading to the suppression of damage associated with target protein [2]. Scientists identified many plant compounds that regulate the nuclear factor kappa B (NF-κB) in diabetes. We can find such regulations in this review in the following pages.

Diabetes is characterized into two categories; Type 1 diabetes (T1D) and Type 2 diabetes (T2D). Absolute lack of pancreatic beta islets leads to insufficient insulin release into the blood, which is the hallmark of T1D. Insulin secreted beta islets of the pancreas are destructed by the immune system of the body, which coincided with the hyperglycaemic condition of blood [3]. In T2D, secretion of insulin by the pancreas is normal, but insulin receptors cannot properly uptake blood insulin into cells; hence, it is called insulin resistance. This condition also increases blood glucose levels and leads to hyperglycemia. Hyperglycemia is common in T1D and T2D, causing too many complications in diabetic patient organs, such as kidney (Diabetic nephropathy), brain (diabetic neuropathy), eye (diabetic retinopathy), liver, heart (diabetic cardiomyopathy), skeletal muscle, endothelium, adipose tissue, and pancreas. Hyperglycemia induces overproduction of reactive oxygen species (ROS) and the formation of advanced glycation end products (AGEs), which initiate endothelial dysfunction and pro-inflammatory response through activation of NF-κB protein [4]. Activated NF-κB enhances the release of vascular cell adhesion molecules, cytokines, chemokines, and transforming growth factors. Subsequently, up-regulation of monocyte chemoattractant protein 1 (MCP-1), Tumor necrosis factor-alpha (TNF-α), interleukin 6 (IL6), interleukin 1β ( IL1β) and the cluster of differentiation 36 (CD36), leads to endothelial cell apoptosis and inflammatory process [5, 6].

NF-κB is a part of the Rel protein family consisting of evolutionarily conserved proteins that regulate many genes associated with inflammation and immunity. Rel family comprises five related proteins, such as NF-κB1/p50, NF-κB2/p52, RelA/p65, RelB and c-Rel [7]. The p50 and p52 are processed subunits from large precursor's p105 and p100, respectively, through the ubiquitin-proteasome pathway. These subunits lose their c-terminal regions holding ankyrin repeats, and they do not contain transactivation domains in their c-terminal region in contrast to RelA, RelB, and c-Rel but playing the main role in controlling the selectivity of NF-κB function [5]. This Rel protein family members together form homo and heterodimers, enter into the nucleus where they bind to deoxyribonucleic acid (DNA) regulatory sites, the so-called κB sites, and

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activates specific gene expression. In general, these dimers present in the cytoplasm of the cell in inactive condition due to the association of inhibitor of NFκB (IκB) include IκBα, IκBβ, IκBγ (NEMO: NF-kappa-B essential modulator) and B-cell lymphoma 3 (Bcl-3) that belongs to IκB family. These inhibitor proteins have 6 to 7 ankyrin repeats, which mediate binding/mask to nuclear localization sequences (NLSs) of NF-κB dimers and retain in the cytosol. In addition to the above inhibitory proteins, large precursor proteins p105 and p100 of p50 and p52, respectively, possess ankyrin repeats; hence, they also kept in the IκB family [8]. During stimulus on various pathological conditions, activation of NF-κB takes place by the degradation of IκB proteins through polyubiquitination, which leads to the relieve of dimers that enter into the nucleus and bind to DNA for expression of genes.

Though there are multiple ways for activation of NF-κB, two major ways are classical/ canonical and alternative/ non-canonical pathways [9] (Fig. **1**). In the classical pathway, extracellular stimulus transforming growth factor b-activated kinase 1 (TAK1) induces the activation of a kinase complex inhibitor of nuclear factor kappa-B kinase-α (IKKα)-IKKβ-NEMO, which, in turn, phosphorylates IκBα to release heterodimer p50-RelA from the complex. On phosphorylation, IκBα is released from the complex to sequester and degraded by the ubiquitin-proteasome complex. Now, the heterodimer enters into the nucleus and triggers the gene expression. In an alternative pathway, upon activation of receptor signals, NF-κB-inducing kinase (NIK) induces IKKα homo dimer activation to phosphorylate p100, which is complexed with RelB protein. Phosphorylated P100 ubiquitinated and then further takes into proteasome processing to release p52; now, it forms p52-RelB heterodimer. This dimer enters into the nucleus and prompts gene expression by binding DNA [10, 11]. Overall, NF-κB is regulated by protein kinases, protein phosphatases, proteasome, ubiquitination and DNA binding phases, and these can be targets for any chemical molecule which may, in turn, inhibit the activity of NF-κB. Thus, the natural compounds may non-selectively inhibit NF-κB activity through the above-said targets, and such compounds have been considered as NF-κB inhibitors.

The explanation in the following pages describes how diabetes affects the organs of diabetic patients and their protection by plant compounds with reference to NF-κB (Table **1**). We also mentioned the mechanism of action of natural plant compounds on the NF-κB pathway (Fig. **2**).

## 2. DIABETIC COMPLICATIONS AND ANTI-DIABETIC COMPOUNDS

### 2.1. Diabetic Kidney

Diabetic nephropathy is an end-stage renal failure and chronic kidney disease associated with cardiovascular mortality in diabetic patients. Around 30 % of patients with diabetes suffer from diabetic nephropathy complications and ultimately undergo renal dialysis or transplantation [12]. The noticeable pathological changes in this condition are decreased glomerular filtration, persistent albuminuria, increased albumin creatinine ratio and interstitial tubule fibrosis [13]. Accumulation of fibroblasts, monocytes, T cells, and macrophages in the kidney of diabetic patients is a key hallmark for intrarenal tissue inflammation. Hyperglycemic condition accumulates AGEs, which activates the NF-κB pathway. IκBα-NF-κB p65-p50 complex dissociated by hyperglycemia, where NF-κB p65-50 translocates into the nucleus to promote the secretion of many pro-inflammatory cytokines, including Transforming growth factor-beta 1 (TGF-β1), interleukin-1 β (IL-1β), IL-6, MCP-1, and TNF-α, which lead to diabetic nephropathy deterioration [14, 15]. MCP-1 and intercellular adhesion molecule-1 ( ICAM-1) facilitate diabetic

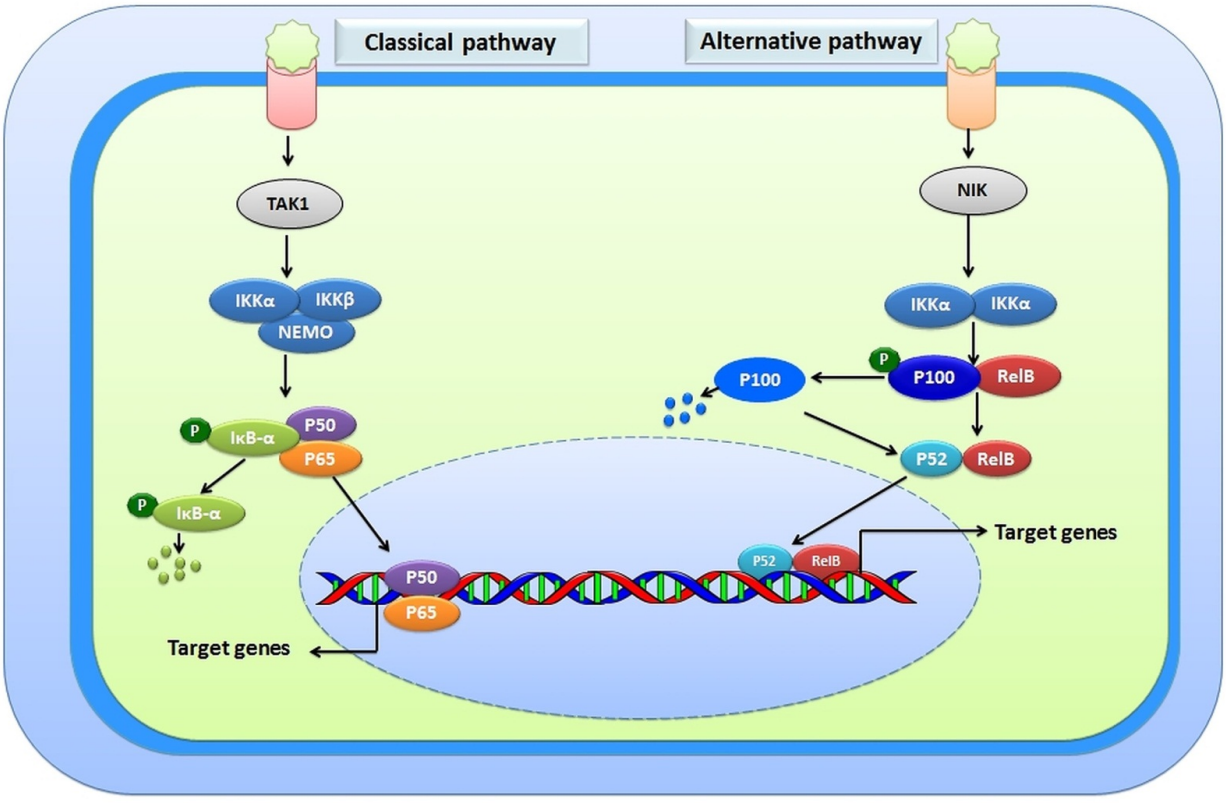



**Fig. (1).** Activation of NF-κB signalling through canonical and alternative pathways. (*A higher resolution / colour version of this figure is available in the electronic copy of the article*).

nephropathy by extravasating macrophages from the blood to the kidney [16]. Hyperglycemia upregulates protein kinase C (PKC), which in turn, activates TGF-β1, a member of the TGF-β family considered as a predominant pathogenic agent because it regulates tubulointerstitial and glomerular fibrosis by activating NF-κB canonical pathway and promoting massive production of collagen along with fibronectin in the kidney [17,18]. Nitric oxide (NO) plays a crucial role in modulating intraglomerular hemodynamics and in accumulating extracellular matrix in the kidney in chronic diabetic patients. One of the nitric acid synthase (NOS) isoform, i.e., inducible nitric acid synthase (iNOS), synthesizes a large amount of NO upon inflammatory stimulation. NO excess production in diabetic condition coincides with the adaptation of the renal tissue to dietary salt intake, diuresis and natriuresis [19, 20]. Oxidative stress is one of the most important factor for the development of renal complications in diabetes. The main reason for oxidative stress is the overproduction of ROS in the kidney. The mitochondrial protein sirtuin 3 (SIRT3) prevents this stress in diabetes and is responsible for the activation of cellular antioxidant superoxide dismutase (SOD) [21]. Additionally, nuclear factor erythroid-derived 2-related factor 2 (Nrf2) is a transcription factor that manages oxidative stress by activating oxidative enzymes that subsequently sustain cellular redox potential. Heme oxygenase-1 (HO-1) and NAD(P)H quinone oxidoreductase 1 (NQO1) are the Nrf2 upregulating genes for stress response. HO-1 and NQO1 both act as antioxidants and scavenge the diabetic induced ROS [22, 23]. Forkhead box O3a (FOXO3a) is a transcriptional activator that activated by sirtuin 1 (SIRT1), which in turn activates the cellular antioxidant genes, including catalase (CAT) and SOD which prevent the lipid peroxidation [24]. Nucleotide-binding oligomerization domain, leucine-rich repeat and pyrin domain 3 (NLRP3) inflammasome can involve in the cleavage of pro-inflammatory cytokines such as pro-IL-1β and pro-interleukin-18 (pro-IL-18) to IL-1β and IL-18 mature form respectively in diabetic nephropathy. Thioredoxin-interacting protein (TXNIP) acts as a mediator of oxidative stress by inhibiting thioredoxin during oxidative stress and hyperglycemic state. Importantly, TXNIP interacts with NLRP3 and causes insulin resistance in diabetes [25, 26]. SIRT1 enzyme plays a key role in the deacetylation of many regulatory proteins of the cell. Recently, it was noted that SIRT1 closely associates with metabolic adaptations of obesity and plasma glucose maintenance by regulating insulin secretion [27, 28]. Toll-like receptor 4 (TLR4) is a membrane receptor that involves a cascade of events when it is stimulated by lipopolysaccharide through lipopolysaccharide-lipopolysaccharide binding protein complex. In addition, activated TLR4 binds to the myeloid differentiation factor 88 (MyD88) for the production of pro-inflammatory cytokines (TNF-α, IL-1, and IL-6) via NF-κB mediator in the diabetic kidney [29]. Hyperglycemic condition enhances the formation of AGEs that interact on different cells with the receptor for advanced glycation end products (RAGE) and activates signals to produce cytokines such as NF-κB, TGF-β1 and TNF-α. These molecules increase extracellular matrix, induce thickening of the glomerular basement membrane and activation of myofibroblasts leads to irreversible tubular damage in the kidney [30, 31]. Besides, matrix metalloproteinases (MMP) such as MMP-2 and MMP-9 are proteolytic enzymes, which play an important role in regulating the extracellular matrix and the proliferation of mesangial cells. Thus, their significant overexpression has been identified in diabetic nephropathy [32].

### *2.1.1. Diabetic Kidney Protection by Plant Compounds*

The anti-inflammatory effect of astragaloside IV was proved in streptozotocin (STZ) induced diabetic rats. Renal tissue inflammation of diabetic rats was decreased by the astragaloside IV through inhibiting NF-κB pathway associated genes expressions such as collagen, ICAM-1, TNF-α, MCP-1 and NF-κB p65 [33]. In another study, a natural iridoid glucoside compound aucubin protected kidney cells of high-fat diet and STZ induced diabetic nephropathy in C57BL/6 mice. Aucubin has elevated the antioxidant defense in diabetic mice by triggering NQO1, HO-1, SOD, CAT, Nrf2, FOXO3a, SIRT1, and SIRT3 genes. Nephropathy associated inflammation was significantly reduced by modulating expression levels of TNF-α, IL-6, IL-1β, Phospho-IκBα (p-IκBα), IκBα and NF-κB p65 [34]. A flavonoid baicalein compound has been tested for nephroprotective effects on a high-fat diet and STZ-induced T2D wistar strain rats. By preventing NF-κB activation, suppressing iNOS, and TGF-β1 expression, baicalein mitigated oxidative stress and reduced inflammation. This compound also reduces the pro-inflammatory cytokine levels, such as TNF-α, IL-1β and IL-6 [35]. Another natural compound berberine is an isoquinoline alkaloid present in *Cortex phellodendri,* and *Berberis vulgaris* plants exhibited renal protection in STZ induced diabetic rats. Berberine reduced renal inflammation by decreased control of IL-1β, IL-6, MCP-1 and inhibition of p65, IκBα and TLR4 indicates that compound protected renal tissue through blockage of TLR4/NF-κB pathway [36]. Cepharanthine and piperine have protected the diabetic nephropathy in Sprague dawley diabetic rats induced by STZ. These compounds protected the kidney by modulating expression levels of the inflammasome, such as TXNIP, NLRP3, IL-1β, TNF-α and NF-κB [37]. In STZ-induced diabetic male sprague-dawley rats, diabetic nephropathy complication, the nephron inflammation and chlorogenic acid anti-inflammatory property were focused by Bao *et al*. (2018). Chlorogenic acid exhibited renal tissue protection in diabetes by activating Nrf2/HO-1 that inhibits NF-κB transcriptional cascade [38]. Diosmin exhibited nephroprotective property in diabetic wistar strain rats induced by alloxan monohydrate through controlling inflammatory cytokines and oxidative stress markers. Diosmin elevated the endogenous antioxidant enzymes, such as SOD, CAT and reduced the lipid peroxidation. Diabetic rats treated with diosmin showed that downregulation of inflammatory mediators such as IL1β, IL-6, TNF-α and NF-kB -p65 [39]. Renal tissue ameliorative effect of ellagic acid was taken to attention in high-fat diet supplement and STZ induced diabetic rats (HFD/STZ). HFD/STZ complications of diabetic nephropathy were significantly reduced by the ellagic acid by suppressing TGF-β, fibronectin in renal tissue. Ellagic acid also reduced the pro-inflammatory cytokines, such as IL-1β, TNF-α in serum. Moreover, ellagic acid inhibited the NF-κB activation in high glucose stress-mediated NRK52E proximal tubular epithelial cells of rats in *invitro* [40]. Genistein also nullified renal podocyte abnormality, inflammation and fibrosis by reducing the expressions of NF-κB p65, TGF-β1 and RAGE in the renal tissue [41]. Diabetic kidney in STZ-induced wistar strain male albino rats was protected by hesperidine and quercetine through elevating the SOD, CAT and SIRT1 levels. Both compounds significantly reduced the oxidative stress in the kidney. These also decreased the lipid peroxidation (Malondialdehyde (MDA) content) and NF-κB expression in diabetic conditions [42]. The effect of marein, a natural compound from *Coreopsis tinctoria,* was tested in rat mesangial cells for anti-renal inflammation under a high concentration of glucose. Marein potentially inhibited hyperglycemia-induced inflammation by down-regulating MCP-1, NF-κB p65 proteins in rat mesangial cells [43]. The renal protective function of naringenin in high-fat diet and STZ induced diabetes in male BALB/cA mice were tested at different doses. Naringenin nullified the kidney inflammation by reducing inflammatory markers such as NF-κB, IL-1β, IL-6, MCP-1, TGF-β1, NF-κB p65, NF-κB p50, PKC and collagen [44]. Diabetic nephropathy complications were ameliorated by salvianolic acid B in high glucose-induced mesangial cells. Salvianolic acid B exhibited potentiality against hyperglycemia by modulating MMP-9 and MMP-2 activities by way of NF-κB inhibition [45]. In another study, male wistar strain albino rats induced to diabetes by fed with a high-fat diet and a low dose of STZ. When they were treated with swertiamarin, the kidney was protected by decreasing NF-κB p65 by suppressing the expression of pro-inflammatory genes, such as IL-6, TNF-α and IL-1β in both tissue and plasma [46]. Ursolic acid present in many

plants was exhibited anti-inflammatory properties in diabetic rats and kidney cells *in vitro*. Ursolic acid prevented the diabetic nephropathy by modulating the expression levels of TLR4 pathway associated genes such as TLR4, MyD88, NF-κB, TNF-α, IL-1β, IL-6 and IL-18 levels in kidney of diabetic rats and hyperglycaemic kidney cell lines *in vitro* [47].

### 2.2. Diabetic Brain

Diabetic neuropathy is a common pathological condition in diabetes which impair both somatic and autonomous nervous system. The plethora of changes such as loss of sensation, impaired cardiovascular control, and diarrhoea, problems of diabetic foot, and impotence and tendon reflexes in patients with diabetes affects the quality of life, and sometimes life risks [48]. Molecular evidences in experimental animals revealed that AGEs, oxidative stress, polyol pathway activity, alteration in cholesterol and fatty acid metabolism in neuropathy consequences changes in signalling pathways, such as mitogen-activated protein kinases (MAPKs), NFκ-B p50/p65 and poly(ADP-ribose) polymerase (PARP). Expressed NFκ-B further initiates the inflammation in nerve cells by producing pro-inflammatory cytokines, such as TNF-α, IL-1β, IL-6 [49]. IKKβ/NF-κB inflammatory pathway is identified as a critical hallmark in the development of hypothalamic insulin resistance and glucose tolerance. Whereas, reduced neuropathy complications were observed in IKKβ/NF-κB inhibited high-fat diet-induced obesity and associated diabetic animals [50]. Elevated blood glucose is closely linked to neuronal damage. Glucose toxicity in neurons is due to intracellular oxidation of glucose that leads to excessive ROS generation and decreases antioxidant enzymes such as SOD, CAT and Glutathione (GSH) content [51]. Clinical studies have found that neuronal disruption was coinciding with elevated glucose levels in diabetic patients. In animal studies, diabetes induced by STZ and infused glucose was promoting apoptosis in neurons and schwann cells. Oxidative stress can stimulate changes in animals with diabetes, including apoptotic caspase-3 [52]. Nrf2 is a transcription factor, reported to reduce ageing and other chronic diseases that occurred from oxidative stress. An increased level of Nrf2 by many natural compounds in diabetic rats improves the cytoprotective and antioxidant enzyme HO-1[53]. The upregulation of cyclooxygenase-2 (COX-2) is occurred in neurons of diabetic animals by inflammatory stimuli, oxidative stress, hyperglycemia, and PKC activation [54]. In ischemic diabetic brain injury, high-mobility group box1 (HMGB1), a non-histone DNA binding protein induces severe inflammation of the brain through the NF-κB pathway [55].

#### *2.2.1. Diabetic Brain Protection by Plant Compounds*

Male mice (C57BL/6J) transferred into diet-induced experimental diabetic animals and supplemented with a natural dietary flavonoid butein compound to know the anti-diabetic character. By inhibiting IKKβ/NF-κB signalling, butein significantly prevented inflammation of the hypothalamus nerves in high-diet induced obesity animals [56]. Chrysin is a naturally occurring flavonoid compound that exhibits neuroprotective property in STZ induced diabetes rats. Oxidative stress, altered inflammatory markers (NF-κB p65, IL-6, IL-1β, TNF-α) and apoptosis (caspase-3) were observed in the diabetic cerebral cortex and hippocampus. Chrysin reduced oxidative stress, inflammation and apoptosis via the NF-κB pathway in diabetic rats [57]. A flavonoid compound fisetin was shown therapeutic potential in diabetic neuropathy of diabetic rats induced by STZ. Fisetin therapeutic benefit was confirmed by its regulating effect on Nrf2, IL-6, COX-2, HO-1 and NF-κB profile in sciatic nerves [49]. Quinolizidine alkaloid, the oxymatrine, has declined the diabetes-associated cognitive impairments in STZ induced wistar strain male albino rats. Oxymatrine declined the diabetic complications such as Oxidative stress through decreasing lipid peroxidation, increasing SOD activity and GSH content, inflammation by inhibiting IL-1β, TNF-α and NF-κB p65 expressions; and apoptosis by suppressing caspase-3 activity on the dose-dependent manner in cerebral cortex and hippocampus of the diabetic brain [58]. Rosmarinic acid exhibited neuroprotective activity in STZ induced diabetic rats. It was noted that the rosmarinic acid protective role related to decreased brain edema, inhibited NF-κB p50/p65 and reduced HMGB1 expression [55]. By targeting Nrf2/HO-1/NF-κB and COX signalling cascades, rutin combination with nimesulide exhibited neuroprotective role in diabetic rats induced by STZ. Rutin significantly decreased the oxidative stress through elevating SOD, CAT activity and GSH content. Rutin protected the sciatic nerves from inflammation and apoptosis by decreasing NF-κB p65, TNF-α, Nrf2, HO-1 and caspase-3 markers in diabetic rats [59]. Tocotrienol prevented diabetes neuropathy complications in STZ induced diabetic rats by suppressing inflammation and apoptosis. Hyperglycemia associated inflammation was suppressed by tocotrienol through the anti-inflammatory property by reducing expression levels of NFκB p65, TNF-α and IL-1β. It also prevented the tissue damage from caspase-3 expression, an apoptotic marker in the hippocampus and cerebral cortex of diabetic rats [60].

### 2.3. Diabetic Eye

Oculopathy in diabetic patients is closely associated with microvascular complications, which lead to blindness, also called diabetic retinopathy. Based on ophthalmoscopically visible vascular lesions, diabetic retinopathy is divided into proliferative, non-proliferative, and diabetic macular oedema [61]. In proliferative, the occurrence of characteristic fragile new aberrant vessels is visible whereas, symptoms in non-proliferative include retinal haemorrhages, lipid exudates and microaneurysms vascular tortuosity. Diabetic macular oedema associate with the accumulation of fluid in the neural retina, thickening the retina and cystoid macula oedema [62]. The prevalence of diabetic retinopathy from 2.6 million people in 2015 to 3.2 million people in 2020 poses an unprecedented global burden [63]. Diabetic retinopathy occurs in many pathways but, NF-κB activation and resulted cascade of events are playing a crucial role. Hyperglycemic condition in diabetic patients increases the accumulation of AGEs and ROS. These activate the NF-κB p65, which, in turn, is responsible for the production of pro-inflammatory cytokines (IL-6, IL-1β), chemokines, and acute-phase proteins. All these substances are accountable for the inflammatory response in the eye by recruiting monocytes and leukocytes [64]. A pleiotropic cytokine TNFα has multiple roles in cellular functions. In retinal pathology, it is associated with diabetic macular oedema, neovascular age-related macular degeneration, diabetic retinopathy, and retinal venous occlusion [65-67]. Ca2+/calmodulin dependant protein kinase II (CaMKII) is a threonine/serine kinase that synchronizes damage of retinal ganglion cells and also releases inflammatory mediators through the mediators of the NF-κB pathway. The most common symptoms in diabetic retinopathy are inflammation and microvascular complications of retinal cells, which correlate with the release of ICAM-1, iNOS, and vascular endothelial growth factor (VEGF) by activated CaMKII / NF-kB [68]. Excess generation of free radicals in different parts of the eye leads to oxidative stress. The cellular antioxidant enzyme system involves the transfer of electrons from the substrate to free radicals. The most important antioxidants present and protect the eye from ROS is SOD, CAT, and GSH content of cell [69].

#### *2.3.1. Diabetic Eye Protection by Plant Compounds*

Catechin, flavan-3-ol, a type of natural phenol and antioxidant, was examined for anti-diabetic retinopathy in STZ induced diabetic rats. Downregulation of NF-κB p65 and p-NF-κB p65 and TNF-α, IL-1β, and IL-6 in catechin treated diabetic rats conformed that catechin prevented retinal inflammation by inhibiting NF-κB pathway [70]. TNFα is a cytokine induces pro-inflammatory changes in diabetic retinopathy. Chebulagic acid, chebulinic acid, and gallic acid were tested for TNFα induced pro-inflammatory changes in retinal-choroid microvascular endothelial cells (RF/6A). These

compounds were inhibited TNFα induced pro-inflammatory changes in RF/6A cells by preventing phosphorylation on NFκB [67]. Curcumin's anti-inflammatory activity prevented the complications of the diabetic retinopathy associated pathway, such as CaMKII / NF-kB and its downstream proteins VEGF, iNOS and ICAM-1in alloxan-induced diabetic male spargue–dawley rats [68]. The protective role of naringin on diabetic retinopathy complications was proved in male experimental rats and muller cell lines (rMC1). STZ induced diabetic rats and high glucose-induced rMC1 treated with naringin exhibited decrease diabetic retinopathy complications through its antioxidant property by up-regulating GSH, SOD and CAT; and down-regulating anti-inflammatory markers, such as TNF-α, IL-1β, IL-6 and NF-κB p65 [71]. Resveratrol is a polyphenolic phytoalexin, which is abundant in many fruits. It exhibited inhibition of diabetic retinopathy in streptozotocin-nicotinamide induced diabetic male wistar rats. Resveratrol showed this property by scavenging free radicals induced oxidative stress by modulating SOD, Glutathione disulphide (GSSG)/GSH ratio and 8-isoprostane; and anti-inflammatory action through decreasing NF-κB p65 expression in retina [72].

### 2.4. Diabetic Liver

Insulin and its counter-regulatory hormones are targeting the liver. The most important thing to notice is that chronic liver disease coincided with glucose intolerance and diabetes. Chronic liver injury is acquaintance with inflammation and its promotion for a long time leads to hepatic fibrosis and hepatocellular carcinoma. In the mouse model, removal of NF-κB regulators causes unstructured liver injury, fibrosis and liver cancer [73]. In insulin resistance diabetes, IkB kinase complex (IKKα and IKKβ) is essential to control the stimulated activation of NF-κB p50/p65. A previous study reported that activated IL-6 and TNF-α by NF-κB p50/p65 again activate the insulin receptor substrate 1 (IRS-1) to withstand the development of insulin resistance [74]. In diabetic patients, several pathways have been identified that cause liver damage. The causative factors of liver damage are hyperglycemia and compensatory hyperinsulinemia. Among insulin-sensitive tissues, the liver is the one affected by the hyperglycemia-induced oxidative tissue damage. Oxidative stress decreases the activity of antioxidant enzymes such as SOD and CAT, also increases lipid peroxidation in the liver [75]. TLR4 is one of the receptors involved in inflammatory diseases, which leads to macrophage infiltration contributing to liver damage in experimental models of diabetes. TLR4 activates the NF-κB pathway through an intermediate MyD88, which results in the production of pro-inflammatory cytokines like IL-1β, IL-6 and TNF-α. Downregulation of TLR4/ MyD88/NF-κB genes in diabetic animal models exhibited a remarkable reduction of liver damage and fibrosis [76-78]. The farnesyl X receptor (FXR) is a member of nuclear receptor family present ubiquitously in all tissues but highly existent in the liver. FXR maintains levels of bile acids, glucose, cholesterol and lipids by promoting bile acids released from the liver, inhibiting bile acids synthesis and intestinal absorption [79]. It regulates energy homeostasis, insulin sensitivity and lipid metabolism, which are closely associated with diabetes. FXR activation increases hepatic glycogen synthesis, glycogen content and suppresses hepatic gluconeogenic expression through a mechanism involving enhanced insulin sensitivity [80]. Also, it regulates many downstream genes responsible for liver cirrhosis, toxic liver damage and hepatitis. FXR interacts and suppresses the activity of the NF-κB, which results in prevention of liver damage from inflammation [81, 82].

#### *2.4.1. Diabetic Liver Protection by Plant Compounds*

Han *et al.* (2016) attempted to elucidate the liver-protective role of celastrol in T2D caused by a high-fat diet. Real-time polymerase chain reaction (RT-PCR) analysis found that up-regulation of TLR4, MyD88, NF-κB, IL-1β, and TNF α in diabetic conditions. Whereas, all expression levels of the above said the treatment with celastrol downregulated inflammatory markers in the liver. It is clear that celastrol prevented liver damage by inhibition of TLR4/MyD88/NF-κB signaling pathway [78]. Luo *et a.l* (2015) had been designed to test whether or not kaempferol could minimize insulin resistance by inhibiting inflammatory cascade in hepatic tissue of diabetic rats. STZ induced diabetic rats fed with high-fat diet were treated with kaempferol revealed the inhibition of phosphorylation of IRS-1, NF-κB p65, IKKα, IKKβ, TNF-α and IL-6 levels. It is clear that kaempferol induces down-regulation of IKK and subsequent inhibition of NF-κB pathway in diabetes conditions [74]. Leonurine /SCm-198 is an alkaloid found in Herba *leonuri* plant reduced T2D in db/db mice at 200 mg/kg of body weight. After 3 weeks of treatment, leonurine reduced diabetes complications in the liver by inhibiting the NF-κB/IKK pathway [83]. Diabetic liver in STZ-induced wistar strain male albino rats was protected by hesperidine and quercetine through elevating the SOD and CAT levels. They also decreased lipid peroxidation (MDA content) and NF-κB expression in diabetic conditions [42]. In C57BL/6 mice liver and HepG2 (ATCC) cells, silymarin, a natural compound that nullifies high-fat diet, caused complications, such as obesity, hyperglycemia, insulin resistance and fatty liver through FXR/NF-κB pathway. High-fat diet complications associated closely with inflammation. FXR signal modulates the inflammation by NF-κB in these conditions [82]. A high-fat diet and a low dose of STZ induced diabetic rats treated with swertiamarin were protected by decreasing NF-κB p65 in the liver tissue, whereas expression of pro-inflammatory genes such as IL-6, TNF-α and IL-1β in both tissues and plasma were suppressed [46].

### 2.5. Diabetic Heart

Cardiomyopathy and heart failure are the main causes of two-thirds of diabetic patient deaths. Diabetic cardiomyopathy leads to systolic and diastolic dysfunction due to decreased compliance, excessive relaxation and diminished contractility of the heart [5]. Increased ROS results in the production of inflammatory cytokines. In myocardial injury, the up-regulation of IL-6, IL-1β, and TNF-α takes place [84]. Patients with heart failure for various reasons revealed the activation of NF-κB p65 and its regulated genes. In diabetic patients, a high amount of circulating glucose, low-density lipoproteins and very-low-density lipoproteins stimulate the NF-κB activation [85]. Cardiac inflammation in diabetes is preceded by the augmented expression of VCAM-1 and ICAM-1. These molecules facilitate the transendothelial movement of immunocompetent cells into heart tissue due to its particular counter receptors, such as macrophage integrins and leukocyte integrins. These invading cells and also cardiomyocytes produce pro-inflammatory cytokines like TNF-α, IL-18 and IL-1β [86]. During chronic hyperglycemia, AGEs are produced extra and intracellularly. AGEs interact with RAGEs, which leads to a cascade of events, such as extracellular matrix accumulation, oxidative stress, and increased inflammation, which promote the myocardial tissue damage [87]. Hyperglycemia induced superoxide radicals favour augmented expression of iNOS through the activation of NF-κB. iNOS involves excess production of NO; consequently, its active products attack biomolecules of the myocardium, leading to cardiovascular dysfunction [88]. Nrf2 is a transcription factor essential for the activation of HO-1, NQO-1 and SOD. These enzymes play an important role in the attenuation of free radicals generated by oxidative stress in the heart by diabetic inducers [89]. Hyperglycemia in STZ rats increases the apoptotic protein Bcl-2 associated X (Bax) and decreases the Bcl-2 suggesting that the toxicity of glucose in the heart causes tissue damage by apoptosis [90].

#### *2.5.1. Diabetic Heart Protection by Plant Compounds*

High glucose supplemented human coronary artery endothelial cells (HCAECs) are used as diabetic experimental cell lines. HCAECs are treated with cannabidiol exhibited anti-glycaemic property. This compound protected the cardiac cells by inhibiting

the genes associated with hyperglycemic complications such as ICAM-1, VCAM-1, IκB-α, NF-κB-p65 and iNOS; also reduced the monocyte adhesion to the endothelial cells, disrupted endothelial barrier function, mitochondrial superoxide radical and 3-NT formation [91]. Luteolin, a flavonoid was examined for the cardioprotective role in STZ induced diabetic mice and H9C2 cells in *in-vitro*. Luteolin reduced the cardiac dysfunction, hypertrophy, fibrosis, inflammation by modulation of Nrf2 mediated oxidative stress (Nrf2, HO-1, NQO-1 and SOD), and inflammatory responses mediated by NF-κB (IκBα, TNF-α, VCAM, iCAM, IL-6, IL-1β and MCP-1) in diabetic cardiomyopathy [92]. Mangiferin exhibited a cardioprotective role in high-fat diet and low dose STZ induced diabetic rats due to its anti-inflammatory, anti-diabetic properties. Mangiferin declined the inflammatory mediators (TNF-α, IL-1β, NF-κB p65), reduced AGEs formation by inhibiting RAGE and prevention of ROS production [93]. Piceatannol is a resveratrol analogue improved the myocardial function in diabetic cardiomyopathy in both hyperglycaemic H9C2 cardiac myoblasts cell lines and STZ induce diabetic male Sprague–Dawley rats. Piceatannol reduced the inflammatory cascade markers TNF-α, IL-6, Nrf2, HO-1 and NF-κB p65 and also inhibited the apoptosis by decreasing Bax and Bcl-2 proteins levels in cardiac cell lines. Similarly, piceatannol also exhibited cardiac protection in animal models by declining oxidative stress, inflammation and apoptosis, as mentioned in hyperglycaemic H9C2 [92]. Diabetic male Sprague–Dawley rats induced by STZ were treated with triptolide reduces the complication accompanying with diabetic cardiomyopathy. Western blotting and RT-PCR analysis explored that triptolide reverses the expression of STZ induced inflammatory markers, such as TNF-α, IL-1β, iCAM-1, VCAM-1, NF-κB-p65 in cardiac tissue of diabetic rats. In hyperglycemic H9C2 rat cardiac cell lines, triptolide also decreased the expression levels of TNF-α and NF-κB p65 [94].

### 2.6. Diabetic Skeletal Muscle

Diabetic patients regularly suffer from muscle atrophy, are caused by increasing molecular events like contractile protein degradation by caspase-3 mediated apoptosis, activation of lysosomal-proteasome and ubiquitin-proteasome. Much scientific evidences indicate that inflammation-sensitive NF-κB pathway leads to muscle atrophy in diabetes. It has been demonstrated that free fatty acids activate NF-κB and its nuclear translocation. This has impaired the sensitivity to insulin in skeletal muscle cells [95].

#### *2.6.1. Diabetic Skeletal Muscle Protection by Plant Compounds*

An experiment with *Astragalus* polysaccharide (APS) was tested for anti-diabetic property in palmitate prompted insulin resistance in C2C12 skeletal muscle myotubes. In Palmitate induced insulin resistance model, APS regulated the NF-κB pathway by inhibiting expression of NF-κB p65, activation of stress kinase IKKα/β and the restoration of IκBα [96].

### 2.7. Diabetic Endothelial Cells

Diabetic endothelial dysfunction is associated with adhesion of leukocytes to the endothelium and expression of cell adhesion molecules (CAMs). Endothelial selectin (E-selectin) and VCAM-1 are CAMs that are over-expressed by endothelial cells under hyperglycemia. Owing to the large number of leucocytes adhering to vascular endothelium, the endothelium transmigration, and dysfunction can occur [97, 98]. An apoptosis warning due to mitochondrial damage was observed in endothelial cells treated with high glucose [99]. A previous study reported decreased concentration of anti-apoptotic protein Bcl-2 whereas, increased concentration of apoptotic proteins such as bax, cytochrome c and caspase-3 in endothelial cells under high glucose condition. It also found that the hyperglycemic state increased the development of ROS, which regulates the inflammatory marker proteins IκB-α and P65 in endothelial cells [100].

#### *2.7.1. Diabetic Endothelial Cells Protection by Plant Compounds*

Wang *et al*. (2010) conducted an experiment with human umbilical vein endothelial cells (HUVECs) induced by high glucose and treated with geniposide. Geniposide inhibited the cell adhesion, expression of E-selectin, and VCAM-1 by reducing ROS production and NF-κB pathway under hyperglycemia [101]. High glucose-mediated inflammation of the endothelial cells and apoptosis is significantly reduced by pre-treatment of the alkaloid neferine in HUVECs. Neferine decreased apoptosis by cleavage of caspase-3 and increasing the expression of Bcl-2 protein; decreasing Bax and cytochrome C. It also suppressed the endothelial cells' inflammation by decreasing IκB-α and p65 protein expression [100].

### 2.8. Diabetic Adipose Tissue

Adipose tissue is not only the tissue that stores fats and regulation of lipid metabolism but also involved in immune functions [102]. Adipocytes secrete mediators such as TNF-α, IL-1β, IL-6 and MCP-1 and many others [103]. Systemic diabetic insulin resistance can induce the production of pro-inflammatory cytokines in adipose tissue. An increased level of MCP-1 was observed in the adipose tissue of diabetic patients. MCP-1 functionally induces monocyte infiltration in adipose tissue, which in turn promotes pro-inflammatory cytokines release from adipocytes and invasive macrophages [104]. Increased levels of TNF-α, IL-1β were identified in Vietnamese patients with T2D [105]. Nitrosative stress in adipose tissue by iNOS enzyme produced NO acts with ROS playing an important role in the impairment of adipocyte function [106]. NF-κB and c-Jun N-terminal Kinase (JNK) are very critical pathways under insulin resistance which are involved in inflammation of adipocytes. JNK and IKKβ activities are both increased in high fat diet-induced obese mice and humans with inflamed adipose tissue. In addition, knockout of IKKβ or JNK in immune cells protect mice from the insulin resistance in adipose tissue caused by a high-fat diet [107-109]. Treatment of inflamed adipose tissue under hyperglycemia with plant compounds upregulates the anti-inflammatory agents such as IL-10, C-Type Lectin Domain Containing 7A (Clec7a), Macrophage galactose-type lectin 1 (MGL1) and arginase 1 [110]. Peroxisome proliferator-activated receptor (PPAR) is primarily localized highly in the brown adipose tissue and liver, whereas, it is the present to a lesser extent in kidney, heart and skeletal muscle. Based on the distinct distribution of PPARs that can be divided into three isoforms such as α, β and γ, PPARγ again divided into two subforms such as PPARγ1 and PPARγ2. PPARs are type II nuclear hormone receptors that contribute to the regulation of carbohydrate and fatty acid metabolism. PPARs also regulate the activity of nuclear factors belonging to inflammatory and immune-modulatory responses [111]. In diabetes, PPARα exhibits anti-inflammatory property by negatively regulating NF-κB and activator protein-1 (AP-1) and upregulating IκBα, an NF-κB inhibitor. PPARα is also reducing adipose tissue inflammation and fat-beta oxidation genes expression. In addition to this, it also regulates the COX-2, VCAM-1 and IL-6 as a part of anti-inflammatory activity. Besides, the anti-inflammatory action of PPARβ is carried via NF-κB by suppressing COX-2 and iNOS. On the other hand, PPARγ also exhibits the anti-inflammatory property by inhibiting cytokines, chemokines via NF-κB [112, 113]. In T1D rats, mice and humans isolated macrophages and monocytes exhibited overexpression of long-chain acyl-CoA synthetase 1 (ACSL1), an enzyme that involved in thioesterification of fatty acids [114].

#### *2.8.1. Diabetic Adipose Tissue Protection by Plant Compounds*

Takimoto *et al*. (2014) isolated 4β-Hydroxywithanolide E (4βHWE) compound from *Physalis pruinosa calyx* and its anti-diabetic ability was examined in adipocyte culture and db/db mice with emphasize on inflammation. The NF-κB activity was inhibited by the compound by blocking NF-κB translocation into the nucleus. In addition, 4βHWE reduced the pro-inflammatory cytokines IL-6,

**Table 1. Representation of anti-diabetic plant compounds targeting NF-κB.**

| S.No | Compound Name | Compound class | Dose studied | Pubchem Id | Source of plant | Reference |
|---|---|---|---|---|---|---|
| **Kidney protective compounds** | | | | | | |
| 1 | Astragaloside IV | Terpenoid | 10 mg/kg/b.w rats | 13943297 | *Astragalus membranaceus,* | [33] |
| 2 | Aucubin | Iridoid | 80 mg/kg/b.w mice | 91458 | *Aucuba japonica, Eucommia ulmoides, Plantago asiatica, Galium aparine* | [34] |
| 3 | Baicalein | Flavonoid | 20 mg/kg/b.w rats | 5281605 | *Oroxylum indicum,Scutellaria baicalensis* | [35] |
| 4 | Berberine | Alkaloid | 200 mg/kg/b.w rats | 2353 | *Argemone mexicana, Berberis aquifolium, Berberis aristata, Berberis vulgaris,Coptis chinensis* | [36] |
| 5 | Cepharanthine | Alkaloid | 10 mg/kg/b.w rats | 10206 | *Stephania* | [37] |
| 6 | Chlorogenic acid | Phenolic acid | 10 mg/kg/b.w rats | 1794427 | *Phyllostachys edulis, Calluna vulgaris* | [38] |
| 7 | Diosmin | Flavonoid | 100 mg/kg/b.w rats | 5281613 | *Hyssopus officinalis, Hyssopus decumbens,* | [39] |
| 8 | Ellagic acid | Tannin | 40 mg/kg/b.w rats | 5281855 | *pomegranates, persimmon, raspberries, black raspberries* | [40] |
| 9 | Genistein | Isoflavanol | 1 mg/kg/b.w rats | 5280961 | *Genista tinctoria, Flemingia vestita, Flemingia macrophylla* | [41, 132] |
| 10 | Hesperidin | Flavonoid | 100 mg/kg/b.w rats | 10621 | *Citrus aurantium, Zanthoxylum gilletii, Agathosma serratifolia* | [42] |
| 11 | Marein | Phenolic acid | 400 μM cell lines | 6441269 | *Coreopsis tinctoria* | [43] |
| 12 | Naringenin | Flavonoid | 80 mg/kg/b.w rats | 439246 | *Citrus aurantium, Prunus cerasus, Solanum lycopersicum, Mentha aquatica* | [44] |
| 13 | Piperine | Alkaloid | 30 mg/kg/b.w rats | 638024 | *Piper nigrum, Piper longum* | [37] |
| 14 | Quercetin | Flavonoid | 100 mg/kg/b.w rats | 5280343 | *Capparis spinosa, Morus alba, Centella asiatica, Aleum cepa.* | [42] |
| 15 | Salvianolic Acid B | Phenolic acid | 10 μM cell lines | 11629084 | *Salvia miltiorrhiza,* | [45] |
| 16 | Swertiamarin | Iridoid | 50 mg/kg/b.w rats | 442435 | *Enicostemma littorale* | [46] |
| 17 | Ursolic acid | Phenolic acid | 25 mg/kg/b.w mice | 64945 | *Eugenia jambolana, Mentha piperita, Rosmarinus officinalis and many others* | [47] |
| **Brain protective compounds** | | | | | | |
| 1 | Butein | Phenolic acid | 1 mg/kg/b.w mice | 5281222 | *Peumus boldus* | [56] |
| 2 | Chrysin | Flavonoid | 100 mg/kg/b.w rats | 5281607 | *Passiflora caerulea, Passiflora incarnata,* | [57] |
| 3 | Fisetin | Flavonoid | 10 mg/kg/b.w rats | 5281614 | *Acacia greggii, Acacia berlandieri, Gleditschia triacanthow* | [49] |
| 4 | Oxymatrine | Alkaloid | 120 mg/kg/b.w rats | 114850 | *Sophora flavescens* | [58] |
| 5 | Rosmarinic acid | Phenolic acid | 200 mg/kg/b.w rats; 9 μM cell lines | 5281792 | *Rosmarinus officinalis, Melissa officinalis, Origanum majorana, Ocimum basilicum* | [55] |
| 6 | Rutin | Flavonoid | 200 mg/kg/b.w rats | 5280805 | *Ruta graveolens, Amaranth hypochondriacus, Carpobrotus edulis, Rubus ursinus* | [59] |
| 7 | Tocotrienol | Phenolic acid | 100 mg/kg/b.w rats | 9929901 | *Bixa orellana, Elaeis guineensis and many others* | [60] |

**(Table 1) Contd....**

| S.No | Compound Name | Compound class | Dose studied | Pubchem Id | Source of plant | Reference |
|---|---|---|---|---|---|---|
| **Eye protective compounds** | | | | | | |
| 1 | Catechin | Flavonoid | 100 mg/kg/b.w rats | 9064 | *Camellia sinensis,Theobroma cacao* | [70] |
| 2 | Chebulagic acid | Tannin | 100 µM cell lines | 442674 | *Emblica officinalis, Terminalia bellerica, Terminalia chebula* | [67] |
| 3 | Chebulinic acid | Tannin | 100 µM cell lines | 72284 | *Emblica officinalis, Terminalia bellerica, Terminalia chebula* | [67] |
| 4 | Curcumin | Phenolic acid | 100 mg/kg/b.w rats | 969516 | *Zingiberaceae, Curcuma longa* | [68] |
| 5 | Gallic acid | Phenolic acid | 100 µM cell lines | 370 | *Emblica officinalis, Terminalia bellerica, Terminalia chebula* | [67] |
| 6 | Naringin | Flavonoid | 80 mg/kg/b.w rats | 442428 | *Citrus paradisi* | [71] |
| 7 | Resveratrol | Phenolic acid | 5 mg/kg/b.w rats | 445154 | *Vitis vinifera, Arachis hypogaea, Pistacia vera, Vaccinium corymbosum.* | [72] |
| **Liver protective compounds** | | | | | | |
| 1 | Celastrol | Phenolic acid | 500 µg/kg/b.w rats | 122724 | *ripterygium wilfordii, Celastrus orbiculatus, Celastrus aculeatus* | [78] |
| 2 | Hesperidin | Flavonoid | 100 mg/kg/b.w rats. | 10621 | *Citrus aurantium, Zanthoxylum gilletii, Agathosma serratifolia* | [42] |
| 3 | Kaempferol | Flavonoid | 150 mg/kg/b.w rats. | 5280863 | *Glycine max, Hypericum perforatum, Pinus sylvestris* | [74] |
| 4 | Leonurine (SCm-198) | Alkaloid | 200 mg/kg/ b.w. mice | 161464 | *Herba leonuri* | [83] |
| 5 | Quercetin | Flavonoid | 100 mg/kg/b.w rats. | 5280343 | *Capparis spinosa, Morus alba, Centella asiatica, Aleum cepa.* | [42] |
| 6 | Silymarin | Phenolic acid | 40 µg/ml cell lines; 40 mg/100g diet/ mice | 31553 | *Silybum marianum* | [82] |
| 7 | Swertiamarin | Iridoid | 50 mg/kg/b.w. rats | 442435 | *Enicostemma littorale* | [46] |
| **Heart protective compounds** | | | | | | |
| 1 | Cannabidiol | Phyto Cannabi-noid | 4 µM cell lines | 644019 | *Cannabis sativa, Cannabis ruderalis* | [91] |
| 2 | Luteolin | Flavonoid | 20 mg/kg/b.w mice | 5280445 | *Aiphanes aculeate, celery, broccoli, green pepper, parsley, thyme* | [92] |
| 3 | Mangiferin | Phenolic acid | 20 mg/kg/b.w. rats | 5281647 | *Mangifera indica, Iris unguicularis, Anemarrhena asphodeloides.* | [93] |
| 4 | Piceatannol | Phenolic acid | 50 µM cell lines 10 mg/kg/b.w. rats | 667639 | *Arachis hypogaea, Vitis vinifera, Rheum rhabarbarum, Saccharum officinarum, Passiflora edulis* | [90] |
| 5 | Triptolide | Terpenoid | 400 µg/kg/b.w. rats | 107985 | *Tripterygium wilfordii* | [94] |
| **Skeletal muscle protective compounds** | | | | | | |
| 1 | Polysaccharide | Carbohydrate | 0.2 µg/ml cell lines | - | *Astragalus propinquus* | [96] |
| **Endothelia protective compounds** | | | | | | |
| 1 | Geniposide | Iridoid | 20 µM/L cell lines | 107848 | *Gardenia jasminoides ellis* | [101] |
| 2 | Neferine | Alkaloid | 30 µM/L cell lines | 159654 | *Nelumbo nucifera* | [100] |

**(Table 1) Contd....**

| S.No | Compound Name | Compound class | Dose studied | Pubchem Id | Source of plant | Reference |
|---|---|---|---|---|---|---|
| **Adipose tissue protective compounds** | | | | | | |
| 1 | 4β-Hydroxywithanolide E | Steroid | 30 mg/kg/ b.w. mice | 73621 | *Physalis pruinosa* | [115] |
| 2 | Catalpol | Iridoid | 100 mg/kg/b.w. mice | 91520 | *Globularia alypum, Globularia cordifolia, Globularia meridionalis* | [110] |
| 3 | Tilianin | Flavone | 10 µM cell lines<br>60 mg/Kg/ b.w. rats | 5321954 | *Agastache rugosa, Agastache Mexicana.* | [116] |
| **Pancreas protective compounds** | | | | | | |
| 1 | Formononetin | Isoflavonol | 10 µmol/L cell lines | 5280378 | *Maackia amurensis* | [128] |
| 2 | Genistein | Isoflavanol | 1 mg/kg/b.w. rats | 5280961 | *Genista tinctoria, Flemingia vestita, Flemingia macrophylla* | [41, 20] |
| 3 | Icariin | Flavonoid | 10 µM cell lines | 5318997 | *Epimedium alpinum* | [130] |
| 4 | Swertiamarin | Iridoid | 50 mg/kg/b.w.rats | 442435 | *Enicostemma littorale* | [46] |
| 5 | Tetrandrine | Alkaloid | 100 mg/kg/b.w.rats | 73078 | *Stephania tetrandra,* | [130] |

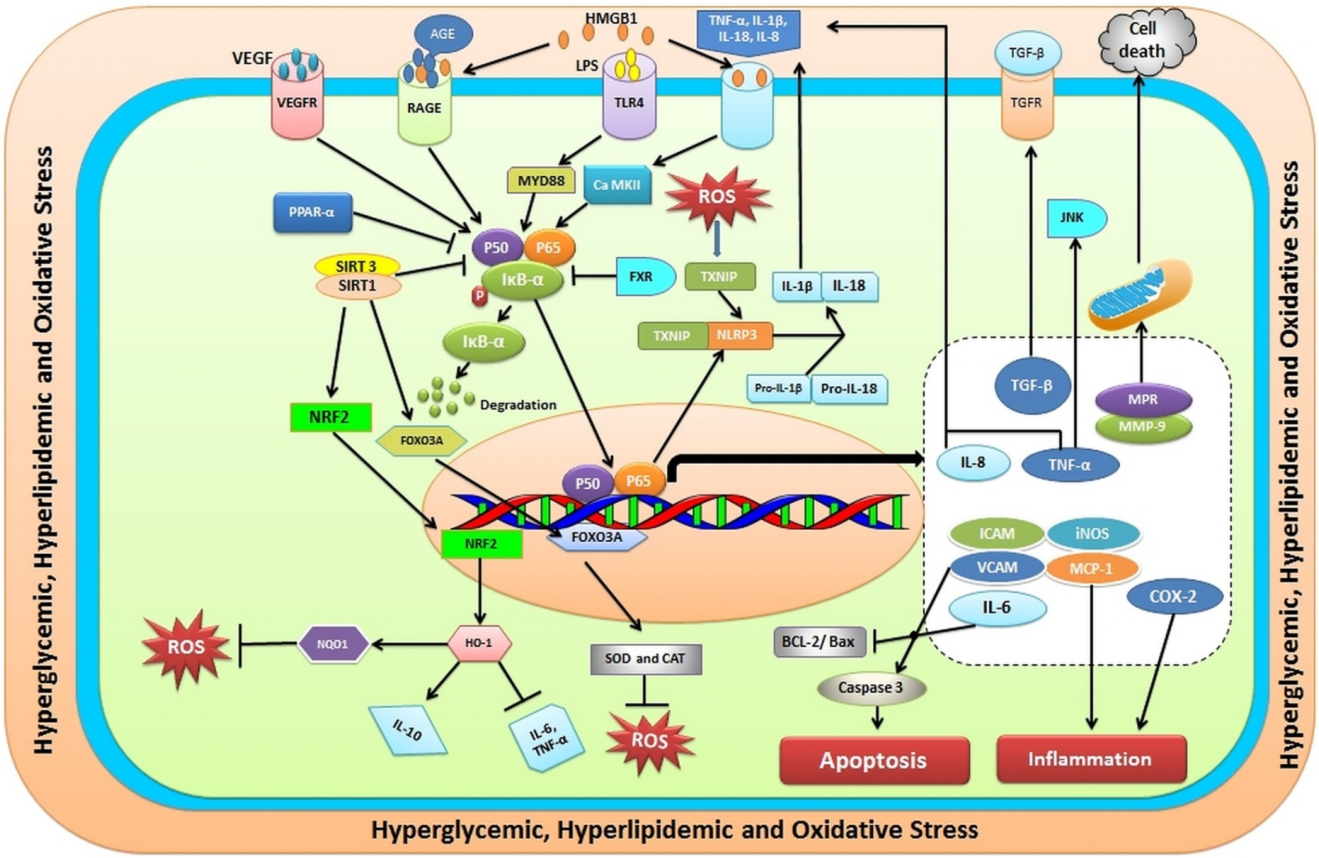



**Fig. (2).** Schematic representation of the proposed mechanism in which NF-κB acts as a central agent responsible for tissue damage in diabetes through inflammation and apoptosis. (*A higher resolution / colour version of this figure is available in the electronic copy of the article*).

TNF-α and MCP-1 in diabetic conditions [115]. Catalpol exhibited hypoglycemic property in high-fat diet-induced diabetic male C57BL/6J mice. Catalpol reversed the adipose tissue inflammation through decreasing macrophage infiltration, IL6, IL-1β, iNOS, MCP-1, and TNF-α. On the other hand, catalpol increased the expression level of anti-inflammatory genes such as IL-10, Clec7a, MGL1 and arginase 1 in adipose tissue. Catalpol also inhibited NF-kB and JNK pathways by suppressing NF-κB subunit p50, phos-

phorylation of both JNK and IKKβ [110]. Anti-hyperlipidemic, anti-diabetic and anti-inflammatory properties of tilianin were found in non-insulin-dependent diabetes mellitus and 3T3-L1 adipose cell lines. Tilianin exhibited hyperlipidemic activity by diminishing triacylglycerides and cholesterol; anti-inflammatory nature due to decreasing IL-1β and IL-18, NF-κB expressions in diabetic condition. In 3T3-L1 cells, tilianin increased PPARα and ACSL1 expression levels, given clarity that it has anti-hyper lipidic property [116].

### 2.9. Diabetic Pancreas

Diabetes mellitus is a progressive disease induced by chronic hyperglycemia and insulin resistance in which the pancreas is the organ most affected. The size of the pancreas decreased in T1D and T2D due to the loss of beta islets and next to apoptosis [117,118]. Caspase-3 is an apoptotic protein. Caspase-3 knocked mice supplemented with diabetic inductive agent STZ showed no diabetes complications in beta islets of the pancreas. Hence, caspase-3 is obvious to be the most important protein in pancreatic islet apoptosis [119]. Bcl-2 is a pro-survival protein of apoptosis, indicating that increased Bcl-2 decreases apoptosis. At the same time, bax is a pro-apoptotic protein that increases cell death by promoting caspase cascade [120]. There has been scientific evidence that damage the viability of beta-cells is caused by the infiltration of immune cells and inflammatory cytokines resulted in oxidative stress and endoplasmic reticulum stress. In the initial stages of diabetes, inflammatory cell infiltration encourages cytokines to release such as IL-1β, interferon γ (IFN γ) and TNF α through the NF-κB pathway. In addition, the combination of IL-1β/IFN or IL-1β/TNF α or IL-1β alone activates the iNOS enzyme that induces NO production in the beta islets of the diabetic pancreas [121-124]. Excessive production of NO causes insulin secretion impairment and triggers β cell death due to protein modification, mitochondrial metabolism dysfunctions and DNA damage [125]. SIRT1is a member of histone/protein deacetylases involved in the inhibition of inflammation. Its expression has been observed in endocrine cells of the Langerhans islets. It prevents the inflammation in β-islets by inhibiting NF-κB by deacetylating p65. In the diabetic pancreas, overproduction of ROS causes declined antioxidant enzyme SOD and increased lipid peroxidation [126, 127].

#### 2.9.1. Diabetic Pancreas Protection by Plant Compounds

INS-1, a rat insulinoma cell lines, were supplemented with IL-1β for the induction of cell apoptosis. INS-1 treated with formononetin significantly prevented the apoptosis induced by IL-1β by reducing the Caspase-3 and Bax / Bcl-2 ratios. It also protected the pancreatic cells by preventing the NO production through inhibition of NF-κB, which is essential for the production of iNOS [128]. Genistein was tested for the anti-inflammatory agent in ovariectomized diabetic rats induced by STZ. Pancreatic tissue inflammation was observed in diabetic rats, but the same was declined in genistein-treated diabetic rats due to reduced expression of inflammatory agents such as IL-1β, NF-κB and increased SIRT1 [129]. In another experiment, cytokines IL-1β and IFN-γ stimulated inflammation in RINm5F cells were abrogated by the natural flavonoid compound icariin. Destruction of insulin-producing pancreatic β cells occurs in T1D due to the action of autoimmune cells. Icariin inhibited cytokines induced inflammatory pointers such as NO production, caspase-3, cleavage of PARP and NF-κB p65 [130]. In an experiment with male Wistar strain albino rats induced to diabetes by fed with a high-fat diet and a low dose of STZ treated with swertiamarin was protected by decreasing NF-κB p65 in the pancreas whereas, expression of pro-inflammatory genes such as IL-6, TNF-α and IL-1β in both tissues and plasma were suppressed [46]. Tetrandrine reduces diabetes mellitus in allaxon induced rats. This compound exhibited ant-diabetic property by decreasing oxidative stress (SOD, MDA, and ROS), downregulating TNF-α ,NF-κB, and upregulating IκBα in pancreatic islets [127].

## CONCLUSION

By having gathered all information, we conclude that diabetes is the metabolic disorder that causes alterations in the homeostasis of cells in association with hyperglycemia and insulin resistance. Oxidative stress, inflammation, and apoptosis are the major culprits in organs, such as kidney, brain, eye, liver, heart, skeletal muscle, endothelium, adipose tissue, and pancreas of diabetic patients. NF-κB plays a crucial role because of its link in the expression of genes that are responsible for tissue damage of organs by inflammation, apoptosis and oxidative stress in the development of diabetic complications. Activation of PPAR-α, SIRT3/1, and FXR through many cascades by the chemical classes of plant compounds, such as terpenoids, iridoids, flavonoids, alkaloids, phenols, tannins, carbohydrates, and phytocannabinoids in different experimental diabetic models proved their anti-diabetic property. Alongside, compounds of chemical classes of plants exhibit prevention of NF-κB translocation into the nucleus by inhibiting NF-κB activators, such as VEGFR, RAGE and TLR4 receptors, which in turn, prevent the activation of many genes which are responsible for tissue damage. Hence, plant compounds are the best choice to find potential anti-diabetic drugs by targeting therapeutic components of the NF-κB activators and inhibitors. In addition, plant compounds have exhibited anti-diabetic properties by reducing blood glucose levels and modulating insulin resistance. Therefore, it is advisable to choose the plant natural resources as alternative medicine in treating diabetes. Current knowledge on the treatment of diabetes by targeting NF-κB is limited. Hence, further research on this aspect is to be focused by scientists both in pre-clinical to clinical studies.

## AUTHORS' CONTRIBUTION

The first and second authors played a substantial role in data acquisition, analysis, interpretation and manuscript preparation. The other co-authors contributed their efforts equally towards acquiring additional data for making the script in a good way. The corresponding author critically revised and finalized the manuscript for publication.

## CONSENT FOR PUBLICATION

Not applicable.

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## CONFLICT OF INTEREST

The authors declare no conflict of interest, financial or otherwise.

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**THE REPRESENTATION OF IDENTITY IN CHARLES DICKENS "A TALE OF TWO CITIES"**

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# THE REPRESENTATION OF IDENTITY IN CHARLES DICKENS "A TALE OF TWO CITIES"

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**ABSTRACT:** Charles Dickens (1812 to 1870) is a foremost representative novelist of the Victorian Era, a great story teller and a social reformer. Dickens was not only the first great urban novelist in England, but also one of the most important social commentators who used fiction effectively to criticize economic, social, and moral abuses in the Victorian era. Dickens showed compassion and empathy towards the vulnerable and disadvantaged segments of English society, and contributed to several important social reforms. A Tale of Two Cities is set in London and Paris before and after French Revolution. The novel depicts the plight of the French Peasantry demoralized by the French aristocracy in the year leading up to the revolution. It has always been one of his best loved novels. The novel is about the Identity and reunion of father DoctorManatee and a daughter lucie Manatee after 18 years. The novel consists of two heroes Charles Draney and Sydney Carton having the same identical features and both of them love one girl Lucie.In the novel there exhibits an admirable honesty to reveal Doctor Manatee his true identity as a member of the infamous evermonde family

**Key words:** Charles Dickens,Identity and A Tale of Two cities

**INTRODUCTION:**Charles Dickens is remembered today as one of the greatest and most popular writers of the novel ever to have lived in Victorian period. All the important people of the day read at least one of his novels. Queen Victoria was a great fan of him.Dickens captured the spirit of his age in both a profound and entering way.He wrote with wit and humour,he also wrote about every day tragedies he saw around him.He put all this in the context of Victorian society.

**Representation of Identity: A Tale of Two Cities**

The novel opens with the opening lines "It was the Best of times, it was the worst of times, it was the age of wisdom, it was the age of foolishness". This novel takes place during French Revolution. Mr. Jarvis Lorrie working in Telson bank in London is a good friend of Mr. Alexander Manatee. Lorrie came to know about his friend Manatee living in Paris was alive and safe with his old servantMonsieur defarge in Paris who was a vendor of wine, as Manatee was imprisoned by evermonde family for a small mistake for 16 years.

Mr.Lorrie along with Lucie Manatee and Pros reaches Paris and met Alexander Manatee and decides to take Manatee along with them to England.At the same time Charles Draney ,who belongs to Evermonde family of nobles, one of the hero in the novel,advices ll the nobles to stop slavery on people,otherwise there would be a revolution from people.Mr.Charles Darney decides to leave France and move to England to make his on living by his own labour.While leaving to England Draney promises to his old servant that he would help him in any trouble.

Mr.charles Draney leaves all his properties and move to England. All the people from Paris Mr.Lorrie, Mr. Manatee,Miss Lucie and Mr.Darney travels in the same ship to reach England.In the travel for the first time Mr.Darney and Miss Lucie met one another.Mr .Darney also helps Manattee in the travel.But,few months later Mr.Darney was imprisoned in a case as a spy. Mr. Manatee and Lucie were called as the witness for Darney case.Darney was declared as a spy moving from England to France, but the witness of Lucie and Manatee was not accepted as there was strong witness named Mr.Barsad who was the real spy,but he accepts Darney as the spy.

"Barsad,was a hired Spy and traitor,an unblushing trafficker in blood,and one of the greatest scoundrels upon the earth since accursed Judas-Which he certainly did look rather like"(TTC.P.62)

For the first time two identical figures were seen in the court.Mr.Sydney Cartoon, another hero of the novel,enters the court with another witness and proves Charles Darney was innocent in the case.As he resembles same to Darney,he save Darney by presenting himself in the court.All the three people fell in love.Charles Darney loves Lucie ,Sydney Cartoon loves lucie but Lucie loves Charles Darney.But all the three never expressed their love to one another.

"Charles Darney loved Lucie Manatee from the hour of his danger.He had never heard a sound as sweet and dear as the sound of her compassionate voice; with his own on the edge of the grave that had been dug for him.But he had not yet spoken to her on the subject; the assassination at the deserted chateaufar away beyond the heaving water and the long, tong ,dusty roads the solid stone chateau which had itself become the mere mist of a dream had been done a year,and he had never yet, by so much as a single spoken word,disclosed to her the state of his heart"(TTC.P.104)

Lucie father accepts the love of Darney and decides to marry them.At that time Darney reveals him the truth that he belongs to Evermonde family and his actual name was Charles Evermonde Darney.Lucie father without knowing that darney belongs to Evermonde family accepted their love and marriage.At the same time Sydney Cartoon enters the house of lucie to propose his love for her.But the engagement is announced for Lucie and Darney by Manatee.

Sydney never revealed his love for Lucie.Lucie was married to Darney and they had a baby girl.On one occasion Darney reveals the secret to lucie that Sydney also loved her so deeply.After 5 years of period,Sydney meets Lucie family and spends his time happily with them.At that occasion Lucie requests Sydney to marry another girl and lead a happy life.But Sydney refuses to marry, and on the same situation Sydney promises lucie that He would do any sacrifice to her in this world and indeed,he would give his life for her sake

"No man ever really loved a woman ,lost her ,and knew her with a blameless though an unchanged mind, when she was a wife and a mother, but her children had a strange sympathy with him an instinctive delicacy of pity for him"(TTC.P.164)

A few days later,revolution started in France for republic of the people against Evermondes.People were against the slavery. All the Nobles of Evermonde family were imprisoned and decided to cut down their heads on the republic day.Sydney receives a letter from his old servant and came to know about the revolution in France and the help needed to him from Darney,as he already promised.

"Cannon,muskets,fire and smoke; but,still the deep ditch,the single drawbridge, the massive stone walls and the eight greattowers. Slight displacements of the raging sea,made by the falling wounded.Flashing weapons,blazing torches,smoking wagonloads of wet straw,hard work at neighbouring barricades in all rections,hrieks,volleys,xecrations,bravery without stint,boom smash and rattle and the furious sounding of the living sea"(TTC.P.167)

Charles move to France to help the servant and release him as he promised without informing his family.Charles was imprisoned in France as he belongs to Evermonde family,his uncle Mr. Manatee was helpless and was not able to help Darney though, he is a citizen of France.Sydney Cartoon come to know France and learns about the incident happend .Sydney decided to help Darney and save his life,as he promised to lucie that he would sacrifice his life for her sake.

Darney and Sydney had same identical features.Sydney took the help of Barsad a spy in France and entered into the prison of Darney and escaped Darney from the prison by making him unconscious with a medicine and replaced his place as Charles Darney by exchanging his dress,as they have identical features no one guessed of it or came to know about this incident.The day came for his sacrifice.Charles and his family were sent safely to England with the help of Mr.Lorrie and Miss. Pros.

The last words spelled by Sydney Cartoon were:

"It is a far, far better thing that Ido, thanI have ever done; it is a far, far better rest that I go to than I have ever known"(TTC.P288)

Mr. Sydney carton was made to cut down his head in the place of Darney.Lucie came to know about the real fact happened and remembered about the promise given by Sydney to her.

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# రాయలసీమ కరువుసంస్కృతి

## (మొలకల పున్నమి - వింజమూరుగారికి)

[redacted]

మానవ జీవన విధానం లోని విస్మరణలే సంస్కృతి. ఇది ఒక్కో సమూహానికి ఒక్కో విధంగా వుంటుంది . మానవాళికి ప్రపంచ,దేశ,ప్రాంతీయ సంస్కృతులున్నాయి. ప్రపంచ సంస్కృతి మానవజీవన విధానాన్ని తెలుపుతుంది. దేశ సంస్కృతి మానవ ధర్మాన్ని విస్తరిస్తుంది. ప్రాంతీయ సంస్కృతి మానవ జీవన విధానం నుంచి ఉద్భవిస్తుంది.మనిషి పుట్టుక,గిట్టుక, ఆహారం,విహారం, పండుగలు అయా సందర్భాల్లో మనం అనుసరించే సంప్రదాయాలన్నీ శాస్త్రీయతను ముడివేసుకొని మానవుడు ఆనందంగా, ఆరోగ్యంగా, శాంతియుతంగా జీవించే ధర్మాన్ని బోధిస్తుంటాయి. ఇది దేశసంస్కృతి .

ప్రాంతీయ సంస్కృతుల్లోని పండుగలు, ఆచారాలు, విశ్వాసాలు వాని ఔచిత్యాసంగతుల నుంచి ఉద్భవిస్తాయి.దీనిని భారతదేశంలో వీళ్ళు పుష్కలంగా ఉన్న కోస్తా ప్రాంతం ఆరోగ్యంగా, శాంతియుతంగా,కళలు కళాత్మకంగా కన్పిస్తుంది. వారి ప్రతి సంప్రదాయం లోనూ ఆ పుష్కలత్వం కన్పిస్తుంది. కరువు అనగానే మనకు గుర్తుకొచ్చే ప్రాంతం రాయలసీమ. వీళ్లు కరువై, భూమి చీలలు వారి అన్నిటి ప్రాంతం వారి కళ్ళన్నీ వానమ్మ కోసం ఆకాశంవైపు ఆశగా, అలా ఎదురుచూస్తూవుంటాయి. వీరుపే ప్రతి పనిలోనూ, వీరు ఆచరించే ప్రతి విశ్వాసంలోనూ, జానపద కళల్లోనూ ,జానపదగేయాల్లోనూ,ఊరేగింపుల్లోనూ కరువుదర్శనంనుంచి బయటపడ్డ ఆశ, ప్రయత్నము కన్పిస్తుంది. అదే ఆ ప్రాంత సంస్కృతిగా వెలసింది.

పాపికొండలు సోమశిలదర్శనం,తుంగభద్రగుణ వచ్చిన వందలాది,వేలాది రచనల్లో వింజమూరుగారి రచనలకు ప్రముఖ స్థానం కరువుసీమ వనితయిన అక్కన్నని రచయిత్రి. ఆమె రచన లోపెనుగొండ 8,2014 నుంచి పెనుగొండ 26,2014 వరకు అంతర్జాల పత్రికలో తొలి

పాఠశాల్లో ప్రైవేట్ ట్రావెల్ ట్రావెల్ బోర్డు ద్వారా విక్రయించే టెండర్లలో 150 ని ఇయుంచి పురస్కరించుకొని ఏప్రిల్, 27, 2011 నుంచి మే 7,2011 వరకు అంబేద్కర్ లో పర్యటించారు. వీరి పదవులన్నీ రాయలసీమ పంచ్యాతీని ప్రపంచస్థాయి అక్కడి మర్యాదలన్నీ ముగించుకున్నాయి.ఈ వేదిక నుంచి వచ్చి 2011లో లో కేంద్రపాలిత యుపుంచ్యాంచాన్ని అందుకున్న 13వరు సంపుటి మొలకలుచున్నవి. అన్ని టివిలోనూ అరణ్య, అక్షరాపాలుటాయన్ని గుంటూరి తొంగ మాటలకు ఈ కథలు అవసరాయి. ఈ యుద్ధంలో గెలుపుకోసం కథను ఉన్నంత వాతావరణంలా కన్నంత దేవుడుకోసం; అవిర్భ అక్షరం కారణం కన్నంత పాపాత్ర శక్తులకోసం దిని పొరాడుతూని ఉంటారు.ఈ పొరాటంలా రాయలసీమ పంచ్యాతీలా వినిపిచోయింది . ఈ పొరాటంలని వచ్చిన పంచ్యాతీని ,పాత్రల పేరుచ్యాన్ని పరిశీలించడమే ఈ వ్యాస లక్ష్యం.

**జానపదుల విశ్వాసాలు:**

**యుమాలుస్వామి గుర్తం – జానపద కళారూపం :**

ప్రకృతి విస్మయాన్ని చూసినప్పుడు ,తన మనుగడకోసం దేవుడుమీద భారంనిని అలు ప్రకృతిని , అలు శక్తులను పూజిస్తూ అనేకరకాలైన పండుగలాలు అయుంచి అవి అప్పాంచ్యు పంచ్యాతీలా వినిపిచోయాయి. అందులోది యుమాలుస్వామి గుర్తం.

రాయలసీమలో ప్రసిద్ధిగాంచిన విశ్వాసం కథను చుట్టూ పరిభ్రమిస్తూఉంటుంది. ఏ ఊరులోనే యుమాలుస్వామి గుర్తం తిరుగుతుంటే ఆ ఊరులో కథను ఊడదని ,ఆ పైంటి మంచిది గా ఉంటుందని ఆ పైంటిని వాసుల విశ్వాసం. ఈ జానపద కళారూపాన్ని ప్రదర్శించేవారు పథను బట్టలు ధరించి పెద్దటలుపాగా చుట్టుకొని బలిష్టమైన గుర్రపు ఊరూ తిరుగుతూ విన్యాసాలు చేస్తుంటారు.వారిలో కొన్ని.

1.గుర్రాన్ని తొడుతీయిస్తూ దానిపై మంచి ఇనుకలో మన్ను తూపాయని అందులోవడం.

2.రెండు బాళ్ళను ప్రేక్షకులి పిల్లలు చేయించడం.

3. విప్పులగుండ్ని దాటించడం

4. పెద్దపెద్ద బాధ్యతలను అవది ఉందని తెలిసేలా దాటించడం. ఇక్కడ విన్యాసానికి ప్రాధాన్యత ఇస్తారు. ఈ విషయాన్ని కథారచయిత యామలపల్లి గుర్తు కథలో హృద్యంగా వివరించారు.

**జానపద సంస్కృతి :**

**మానుసంస్కృతి – శిలలండి:**

జానపద సంస్కృతిలో గ్రామదేవతలను పూజించడం. పూజావిధానంలో భాగంగా జాతరలు చేయడం,మ్రొంతులను లలి ఇవ్వడం,ఆ సందర్భంగా వారికథలను వినిపించడం అనాయితీ.ఒక్కో దేవత వెనుక ఒక్కో కథ దాగి ఉంటుంది.కొన్ని జానపద ఇతివృత్తాలైతే, కొన్ని చారిత్రక నేపథ్యం కలవి.ఇందులో అంకాళమ్మకు జరిగే శిలలండి ఉత్సవానికి,నేడు విజయనగరంలో జరిగే పైడితల్లి ఉత్సవాలకు సామ్యత ఉంది.ఈ రెండు అమ్మవారుల చరిత్ర వెనుక చారిత్రక నేపథ్యం కలదు. అంకాళమ్మ వెనుక విజయనర సామ్రాజ్యపు దొరతనం కనిపిస్తుంది.ప్రజల కష్టాలు చూడలేక ఆ ప్రాంతపు సామంతపు ప్రభువు వీరదర్జారెడ్డి రాయల వారసులకు కప్పం కట్టకుండా దండకారుణ్యం నుంచి పిన్నానపికి పోరంగం తప్పించి వీటి ఊరును మర్థించాడు.ఈ నాడు భూగర్భజల పంపిణీ వ్యవస్థ ద్వారా ప్రతి ఇంటికి నీళ్ళు అందించాలన్నది భగీరథమిషన్.నాడి ఇలాంటి వ్యవస్థ ఉందని ఈ కథ వివరిస్తుంది.కప్పం కట్టని కారణంగా వీరభద్రారెడ్డిని బంధించి చంద్రగిరిలోని చెరసాలకు తరలిస్తుండగా, అతని భార్య అంకమ్మ గ్రామస్థులతో కలసి ప్రభువులను ఎదిరిస్తుంది. అపేం పట్టలేక ప్రభువులు వీరభద్రారెడ్డి తలను నరికి చెట్టుకు వేలాడదీసారు. అతని భార్య కూడా అక్కడి తలను వదుక్కుంటుంది. గ్రామం కోసం అసువులు బాసిన అమకు ఆ అరణ్యమధ్యలోనే గుడికట్టించి,ప్రతి పది సంవత్సరాలకు ఒకసారి జాతర నిర్వహిస్తారు. ఆజాతరలో మ్రొక్కుబడి శిలలండి.

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ఎర్రబండిపై ఎక్కిన తరిమానును నిలిపి దాని వివరణ మేకపోతును కొయ్యానికి వేలాడదీసి, ఉరిగించి మూడోరోజు దాన్ని లలి ఇచ్చి ,దానిరక్తంతో శిలను తడుపుతారు. ఈ సందర్భంగా

దున్నపోతుల బలి కూడా జరుగుతుంది. ఇవి సంస్కృతి పల్లేరు బళ్లారి కలుపాయమ్మ జాతర లో కూడా జరుగుతుంది. ఈ ఉత్సవాన్ని 12 మంది ఆ కోమటి జరుపుతారు.ఉత్తరాంధ్ర లోని విజయనగరంలో పైడితల్లి ఉత్సవాల్లో పిరమిడ్‌నిర్మాణం ప్రసిద్ధి. ఇక్కడ చిన్నగా పిరమిడ్‌ను పూజారిని కూర్చోబెడతారు.బలులు లేని ఈ ఉత్సవం సంస్కృతి అదుపెరగకుండు ప్రతీక.

అత్యాధునికమైన స్త్రీదేవతల ఆరాధనలో ఈ మాను సంస్కృతి కన్పిస్తుంది.ఈ మానును పల్లారు బళ్లా,కలుపాయిలో గుడిమాను, విజయనగరం లో పిరిమను,కడపలో తెలుగుడి అని పిలుస్తున్నారు. ఈ మానుకు క్రమంగా నేవ,చింత,తాటి మానులను ఉపయోగించారు. ఈ దేవతల గుడులన్నీ అరణ్య ప్రాంతాల్లోని మిరప పొలమధ్యలో ప్రత్యేకత.

జంతువులను బలివ్వడం అనాదిగానున్నా వేటికి ఈ ఆచారం గ్రామక్షేమాల శాంతి కోసం ఈ మూఢ విశ్వాసం కొనసాగుతూనే ఉంది. జంతుబలులో కాదు బలిదానాల సంస్కృతి కన్పిస్తోంది. " ఫలాలు కష్టాలు పోవాలి.. పాపాలు పోవాలి..కన్నీళ్లు పోవాలి..పిల్ల ... పిల్ల...కు 68 / 350 నిలుపా తడవాలి,పెరుగు నిండాలి,పంటలు పండాలి.. కరువుపోవాలి..మాండుసిరి పాలు, ఎన్ని నా అమ్మ బలిదానం పిచ్చో..పిచ్చో.. అన్ని." అని 'మాండవ్యం' కథలో ఊరిలాగు కోసం, వాని కోసం పార్వతి బలిదానం కన్పిస్తుంది.

**చారిత్రక సంస్కృతి :**

చారిత్రాత్మక కట్టడాలు, చరిత్రకు సాక్ష్యాలైన కట్టడాలు అయా దేశ ప్రాంత చరిత్రను తెలియజేస్తుంటాయి.తాతమాలే మనదేశ సంస్కృతికి చిహ్నం. అలాగే ఏడు లాంతర్ల సెంటరు', 'దీపమాను' (కథలు)లు రాయలసీమ చరిత్రకు చిహ్నాలు.

**ఏడు లాంతర్ల సెంటరు:**

దొరల అత్యాచారాలకు, దేశ ప్రజల స్వాతంత్ర్య కాంక్షకు ఈ సెంటరు ప్రత్యక్ష సాక్ష్యం.దొరల మాటనని వారి వరలలులు,ఉరిశిక్షలు, గాంధీజీ దేశభక్తి ప్రసంగాలకు ఇది నిదర్శన సాక్ష్యం. స్వాతంత్ర్యోద్యమ కాలంలో వెల్లదొర గుర్రపు బండిని వదిలేసాడు వీరనాయుడు. గాంధీజీ ప్రసంగాలతో స్ఫూర్తిని నింపుకున్న వీరనాయుడు శ్వేత ఇండియా అంటూ దొరలండిపై నుంచే భారతదేశ జాతీయతాభావాన్ని ఏడులాంతర్ల సెంటరుపై గుర్తించము. అతనిని దొర కాల్చడముజరిగిపోయాయి. దీనికి ప్రత్యక్ష

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పాశ్చాత్యం ఇది విడిచి పోయింది. భారతీయుడి అహింసా సిద్ధాంతానికి, వ్యవహార హింసావాదానికి ఇది ప్రతీక. వీరాయుడికి దొరను చంపే అవకాశమున్నా చంపలేదు. భారతీయుడు బానిసత్వాన్ని చంపి స్వాతంత్ర్యాయువులు పీల్చాలనుకున్నాడు .కాని వ్యవహారం మనుషులను చంపాలనుకున్న హింసావాది. భారతీయ శాంతి సంస్కృతికి ఇది చిహ్నం.

**దీపమాను:**

లేనివాడికి అన్నం పెట్టడం, చిలువ పిదలనివాడికి పిడకల్నించడం,కష్టం లో ఉన్నవాడిని కాపాడడం, భారతీయ సంస్కృతిలో భాగం.కొన్ని సంవత్సరాల క్రితం కూడా పల్లెల్లో ఉన్న కుటుంబాలు పిల్లలకు పాలుమార్చి పోయడం, పిడ్డలువ్య పెట్టడం,ఇ సంస్కృతిలో భాగాలుగా కన్పిస్తుంటాయి. ఇలాంటి ఔదార్యాన్ని తెలిపే కథ లో ఇంత సంగతేది పెట్టి గండి పోసింది ఆ రాతిమడ. ప్రజల సంక్షేమం కోసం తనను తాను కూల్చుకున్న ఇనివృక్షం రాతిమడది. దీని యజమాని పీర శివారెడ్డి.అపరకర్ణుడు. ఎడ్డల పందెం లో గెలిచిన అరుగూర్ల పుట్ట పడ్డను పీదలకు పంచిన మహానీయుడు. కరువు రక్కసి మంచి తన ఊరి కాపాడడం కోసం ప్రాణత్యాగం కాలవ తవ్వించిన మహనీయుడు. చివరకు తనకు పంతాదారుగా వచ్చిన రాతిమడను పీదల ఆకలి తీర్చడానికి కూల్చి, కూలిన వ్యక్తి వీరశివారెడ్డి. అవ్యక్తి కి గుర్తుగా ఆ వ్యక్తి సమాధిని కోవెలగా, ఆ తీపుని సంకేతంగా ఆ సమాధిలో దీపం ఎప్పుడూ ఆరి పోకుండా చూసుకుంటూ ఉంటారు. అది వెలుగొంది ఆ సమాధి దీపమానుగా ప్రసిద్ధికెక్కింది.

**ఆధునిక సంస్కృతి:**

ఎన్ని మార్పులు వచ్చి పోతి తరాల్లో కరువులో ఎండి పీలలు వారిన వారి జీవితాన్ని చదువు వెక్కిరించే దిగులిను దేనుకోవాలన్న వారి ఆశలపై ఆధునికతనాగరికత పీడుతో విష సంస్కృతి నేటి యువతపై కోరలు చాచి ఎలా విషం చిమ్ముతుందో మూడు పదన్ల వాన దృశ్యమానం చేస్తోంది. ఈ కథ భూమిమ్మి పీజాల కోసం, ఖర్చుల కోసమని తనకు వచ్చే కోడుకు నిరంజన్ దారి చూసి నివ్వెరపోయాడు "జలపాలు చెవుల మీద నుండి మెడలు మీద నుండి దుజాలను తాకి గాలికి వినుడుగా కదులుతున్నాయి. ఎడమ చెవి తమ్మకు బంగారు కమ్మకు తళుక్కుమంది. అంతేకాక

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మనసు కళ్ళుక్కుమంది. తొడలదాక గోర్లోల మాదిరి చేతులులేని మందం చొక్కా చేతిలో పిల్లోనీ.. వేర్లలో ఏ గుల్కా లాంటిదో నములు కళ్ళముందు విరంజనీ'.

మారిపోయిన కొడుకును చూసి తన ఆశలన్నీ ఎటుపోతుయాయో తెలియని నాన్నతో ఇలా లేక పోతే ఎక్కడి సమాజము అలగీకరించాడదు అన్న కొడుకుది మరో సమస్య. మారుతున్న సమాజంలో ఏది మంచో, ఏది చెడో తెలుసుకోలేక తప్పు దోవ పడుతున్న యువత కథే ఇది. ప్రతిదకు గుర్తింపును, అందుకోవాల్సిన సాంకేతికపరిజ్ఞానాన్ని అందుకోకుండా, లాభా పొందడానికి ప్రాధాన్యత ఇవ్వడం, చెడు అలవాట్లకు బానిసలు కావడం, మొదలైన అంశాలను కథా రచయిత చర్చించాడు.

తనకున్నదంతా అమ్మి కూతురి పెళ్లిచేసి, కొడుకును అమెరికా పంపడానికి పెచ్చిస్తే, కొడుకు ఇతరుల చేతిలో మోస పోయి మోసపోయిన కొడుకు వృత్తాంతం. నేటి ఆధునిక విష సంస్కృతి అమాయకులైన కాయలసీమ విద్యార్థులను ఎలా ఆకర్షించి మోసంచేస్తుందో తెలియవస్తుంది.

**పండుగ సంస్కృతి – మొలకల పున్నమి:**

ఈ కథా సంపుటి మొత్తం లో కదువుతో వానతో సంబంధం లేకుండా కనిపించే కథ మొలకల పున్నమి' . ప్రేమ కథ ఇవ్వగ్రాంతంతో పాటు మొలకల పున్నమి పండుగను వివరించాడు కథా రచయిత . గోదమ్మ ర్యాడం, కోలన్నకర్రాలాట(కోలాటం),చెక్కభజనలు ,కులుకరజనులు . ఇవన్నీ కానవిదుల వరలంతా ఏనిమిది రాత్రి వినోదం కోసం వేస్తుకునే కళారూపాలు . వీటన్నింటిని పండుగ వాతావరణంలో ఆనందంగా ప్రదర్శించే కళారూపాలు.

మొలకల పున్నమి పెద్దలాని అడపిల్ల చేసే పండుగ . పుట్టమట్టినిచ్చి నవధాన్యాలతో మొలకలు తెప్పించి,వాటిని గంగమ్మ దేవాలయంలోనికి తెస్తారు. వానలిచ్చిన దియ్యంలో వళ్ల నూగులు,బియ్యం కలిపి ప్రసాదంగా పంచుకుంటారు. మర్థి ప్రమిదల్లో దీపాలు వెలిగించి ఇష్టమైన వారితో వివాహం వివాహం జరగాలని వాటిని నీటిలో వదులుతారు.ఈ సందర్భం లో అనేక జానపద గీతాలను ఆలపిస్తూఉంటారు. ఇదే మొలకల పున్నమి.

**ముగింపు:**

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తెలుగు కథానిక మొదటినుంచి సమాజాన్ని ప్రజాస్వామ్యీకరణ చేయడానికి కృషి చేస్తోంది. గిడసబారిపోయిన మానవ జీవితాన్ని, సమాజాన్ని అజ్ఞానం లోనుంచి జ్ఞానం లోకి, చీకటి లోనుంచి వెలుగులోకి, అసమానత్వంలోనుంచి సమానత్వం లోకి నడిపించడానికి కృషి చేస్తూనే ఉంది. అందులో ని కొన్ని దారిచ్చేగులే వేంపల్లి గంగాధర్ రచనలు.కనుకమేము లాంటి రాయలసీమనను ఏంటిసిమా మార్చాలనే ఆకాంక్ష వీరి రచనల్లో కన్పిస్తుంది.వీరిరచనలు సామాజిక చైతన్యంతో పాటు ఆ ప్రాంత సంస్కృతిని,చారిత్రక నేపథ్యాన్ని ప్రతిబింబిస్తూ ఉంటాయి.

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# Utilization of Library and Information Resources in Government and Aided Degree Colleges in SPSR Nellore District Andhra Pradesh: A Study

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**ABSTRACT**

*In this paper I studied usage of library and information resources of in Government and Aided Degree Colleges in SPSR Nellore District in Andhra Pradesh, distributed 2000 questionnaires in colleges and collected 1862 questionnaires. I found in this study the library information resources, services (electronic & print), and library expressed their opinion about library working hours, physical facility, library information resources and services excellent and good.*

**KEYWORDS:** Academic libraries, Government and Aided Degree Colleges, Library and Information resources, Library physical facilities.

## INTRODUCTION

Libraries and information centres play a major role in information transfer cycle. The role of the college libraries is not any limited to the presentation of reading materials but also to ensure that the information needs of the users are met by its own traditional as well as electronic resources and services.

In order to know to what extent the information needs are met by Degree college libraries it is necessary to have a continuous feedback from the students can be obtained by conducting user surveys. The surveys examine the awareness of the students about library resources and services, the use of these resources and services and either satisfaction with them. They also examine to what extent the information needs or the students are met by Degree college libraries. The feedback obtained form them can be used to develop the library collection, to improve the

existing library services, to innovate new services and a plan for future. It is also helpful to orient library and information services to user requirements and to evaluate the resources and service.

## ROLE OF LIBRARIES IN EDUCATION

Recent changes in Educational Philosophy, widening curricula, reforms in examination system, Knowledge explosion and the developments in Information Technology have given an increased awareness of the role of libraries in higher education. College libraries are now to be considered an important resource existing to support the teaching-learning process. So, college libraries should collect and organize relevant information recorded in various print and non-print media and should provide right information to the users at the right time in the educational process. If the colleges are to take maximum possible advantage of the developments in library profession to the greatest benefit of the teachers and students, it is to be ensured that colleges have efficient library systems and qualified and experienced librarians capable of interactions with teachers and students effectively to direct the policies and regulate resources of the library towards the needs of teaching – learning process in the college (Raman Nair, 1996).

**Information Resources and Services:** Information is an important and key resource and an essential input for all. Types of organizations libraries have limited resources with which they have to satisfy the information needs of the users. Therefore, libraries have to build their collections and facilities to meet the requirement s of the users.

The present era is an era of information. Good learning is based upon adequate information. Libraries provide information through their resources and services. Hence libraries particularly academic libraries are playing vital role in shaping a future generation of students by providing required information to them.

## CATEGORIES OF INFORMATION SOURCES

**Primary:** Primary publications are those in which the author for the first--time supplies evidence, describes a discovery, makes or drives a new proposition or brings forward new evidence about previous proposition.

**Secondary:** A document concerning a particular subject of inquiry which is derived from or based on the study and analysis of the primary source of information is called the secondary source of information.

**Tertiary:** Report information that are last to appear and mostly do not contain subject knowledge. It is designed to provide information about information and so acts as a guide to the primary and secondary sources of information.

**Information Needs:** The term information and information needs requires a carful definition. The satisfaction of information seeds however does relate such effect in terms of the individuals receiving and processing of transmitted and previously potentials communication to his needs. However the concept of information need has provided to be exclusive one to define isolate and to measure. Research have been used inter or changeable although they may not be identical. “Krisheals” has defined it as the “recognition of the existence of uncertainty “based on information seeking behavior needs have been categorized as immediate needs or deferred needs.

## LITERATURE OF REVIEWS

**Tripathi (2018)** paper, attempts have been made to identify the Information sources used, for writing thesis or research papers by research scholars. Moreover, this study also examined the researcher’s dependency on Internet, for writing their thesis or research papers. For the study, the survey method was followed by using a well-structured questionnaire. It was identified that, respondents utilizing Information sources namely “E-resources or Internet”

were 62.8%, other's dissertations or thesis were 58.7% and depended on textbooks were 41.5 %. The study concluded that, the there is no significant difference in the researcher's dependency on the Internet for writing thesis/research paper on the respective status of the university.

## Objectives of the Study

The following are the specific objectives of the study.

- To study the extent of use of library resources and services by the students
- To know the purpose of visit to library.
- To examine the students awareness about library resources and services.
- To identify the frequency of use of the library resources and services.
- To find out which library resources are more used between manual and electronic resources.

## SCOPE AND LIMITATIONS OF THE STUDY

This study cover Degree college libraries and students of the Degree colleges, in SPSR Nellore District is Andhra Pradesh. Hence the study has been restricted to Government and Aided Degree College of Nellore District located in the Coastal Andhra Region. As a comprehensive study covering all 9 Government Degree Colleges and 7 Aided Degree are considered for the present study which is presented.

## METHODOLOGY

The basic research method adopted in the present study was the survey method. the present study used questionnaire method to collect data from the Government & Aided Degree Colleges Libraries located in Nellore District. structured questionnaires were developed by the researcher in consultation with the research supervisor for the purpose of this study. I have prepared 2000 questionnaires and personally distributed to the library users of the respective universities and 1862 questionnaires were received from the library users of respected colleges.

### Table-1 Gender-wise distribution of Students

| S.No. | Gender | Students | | Total |
|---|---|---|---|---|
| | | Govt | Aided | |
| 1. | Male | 417(22.39) | 460(24.70) | 877(47.09) |
| 2. | Female | 519(27.87) | 466(25.02) | 985(52.1) |
| **Total** | | **936(50.26)** | **926(9.73)** | **1862(100)** |

It is obvious from Table -1 Out of the total 1862 respondents, 985(52.91%) are female respondents and the remaining 877(47.09%) are female. The proportion of the female respondents was much higher than that of the male.

### Table-2 Branch wise distribution

| S.No. | Branch wise | Students | | Total |
|---|---|---|---|---|
| | | Govt | Aided | |
| 1. | BA | 209(11.22) | 211(1133) | 420(22.56) |
| 2. | BCOM | 323(17.34) | 270(14.50) | 593(31.84) |
| 3. | BSC | 404(21.69) | 445(23.89) | 849(45.59) |
| **Total** | | **936(50.26)** | **926(49.73)** | **1862(100)** |

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From the above table it can be observed that 849(45.59%) are having BSC students, 593(31.84%) are having B. Com students and the remaining 420(22.56%)are having B.A students.

**Table-3: Age Group (years)**

| Age Group | Govt. | | | Aided | | | Total |
|---|---|---|---|---|---|---|---|
| | **B.A** | **B.Com** | **B.Sc.** | **B.A** | **B.Com** | **B.Sc.** | |
| Below 18 | 26(1.39) | 38(2.04) | 50(2.86) | 32(1.71) | 30(1.61) | 63(3.38) | 239(12.83) |
| 18-19 | 68(3.65) | 84(4.51) | 154(8.27) | 48(2.57) | 56(3.00) | 78(4.18) | 488(26.21) |
| 20-21 | 72(3.86) | 136(7.30) | 138(7.41) | 106(5.69) | 118(6.33) | 142(7.62) | 712(38.23) |
| Above 21 | 43(2.31) | 65(3.49) | 62(3.32) | 25(1.34) | 66(3.54) | 162(8.71) | 423(22.71) |
| **Total** | **209(11.22)** | **323(17.34)** | **404(21.69)** | **211(11.33)** | **270(14.50)** | **445(23.89)** | **1862(100)** |

It is evident from Table-3 that the age group of the respondents is are categorized into four groups. A majority of the respondents (students) i.e. 712(38.23) belong to the age group 20-21 years, whereas 488(26.21%) respondents are in the 18-19 years age group, 423(22.71) are students above 21 years and the remaining 239(12.83) respondents are below 18 years. Hence, it can be concluded that majority of the respondents are below 20-21 years age group.

**Table-4: Frequency of visit to the Library for Internet usage**

| visit the Library | Govt. | | | Aided | | | Total |
|---|---|---|---|---|---|---|---|
| | **B.A** | **B.Com** | **B.Sc.** | **B.A** | **B.Com.** | **B.Sc.** | |
| **Daily** | 18(0.96) | 36(1.93) | 86(4.61) | 46(2.47) | 46(2.47) | 64(3.43) | **272(14.61)** |
| **Once in a week** | 35(1.87) | 92(4.94) | 104(5.58) | 56(3.00) | 68(3.65) | 126(6.76) | **481(25.83)** |
| **Twice in a week** | 42(2.25) | 78(4.18) | 118(6.33) | 64(3.43) | 72(3.86) | 96(5.15) | **470(25.24)** |
| **Once in a fortnight** | 24(1.24) | 63(3.38) | 60(3.22) | 42(2.25) | 38(2.04) | 62(3.33) | **289(15.52)** |
| **Once in month** | 58(3.11) | 30(1.61) | 20(1.07) | 18(0.96) | 28(1.50) | 54(2.90) | **208(11.17)** |
| **Occasionally** | 32(1.71) | 14(0.75) | 16(0.85) | 09(0.48) | 18(0.96) | 43(2.31) | **132(7.08)** |
| **Total** | **209(11.22)** | **323(17.34)** | **404(21.69)** | **211(11.33)** | **270(14.50)** | **445(23.89)** | **1862(100)** |

Table-4 shows that 481(25.83) visiting the library once in a week, followed by 470(25.24%) are visiting twice in a week, 289(15.52%) visiting the library Once in a fortnight, 272(14.61%) users who are visiting the library daily and remaining 208(11.17%)of the users visiting the library once in a month.

**Table-5: Time spent in the library**

| Time spent | Govt. | | | Aided | | | Total |
|---|---|---|---|---|---|---|---|
| | B.A | B.Com | BSc | B.A | B.Com | BSc | |
| less than 1 hour | 42(2.25) | 46(2.47) | 86(4.61) | 56(3.00) | 62(3.32) | 174(9.34) | 466(25.02) |
| 1 to 2 hours | 76(4.08) | 132(7.08) | 154(8.27) | 68(3.65) | 82(4.40) | 136(7.30) | 648(34.80) |
| 2 to 3 hours | 54(2.90) | 84(4.51) | 112(6.01) | 32(1.71) | 68(3.65) | 89(4.7) | 439(23.57) |
| 3 to 4 hours | 25(1.34) | 43(2.30) | 28(1.50) | 25(1.34) | 42(2.25) | 28(1.50) | 191(10.25) |
| More than 4 hours | 12(0.64) | 18(0.96) | 24(1.28) | 30(1.61) | 16(0.85) | 18(0.96) | 118(6.33) |
| **Total** | **209(11.22)** | **323(17.34)** | **404(21.69)** | **211(11.33)** | **270(14.50)** | **445(23.89)** | **1862(100)** |

The duration of visit is taken as less than one hour, 1 to 2 hours, 2 to 3 hours, more than 3 hours. From the above table-5 shows that 648(34.80%) of respondents spent time 1 to 2 hours per day in the library, followed by 466(25.02%) spent time less than 1 hour in the library, 439(23.57%) spent time 2 to 3 hours, 191(10.25%) spent time 2 to 3 hours and the remaining 118(6.33) spent time more than 4 hour in the library.

**Table-6: Purpose of visit to library**

| Purpose of visit to library | Govt. | | | Aided | | | Total |
|---|---|---|---|---|---|---|---|
| | B.A | B.Com | B.Sc. | B.A | B.Com. | B.Sc. | |
| To borrow/return books | 72(3.86) | 98(5.26) | 124(6.65) | 42(2.25) | 60(3.22) | 148(7.94) | 544(29.21) |
| To read Newspaper/magazines | 34(1.82) | 82(4.40) | 102(5.47) | 36(1.93) | 54(2.90) | 106(5.69) | 414(22.23) |
| To collect subject specific information | 26(1.39) | 46(2.47) | 56(3.00) | 28(1.50) | 26(1.39) | 56(3.00) | 238(12.78) |
| To use Electronic resources | 18(0.96) | 32(1.71) | 36(1.93) | 24(1.28) | 19(1.02) | 42(2.25) | 171(9.18) |
| To use Internet | 20(1.07) | 28(1.50) | 40(214) | 30(1.61) | 28(1.50) | 23(1.23) | 169(9.07) |

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| | | | | | | | |
|---|---|---|---|---|---|---|---|
| To prepare for Assignments | 21(1.12) | 24(1.28) | 30(1.61) | 28(1.50) | 36(1.93) | 35(1.87) | 174(9.34) |
| To take Photocopies (Xerox) | 12(0.64) | 05(0.26) | 08(0.42) | 12(0.64) | 24(1.28) | 23(1.23) | 84(4.51) |
| Any other (pi. Specify) | 06(0.32) | 08(0.2) | 08(0.42) | 11(0.59) | 23(1.23) | 12(0.64) | 68(3.65) |
| **Total** | **209(11.22)** | **323(17.34)** | **404(21.69)** | **211(11.33)** | **270(14.50)** | **445(23.89)** | **1862(100)** |

Respondents were asked to indicate their main purpose of using Library. From the above table-6 it is seen that the maximum number 544(29.21%) of respondents were borrow/return books purpose, followed by 414(22.23%) of respondents purpose of read Newspaper/magazines, 238(12.78%) of respondents are collect subject specific information, 174(9.34%) respondents are prepare for Assignments, 171(9.18%) respondents are To use Electronic resources, 169(9.07%) respondents are use Internet, 84(4.51%) respondents are To take Photocopies (Xerox) and remaining 68(3.65%) respondents are other information.

**Table-7: frequently do you use the following information sources in your Library**

| **information sources** | **Most Frequently** | **Frequently** | **Occasionally** | **Not at all** | **Total** |
|---|---|---|---|---|---|
| books | 216(11.60) | 108(5.80) | 152(8.16) | - | 476(25.56) |
| Journals | 62(3.32) | 174(9.34) | 86(4.61) | 45(2.41) | 367(19.71) |
| Newspapers/Magazines | 124(6.65) | 168(9.02) | 72(3.86) | 18(0.96) | 382(20.51) |
| Project Reports | 28(1.50) | 36(1.93) | 105(5.64) | 14(0.75) | 183(9.83) |
| Government Publications | 32(1.71) | 48(2.57) | 52(2.79) | 40(2.14) | 172(9.23) |
| E-resources | 74(3.97) | 106(5.69) | 70(3.75) | 32(1.2) | 282(15.14) |
| **Total** | **536(28.81)** | **640(34.41)** | **537(28.87)** | **149(8.01)** | **1862(100)** |

Table-7 indicates that majority of the respondents 476(25.56%) of the respondents are books use information sources in Library , 382(20.51%) of the respondents using Newspapers/Magazines, 367(19.71%) of the respondents are using Journals, 282(15.14)%) of the respondents using e-resources and the remaining respondents using 183(9.83%) are Project Reports/ Government Publications.

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**Table-8: type of e-resources**

| Type of e-Resources | Govt. | | | Aided | | | Total |
|---|---|---|---|---|---|---|---|
| | B.A | B.Com. | B.Sc. | B.A | B.Com | B.Sc. | |
| E- Journals | 48(2.57) | 82(4.40) | 96(5.15) | 56(3.00) | 28(1.50) | 74(3.97) | 384(20.62) |
| E-Books | 36(1.93) | 54(2.0) | 82(4.40) | 34(1.82) | 22(1.18) | 62(3.32) | 290(15.7) |
| Bibliographical Databases | 24(1.34) | 36(1.93) | 76(4.08) | 28(1.50) | 18()0.96 | 64(3.43) | 266(14.28) |
| Full Text Databases | 50(2.68) | 66(3.54) | 68(3.65) | 38(2.04) | 76(4.08) | 56(3.00) | 354(19.01) |
| Open Access Materials | 34(1.82) | 62(3.32) | 46(2.47) | 30(1.61) | 52(2.79) | 80(4.29) | 304(16.32) |
| E-Learning Resources | 17(1.9) | 23(1.23) | 36(1.93) | 25(1.34) | 74(3.97) | 89(4.78) | 264(14.17) |
| **Total** | **209(11.22)** | **323(17.34)** | **404(21.69)** | **211(11.33)** | **270(14.50)** | **445(23.89)** | **1862(100)** |

Table-8 indicates that majority of the respondents 384(20.62%) of the respondents use e-journals followed by 354(19.01%) of the respondents using full-text databases, 304(16.32%) of the respondents using open access materials, 290(15.7%) of the respondents using e-books, 266(14.28%) of the responds using Bibliographical Databases and the remaining respondents using 264(14.17%) of the respondents E-Learning Resources. Hence it can be concluded that one by fourth of the respondents 384(20.62%) of the respondents e-journals using frequently.

## FINDINGS

1. Majority of the users 985(52.91%) are female respondents and the remaining 877(47.09%) are male. The proportion of the female respondents was much higher than that of the male.
2. observed that 849(45.59%) are having BSC students, 593(31.84%)
3. A majority of the respondents (students) i.e. 712(38.23) belong to the age group 20-21 years, whereas 488(26.21%) respondents are in the 18-19 years age group,
4. Majority of the users 481(25.83) visiting the library once in a week , followed by 470(25.24%) are visiting twice in a week, 289(15.52%) visiting the library Once in a fortnight.
5. Majority of the users 648(34.80%) of respondents spent time 1 to 2 hours per day in the library, followed by 466(25.02%) spent time less than 1 hour in the library, 439(23.57%) spent time 2 to 3 hours.
6. Majority of the users 544(29.21%) of respondents were borrow/return books purpose, followed by 414(22.23%) of respondents purpose of read Newspaper/magazines.
7. majority of the respondents 476(25.56%) of the respondents are books use information sources in Library , 382(20.51%) of the respondents using Newspapers/Magazines.
8. majority of the respondents 384(20.62%) of the respondents use e-journals followed by 354(19.01%) of the respondents using full-text databases, 304(16.32%) of the respondents using open access materials.

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## SUGGESTIONS

- To improve for reading, Internet facility, journal and bibliography details.
- More computers required with internet facility in users.
- Training the User for necessary digital literacy skills can bring about knowledge in the use of ICT.
- The libraries are expected to introduce new services like Remote Access, Discovery tools to access to e-resources remotely.

## CONCLUSION

The survey highlighted availability and use of the library information resources and services of the selected degree college libraries in Nellore district, Andhra Pradesh, India and what will be somewhat helpful to the students in communicate realistic education to their present generation for a better tomorrow. In this study majority of library users satisfied on library resources and services of degree college libraries. It provides access to various e-journals, full-text databases, bibliographic databases, etc to the colleges. These resources will provide information in many disciplines for learning, teaching and research in the educational institutions. The following are recommended based on the results of the study.

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# Orange–red fluorescence features of $SrAl_2O_4$: $Sm^{3+}$ phosphors

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A series of $SrAl_2O_4$: $xSm^{3+}$ ($x$ = 0, 0.1, 0.5, 1.0 and 2.0 mol.%) nanophosphors were synthesized by the conventional solid-state reaction method and characterized. The structural and morphological properties were analyzed through powder X-ray diffraction (PXRD), Fourier transform infrared, Fourier transform Raman, scanning electron microscopy and transmission electron microscopy studies. The fluorescence features were examined through photoluminescence-excitation and emission studies. The investigated phosphor materials show intense orange–red fluorescence at 400 nm excitation. For intense and effective fluorescence, the $Sm^{3+}$ -doping concentration was optimized as 1.0 mol.%. The cross-relaxation mechanism responsible for fluorescence quenching beyond the optimum concentration was discussed. The color perception of emitted fluorescence was analyzed by evaluating Commission International de I'Eclairage (CIE) 1931 coordinates. The experimental results confirmed the candidature of orange–red emitting $SrAl_2O_4$: 1.0 $Sm^{3+}$ nanophosphor for various lighting applications.

*Keywords*: Phosphors; powder XRD; fluorescence; optoelectronic devices.

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## 1. Introduction

Currently, the lighting technology is a rapidly growing field that is progressively replacing the old technologies such as incandescent lamps, halogen lamps, fluorescent lamps, discharge lamps, etc. Replacing old technologies with novel and advanced solid-state lighting (SSL) devices could reduce the energy needed for the upcoming generations. The luminescent materials such as crystals, glasses and phosphors based on *f–f* transitions of trivalent rare earth (RE) ions play a significant role in lighting technology. In recent years, single phase phosphors at nanoscale have drawn much attention in the field of SSL technology due to reduction in internal light scattering.[1,2] Such ultra-fine nanophosphors have the potential to improve the efficiency of luminescent displays, fluorescent lamps, etc. The RE ions activated single phase nanophosphors play a crucial role in the design of light emitting diodes (LEDs), field emission displays (FEDs), plasma display panels (PDPs), gas sensors, etc.[3–5]

The synthesis of phosphors by traditional solid-state reaction methods at low sintering temperatures and relatively short calcining time results in considerable mass production. It is known that the fluorescence efficiency could remain very high when the quality of crystalline phase of nanophosphors is certain. Unluckily, most of the techniques that currently fabricate nanophase phosphors, for example, sol–gel, solvothermal, precipitation techniques, etc., are not much efficient for considerable mass production. Compared to borate, silicate, molybdate, vanadate, tungstate, phosphate phosphors, the $SrAl_2O_4$ phosphors show outstanding fluorescence properties due to their excellent ultra-violet (UV) absorption, greater thermo-mechanical behavior, good chemical durability and eco-friendly behavior.[6–8] The importance of $SrAl_2O_4$ nanophosphors crystallized into monoclinic structure for diverse lighting applications has been explored in our previous work.[9,10]

Depending upon the host environment, the $Sm^{3+}$ ions emit intense orange and/or orange–red fluorescence under suitable near UV excitation. In most of the hosts, the fluorescence spectra of $Sm^{3+}$ ions reveal $^4G_{5/2} \rightarrow {}^6H_{5/2}$, $^4G_{5/2} \rightarrow {}^6H_{7/2}$, $^4G_{5/2} \rightarrow {}^6H_{9/2}$ and $^4G_{5/2} \rightarrow {}^6H_{11/2}$ transitions. $Sm^{3+}$-doped $GdAl_3(BO_3)_4$, $Na_2Gd(PO_4)_2$ and $YAl_3(BO_3)_4$ phosphors have been fabricated for orange and/or orange–red fluorescence sources.[11–13] Many other researchers also reported the $Sm^{3+}$-doped $NaGd(MoO_4)(WO_4)$, $Ba_3Y(PO_4)_3$, $CaAl_4O_7$, $CaY_{0.5}Ta_{0.5}O_3$ phosphors, etc., for the red emitting light sources.[14–17] Hingwe *et al.* synthesized $SrAl_2O_4$: Sm phosphor by solution combustion

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method and optically analyzed for red light emitting source.[18] However, it is crucial to develop new class of orange–red exhibiting phosphor materials with superior fluorescence efficiency to meet the needs of current lighting technology. This research paper reports the basic study of fluorescent features of orange–red emitting $SrAl_2O_4:Sm^{3+}$ nanophosphor based on *f–f* transitions of $Sm^{3+}$ ions through structural, morphological and concentration dependent studies for various lighting applications in different fields like scientific research, electronic industry, etc.

## 2. Experimental Techniques

### 2.1. *Materials and method of synthesis*

New class of orange-red emitting $Sr_{(1-x)}Al_2O_4$: $xSm^{3+}$ ($x$ = 0, 0.1, 0.5, 1.0 and 2.0 mol.%) nanophosphors were synthesized by conventional solid-state reaction method. These materials were prepared using stoichiometric ratios of $SrCO_3$ (99%, Sigma), $Al_2O_3$ (99.9%, Himedia) and $Sm_2O_3$ (99.99%, Aldrich) including 2.0 wt.% of $H_3BO_3$ (99.5%, Merck) as a flux material. The homogeneous powders of the starting materials were heat treated at 200 °C for 3 h and then calcined at 1050 °C for 3 h with intermediate grinding to produce milky-white $SrAl_2O_4$: $xSm^{3+}$ nanophosphors. These materials were labeled as SAOSm0, SAOSm01, SAOSm05, SAOSm10 and SAOSm20 for $x$ = 0, 0.1, 0.5, 1.0 and 2.0 mol.%, respectively.

### 2.2. *Characterizations*

The phase purity of SAOSm$x$ nanophosphors was confirmed with X′ Pert-Pro Materials-Research-diffractometer provided with CuK$\alpha$ emission of wavelength 1.5406 Å. The functional groups present were examined by Fourier-transform infra-red (FT-IR) spectral profile recorded with Perkin Elmer Spectrum One: FT-IR spectrometer in the wave length range of 400–4000 $cm^{-1}$ following the KBr pellet method. The Raman analysis was carried out with Bruker RFS27 FT-Raman spectrometer ($\lambda_{Nd:YAG}$ = 1064 nm). The scanning electron microscopy and energy dispersive X-ray (SEM-EDX) investigations were carried out with Hitachi SU-70 scanning electron microscope equipped with Bruker Nano GmbH EDX device. The morphology was studied with FEI TECNAI G2 F20 high-resolution transmission electron microscope (HR-TEM). The photoluminescence excitation and emission studies were carried out with JOBIN YVON FLUOROLOG-3 spectrophotometer equipped with xenon flash lamp (300 < $\lambda$ < 1300 nm). All the characterizations were recorded at room temperature.

## 3. Results and Discussions

The phase purity of SAOSm$x$ nanophosphors has been confirmed by powder X-ray diffraction (PXRD) studies.

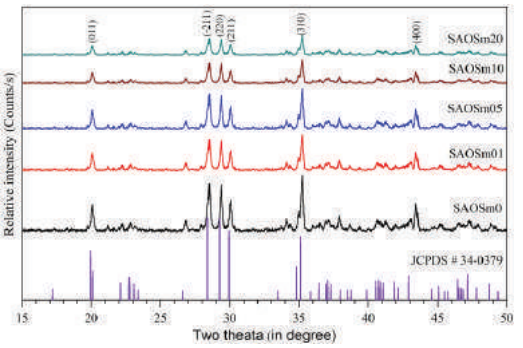



Fig. 1. PXRD patterns for SAOSm$x$ ($0 \le x \le 2.0$ mol.%) nanophosphors.

The studied PXRD patterns shown in Fig. 1 are well matched with JCPDS No. 34-0379.

The synthesized materials are crystallized into monoclinic phase with unit cell parameters, $a$ = 8.4424 Å, $b$ = 8.8221 Å and $c$ = 5.1607 Å.[19] In our previous work, the unit cell parameters have been obtained by Rietveld refinement program (Fullprof software) and they are found to be $a$ = 8.4419 Å, $b$ = 8.8217 Å and $c$ = 5.1592 Å.[20] A schematic representation of packing arrangement of monoclinic SAOSm0 nanophosphor is described in Fig. 2.

As seen from Fig. 1. one can note that the addition of small amounts of $Sm_2O_3$ results a quenching in intensity of PXRD peaks. A detailed explanation for the quenching of intensity of PXRD patterns was presented in our earlier work on $SrAl_2O_4$: $Tb^{3+}/Bi^{3+}$ nanophosphors.[21] The size of SAOSm$x$ crystallites has been predicted as ~58 nm using the Scherrer's equation, $D_{hkl} = 0.9\lambda/\beta \cos\theta$, where $\lambda$ represents the wavelength of X-rays used, $\beta$ represents the full-width at half maximum (FWHM) and $\theta$ represents the angle of diffraction.

The FT-IR spectral profile of SAOSm0 shown in Fig. 3 reveals 13 IR bands at around 3440, 2918, 1713, 1631, 1441, 1365, 1222, 895, 850, 785, 646, 500 and 446 $cm^{-1}$. A broad

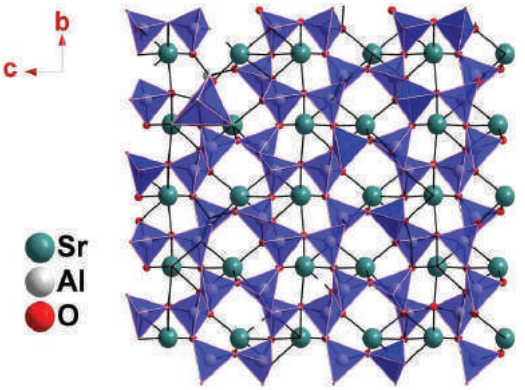



Fig. 2. Packing arrangement of monoclinic SAOSmo.

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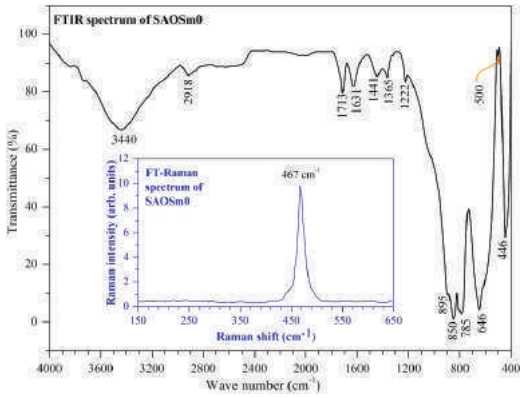



Fig. 3. FT-IR and FT-Raman profiles of SAOSm0.

IR absorption band noticed at 3440 $cm^{-1}$ with a sub-peak at 2918 $cm^{-1}$ has been ascribed to the symmetric stretching vibrations of $OH^{-1}$ group. Two sharp and less intense IR bands at 1713 $cm^{-1}$ and 1631 $cm^{-1}$ have been attributed to the deformation mode of $H_2O$ molecules get absorb in compaction of SAOSm0 with KBr.[22] The IR bands around 1441, 1365 and 1222 $cm^{-1}$ have been assigned to the B-O stretching vibrations.[23] The IR bands noticed at 895 $cm^{-1}$ and 850 $cm^{-1}$ represent the formation of $SrAl_2O_4$, while the band at 785 $cm^{-1}$ belongs to the aluminate ($AlO_4$) group.[24,25] The FT-IR bands located at 646, 500 and 446 $cm^{-1}$ are assigned to the Sr–O, Al–O and O–Al–O vibrations, respectively.[26]

The inset of Fig. 3. represents the FT-Raman spectrum of SAOSm0 and it is analogous to the Raman profile of $SrAl_2O_4$ nanoparticles.[27] The FT-Raman spectrum consists of a sharp band positioned at ~467 $cm^{-1}$ which confirms the monoclinic phase of SAOSm0 nanophosphor. The Raman selection rules explore that nearly 81 active vibrational modes are feasible for $SrAl_2O_4$ monoclinic phase.[28] In this research, the FT-Raman profile of SAOSm0 exhibits nearly ten fever bands in addition to an intense FT-Raman band at 467 $cm^{-1}$ which belongs to O–Al–O bending vibrations.[29] The FT-Raman observations support the FT-IR observations described above. These experimental results confirm the monoclinic phase of SAOSm*x* nanophosphors.

The distribution of particles and the elemental analysis of SAOSm*x* nanophosphors have been examined by SEM-EDX studies of SAOSm10 and it is shown in Fig. 4. The SEM analysis make known a grain like morphology with agglomerated particles distributed homogeneously. The EDX profile make known the presence of oxygen (72.34 atm. wt.%), aluminum (10.53 atm. wt.%), strontium (12.76 atm. wt.%) and samarium (4.37 atm. wt.%) confirming the composition of SAOSm*x* nanophosphors.

The surface morphology of SAOSm0 powder has been investigated by TEM analysis and is shown in Fig. 5. As examined from the TEM image illustrated in Fig. 5(a), the

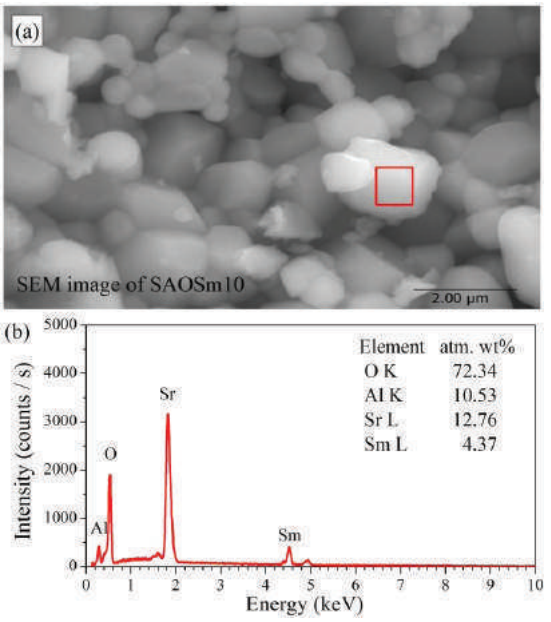



Fig. 4. SEM image (a) and EDX spectrum (b) of SAOSm10 nanophosphor.

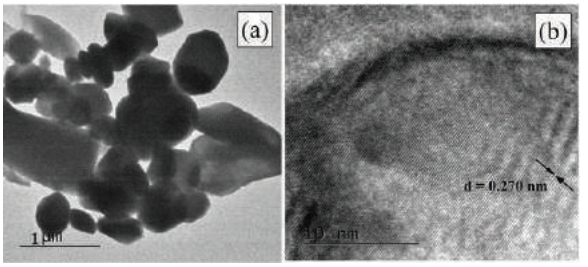



Fig. 5. TEM (a) and HRTEM (b) images of SAOSm0.

average size of the crystallite is estimated to be in the order of hundred nanometers. These results confirm that the studied phosphors have been crystallized into nanoscale. The HR-TEM image shown in Fig. 5(b) provides further insight into the structure of SAOSm*x* nanophosphors. The observed lattice fringes reveal that the distance between the adjacent fringes is estimated to be 0.270 nm which corresponds to the (310) crystal plane of $SrAl_2O_4$ nanophosphors.

The fluorescence features of $Sm^{3+}$ ions in SAOSm*x* nanophosphors have been investigated through photoluminescence excitation (PLE) and emission studies. The PLE spectra monitoring the emission at 603 nm corresponding to $^4G_{5/2} \rightarrow {}^6H_{7/2}$ transition of $Sm^{3+}$ ions reveal thirteen excitation bands owing to $^6H_{5/2} \rightarrow {}^4G_{7/2}$ (334 nm), $^6H_{5/2} \rightarrow {}^4K_{15/2}$ (347 nm), $^6H_{5/2} \rightarrow {}^4F_{9/2}$ (364 nm), $^6H_{5/2} \rightarrow {}^4D_{1/2}$ (377 nm), $^6H_{5/2} \rightarrow {}^4L_{15/2}$ (390 nm), $^6H_{5/2} \rightarrow {}^4L_{13/2}$ (400 nm), $^6H_{5/2} \rightarrow {}^4M_{19/2}$ (419 nm), $^6H_{5/2} \rightarrow {}^4G_{9/2}$ (442 nm), $^6H_{5/2} \rightarrow {}^4I_{18/2}$ (464 nm), $^6H_{5/2} \rightarrow {}^4I_{11/2}$ (471 nm), $^6H_{5/2} \rightarrow {}^4M_{15/2}$ (475 nm), $^6H_{5/2} \rightarrow {}^4I_{9/2}$ (487 nm) and $^6H_{5/2} \rightarrow {}^4G_{7/2}$ (493 nm) transitions.[30] Since

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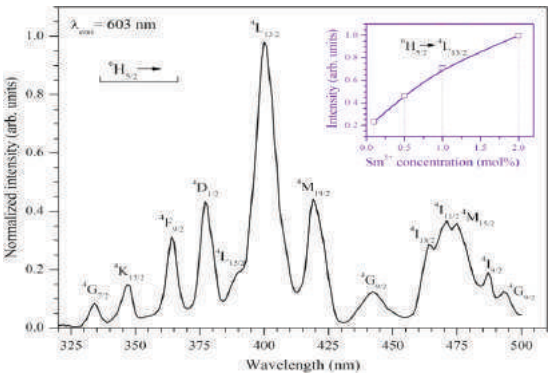



Fig. 6. Excitation spectrum ($\lambda_{emi}$ = 603 nm) of SAOSm10 nanophosphor. Inset is the variation of intensity of $^6H_{5/2} \rightarrow {}^4L_{13/2}$ transitions as a function of $Sm^{3+}$ concentration.

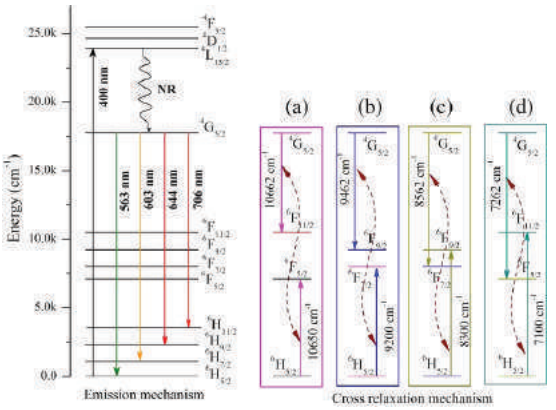



Fig. 8. Partial energy level diagram showing the emission and cross-relaxation mechanisms of $Sm^{3+}$ ions in SAOSm*x* nanophosphors.

the environment around the $Sm^{3+}$ ions and the experimental conditions are the same, the excitation profiles are identical for all the samples under investigation. However, considerable change in intensity of observed excitation bands is noticed. Figure 6 describes the excitation spectral profile of SAOSm10 nanophosphor along with the assignment of excitation bands.

The intensity of excitation bands enhances with the increase of concentration of $Sm^{3+}$ ions. The inset figure described in Fig. 6 shows the deviation of intensity of $^6H_{5/2} \rightarrow {}^4L_{13/2}$ (400 nm) transition versus $Sm^{3+}$ ions concentration. As observed from the PLE profiles, the intensity of $^6H_{5/2} \rightarrow {}^4L_{13/2}$ (400 nm) transition is found to be more prominent than other transitions. Thus, the wavelength related to this PLE transition is more suitable to produce intense and efficient fluorescence from the SAOSm*x* nanophosphors.

The fluorescence spectral features of SAOSm*x* nanophosphors have been studied by exciting at 400 nm wavelength of xenon flash lamp. The emission spectra in the spectral range from 525 nm to 725 nm shown in Fig. 7 exhibit four characteristics transitions of $Sm^{3+}$ ions. The observed emission transitions with peak maximum at around 563, 603, 644 and 706 nm have been ascribed to $^4G_{5/2} \rightarrow {}^6H_{5/2}$, $^4G_{5/2} \rightarrow {}^6H_{7/2}$, $^4G_{5/2} \rightarrow {}^6H_{9/2}$ and $^4G_{5/2} \rightarrow {}^6H_{11/2}$ transitions, respectively.[30]

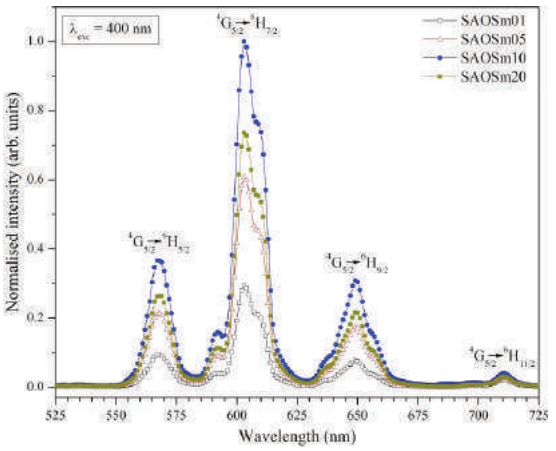



Fig. 7. Emission spectra ($\lambda_{exc}$ = 400 nm) of SAOSm*x* nanophosphors.

Upon 400 nm excitation, the incident light photons stimulate the ground state $Sm^{3+}$ ions resulting to excite them to $^6H_{5/2} \rightarrow {}^4L_{13/2}$ (400 nm) energy level. These excited ions decays quickly to $^4G_{5/2}$ meta-stable level via non-radiative (NR) process. Initially, one of the $Sm^{3+}$ ions at meta-stable level de-excites radiatively to lower energy levels releasing photons via spontaneous emission. The emitted photons trigger the other $Sm^{3+}$ ions at meta-stable level causing stimulated emission through $^4G_{5/2} \rightarrow {}^6H_J$ ($J$ = 5/2, 7/2, 9/2 and 11/2) transitions. The emission mechanism of SAOSm*x* nanophosphors at 400 nm excitation is described in Fig. 8.

The emission spectra of SAOSm*x* nanophosphors are similar to $GdAl_3(BO_3)_4$:$Sm^{3+}$, $Na_2Gd(PO_4)_2$:$Sm^{3+}$, $YAl_3(BO_3)_4$:$Sm^{3+}$ and $CaAl_4O_7$: $Sm^{3+}$ phosphors.[11–13, 15] When compared to $SrAl_2O_4$: Sm phosphor prepared by solution combustion method, this work explores more details on structural and concentration-dependent optical analysis.[18]

The color perception of SAOSm*x* nanophosphors has been investigated by evaluating the Commission International de I'Eclairage (CIE) 1931 coordinates using the emission spectral profiles shown in Fig. 7 and they are found to be (0.598, 0.359), (0.601, 0.360), (0.605, 0.362) and (0.603, 0.365) for SAOSm01, SAOSm05, SAOSm10 and SAOSm20 nanophosphors, respectively. The evaluated chromaticity coordinates of SAOSm10 (0.605, 0.362) are found close to those reported for $Ca_{2.96}Sm_{0.02}Na_{0.02}B_2O_6$ (0.608, 0.365) and $NaSrPO_4$:$Sm^{3+}$ (0.60, 0.39) phosphors.[31, 32]

Figure 9 shows the location of CIE chromaticity coordinates of SAOSm*x* nanophosphors. The CIE-1931 chromaticity diagram of SAOSm*x* nanophosphors shows that the chromaticity coordinates are well located in the orange–red region. The color of emitted fluorescence vary from orange

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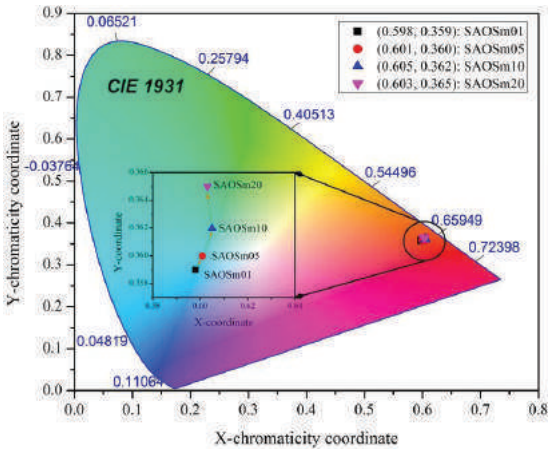



Fig. 9. CIE -1931 chromaticity diagram of SAOSm*x* nanophosphors. Inset shows the tuning of emitted color with $Sm^{3+}$ ions concentration.

for low concentrations i.e. $x = 0.1$ and 0.5 mol.% to orange–red for higher concentrations i.e. $x = 1.0$ and 2.0 mol.%. The inset of Fig. 9 shows the tuning of emitted fluorescence from orange to orange–red region with $Sm^{3+}$ ions concentration. Thus, the SAOSm10 nanophosphor emits intense orange–red fluorescence than the other studied materials.

In order to confirm the orange–red fluorescence of SAOSm10 nanophosphor, its CIE chromaticity coordinates together with the CIE chromaticity coordinates of National Television Standard Committee (NTSC) (0.67, 0.33) and commercial red emitting phosphor $Y_2O_3$:$Eu^{3+}$ (0.655, 0.345) are located in Fig. 10. As seen in CIE 1931 chromaticity diagram, it is clear that compared to the CIE chromaticity coordinates of NTSC and commercial red phosphor, the CIE chromaticity coordinates of SAOSm10 nanophosphor are located in the orange–red region. Thus, the SAOSm10 nanophosphor is more desirable to develop a new class of orange–red emitting phosphors for lighting applications.

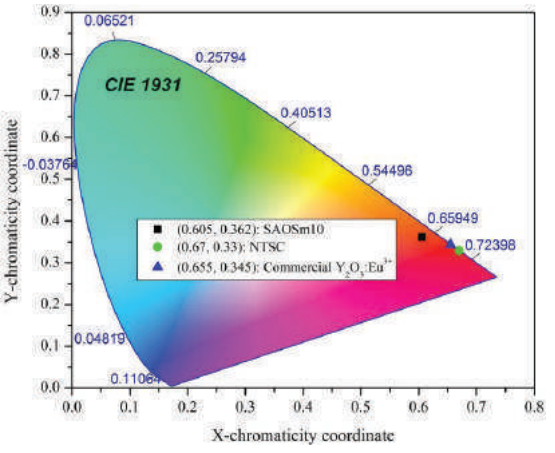



Fig. 10. Location of CIE-1931 chromaticity coordinates of SAOSm10, NTSC and commercial red phosphor.

As seen, the emission spectra shown in Fig. 7, the fluorescence intensity of observed transitions enhance with the addition of concentration of $Sm^{3+}$ ions reaches maximum and then decreases for further increase in concentration leading to fluorescence quenching. In case of SAOSm*x* nanophosphors excited at 400 nm wavelength, fluorescence quenching has been noticed beyond $x = 1.0$ mol.%. In general, for lowest concentrations ($x \leq 0.1$ mol.%), no transfer of energy takes place among the $Sm^{3+}$ ions as the active ions are dispersed at relatively large distances. As long as the concentration of $Sm^{3+}$ ions increases (for example, $0.5 \leq x \leq 1.0$ mol.%), the population of metastable level becomes high enough resulting in intense fluorescence. At higher concentrations ($x > 1.0$ mol.%), the $Sm^{3+}$ ion density ($Sm^{3+}$ ions per unit volume) increases causing NR transitions through exchange or dipole–dipole or dipole–quadrupole or quadrupole–quadrupole interactions among the excited $Sm^{3+}$ ions. These NR transitions are responsible for fluorescence quenching.

The fluorescence quenching at higher $Sm^{3+}$ ions concentration ($x > 1.0$ mol.%) in SAOSm*x* nanophosphors could be due to the transfer of energy among the excited $Sm^{3+}$ ions. One of the possible reasons for the transfer of energy is NR transitions through cross-relaxation mechanism. In case of $Sm^{3+}$ ions, the most promising cross-relaxation channels responsible for fluorescence quenching in SAOSm*x* nanophosphors are shown below and they are illustrated in Fig. 8.

$$\text{(a)}: [{}^4G_{5/2}, {}^6H_{5/2}] \rightarrow [{}^6F_{11/2}, {}^6F_{5/2}],$$

$$\text{(b)}: [{}^4G_{5/2}, {}^6H_{5/2}] \rightarrow [{}^6F_{9/2}, {}^6F_{7/2}],$$

$$\text{(c)}: [{}^4G_{5/2}, {}^6H_{5/2}] \rightarrow [{}^6F_{7/2}, {}^6F_{9/2}],$$

$$\text{(d)}: [{}^4G_{5/2}, {}^6H_{5/2}] \rightarrow [{}^6F_{5/2}, {}^6F_{11/2}].$$

## 4. Conclusions

The $Sm^{3+}$-doped SAOSm*x* ($x = 0, 0.1, 0.5, 1.0$ and 2.0 mol.%) nanophosphors have been synthesized by solid-state reaction method and characterized for lighting applications. The morphological studies show homogeneous distribution of particles that are agglomerated. The HR-TEM results show that the distance between the adjacent fringes is ~0.270 nm corresponding to (310) plane of SAOSm0 nanophosphor. The studied phosphors have been excited effectively at 400 nm wavelength to generate intense orange–red fluorescence. The CIE 1931 chromaticity coordinates of SAOSm10 nanophosphor are found to be (0.605, 0.362) which corresponds to orange–red fluorescence. The experimental results conclude that the SAOSm10 nanophosphor emitting orange–red fluorescence at 400 nm excitation has more potentiality for various lighting applications.

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# Co-Fuzzy Sub Ordered Finite Gamma Near Rings

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## ABSTRACT

***In this paper, we introduce and study the concept of Co-fuzzy sub ordered finite $\Gamma$ - near rings and L-fuzzy sub ordered finite $\Gamma$ - near rings with maximum and infimum conditions, where L stands for a complete lattice satisfying the infinite meet distributive law. We discuss the concept of intersection and union of co-fuzzy sub ordered finite $\Gamma$ - near rings. We also prove theorems on homomorphism of finite $\Gamma$ - near rings.***

***Keywords***— *Fuzzy set, L – Fuzzy set, co-fuzzy sub ordered finite $\Gamma$ - near ring, homomorphism of finite $\Gamma$ - near rings.*

## 1. INTRODUCTION

We know the importance of fuzzy sets. It is being used in different areas like physics, Electronics, Robotics, Computer Languages, Military control, Artificial intelligence, Law, Psychology, Economics and Medical sciences.

The notion of fuzzy set was introduced by Zadeh L.A [12] in 1965 as function from a nonempty set $X$ into $[0,1]$.Goguen[5] further generalized Zadeh definition of a fuzzy subset of $X$ as a mapping of $X$ into a Lattice L. Further more so many authors introduced the fuzzy set concept in algebraic structures, like groups, semi groups, rings and $\Gamma-$near rings etc. The concept of a Gamma – ring, a generalization of a ring was introduced by Nobusawa[4] and was generalized by Barnes. The concept of near ring was introduced by Pilz.G[6]. The common generalization of concepts of Near ring and $\Gamma-$near ring, namely $\Gamma-$near ring was introduced by Satyanarayana. Bh[9][10] and the ideal theory of $\Gamma-$near rings was studied by Satyanarayana.Bh and Booth.G.L[2]. Fuzzy ideals in rings were introduced by Liu.W and they have been studied by several authors.

In this paper, we define Co-Fuzzy sub ordered finite $\Gamma-$near ring. We prove the intersection and union of two Co-Fuzzy sub ordered finite $\Gamma-$near rings theorems. We also prove the homomorphic image and pre-image of Co-Fuzzy sub ordered finite $\Gamma-$near ring is again a Co-Fuzzy sub ordered finite $\Gamma-$near rings. We also prove some necessary and sufficient conditions for a Fuzzy set to be Co-Fuzzy sub ordered finite $\Gamma-$near ring. Throughout this chapter $\mathcal{N}$ stands for finite $\Gamma-$near ring.

## 2. PRELIMINARIES

In this section we recall some of the fundamental definitions, which are necessary for this paper.

**Definition 2.1:** A triplet $(\mathcal{N},+,\cdot)$ is said to be a near ring if

1. $(\mathcal{N},+)$ is a group (Not necessarily abelian group)
2. $(\mathcal{N},\cdot)$ is a semi-group
3. $(a+b)\cdot c = a\cdot c + b\cdot c \;\forall\; a,b,c \in \mathcal{N}$ (Right distribution law).

**Definition 2.2:** A near ring $(\mathcal{N},+,\cdot)$ is said to be finite near ring if $\mathcal{N}$ has finite Number of elements.

**Definition 2.3:** Let $\mathcal{N}$ be a non-empty finite set. If

1. $(\mathcal{N},+)$ is a group. (Not necessarily abelian group)
2. $\Gamma$ is the set of binary operations such that $(\mathcal{N},+,\alpha)$ is a near ring.

Where $\alpha \in \Gamma$.

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3. $a\alpha(b\beta c) = (a\alpha b)\beta c, \forall\ a,b,c \in \mathcal{N}$ and $\alpha,\beta \in \Gamma$.

Then $(\mathcal{N}, +, \Gamma)$ is a finite $\Gamma$ - near ring.

**Example 2.4:** Let G be any finite non-abelian group and $X(\neq \phi)$ be any finite set.

Let N $= \{f / f : X \to G \text{ is a function}\}$

Then $(\mathcal{N}, +)$ is a group with respect to point wise addition of functions, but $(\mathcal{N}, +)$ is not commutative. Let us choose $a, b \in G$ such that $a + b \neq b + a$.

Define $f_a : X \to G$ and

$f_b : X \to G$ such that

$f_a(x) = a$ & $f_b(x) = b\ \forall x \in X$.

$$Then\ (f_a + f_b)(x) = f_a(x) + f_b(x)$$
$$= a + b \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2.4.1)$$

But

$$(f_b + f_a)(x) = f_b(x) + f_a(x)$$
$$= a + b \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2.4.2)$$

From the equations (2.4.1) and (2.4.2),

$$(f_a + f_b)(x) \neq (f_b + f_a)(x)$$
$$f_a + f_b \neq f_b + f_a$$

Thus $(\mathcal{N}, +)$ is a not commutative group.

Now take $\Gamma = \{g / g : G \to X \text{ is a function}\}$

Then by defining $\Gamma : \mathcal{N} \times \mathcal{N} \to \mathcal{N}$ by $f_1 g f_2$ as composition of mappings. Then $(\mathcal{N}, +, \Gamma)$ is a finite $\Gamma$ - near ring.

Clearly,

$$((f_1 + f_2)gf_3)(x) = (f_1 + f_2)(g(f_3(x)))$$
$$= f_1(g(f_3(x))) + f_2(g(f_3(x)))$$
$$= (f_1 g f_3)(x) + (f_2 g f_3)(x)$$
$$= (f_1 g f_3 + f_2 g f_3)(x)$$

$\forall x \in X, f_1, f_2, f_3 \in \mathcal{N}$ and $g \in \Gamma$

i.e., $(f_1 + f_2)gf_3 = f_1 g f_3 + f_2 g f_3$

i.e., the right distribution law hold in $\mathcal{N}$.

But left distribution law is not satisfied in $\mathcal{N}$.

Let us take $z_0(\neq 0) \in G$

Define $f_1 : X \to G$ such that $f_1(x) = z_0, \forall x \in X$ *and* $g : G \to X$ *such that* $g(x) = u, \forall x \in G$

Where $u \in X$

Now $(f_1 g(f_2 + f_3))(x) = z_0 \ldots\ldots (2.4.3)$

But

$$(f_1 g f_2 + f_1 g f_3)(x) = (f_1 g f_2)(x) + (f_1 g f_3)(x)$$
$$= f_1(g(f_2(x))) + f_1(g(f_3(x)))$$
$$= f_1(u) + f_1(u) = z_0 + z_0 ----------- (2.4.4)$$

From equations (2.4.3) and (2.4.4),

$(f_1 g(f_2 + f_3))(x) \neq (f_1 g f_2 + f_1 g f_3)(x)$.

Clearly

$f_1 g_1 (f_2 g_2 f_3) = (f_1 g_1 f_2) g_2 f_3$ holds in $\mathcal{N}$ with respect to composition of functions

Hence $(\mathcal{N}, +, \Gamma)$ is a finite $\Gamma$ – near ring.

**Definition 2.5 :** Let $(\mathcal{N}, +, \Gamma)$ is a finite $\Gamma$ –near ring. Then a subset S of $\mathcal{N}$ is said to be sub $\Gamma$ –

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near ring of $(\mathcal{N}, +, \Gamma)$, if

1. $x + y \in S$
2. $x\alpha y \in S, \forall x, y \in S \text{ and } \alpha \in \Gamma$

**Definition 2.6:** A non-empty set P is said to be POSET (partial ordering set), if there exists a relation $\leq$ on P such that

1. $a \leq a$
2. $a \leq b \text{ and } b \leq a \Rightarrow a = b$
3. $a \leq b, b \leq c \Rightarrow a \leq c \ \forall a, b, c \in P$

**Definition 2.7 :** Finite $\Gamma$ - near ring $\mathcal{N}$ is said to be finite ordered $\Gamma$ - near ring , if $(\mathcal{N}, \leq)$ is a POSET.

**Definition 2.8: A** POSET L is said to be a lattice if every two elements $a, b \in L$ have suprimum and infimum. Generally, we denote

$$\sup\{a, b\} = a \vee b$$

$$Inf\{a, b\} = a \wedge b$$

Where $\vee, \wedge$ are respectively called join and meet.

**Definition 2.9:** If every non empty sub set of lattice L has suprimum and inifimum then L is called complete lattice.

**Definition 2.10:** If X be a non-empty set and $f : X \to [0,1]$ is a mapping then the pair $(X, f)$ is called fuzzy set and $f$ is called fuzzy sub set of X.If $[0,1] = L$ where L stands for lattice then $f$ is called L - fuzzy sub set of X. It is denoted by $f_L$.

**Definition 2.11:** Let X be a non empty set and L is a lattice. If $f_L : X \to L$ is a mapping then $f_L$ is Called L-fuzzy sub set of X.

**Definition 2.12:** Let $f_L$ be a L - fuzzy sub set of X. The set $\{x \in X / f_L(x) < s\}$.Where $s \in L$ is called level sub set of $f_L$. It is denoted by $f_s$.

This $f_s$ is called $s$ - cut of $f_L$.

$$\therefore f_s = \{x \in X / f(x) < s\}$$

**Definition 2.13:** Let $f_L \text{ and } g_L$ be two L-fuzzy sub sets of X. If $f_L(x) \leq g_L(x)$, $\forall x \in X$ then $f_L$ is said to be contained in $g_L$. It is denoted by $f_L \subseteq g_L$.

## 3. CO-FUZZY SUB ORDERED FINITE $\Gamma$ - NEAR RING

In this section we define the intersection and union of co-fuzzy sub sets of non-empty set $X$. We prove the intersection of two co-fuzzy sub ordered finite $\Gamma$ - near rings is also co-fuzzy sub ordered finite $\Gamma$ - near ring. But the union of two co-fuzzy sub ordered finite $\Gamma$ - near rings need not be co-fuzzy sub ordered finite $\Gamma$ - near ring and also, we give suitable illustrations.

**Definition 3.1:** Let $f \text{ and } g$ be two fuzzy sub sets of $X$. Then their intersection and union are denoted by $f \cap g \text{ and } f \cup g$ respectively and defined as follows

$$(f \cap g)(x) = \min\{f(x), g(x)\}$$

and

$$(f \cup g)(x) = \max\{f(x), g(x)\}$$

**Definition 3.2:** For any sub set A of a set $X$, the co-fuzzy characteristic set $\delta_A$ is defined as follows

$$\delta_A = \begin{cases} 0 & if \ x \in A \\ 1 & if \ x \notin A \end{cases}$$

**Definition 3.3:** Let $M_1 \text{ and } M_2$ be two non-empty sets and $\mu : M_1 \to M_2$ is a mapping. If $f$ is a fuzzy sub set of $M_1$ then $g$ be a fuzzy sub set of $M_2$ defined by

$$g(y) = \begin{cases} \underset{z \in \mu^{-1}(y)}{Inf} f(z) & if \ \mu^{-1}(y) \neq \phi \\ 0 & if \ \mu^{-1}(y) = \phi \end{cases}$$

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Where $\mu^{-1}(y)=\{x\in M_1 / \mu(x)=y\}$

If $g$ is fuzzy sub set of $M_2$ then $f$ be a fuzzy sub set of $M_1$ defined by

$$f(x)=g(\mu(x)),\ \forall x\in M_1$$

**Definition 3.4:** Let $f$ be a fuzzy sub set of finite ordered $\Gamma$ - near ring $(\mathcal{N},+,\Gamma)$. Then $f$ is said to be co-fuzzy sub ordered finite $\Gamma$ - near ring of $(\mathcal{N},+,\Gamma)$, if

1. $f(x+y)\le \max\{f(x),f(y)\}$
2. $f(x\alpha y)\le \max\{f(x),f(y)\}$
3. $x\le y\Rightarrow f(x)\le f(y),\ \forall x,y\in\mathcal{N}$ and $\alpha\in\Gamma$

**Definition 3.5:** Let $f_L$ be a L-fuzzy sub set of a finite ordered $\Gamma$ - near ring $(\mathcal{N},+,\Gamma)$. Then $f_L$ is Said be a co-fuzzy sub ordered finite $\Gamma$ - near ring of $(\mathcal{N},+,\Gamma)$, If

1. $f_L(x+y)\le f_L(x)\vee f_L(y)$
2. $f_L(x\alpha y)\le f_L(x)\vee f_L(y)$
3. $x\le y\Rightarrow f_L(x)\le f_L(y)$ , $\forall x,y\in\mathcal{N}$ and $\alpha\in\Gamma$.

**Example 3.6:** Let $S=\{1,2,3,4\}$ and $\mathcal{N}=P(S)$ is the power set of $S$ .Then $\mathcal{N}$ is a group with respect to symmetric difference of two sets.
Where the symmetric difference of two sets A and B is defined as

$$A\Delta B=(A\cup B)-(A\cap B)$$

Let us take $L=\Gamma=\{\{1\},\{2\},\{1,2\},\{1,2,3\}\}$

Define the mapping $\mathcal{N}\times\Gamma\times\mathcal{N}\to\mathcal{N}$, by $A\alpha B$ is the intersection of the sets $A,\alpha,B$. Where $A,B\in\mathcal{N}$ and $\alpha\in\Gamma$.
It is clear that 1. $(\mathcal{N},\Delta,\Gamma)$ is finite $\Gamma$ –near ring.
2. $(\mathcal{N},\subseteq)$ is a poset and $(L,\subseteq)$ is lattice.

Then $(\mathcal{N},\Delta,\Gamma)$ is finite ordered $\Gamma-$ near ring.

Now define $f_L:\mathbf{N}\to L$ such that

$$f_L(A)=\begin{cases}\{1,2,3\} & if\ \ A\neq\phi\\ \phi & if\ \ A=\phi\end{cases}$$ Where $A\in\mathcal{N}$.

Let us take $A,B\in\mathcal{N}$ and $\alpha\in\Gamma$

*Case* $(i)$: *Let* $A\neq\phi,B\neq\phi,A\Delta B\neq\phi,$ *and* $A\alpha B\neq\phi$

$f_L(A)=\{1,2,3\}$ *and* $f_L(B)=\{1,2,3\}$

*and* $f_L(A\Delta B)=\{1,2,3\}$

$f_L(A\alpha B)=\{1,2,3\}$ *and* $f_L(A)\vee f_L(B)=\{1,2,3\}$.

*Case* $(ii)$: *Let* $A\neq\phi,B=\phi$ *then* $A\Delta B=A,$ *and* $A\alpha B=\phi$

$f_L(A)=\{1,2,3\}$ *and* $f_L(B)=\phi$

$f_L(A\Delta B)=\{1,2,3\}$

$f_L(A\alpha B)=\phi$ *and* $f_L(A)\vee f_L(B)=\{1,2,3\}$

*Case* $(iii)$: *Let* $A\neq\phi,B\neq\phi$ *and* $A\Delta B=\phi,$ *and* $A\alpha B\neq\phi$

$f_L(A)=\{1,2,3\}$ *and* $f_L(B)=\{1,2,3\}$

$\therefore f_L(A\Delta B)=\phi,f_L(A\alpha B)=\{1,2,3\}$ *and* $f_L(A)\vee f_L(B)=\{1,2,3\}$

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$Case\ (iv): Let\ A=\phi, B=\phi, Then\ A\Delta B=\phi,\ and\ A\alpha B=\phi$

$f_L(A)=\phi\ and\ f_L(B)=\phi$

$\therefore f_L(A\Delta B)=\phi, f_L(A\alpha B)=\phi\ and\ f_L(A)\vee f_L(B)=\phi.$

$Case\ (v): Let\ A\neq\phi, B\neq\phi\ and\ A\Delta B=\phi, A\alpha B=\phi$

$\therefore f_L(A)=\{1,2,3\}\ and\ f_L(B)=\{1,2,3\}$

$\therefore f_L(A\Delta B)=\phi, f_L(A\alpha B)=\phi\ and\ f_L(A)\vee f_L(B)=\{1,2,3\}$

$Case\ (vi): Let\ A\neq\phi, B\neq\phi\ then\ A\Delta B\neq\phi,\ and\ A\alpha B=\phi$

$f_L(A)=\{1,2,3\}\ and\ f_L(B)=\{1,2,3\}$

$\therefore f_L(A\Delta B)=\{1,2,3\} f_L(A\alpha B)=\phi\ and\ f_L(A)\vee f_L(B)=\{1,2,3\}$

In above all the cases,

1. $f_L(A\Delta B)\leq f_L(A)\vee f_L(B)$
2. $f_L(A\alpha B)\leq f_L(A)\vee f_L(B)$

and it is clear that $A\subseteq B\Rightarrow f_L(A)\subseteq f_L(B)$

Hence $f_L$ is a L - fuzzy sub ordered finite $\Gamma$ - near ring of $(\mathcal{N}, \Delta, \Gamma)$.

Now, we prove a necessary and sufficient condition for $f$ to be a co-fuzzy sub ordered finite $\Gamma-$ near ring.

**Theorem3.7:** Let $f$ be a fuzzy sub set of finite ordered $\Gamma$ - near ring $(\mathcal{N}, +, \Gamma)$. Then $f$ is a co-fuzzy sub ordered finite $\Gamma$ - near ring of $\mathcal{N}$ if and only if for each $\delta\in(0,1]$, the $\delta$ -cut $f_\delta=\{x\in\mathcal{N}\ /f(x)<\delta\}$ is a sub ordered $\Gamma$ - near ring of $\mathcal{N}$.

**Proof:**

Let $f$ be a co-fuzzy sub ordered $\Gamma$ - near ring of $\mathcal{N}$. We need to prove that the $\delta$ - cut $f_\delta=\{x\in\mathcal{N}\ /f(x)<\delta\}$ is a sub ordered $\Gamma$ - near ring of $\mathcal{N}$.

$Let\ x, y\in f_\delta$

$\therefore f(x)<\delta\ and\ f(y)<\delta$

$Now\ f(x+y)\leq\max\{f(x), f(y)\}<\delta$

$\therefore x+y\in f_\delta$

$Let\ x, y\in f_\delta\ and\ \alpha\in\Gamma$

$\therefore f(x\alpha y)\leq\max\{f(x), f(y)\}<\delta$

$\therefore x\alpha y\in f_\delta$

Thus $f_\delta$ is a sub ordered $\Gamma$ - near ring of $\mathcal{N}$.

Conversely assume that $f_\delta$ is a sub ordered $\Gamma$ - near ring of $\mathcal{N}$. for all $\delta\in(0,1]$

We have to prove that $f$ is co-fuzzy sub ordered finite $\Gamma$ - near ring of $\mathcal{N}$.

If possible, let $\exists\ x_0, y_0\in\mathcal{N}$ ∋

$f(x_0+y_0)>\max\{f(x_0), f(y_0)\}$

$Choose\ \delta=\dfrac{f(x_0+y_0)+\max\{f(x_0), f(y_0)\}}{2}$

$\therefore f(x_0+y_0)>\delta\ and\ \max\{f(x_0) f(y_0)\}<\delta$

$\therefore x_0, y_0\in f_\delta\ and\ x_0+y_0\notin f_\delta$

This is a contradiction to the fact that $f_\delta$ is a sub ordered $\Gamma$ - near ring.

$\therefore f(x+y)\leq\max\{f(x), f(y)\}\ \ \forall x, y\in\mathcal{N}$.

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Again, if possible let $\exists\ x_0, y_0 \in \mathcal{N}$. ∋

$$f(x_0 \alpha y_0) > \max\{f(x_0), f(y_0)\} \text{ for some } \alpha \in \Gamma$$

$$\text{Choose } \delta = \frac{f(x_0 \alpha y_0) + \max\{f(x_0), f(y_0)\}}{2}$$

$$\therefore f(x_0 \alpha y_0) > \alpha \text{ and } \max\{f(x_0), f(y_0)\} < \delta$$

$$\therefore x_0 \alpha y_0 \notin f_\delta \text{ and } x_0, y_0 \in f_\delta$$

Which is a contradiction

$\therefore f(x\alpha y) \le \max\{f(x), f(y)\}\ \forall x, y \in \mathcal{N}$ and $\alpha \in \Gamma$

Let $x, y \in \mathcal{N}$ and $x \le y$

If possible, let $f(x) > f(y)$

$\therefore$ choose a $\delta \in (0,1)$ such that $f(x) > \delta > f(y)$

$\therefore x \notin f_\delta$ *and* $y \in f_\delta$

Which is a contradiction

Hence $x \le y \Rightarrow f(x) \le f(y)$

$\therefore\ f$ is a co-fuzzy sub ordered finite $\Gamma$ - near ring of $\mathcal{N}$.

**Theorem3.8:** The intersection of two co-fuzzy sub ordered finite $\Gamma$ - near rings of a finite ordered $\Gamma$ - near ring $(\mathcal{N}, +, \Gamma)$ is a co-fuzzy sub ordered finite $\Gamma$ - near ring of $\mathcal{N}$.

**Proof:**

Let $f$ and $g$ are two co-fuzzy sub ordered finite $\Gamma$ - near rings of finite ordered $\Gamma$ - near ring $(\mathcal{N}, +, \Gamma)$.

We have to show that $(f \cap g)$ is a co-fuzzy sub ordered finite $\Gamma$ - near ring of $\mathcal{N}$.

Let $x, y \in \mathcal{N}$ and $\alpha \in \Gamma$.

$$i.\ (f \cap g)(x+y) = \min\{f(x+y), g(x+y)\}$$
$$\le \min\{\max\{f(x), f(y)\}, \max\{g(x), g(y)\}\}$$
$$= \max\{(f \cap g)(x), (f \cap g)(y)\}$$
$$\therefore (f \cap g)(x+y) \le \max\{(f \cap g)(x), (f \cap g)(y)\}$$

$$ii.\ (f \cap g)(x\alpha y) = \min\{f(x\alpha y), g(x\alpha y)\}$$
$$\le \min\{\max\{f(x), f(y)\}, \max\{g(x), g(y)\}\}$$
$$= \max\{(f \cap g)(x), (f \cap g)(y)\}$$
$$\therefore (f \cap g)(x+y) \le \max\{(f \cap g)(x), (f \cap g)(y)\}$$

*iii. Let* $x, y \in$ N and $x \le y$

$$\therefore f(x) \le f(y) \text{ and } g(x) \le g(y)$$
$$\text{Now } (f \cap g)(x) = \min\{f(x), g(x)\}$$
$$\le \min\{f(y), g(y)\}$$
$$= (f \cap g)(y)$$

Hence $f \cap g$ is a co-fuzzy sub ordered finite $\Gamma$ - near ring of $\mathcal{N}$.

**Theorem 3.9:** The union of two co-fuzzy sub ordered finite $\Gamma$ - near rings of a finite ordered $\Gamma$ - near rings $\mathcal{N}$ is a co-fuzzy sub ordered finite $\Gamma$ - near ring if one is contained in other.

**Proof:** Let $f$ and $g$ be two co-fuzzy sub ordered finite $\Gamma$ - near rings of $\mathcal{N}$ such that $f \subseteq g$ or $g \subseteq f$.

With out less of generality, assume that $f \subseteq g$

i. Let $x, y \in \mathcal{N}$

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$\therefore f(x) \le g(x)$ *and* $f(y) \le g(y)$

$$Now\ (f \cup g)(x+y) = \max\{f(x+y), g(x+y)\}$$
$$\le \max\{\max\{f(x), f(y)\}, \max\{g(x), g(y)\}\}$$
$$\le \max\{\max\{f(x), g(x)\}, \max\{f(y), g(y)\}\}$$
$$= \max\{(f \cup g)(x), (f \cup g)(y)\}$$

ii. Let $x, y \in \mathcal{N}$ and $\alpha \in \Gamma$

$$\therefore (f \cup g)(x\alpha y) = \max\{f(x\alpha y), g(x\alpha y)\}$$
$$\le \max\{\max\{f(x), f(y)\}, \max\{g(x), g(y)\}\}$$
$$\le \max\{\max\{f(x), g(x)\}, \max\{f(y), g(y)\}\}$$
$$= \max\{(f \cup g)(x), (f \cup g)(y)\}$$

iii. let $x, y \in \mathcal{N}$ and $x \le y$

$$\therefore (f \cup g)(x) = \max\{f(x), g(x)\}$$
$$\le \max\{f(y), g(y)\}$$
$$= (f \cup g)(y)$$

Hence $f \cup g$ is a co-fuzzy sub ordered finite $\Gamma$ - near ring of $\mathcal{N}$.

**Note 3.10:**

The converse of the above theorem need not be true, i.e., even if the union of two co-fuzzy sub ordered finite $\Gamma$ - near rings of finite ordered $\Gamma$ - near ring $\mathcal{N}$ is a co-fuzzy sub ordered finite $\Gamma$ - near rings of $\mathcal{N}$, one may not contained in the other.

**Example 3.11:** Let $S = \{1,2,3,4\}$ then $(P(S), \Delta, \Gamma)$ is a finite ordered $\Gamma$ - near ring. Where $\Gamma = \{\{1\}, \{1,2\}\}$

Define $f : P(S) \to [0,1]$ and $g : P(S) \to [0\ 1]$ such that

$$f(A) = \begin{cases} 0.5 & if \quad A \neq \phi \\ 0.4 & if \quad A = \phi \end{cases}$$

and

$$g(A) = \begin{cases} 0.6 & if \quad A \neq \phi \\ 0.3 & if \quad A = \phi \end{cases}$$ are two co-fuzzy sub ordered finite $\Gamma$ - near rings of $(P(S), \Delta, \Gamma)$.

Then clearly $(f \cup g)$ is a co-fuzzy sub ordered finite $\Gamma$ - near ring of $(P(S), \Delta, \Gamma)$. But one is not contained in the other.

i.e., $f \not\subset g$ and $g \not\subset f$.

**Theorem 3.12:**

The necessary and sufficient condition for two level subsets $f_{\delta_1}$ and $f_{\delta_2}$ of a finite ordered $\Gamma$ - near ring $(\mathcal{N}, +, \Gamma)$ are equal is there exists, no $x \in \mathcal{N}$ such that $\delta_1 \le f(x) < \delta_2$.

Where $0 < \delta_1 < \delta_2 \le 1$

**Proof:**

Let the two level subsets $f_{\delta_1}$ and $f_{\delta_2}$ are equal.

Suppose, let $\exists x \in \mathcal{N}$ ,ə $\delta_1 \le f(x) < \delta_2$

$\therefore x \notin f_{\delta_1}$ *and* $x \in f_{\delta_2}$

This is a contradiction to $f_{\delta_1} = f_{\delta_2}$

$\therefore \exists$ no $x \in \mathcal{N}$ ə $\delta_1 \le f(x) < \delta_2$

Conversely assume that $\therefore \exists$ no $x \in \mathcal{N}$ ə $\delta_1 \le f(x) < \delta_2$

Suppose let $f_{\delta_1} \neq f_{\delta_2}$

$\therefore f_{\delta_1} \subset f_{\delta_2}$

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$\Rightarrow$ There exist $x \in f_{\delta_2}$ such that $x \notin f_{\delta_1}$

$\Rightarrow \delta_1 \le f(x) < \delta_2$

This is a contradiction to our assumption

Hence $f_{\delta_1} = f_{\delta_2}$. □

## 4. HOMOMORPHISM OF FINITE ORDERED $\Gamma-$ NEAR RINGS

In this section we define homomorphism between two finite ordered $\Gamma-$ near rings and prove that homomorphic image and pre image of co-fuzzy sub ordered finite $\Gamma-$ near rings are also co-fuzzy sub ordered finite $\Gamma-$ near rings.

**Definition 4.1:** Let $(\mathcal{N}_1, +, \Gamma)$ and $(\mathcal{N}_2, +, \Gamma)$ be two finite ordered $\Gamma$ - near rings and $f: \mathcal{N}_1 \to \mathcal{N}_2$ be a mapping. Then $f$ is said to be homomorphism if

1. $f(a+b) = f(a) + f(b)$
2. $f(a\gamma b) = f(a)\gamma f(b)$
3. $a \le b \Rightarrow f(a) \le f(b)$ , $\forall a,b \in \mathcal{N}_1$ and $\gamma \in \Gamma$

**Definition 4.2:** Let $(\mathcal{N}_1, +, \Gamma_1)$ and $(\mathcal{N}_2, +, \Gamma_2)$ be two finite ordered $\Gamma$ - near rings. $f: \mathcal{N}_1 \to \mathcal{N}_2$ and $g: \Gamma_1 \to \Gamma_2$ be two mappings. Then $(f, g)$ is said to be homomorphism from $\mathcal{N}_1$ to $\mathcal{N}_2$ if

1. $f(a+b) = f(a) + f(b)$
2. $f(a\gamma b) = f(a)g(\gamma)f(b)$
3. $a \le b \Rightarrow f(a) \le f(b)$ , $\forall a,b \in \mathcal{N}_1$ and $\gamma \in \Gamma_1$

**Definition 4.3:** Let $(\mathcal{N}_1, +, \Gamma)$ and $(\mathcal{N}_2, +, \Gamma)$ be two finite ordered $\Gamma$ - near rings and the function $f: \mathcal{N}_1 \to \mathcal{N}_2$ is a homomorphism from $\mathcal{N}_1$ to $\mathcal{N}_2$. If $\mu$ is a fuzzy subset of $\mathcal{N}_1$. Then $f(\mu)$ is a fuzzy subset of $N_2$ defined by

$$(f(\mu))(y) = \begin{cases} \inf_{z \in f^{-1}(y)} \mu(z) & \text{if } f^{-1}(y) \neq \phi \\ 0 & \text{if } f^{-1}(y) = \phi \end{cases} \quad \forall y \in \mathcal{N}_2$$

**Definition 4.4 :** Let $(\mathcal{N}_1, +, \Gamma)$ and $(\mathcal{N}_2, +, \Gamma)$ be two finite ordered $\Gamma$ - near rings and the function $f: \mathcal{N}_1 \to \mathcal{N}_2$ is a homomorphism from $\mathcal{N}_1$ to $\mathcal{N}_2$. If $\sigma$ is a fuzzy subset of $\mathcal{N}_2$, then its inverse image $f^{-1}(\sigma)$ is a fuzzy subset of $\mathcal{N}_1$ defined by

$$(f^{-1}(\sigma))(x) = \sigma(f(x)) \ \forall x \in \mathcal{N}_1$$

Now, we prove some theorems related to homomorphism.

**Theorem 4.5:** Let $(\mathcal{N}_1, +, \Gamma)$ and $(\mathcal{N}_2, +, \Gamma)$ be two finite ordered $\Gamma$ - near rings. The function $f: \mathcal{N}_1 \to \mathcal{N}_2$ is a homomorphism. If $\sigma$ is a co-fuzzy sub ordered finite $\Gamma$ - near ring of $\mathcal{N}_2$, then its inverse image $f^{-1}(\sigma)$ is a co-fuzzy sub ordered finite $\Gamma$ - near ring of $\mathcal{N}_1$.

**Proof:**

Given $f: \mathcal{N}_1 \to \mathcal{N}_2$ is a homomorphism and $\sigma: \mathcal{N}_2 \to [0,1]$ is a co-fuzzy sub ordered finite $\Gamma$ - near ring of $\mathcal{N}_2$.

We have to prove that $f^{-1}(\sigma)$ is a co-fuzzy sub ordered finite $\Gamma$ - near ring of $\mathcal{N}_1$.

Let $x, y \in \mathcal{N}_1$ and $\alpha \in \Gamma$.

$$i.\ (f^{-1}(\sigma))(x+y) = \sigma(f(x+y))$$
$$= \sigma(f(x) + f(y))$$
$$\le \max\{\sigma(f(x)), \sigma(f(y))\}$$
$$= \max\{(f^{-1}(\sigma))(x), (f^{-1}(\sigma))(y)\}$$

$$(f^{-1}(\sigma))(x+y) \le \max\{(f^{-1}(\sigma))(x), (f^{-1}(\sigma))(y)\}$$

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*ii.* $\left(f^{-1}(\sigma)\right)(x\alpha y)=\sigma\left(f(x\alpha y)\right)$

$=\sigma\left(f(x)\alpha f(y)\right)$

$\le \max\left\{\sigma\left(f(x)\right),\sigma\left(f(y)\right)\right\}$

$=\max\left\{\left(f^{-1}(\sigma)\right)(x),\left(f^{-1}(\sigma)\right)(y)\right\}$

$\left(f^{-1}(\sigma)\right)(x\alpha y)\le \max\left\{\left(f^{-1}(\sigma)\right)(x),\left(f^{-1}(\sigma)\right)(y)\right\}$

*iii.* $x\le y \Rightarrow f(x)\le f(y)$

$\Rightarrow \sigma\left(f(x)\right)\le\sigma\left(f(y)\right)$

$\Rightarrow \left(f^{-1}(\sigma)\right)(x)\le\left(f^{-1}(\sigma)\right)(y)$

$x\le y \Rightarrow \left(f^{-1}(\sigma)\right)(x)\le\left(f^{-1}(\sigma)\right)(y)$

Hence $f^{-1}(\sigma)$: $\mathcal{N}_1\to[0,1]$ is a co-fuzzy sub ordered finite Γ - near ring of $\mathcal{N}_1$.

**Theorem 4.6:** Let ( $\mathcal{N}_1$ ,+, Γ ) and ( $\mathcal{N}_2$ ,+, Γ ) be two finite ordered Γ - near rings. The function $f:\mathcal{N}_1\to\mathcal{N}_2$ is an onto homomorphism. If $\mu$ is a co-fuzzy sub ordered finite Γ - near ring of $\mathcal{N}_1$ then it's image $f(\mu)$ is a co-fuzzy sub ordered finite Γ - near ring of $\mathcal{N}_2$.

**Proof:**

Given $f:\mathcal{N}_1\to\mathcal{N}_2$ is an onto homomorphism and $\mu:\mathcal{N}_1\to[0\ 1]$ is a co-fuzzy sub ordered finite Γ - near ring of $\mathcal{N}_1$.

Now we have to prove that $f(\mu)$ is a co-fuzzy sub ordered finite Γ - near ring of $\mathcal{N}_2$ defined by

$$\left(f(\mu)\right)(y)=\begin{cases}\inf\limits_{z\in f^{-1}(y)}\mu(z) & \text{if } f^{-1}(y)\neq\phi\\ 0 & \text{if } f^{-1}(y)=\phi\end{cases}\quad \forall y\in \mathcal{N}_2.$$

Let $x,y\in\mathcal{N}_2$ and $\alpha\in\Gamma$

Since $f$ is onto from $\mathcal{N}_1$ to $\mathcal{N}_2$, $\exists$ $x^1,y^1\in\mathcal{N}_1$, such that $f(x^1)=x$ and $f(y^1)=y$

i. $\left(f(\mu)\right)(x+y)=\inf\limits_{z\in f^{-1}(x+y)}\mu(z)$

*Let* $\mu(x_0)=\inf\limits_{z\in f^{-1}(x)}\mu(z)$ *and* $\mu(y_0)=\inf\limits_{z\in f^{-1}(y)}\mu(z)$

$\therefore f(x_0)=x$ *and* $f(y_0)=y$

*Now* $f(x_0+y_0)=f(x_0)+f(y_0)=x+y$

$x_0+y_0\in f^{-1}(x+y)$

$\therefore \left(f(\mu)\right)(x+y)=\inf\limits_{z\in f^{-1}(x+y)}\mu(z)$

$\le \mu(x_0+y_0)$

$\le \max\left\{\mu(x_0),\mu(y_0)\right\}$

$=\max\left\{\inf\limits_{z\in f^{-1}(x)}\mu(z),\inf\limits_{z\in f^{-1}(y)}\mu(z)\right\}$

$=\max\left\{\left(f(\mu)\right)(x),\left(f(\mu)\right)(y)\right\}$

ii. $\left(f(\mu)\right)(x\alpha y)=\inf\limits_{z\in f^{-1}(x\alpha y)}\mu(z)$

$\le \mu(x_0\alpha y_0)$

$\le \max\left\{\mu(x_0),\mu(y_0)\right\}$

$=\max\left\{\inf\limits_{z\in f^{-1}(x)}\mu(z),\inf\limits_{z\in f^{-1}(y)}\mu(z)\right\}$

$=\max\left\{\left(f(\mu)\right)(x),\left(f(\mu)\right)(y)\right\}$

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iii. $x \le y \Rightarrow f(x) \le f(y)$

$\Rightarrow \inf_{z \in f^{-1}(x)} \mu(z) \le \inf_{z \in f^{-1}(y)} \mu(z)$

$\Rightarrow (f(\mu))(x) \le (f(\mu))(y)$

Hence $f(\mu): \mathcal{N}_2 \to [0,1]$ is a co-fuzzy sub ordered finite $\Gamma-$ near ring of ( $\mathcal{N}_2$, +, $\Gamma$ ). □

**5. CONCLUSION AND FUTURE SCOPE**

In the paper, we proved that the homomorphic image and its pre-image of a co-fuzzy sub ordered finite $\Gamma-$ Near ring is also a co-fuzzy sub ordered finite $\Gamma-$ Near ring. Also the intersection and union of two co-fuzzy sub ordered finite $\Gamma-$ Near rings are co-fuzzy sub ordered finite $\Gamma-$ Near rings under certain conditions. Using this idea we have a scope to develop co-fuzzy ideals in ordered $\Gamma-$ Near rings.

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# CO - FUZZY BI-IDEALS AND CO - FUZZY PRIME IDEALS OF A FINITE Γ- NEAR RINGS

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***Abstract*:** In this paper we introduce and study the concepts of co-fuzzy bi-ideals of a finite $\Gamma$ - near ring and co-fuzzy prime ideals of a finite $\Gamma$ - near ring. We also define normal co-fuzzy bi-ideal and prove its properties. Further we establish a relation between co-fuzzy bi-ideal and principal ideal.

***Keywords***: Fuzzy set, Finite $\Gamma$ - near ring, Bi-ideal, Co-fuzzy bi-ideal, Prime ideal, Co-fuzzy prime ideal, Principal ideal.

## 1. INTRODUCTION:

We know that the concept of fuzzy set was introduced by Zadeh.L.A[1] in 1965 as a function from a non-empty set $X$ into closed interval [0,1]. Later Atanassov.K.T [1,2,3] Gangnen [5] and many mathematicians studied and developed the fuzzy concept. Later it had been introduced in algebraic structures like semi groups, groups, rings and near rings etc. In 1981 Satyanarayana.Bh [7] introduced $\Gamma$ - near rings and introduced the fuzzy set concept in $\Gamma$ - near rings. Swamy.K.L.N and Swamy.U.M [0] studied fuzzy prime ideals of rings. Later Syamprasad.K and Satyanarayana.B[8,9] introduced fuzzy prime ideal in $\Gamma$ - near ring. Further Meenakumari.N and T.Tamizh Chelvam.J [6] introduced the concept of fuzzy bi-ideals in $\Gamma$ - near rings.

Taking the above as origin, in this paper we have introduced co-fuzzy bi-ideal and normal co-fuzzy bi-ideal concepts in finite $\Gamma$ - near ring. We also defined co-fuzzy prime ideal in finite $\Gamma$ - near ring and studied their properties.

## 2. PRELIMINARIES:

In this section we recall some of the fundamental definitions, which are necessary for this paper.

**Definition 2.1:** If $X$ is any non empty set, then a mapping $f : X \to [0,1]$ is called a fuzzy subset of $X$.

**Definition 2.2:** Let $f$ and $g$ be two fuzzy subsets of $X$. If $f(x) \le g(x)$ $\forall x \in X$, then we say that $f$ is contained in $g$ and is denoted by $f \subseteq g$.

**Definition 2.3:** A triplet $(\mathcal{N}, +, .)$ is said to be a near ring, if

1. $(\mathcal{N}, +)$ is a group (Not necessarily abelian)
2. $(\mathcal{N}, .)$ is a semi group
3. $(a+b).c = ab + ac \qquad \forall a, b, c \in \mathcal{N}$.

**Definition 2.4:** Let $\mathcal{N}$ be a finite non-empty set such that

1. $(\mathcal{N}, +)$ is a group (Not necessarily abelian)
2. $\Gamma$ is the set of all binary operations on $\mathcal{N}$. So that $(\mathcal{N}, +, \alpha)$ is a near ring, where $\alpha \in \Gamma$
3. $a\alpha(b\beta c) = (a\alpha b)\beta c \quad \forall a, b, c \in \mathcal{N}$ and $\alpha, \beta \in \Gamma$.

Then the triplet $(\mathcal{N}, +, \Gamma)$ is called a finite $\Gamma$ - near ring.

## 3. CO - FUZZY BI-IDEALS:

In this section we introduce the concept of co-fuzzy bi-ideals and bi-ideals in finite $\Gamma$ - near ring and develop some of their related properties. Also, we introduce normal co-fuzzy bi-ideals in finite $\Gamma$ - near rings and establish related theorems.

**Definition 3.1 :** Let $(\mathcal{N},+,\Gamma)$ is a finite $\Gamma$ - near ring and $f$ is a fuzzy subset of $\mathcal{N}$. Then $f$ is said to be a co-fuzzy bi-ideal of $\mathcal{N}$ if

1. $f(x+y) \le \max\{f(x), f(y)\}$
2. $f(x\alpha y\beta z) \le \max\{f(x), f(z)\} \quad \forall x, y, z \in \mathcal{N}$ and $\alpha, \beta \in \Gamma$

**Definition 3.2 :** Let $A(\neq \phi) \subseteq \mathcal{N}$ is said to be bi-ideal of $\mathcal{N}$ if

1. $x+y \in A \qquad \forall x, y \in A$
2. $x\alpha y\beta z \in A \qquad \forall x, z \in A, y \in \mathcal{N}, \alpha, \beta \in \Gamma$

**Definition 3.3:** If $f$ is a fuzzy subset of a finite $\Gamma$ - near ring $\mathcal{N}$, then the set

$f_t = \{x \in \mathcal{N} / f(x) < t \in [0,1]\}$ is called a level cut of $f$ .

**Definition 3.4 :** Let $f$ be a fuzzy subset of a finite $\Gamma$ - near ring $\mathcal{N}$, then the complement of $f$ is denoted by $f^1$ and defined as $f^1(x) = 1 - f(x), \forall x \in \mathcal{N}$.

**Definition 3.5 :** Let $(\mathcal{N},+,\Gamma)$ be a finite $\Gamma$ - near ring. Then the fuzzy set $f : \mathcal{N} \to [0,1]$ is said to be normal co- fuzzy bi-ideal of $\mathcal{N}$ . If

1. $f(x+y) \le \max\{f(x), f(y)\}$
2. $f(x\alpha y\beta z) \le \max\{f(x), f(z)\} \quad \forall x, y, z \in \mathcal{N}$ and $\alpha, \beta \in \Gamma$
3. $f(0) = 0$

**Definition 3.6:** Let $S = \{1,2,3,4\}$ and $\mathcal{N} = P(S) =$ The power set of $S$ . Then $(\mathcal{N},\Delta,\cap)$ is a finite $\Gamma$ - near ring. Define $f : \mathcal{N} \to [0,1]$ such that

$$f(A) = \begin{cases} 0.7 & if \quad A \neq \phi \\ 0.3 & if \quad A = \phi \end{cases}$$

Then $f$ is a co-fuzzy bi-ideal of $\mathcal{N}$.

**Theorem 3.7:**

Let A be a bi-ideal of a finite $\Gamma$ - near ring $\mathcal{N}$. Then for any $t \in (0,1)$ there exists a co-fuzzy bi-ideal $f$ of $\mathcal{N}$ such that $f_t = A$

**Proof:**

Given A is a bi-ideal of $\mathcal{N}$. Define $f : \mathcal{N} \to [0,1]$ such that

$$f(x) = \begin{cases} 0 & if \quad x \in A \\ t & if \quad x \notin A \end{cases}$$

Now, we prove that $f$ is a co-fuzzy bi-ideal of $\mathcal{N}$.

Let $x, y, z \in \mathcal{N}$ and $\alpha, \beta \in \Gamma$

*I* *i. Let* $x, y \in A$

Then $x+y \in A$ and $f(x) = f(y) = f(x+y) = 0$

$\therefore f(x+y) \le \max\{f(x), f(y)\}$

*ii. Let* $x, y \notin A$

Suppose let $x+y \in A$

Then $f(x+y) = 0, f(x) = f(y) = t$

$\therefore f(x+y) \le \max\{f(x), f(y)\}$

Suppose let $x+y \notin A$

Then $f(x+y)=f(x)=f(y)=t$

$\therefore f(x+y)\le \max\{f(x),f(y)\}$

*iii.* $x\in A$ & $y\notin A$

Then $x+y\notin A$ *and* $f(x+y)=t, f(x)=0, f(y)=t$

$\therefore f(x+y)\le \max\{f(x),f(y)\}$

*II* *i. Let* $x,z\in A$

Then $x\alpha y\beta z\in A$ *and* $f(x)=f(z)=f(x\alpha y\beta z)=0$

$\therefore f(x\alpha y\beta z)\le \max\{f(x),f(z)\}$

*ii. Let* $x,z\notin A$

If suppose $x\alpha y\beta z\notin A$ Then

$f(x\alpha y\beta z)=f(x)=f(z)=t$

$\therefore f(x\alpha y\beta z)\le \max\{f(x),f(z)\}$

If suppose $x\alpha y\beta z\in A$ Then

$f(x\alpha y\beta z)=0$ *and* $f(x)=f(z)=t$

$\therefore f(x\alpha y\beta z)\le \max\{f(x),f(z)\}$

Hence f is a co-fuzzy bi-ideal of $\mathcal{N}$.

Now

$f_t=\{x\in \mathcal{N} / f(x)<t\}$

$=\{x\in \mathcal{N} / f(x)=0\}$

$=A$

**Theorem 3.8:**

The necessary and sufficient condition for a non-empty subset A of a finite $\Gamma$ - near ring $\mathcal{N}$ to be bi-ideal of $\mathcal{N}$ is the fuzzy set $f$ defined by

$f(x)=\begin{cases}0 & if\ x\in A\\ 1 & if\ x\notin A\end{cases}$ is co-fuzzy bi-ideal of $\mathcal{N}$.

**Proof:**

Let A be a bi-ideal of $\mathcal{N}$.

Then by the above theorem (3.7), it is clear that $f$ is a co-fuzzy bi-ideal of $\mathcal{N}$.

Conversely, assume that $f$ is co-fuzzy bi-ideal of $\mathcal{N}$.

We now prove that A is bi-ideal of $\mathcal{N}$.

Let $x,y\in A$

$\therefore f(x)=f(y)=0$

*Now* $f(x+y)\le \max\{f(x),f(y)\}=0$

$\Rightarrow f(x+y)=0$

$\therefore x+y\in A$

Let $x,z\in A, y\in \mathcal{N}$ and $\alpha,\beta\in\Gamma$

$\therefore f(x)=f(z)=0$

*Now* $f(x\alpha y\beta z)\le \max\{f(x),f(z)\}=0$

$\Rightarrow f(x\alpha y\beta z)=0$

$\therefore x\alpha y\beta z\in A$

Thus $A$ is a bi-ideal of $\mathcal{N}$.

**Theorem 3.9:**

Let $f$ be a co-fuzzy bi-ideal of a $\Gamma$ - near ring $\mathcal{N}$. Then $\mathcal{N}_f = \{x \in \mathcal{N} / f(x) = f(0)\}$ is a bi-ideal of $\mathcal{N}$.

**Proof:**

$$Let\ x, y \in \mathcal{N}_f$$

$$\therefore f(y) = f(0), f(x) = f(0)$$

$$Now\ f(x+y) \le \max\{f(x), f(y)\} = f(0)$$

$$f(x+y) \le f(0)$$

$$f(x+y) = f(0)$$

$$\therefore x+y \in \mathcal{N}_f$$

$$Let\ x, z \in \mathcal{N}_f,\ y \in \mathcal{N} \text{ and } \alpha, \beta \in \Gamma$$

$$\therefore f(x) = f(z) = f(0)$$

$$Now\ f(x\alpha y\beta z) \le \max\{f(x), f(z)\} = f(0)$$

$$f(x\alpha y\beta z) = f(0)$$

$$\therefore x\alpha y\beta z \in \mathcal{N}_f$$

Thus $\mathcal{N}_f$ is a bi-ideal of $\mathcal{N}$.

**Theorem 3.10:**

Let $A(\neq \phi) \subseteq \mathcal{N}$, where $\mathcal{N}$ is a finite $\Gamma$ - near ring and a fuzzy set $f_A$ defined by

$$f_A(x) = \begin{cases} p & if\ \ x \in A \\ q & if\ \ x \notin A \end{cases} \quad \forall x \in \mathcal{N}$$

where $p, q \in [0\ 1]$ such that $p < q$. Then $f_A$ is a co-fuzzy bi-ideal of $\mathcal{N}$ iff A is a bi-ideal of $\mathcal{N}$. More over $\mathcal{N}_f = A$

**Proof:**

Let $f_A$ is a co-fuzzy bi-ideal of $\mathcal{N}$.

We have to prove that A is bi-ideal of $\mathcal{N}$

Let $x, y \in A$

$$\therefore f_A(x) = f_A(y) = p$$

Now $f_A(x+y) \le \max\{f_A(x), f_A(y)\} = p$

Since the range of $f_A$ consists only two elements p and q, $f(x+y) \neq p$

$$\therefore f(x+y) = p$$

$$\therefore x+y \in A$$

Let $x, z \in A,\ y \in \mathcal{N}$ and $\alpha, \beta \in \Gamma$

we have $f_A(x) = f_A(z) = p, f_A(y) = q$

Now $f_A(x\alpha y\beta z) \le \max\{f(x), f(z)\} = p$

$$\therefore f_A(x\alpha y\beta z) = p$$

$$\therefore x\alpha y\beta z \in A$$

Thus $A$ is a bi-ideal of $\mathcal{N}$.

Conversely, assume that A is a bi -ideal of $\mathcal{N}$.

In order to prove $f_A$ is a co-fuzzy bi-ideal of $\mathcal{N}$, let as take $x, y, z \in \mathcal{N}$ and $\alpha, \beta \in \Gamma$

**Case I**:

Let $x, y \in A$. Then $x+y \in A$ and $x\alpha z\beta y \in A$

$\therefore f_A(x) = f_A(y) = f_A(x+y) = f_A(x\alpha z\beta y) = p$

$\therefore f_A(x+y) \le \max\{f(x), f(y)\}$

$f_A(x\alpha z\beta y) \le \max\{f_A(x), f_A(y)\}$

**Case II**:

Let $x, y \notin A$ and $x+y \in A$, $x\alpha z\beta y \in A$

Then $f_A(x) = f_A(y) = q$ *and* $f_A(x+y) = f_A(x\alpha z\beta y) = p$

$\therefore f_A(x+y) \le \max\{f_A(x), f_A(y)\}$ and

$f_A(x\alpha z\beta y) \le \max\{f_A(x), f_A(y)\}$

**Case III:**

Let $x, y \notin A$ and one of $x+y \notin A$ and $x\alpha z\beta y \notin A$

$\therefore f_A(x+y) \le \max\{f_A(x), f_A(y)\}$ and

$f_A(x\alpha z\beta y) \le \max\{f_A(x), f_A(y)\}$

**Case IV:**

Let $x, y \notin A$ and $x+y \notin A$, $x\alpha z\beta y \in A$

Then $f_A(x+y) \le Max\{f_A(x), f_A(y)\}$ and

$f_A(x\alpha z\beta y) \le Max\{f_A(x), f_A(y)\}$

**Case V:**

Let $x, y \notin A$ and $x+y \in A$, $x\alpha z\beta y \notin A$

Then $f_A(x+y) \le Max\{f_A(x), f_A(y)\}$ and

$f_A(x\alpha z\beta y) \le Max\{f_A(x), f_A(y)\}$

Thus $f_A$ is a co-fuzzy bi-ideal of $\mathcal{N}$.

Finally $\mathcal{N}_f = \{x \in \mathcal{N} / f(x) = f(0)\}$

Since A is bi-ideal of $\mathcal{N}$, $o \in A$ and Hence $f(0) = p$

$\therefore \mathcal{N}_f = \{x \in \mathcal{N} / f(x) = p\}$

$= A$ □

**Theorem 3.11:**

Let A and B two bi-ideal of $\mathcal{N}$. Then $A \subseteq B$ iff $f_A \supseteq f_B$. Where

$$f_A(x) = \begin{cases} 0 & if \quad x \in A \\ 1 & if \quad x \notin A \end{cases}$$

And

$$f_B(x) = \begin{cases} 0 & if \quad x \in B \\ 1 & if \quad x \notin B \end{cases} \quad for\ all\ x \in \mathcal{N}$$

**Proof:**

Let $A \subseteq B$

Let $x \in \mathcal{N}$

**Case I:** If $x \in A$, then $x \in B$ and $f_A(x) = f_B(x) = 0$

**Case II:** if $x \notin A$, then $x \in B$ *or* $x \notin B$

$\therefore f_A(x) = 1$ and $f_B(x) = 0$ *or* $f_B(x) = 1$

$\therefore f_A \supseteq f_B$

Conversely assume that $f_A \supseteq f_B$

We have to prove that $A \subseteq B$

Let $x \in A$

$\Rightarrow f_A(x) = 0$

$\Rightarrow f_B(x) = 0 \ (\because f_A \geq f_B)$

$\therefore x \in B$

$\therefore A \subseteq B$

Hence the theorem is proved. □

**Theorem 3.12:**

Let $f$ be a fuzzy set of a finite $\Gamma$ - near ring $\mathcal{N}$. Then $f$ is co-fuzzy bi-ideal of $\mathcal{N} \Leftrightarrow$ each level cut $f_s, s \in \mathrm{Im}(f)$ of $f$ is bi-ideal of $\mathcal{N}$.

**Proof:**

Let $f$ be a co-fuzzy bi-ideal of $\mathcal{N}$. We have to prove that $f_s = \{x \in \mathcal{N} / f(x) < s\}$ is bi-ideal of $\mathcal{N}$.

Let $x, y \in f_s$

$\therefore f(x) < s$ and $f(y) < s$

Now $f(x+y) \leq \max\{f(x), f(y)\} < s$

$\therefore x + y \in f_s$.

$\therefore f(x) < s$ and $f(y) < s$

Now $f(x\alpha z\beta y) \leq \max\{f(x), f(y)\} < s$

$\therefore x\alpha z\beta y \in f_s$

Thus $f_s$ is a bi-ideal of $\mathcal{N}$.

Conversely assume that $f_s$ is a bi-ideal of $\mathcal{N}$ for each $s \in \mathrm{Im}(f)$.

To prove $f$ is co-fuzzy bi-ideal of $\mathcal{N}$, let us take $x, y, z \in \mathcal{N}$ and $\alpha, \beta \in \Gamma$

Suppose, let $\exists\ p_0, q_0 \in \mathcal{N}$ such that

$f(p_0 + q_o) > \max\{f(p_0), f(q_0)\}$

Take $s = \dfrac{f(p_0+q_0) + \max\{f(p_0), f(q_0)\}}{2}$

$\therefore s < \dfrac{f(p_0+q_0) + f(p_0+q_0)}{2} = f(p_0+q_0)$ and

$s > \max\{f(p_0), f(q_0)\}$

$\therefore p_0 + q_0 \notin f_s$ and $p_0, q_0 \in f_s$

Which is contradiction

$\therefore f(x+y) \leq \max\{f(x), f(y)\}$

Suppose, let $\exists\ p_0, q_0, r_0 \in \mathcal{N}$ and $\alpha_0, \beta_0 \in \Gamma$ such that

$f(p_0\alpha_0 q_0\beta_0 r_0) > \max\{f(p_0), f(r_0)\}$

Take $s = \dfrac{f(p_0\alpha_0 q_0\beta_0 r_0) + \max\{f(p_0), f(r_0)\}}{2}$

$s < f(p_0\alpha_0 q_0\beta_0 r_0)$ *and* $f(p_0) < s, f(r_0) < s$

$\therefore p_0\alpha_0 q_0\beta_0 r_0 \notin f_s$ *and* $p_0, r_0 \in f_s$

Which is contradiction

$\therefore f(x\alpha y\beta z) \leq \max\{f(x), f(z)\}$

Thus $f$ is co-fuzzy bi-ideal of $\mathcal{N}$.

Hence the theorem is proved. □

**Theorem 3.13:**

If $(\mathcal{N},+,\Gamma)$ is a finite $\Gamma$ - near ring and $f$ is a co-fuzzy bi-ideal of $\mathcal{N}$. Then $f^1$ is also co-fuzzy bi-ideal of $\mathcal{N}$.

**Proof:**

Let $x,y,z \in \mathcal{N}$ and $\alpha,\beta \in \Gamma$ and $f$ is a co-fuzzy bi-ideal of $\mathcal{N}$.

$$(i)\ f^1(x+y) = 1 - f(x+y)$$
$$\leq 1 - \max\{f(x), f(y)\}$$
$$\leq \max\{1-f(x), 1-f(y)\}$$
$$= \max\{f^1(x), f^1(y)\}$$

$$(ii)\ f^1(x\alpha y\beta z) = 1 - f(x\alpha y\beta z)$$
$$\leq 1 - \max\{f(x), f(z)\}$$
$$\leq \max\{1-f(x), 1-f(z)\}$$
$$= \max\{f^1(x), f^1(z)\}$$

Hence $f^1$ is a co-fuzzy bi-ideal of $\mathcal{N}$. □

**Theorem 3.14:**

Let A be a bi-ideal of a finite $\Gamma$ - near ring $\mathcal{N}$. Then the fuzzy set defined by $f_A(x) = \begin{cases} 0 & if \quad x \in A \\ 1 & if \quad x \notin A \end{cases}$ is normal co-fuzzy bi-ideal of $\mathcal{N}$ and $\mathcal{N}_{f_A} = A$.

**Proof:**

By theorem (3.8), $f_A$ is a co-fuzzy bi-ideal of $\mathcal{N}$.

Since $A$ is bi-ideal of $\mathcal{N}$, $0 \in A$

$\therefore$ By the definition of $f_A$, it is clear that $f_A(0) = 0$

$\because$ $f_A$ is normal co-fuzzy bi-ideal of $\mathcal{N}$.

Further more $\mathcal{N}_{f_A} = \{x \in \mathcal{N} / f_A(x) = f_A(0)\}$
$$= \{x \in \mathcal{N} / f_A(x) = 0\}$$
$$= \{x \in \mathcal{N} / x \in A\}$$
$$= A$$

## 4. CO-FUZZY PRIME IDEALS

In this section, we define prime ideal and co-fuzzy prime ideal of a finite $\Gamma$ - near ring and principal ideal and its characteristics. We also prove some theorems related to co-fuzzy prime ideals.

**Definition 4.1:** A sub set $S$ of a finite $\Gamma$-near ring $(\mathcal{N}$ is said to be a left ideal of $\mathcal{N}$ if

1. $x+y \in S, \quad \forall x,y \in S$
2. $y+x-y \in S, \quad \forall x \in S$ and $y \in \mathcal{N}$
3. $a\alpha(x+b) - a\alpha b \in S, \quad \forall x \in S, a,b \in \mathcal{N}$ and $\alpha \in \Gamma$.

**Definition 4.2:** A sub set $S$ of a finite $\Gamma$-near ring $(\mathcal{N},+,\Gamma)$ is said to be a right ideal of $\mathcal{N}$ if

1. $x+y \in S, \quad \forall x,y \in S$
2. $y+x-y \in S, \quad \forall x \in S$ and $y \in \mathcal{N}$
3. $x\alpha a \in S, \quad \forall x \in S, a \in \mathcal{N}$ and $\alpha \in \Gamma$

**Definition 4.3:** A sub set $S$ of a finite $\Gamma$-near ring $(\mathcal{N},+,\Gamma)$ is said to be an ideal of $\mathcal{N}$ if

1. $x+y \in S, \quad \forall x,y \in S$
2. $y+x-y \in S, \quad \forall x \in S$ and $y \in \mathcal{N}$
3. $a\alpha(x+b) - a\alpha b \in S, \forall x \in S, a,b \in \mathcal{N}$ and $\alpha \in \Gamma$
4. $x\alpha a \in S, \quad \forall x \in S, a \in \mathcal{N}$ and $\alpha \in \Gamma$

**Definition 4.4:** A fuzzy sub set $f$ of a finite Γ-near ring $(\mathcal{N},+,\Gamma)$ is said to e a co- fuzzy left ideal of $\mathcal{N}$ if

1. $f(x+y) \le \max\{f(x), f(y)\}$
2. $f(y+x-y) \le f(x)$
3. $f(a\alpha(xb)-a\alpha b) \le f(x), \quad \forall x,y,a,b \in \mathcal{N}$ and $\alpha \in \Gamma$

**Definition 4.5:** A fuzzy sub set $f$ of a finite Γ-near ring $(\mathcal{N},+,\Gamma)$ is said to be a co- fuzzy right ideal of $\mathcal{N}$ if

1. $f(x+y) \le \max\{f(x), f(y)\}$
2. $f(y+x-y) \le f(x)$
3. $f(x\alpha a) \le f(x), \quad \forall x,y,a,b \in \mathcal{N}$ and $\alpha \in \Gamma$

**Definition 4.6:** A fuzzy sub set $f$ of a finite Γ-near ring $(\mathcal{N},+,\Gamma)$ is said to be a co- fuzzy ideal of $\mathcal{N}$ if

1. $f(x+y) \le \max\{f(x), f(y)\}$
2. $f(y+x-y) \le f(x)$
3. $f(a\alpha(x+b)-a\alpha b) \le f(x)$
4. $f(x\alpha a) \le f(x), \quad \forall x,y,a,b \in \mathcal{N}$ and $\alpha \in \Gamma$

**Definition 4.7:** Let $(\mathcal{N},+,\Gamma)$ be a finite $\Gamma$ - near ring. For any two subsets $A$ and $B$ of $\mathcal{N}$, the set $\{x\alpha y / x \in A, y \in B \text{ and } \alpha \in \Gamma\}$ is called product of A and B and is denoted by $A\alpha B$ $(or)$ $AB$.

**Definition 4.8:** Let $(\mathcal{N},+,\Gamma)$ is a finite $\Gamma$ - near ring. An ideal $I$ of $\mathcal{N}$ is said to be prime ideal of $\mathcal{N}$, If for any ideals $A,B \subseteq \mathcal{N}$, $A\gamma B \subseteq I \Rightarrow A \subseteq I$ or $B \subseteq I$, $\forall \gamma \in \Gamma$

**Definition 4.9:** Let $(\mathcal{N},+,\Gamma)$ be a finite $\Gamma$ - near ring and $a \in \mathcal{N}$. An ideal $I$ of $\mathcal{N}$ is said to be principal ideal generated by 'a' if

1. $a \in I$
2. For any ideal $U \subseteq \mathcal{N}$ and $a \in U \Rightarrow I \subseteq U$

The principal ideal generated by 'a' is denoted by $\langle a \rangle$.

**Definition 4.10:** Let $(\mathcal{N},+,\Gamma)$ be a finite $\Gamma$ - near ring. A co-fuzzy ideal ' $f$ ' of $\mathcal{N}$ is said to be co-fuzzy prime ideal of $\mathcal{N}$ if for any co-fuzzy ideals $g$ and $h$, $g\alpha h \subseteq f \Rightarrow g \subseteq f$ $or$ $h \subseteq f$.

$goh : \mathcal{N} \to [0,1]$ is defined as $(goh)(x) = \underset{x=y\alpha z}{Sup\ Inf}\{g(y), h(z)\}$ $\forall x \in \mathcal{N}$.

**Theorem 4.11:**

If $(\mathcal{N},+,\Gamma)$ is a finite $\Gamma$ - near ring and $a \in \mathcal{N}$. Then $\langle a \rangle = \bigcup_{i=0}^{\infty} U_i$, where

$U_0 = \{0\}$ $and$ $U_{k+1} = U_k^{+} \cup U_k^{0} \cup U_k^{++} \cup U_k^{00}$ $\forall k \ge 0$.

And

$U_k^{+} = \{x+y / x,y \in U_k\}$

$U_k^{0} = \{x\alpha p / x \in U_k, p \in \mathcal{N}, \alpha \in \Gamma\}$

$U_k^{++} = \{y+x-y / x \in U_k, y \in \mathcal{N}\}$

$U_k^{00} = \{p\alpha(x+b) - p\alpha b / p,b \in \mathcal{N}, x \in U_k, \alpha \in \Gamma\}$

**Proof:**

First, we prove that $\langle a \rangle = \bigcup_{i=0}^{\infty} U_i$ is an ideal of $\mathcal{N}$

*i.* Let $x, y \in \langle a \rangle$

$\therefore x, y \in U_k$ for some $k$

$\Rightarrow x + y \in U_k^+$

$\Rightarrow x + y \in U_{k+1}$

$\Rightarrow x + y \in \langle a \rangle$

*ii.* Let $x \in \langle a \rangle$ and $y \in \mathcal{N}$

$\therefore x \in \bigcup_k$ for some $k$

$\Rightarrow y + x - y \in U_k^{++}$

$\Rightarrow y + x - y \in U_{k+1}$

$\Rightarrow y + x - y \in \langle a \rangle$

*iii.* Let $x \in \langle a \rangle$ and $p, b \in \mathcal{N}$, $\alpha \in \Gamma$

$x \in \langle a \rangle \Rightarrow x \in U_k$

$p\alpha(x+b) - p\alpha b \in U_k^{00}$

$p\alpha(x+b) - p\alpha b \in U_{k+1}$

$p\alpha(x+b) - p\alpha b \in \langle a \rangle$

*iv.* Let $x \in \langle a \rangle$ and $p \in \mathcal{N}$, $\alpha \in \Gamma$

$\therefore x \in U_k$ for some $k$

$x\alpha p \in U_k^0$

$x\alpha p \in U_{k+1}$

$x\alpha p \in \langle a \rangle$

Thus $\langle a \rangle$ is an ideal of $\mathcal{N}$.

Now, we prove that $\langle a \rangle$ is a principal ideal of $\mathcal{N}$. By the definition of $\langle a \rangle = \bigcup_{i=0}^{\infty} U_i$, it is clear that

$a \in U_0 \Rightarrow a \in \langle a \rangle$

Let $I$ be an ideal of $\mathcal{N}$ such that $a \in I$.

Let $x \in \langle a \rangle$, Then we can easily prove that

$\langle a \rangle \subseteq I$

$\therefore \langle a \rangle$ is a principal ideal in $\mathcal{N}$ generated by 'a'.

**Theorem 4.12:**

If $f$ is a co-fuzzy ideal of a finite $\Gamma$ - near ring $\mathcal{N}$ then $f(x) \le f(a)$ $\forall x \in \langle a \rangle$

**Proof:**

By the theorem(4.11), we know that

$\langle a \rangle = \bigcup_{i=0}^{\infty} U_i$ where $U_0 = \{0\}, U_{k+1} = U_k^+ \cup U_k^0 \cup U_k^{++} \cup U_k^{00}$, and

$U_k^+ = \{x + y / \forall x, y \in U_k\}$

$U_k^0 = \{x\alpha p / \forall x \in U_k, p \in \mathcal{N}, \alpha \in \Gamma\}$

$U_k^{++} = \{y + x - y / \forall x \in U_k, y \in \mathcal{N}\}$

$U_k^{00} = \{p\alpha(x+b) - p\alpha b / p, b \in \mathcal{N} \ \ x \in U_k, \alpha \in \Gamma\}$

Now, let $x \in \langle a \rangle$. We have to prove that

$f(x) \le f(a)$

$$x \in \langle a \rangle \Rightarrow x \in \bigcup_i \ (i \geq 0)$$

We prove the result by mathematical induction.
It is obvious for $i = 0$.
Assume that the result is true for $i = k$.
i.e., $f(x) \leq f(a) \ \ \forall x \in U_k$
We have to prove that the result is true for all $x \in U_{k+1}$

*Case* $(i)$: *Let* $x \in U_k^+$

$$\therefore x = u + v \text{ where } u, v \in U_k,$$

$$\text{Then } f(u) \leq f(a) \text{ and } f(v) \leq f(a)$$

$$\therefore f(x) = f(u+v) \leq \max\{f(u), f(v)\} \leq f(a)$$

$$\Rightarrow f(x) \leq f(a)$$

*Case* $(ii)$: *Let* $x \in U_k^0$

$$\therefore x = u \alpha p \text{ where } u \in U_k \text{ and } p \in \mathcal{N},$$

$$\text{Then } f(u) \leq f(a)$$

$$\therefore f(x) = f(u \alpha p) \leq f(u) \leq f(a)$$

$$\Rightarrow f(x) \leq f(a)$$

*Case* $(iii)$: *Let* $x \in U_k^{++}$

$$\therefore x = y + u - y \text{ where } y \in \mathcal{N} \text{ and } u \in U_k,$$

$$\text{Then } f(u) \leq f(a)$$

$$\therefore f(x) = f(y + u - y) \leq f(u) \leq f(a)$$

$$\Rightarrow f(x) \leq f(a)$$

*Case* $(iv)$: *Let* $x \in U_k^{00}$

$$\therefore x = p\alpha(u+b) - p\alpha b \text{ where } p, b \in \mathcal{N}, u \in U_k \text{ and } \alpha \in \Gamma$$

$$\text{Then } f(u) \leq f(a)$$

$$\therefore f(x) = f(p\alpha(u+b) - p\alpha b) \leq f(u) \leq f(a)$$

$$\Rightarrow f(x) \leq f(a)$$

By the above four cases
$\therefore f(x) \leq f(a) \ \ \forall x \in \langle a \rangle$
Hence by mathematical induction $f(x) \leq f(a) \ \ \forall x \in \langle a \rangle$ □

**Theorem 4.13:**

Let ' $f$ ' be a co-fuzzy ideal of a finite $\Gamma$ - near ring $\mathcal{N}$ and $I$ is an ideal of $\mathcal{N}$ such that $I = \langle a \rangle = \langle b \rangle$ for some $a, b \in \mathcal{N}$. Then $f(a) = f(b)$

**Proof:**

Given $I = \langle a \rangle = \langle b \rangle$
We know that $a \in \langle a \rangle$

$$\Rightarrow a \in \langle b \rangle$$

$$\Rightarrow f(a) \leq f(b) \text{ (By Theorem 4.12) ----------(4.13.1)}$$

Similarly

$$\Rightarrow b \in \langle b \rangle$$

$$\Rightarrow b \in \langle a \rangle$$

$$\Rightarrow f(b) \leq f(a) \text{ (By Theorem 4.12) ----------(4.13.2)}$$

From (4.13.1) & (4.13.2),

$$f(a) = f(b)$$

**Theorem 4.14:**

If $f$ is a co-fuzzy prime ideal of a finite $\Gamma$ - near ring $\mathcal{N}$, Then $f(0)=0$.

**Proof:**

Given $f$ is co-fuzzy prime ideal of $\mathcal{N}$. If possible assume that $f(0)>0$

Since $f$ is not constant function $\exists\ a\in[0,1]$, such that

Let us take $k\in(0,1)$ such that $f(0)<k<f(a)$

Now, define two fuzzy sets $\sigma$ and $\mu$ such that $\sigma(x)=f(a)\ \forall x\in\mathcal{N}$ and $f(0)<f(a)$

$$\mu(x)=\begin{cases} k & if \quad f(x)=f(0) \\ f(0) & if \quad otherwise \end{cases}$$

Since $\sigma$ is a constant function, it is a co-fuzzy ideal we can prove that $\mu$ also a co-fuzzy ideal.

Also

$\sigma(0)=f(a)>f(0)$ *and*

$\mu(0)=k>f(0)$

$\therefore \sigma\not\subseteq f$ and $\mu\not\subseteq f$

Now, Let $p\in\mathcal{N}$

By the definition of $\sigma\alpha\mu$, we have

$$(\sigma\alpha\mu)(p)=\underset{p=x\alpha y}{Sup}\ \min\{\sigma(x),\mu(y)\}$$

*Case I* : *Let* $\mu(y)=k$

$$(\sigma\alpha\mu)(p)=\underset{p=x\alpha y}{Sup}\ \min\{f(a),k\}$$
$$=\underset{p=x\alpha y}{Sup}\ \{k\}$$
$$=k<f(0)\le f(p)$$

($\because$ since $\mathcal{N}$ is zero symmetric finite $\Gamma$ - near ring, $f(x\alpha 0)\le f(x)\Rightarrow f(0)\le f(x)\ \forall x\in\mathcal{N}$)

*Case II* : *Let* $\mu(y)=f(0)$

$$(\sigma\alpha\mu)(p)=\underset{p=x\alpha y}{Sup}\ \min\{f(a),f(0)\}$$
$$=f(0)\le f(p)$$

$\therefore$ By Case I and Case II, $\sigma\alpha\mu\subseteq f$

Since $f$ is co-fuzzy prime ideal, either $\sigma\subseteq f$ *or* $\mu\subseteq f$

This is a contradiction.

$\therefore$ our assumption $f(0)>0$ is wrong.

Hence $f(0)=0$.

## 5. SCOPE AND CONCLUSION:

In this paper we have introduced co-fuzzy bi-ideal and co-fuzzy prime ideals of a finite $\Gamma-$ near ring. We also defined normal co-fuzzy bi-ideal of a finite $\Gamma-$near ring. We established some necessary and sufficient conditions for a fuzzy set $f$ to be co-fuzzy bi-ideal of a finite $\Gamma-$near ring. Having this knowledge, we can develop Dual co-fuzzy bi-ideals of a finite $\Gamma-$near rings.

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# CO-FUZZY IDEALS OF FINITE Γ-NEAR RING

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***ABSTRACT***

*In this paper we introduce and study the concept of ideals of finite Γ-near rings, co-fuzzy ideals of finite Γ-near rings and related theorems. We prove intersection of two co-fuzzy ideals is always a co-fuzzy ideal but union of two co-fuzzy ideals need not be a co-fuzzy ideal of finite Γ-near ring and it is explained by a suitable example. We also introduce homomorphic image and homomorphic pre image of co-fuzzy ideals of finite Γ-near rings and related theorems.*

***Key Words** : finite Γ-near ring, fuzzy set, level subset, union of fuzzy sets, intersection of fuzzy sets, co-fuzzy ideals and homomorphism of co-fuzzy ideals.*

## 1. INTRODUCTION

The fuzzy set theory was developed by Zadeh.L.A. [12] in 1965. The fuzzification of algebraic structure was introduced by Rosenfield.A[7] and he introduced the notation of fuzzy of subgroups in 1971. Swamy K.L.N and Swamy U.M [8] studied fuzzy prime ideals [4,6] Later Satyanarayana. Bh [9] defined Γ-near rings and also he studied ideal theory in Γ-near rings. The notation of fuzzy ideals and its properties were applied to various areas like semi groups [11, 10, 5] and semi rings [1,2] Jun.Y.B [3] considered the fuzzification of ideals of Γ-near rings and investigated the related properties.

In this paper, we have defined co-fuzzy ideal concept of finite $\Gamma-$near ring with less than or equal and maximum conditions and also investigated several properties with the new definitions. Throughout this chapter $\mathcal{N}$ stands for zero symmetric finite $\Gamma-$ near ring.

## 2. PRELIMINARIES

In this section we recall some of the fundamental definitions, which are necessary for this paper.

**Definition 2.1:** A triplet $(\mathcal{N},+,\cdot)$ is said to be a near ring if

1. $(\mathcal{N},+)$ is a group
2. $(\mathcal{N},\cdot)$ is a semi-group
3. $(a+b)\cdot c = a\cdot c + b\cdot c$ (Right distribution law) $\forall\ a,b,c \in \mathcal{N}$.

**Definition 2.2:** A near ring $(\mathcal{N},+,\cdot)$ is said to be finite near ring if $\mathcal{N}$ has finite number of elements.

**Definition 2.3:** Let $\mathcal{N}$ be a non-empty finite set. If

1. $(\mathcal{N},+)$ is a group. (Not necessarily abelian group)
2. Γ is the set of binary operations on $\mathcal{N}$ such that $(\mathcal{N},+,\alpha)$ is a near ring. Where $\alpha \in \Gamma$.
3. $a\alpha(b\beta c) = (a\alpha b)\beta c, \forall\ a,b,c \in \mathcal{N}$ and $\alpha,\beta \in \Gamma$. Then $(\mathcal{N},+,\Gamma)$ is called finite Γ-near ring.

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**Definition 2.4:** If $X$ be a non empty set and $f : X \to [0, 1]$ is a mapping then the pair $(X, f)$ is called fuzzy set and $f$ is called fuzzy sub set of $X$.

**Definition 2.5:** Let $f$ be a fuzzy sub set of the set $X$.Then the set $\{x \in X/f(x) < s\}$ Where $s \in [0,1]$ is called level sub set of $f$ .It is denoted by $f_s$.This $f_s$ is also $s$-cut of $f$ .

$$\therefore f_s = \{x \in X/f(x) < s\}$$

**Definition 2.6:** Let $f$ and $g$ be two fuzzy sub sets of the set $X$. If $f(x) \leq g(x),\ \forall\, x \in X$ then $f$ is said to be contained in $g$.It is denoted by $f \subseteq g$.

**Definition 2.7:** Let $f$ and $g$ be two fuzzy sub sets of the set $X$.Then their intersection and union are denoted by $f \cap g$ and $f \cup g$ respectively and defined as follows,

$$(f \cap g)(x) = Min\{f(x), g(x)\},\ \forall x \in X.$$

and

$$(f \cup g)(x) = Max\{f(x), g(x)\},\ \forall x \in X.$$

**Definition 2.8:** Let $M_1$ and $M_2$ be two non empty sets and $\mu: M_1 \to M_2$ is a mapping. If $f$ is a fuzzy sub set of $M_1$ then $g$ be a fuzzy sub set of $M_2$ defined by

$$g(y) = \begin{cases} \underset{z \in \mu^{-1}(y)}{Inf}\ f(z) \ if\ \mu^{-1}(y) \neq \phi \\ 0 \qquad if\ \mu^{-1}(y) \neq \phi \end{cases}$$

Where $\mu^{-1}(y) = \{x \in M_1/\mu(x) = y\}$

If $g$ is a fuzzy sub set of $M_2$ then $f$ be a fuzzy sub set of $M_1$ defined by

$$f(x) = g(\mu(x)),\ \forall\, x \in M_1.$$

**Definition 2.9:** For any sub set $A$ of the set $X$, the co-fuzzy characteristic set $\delta_A$ is defined as follows,

$$\delta_A(x) = \begin{cases} 0 & if\ x \in A \\ 1 & if\ x \notin A \end{cases}$$

## 3. CO - FUZZY IDEALS OF FINITE Γ-NEAR RINGS

In this section we define ideals and co-fuzzy ideals of a finite Γ-near rings. We prove the intersection of two co-fuzzy ideals of a finite Γ-near ring is always a co-fuzzy ideal. But, the union of two co-fuzzy ideals of a finite Γ-near ring need not be a co-fuzzy ideal and it is explained by a suitable example. We also prove some of related theorems on ideals and co-fuzzy ideals of a finite Γ-near rings.

**Definition 3.1:** A sub set $S$ of a finite Γ-near ring $(\mathcal{N}, +, \Gamma)$ is said to be a left ideal of $\mathcal{N}$ if

1. $x + y \in S, \qquad \forall\, x, y \in S$
2. $y + x - y \in S, \qquad \forall\, x \in S$ and $y \in \mathcal{N}$
3. $a\alpha(x + b) - a\alpha b \in S,\ \forall\, x \in S, a, b \in \mathcal{N}$ and $\alpha \in \Gamma$.

**Definition 3.2:** A sub set $S$ of a finite Γ-near ring $(\mathcal{N}, +, \Gamma)$ is said to be a right ideal of $\mathcal{N}$ if

1. $x + y \in S, \qquad \forall\, x, y \in S$
2. $y + x - y \in S,\ \forall\, x \in S$ and $y \in \mathcal{N}$
3. $x\alpha a \in S, \qquad \forall\, x \in S, a \in \mathcal{N}$ and $\alpha \in \Gamma$.

**Definition 3.3:** A sub set $S$ of a finite Γ-near ring $(\mathcal{N}, +, \Gamma)$ is said to be an ideal of $\mathcal{N}$ if

1. $x + y \in S, \qquad \forall\, x, y \in S$
2. $y + x - y \in S, \qquad \forall\, x \in S$ and $y \in \mathcal{N}$
3. $a\alpha(x + b) - a\alpha b \in S,\ \forall\, x \in S, a, b \in \mathcal{N}$ and $\alpha \in \Gamma$.
4. $x\alpha a \in S, \qquad \forall\, x \in S, a \in \mathcal{N}$ and $\alpha \in \Gamma$.

**Definition 3.4:** A fuzzy sub set $f$ of a finite Γ-near ring $(\mathcal{N}, +, \Gamma)$ is said to be a co-fuzzy left ideal of $\mathcal{N}$ if

1. $f(x + y) \leq \text{Max}\{f(x), f(y)\}$,
2. $f(y + x - y) \leq f(x)$,
3. . $f(a\alpha(x + b) - a\alpha b) \leq f(x), \forall\, x, y, a, b \in \mathcal{N}$ and $\alpha \in \Gamma$.

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**Definition 3.5:** A fuzzy sub set $f$ of a finite Γ-near ring $(\mathcal{N}, +, \Gamma)$ is said to be a co-fuzzy right ideal of $\mathcal{N}$ if

1. $f(x+y) \leq \text{Max}\{f(x), f(y)\}$,
2. $f(y+x-y) \leq f(x)$,
3. $f(x\alpha a) \leq f(x)$, $\forall\, x, y, a \in \mathcal{N}$ and $\alpha \in \Gamma$.

**Definition 3.6:** A fuzzy sub set $f$ of a finite Γ-near ring $(\mathcal{N}, +, \Gamma)$ is said to be a co-fuzzy ideal of $\mathcal{N}$ if

1. $f(x+y) \leq \text{Max}\{f(x), f(y)\}$,
2. $f(y+x-y) \leq f(x)$,
3. $f(a\alpha(x+b) - a\alpha b) \leq f(x)$,
4. $f(x\alpha a) \leq f(x)$, $\forall\, x, y, a, b \in \mathcal{N}$ and $\alpha \in \Gamma$.

**Definition 3.7:** A $L$-fuzzy sub set $f_L$ of a finite Γ-near ring $(\mathcal{N}, +, \Gamma)$ is said to be $L$-fuzzy ideal of $\mathcal{N}$ if

1. $f_L(x+y) \leq \text{Max}\{f_L(x), f_L(y)\}$
2. $f_L(y+x-y) \leq f_L(x)$
3. $f_L(a\alpha(x+b) - a\alpha b) \leq f_L(x)$
4. $f_L(x\alpha a) \leq f_L(x)$ $\forall\, x, y, a, b \in \mathcal{N}$ and $\alpha \in \Gamma$.

Here L is a complete lattice satisfying infinite distribute laws.

**Definition 3.8:** A finite Γ-near ring $(\mathcal{N}, +, \Gamma)$ is said to be zero symmetric if $x\alpha 0 = 0\alpha x = 0 \;\; \forall x \in \mathcal{N}$

**Note 3.9:**

1. $f(x+y) \leq \text{Max}\{f(x), f(y)\}$
2. $f(x-y) \leq \text{Max}\{f(x), f(-y)\}$
3. $f(0) \leq \text{Max}\{f(x), f(-x)\}$
4. $f(0) = f(x\alpha 0) \leq f(x)$, $\forall x, y \in \mathcal{N}$

**Example 3.10:** Let $S = \{1,2,3,4\}$ and $\mathcal{N}$ = P(S) is the power set of $S$.

Let $\Gamma = \{\{1\}, \{2,3\}\}$

Define $f$: $\mathcal{N} \to [0,1]$ such that $f(A) = \begin{cases} \frac{1}{2} & if \quad A \neq \phi \\ \frac{1}{3} & if \quad A = \phi \end{cases}$

Here $f$ is both co-fuzzy left and co-fuzzy right ideal of finite Γ-near ring $(\mathcal{N}, \Delta, \Gamma)$.

Hence $f$ is co-fuzzy ideal of finite Γ-near ring $(\mathcal{N}, \Delta, \Gamma)$.

**Example 3.11:** Let $\mathcal{N}$ be the set of all $2 \times 2$ matrices defined over $Z_5$.Where $Z_5 = \{\bar{0}, \bar{1}, \bar{2}, \bar{3}, \bar{4}\}$ is the set of all residue classes modulo 5 and $\Gamma = \{\bar{1}, \bar{2}, \bar{3}\}$.Then $(\mathcal{N}, +, \Gamma)$ is finite Γ-near ring.

Define $f$: $\mathcal{N} \to [0,1]$ such that $f(A) = \begin{cases} 0.3 & if \quad A = \begin{bmatrix} a & b \\ 0 & 0 \end{bmatrix} \\ 0.5 & if \quad other\ wise \end{cases}$

Then $f$ is a co-fuzzy right ideal of $\mathcal{N}$. But not co-fuzzy left ideal of $\mathcal{N}$.

Define $f$: $\mathcal{N} \to [0,1]$ such that $f(A) = \begin{cases} 0.2 & if\ A = \begin{bmatrix} 0 & a \\ 0 & b \end{bmatrix} \\ 0.6 & otherwise \end{cases}$

Then $f$ is a co-fuzzy left ideal of $\mathcal{N}$. But not co-fuzzy right ideal of $\mathcal{N}$.

Now, we prove some important theorems on co-fuzzy ideals.

**Theorem 3.12:** A fuzzy sub set $f$ of a finite Γ-near ring $(\mathcal{N}, +, \Gamma)$ is a co-fuzzy ideal of $\mathcal{N}$ if and only if for each $\delta \in Im(f)$, the level set $f_\delta$ of $f$ is an ideal of $\mathcal{N}$.

**Proof**: Let $f$ be a co-fuzzy ideal of a finite Γ-near ring $(\mathcal{N}, +, \Gamma)$.

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Now, we have to prove that the level set $f_\delta$ of $f$ is an ideal of $\mathcal{N}$ $\forall \delta \in im(f)$

By the definition of the level set $f_\delta = \{X \in \mathcal{N},\ f(x) < \delta\}$

1. Let $x, y \in f_\delta$
   Then $f(x) < \delta$ and $f(y) < \delta$
   Now $f(x+y) \leq \text{Max}\{f(x), f(y)\} < \delta$
   $\therefore f(x+y) < \delta$
   $\Rightarrow x+y \in f_\delta$
2. Let $x \in f_\delta$ and $y \in \mathcal{N}$
   Then $f(x) < \delta$
   Now $f(y+x-y) \leq f(x) < \delta$
   $\therefore f(y+x-y) < \delta$
   $\Rightarrow y+x-y \in f_\delta$
3. Let $x \in f_\delta$, $a, b \in \mathcal{N}$ and $\alpha \in \Gamma$
   Then $f(x) < \delta$
   Now $f(a\alpha(x+b) - a\alpha b) \leq f(x) < \delta$
   $\therefore f(a\alpha(x+b) - a\alpha b) < \delta$
   $\Rightarrow a\alpha(x+b) - a\alpha b \in f_\delta$
   Then the level set $f_\delta$ of $f$ is a left ideal of $\mathcal{N}$, $\forall\ \delta \in Im(f)$
4. Let $x \in f_\delta$, $a \in \mathcal{N}$ and $\alpha \in \Gamma$
   Then $f(x) < \delta$
   We have $f(x\alpha a) \leq f(x) < \delta$
   $\therefore f(x\alpha a) < \delta$
   $\Rightarrow x\alpha a \in f_\delta$
   Then the level set $f_\delta$ of $f$ is a right ideal of $\mathcal{N}$.
   Hence the level set $f_\delta$ of $f$ is a ideal of $\mathcal{N}$, $\forall \delta \in \text{Im}(f)$
   Conversely assume that $f_\delta$ is an ideal of $\mathcal{N}$
   Now we prove that $f$ is a co-fuzzy ideal of a finite Γ-near ring $(\mathcal{N}, +, \Gamma)$

1. Let $x, y \in \mathcal{N}$
   If possible, let there exists $x_0, y_0 \in \mathcal{N}$ such that
   $f(x_0 + y_0) > Max\{f(x_0), f(y_0)\}$
   Let $\delta = \frac{1}{2}\{f(x_0+y_0) + Max\{f(x_0), f(y_0)\}\}$
   Then $\delta < \frac{1}{2}\{f(x_0+y_0) + f(x_0+y_0)\}$
   $\Rightarrow \delta < f(x_0+y_0)$
   $\Rightarrow x_0 + y_0 \notin f_\delta$
   And $\delta > \frac{1}{2}\{2\ Max\{f(x_0), f(y_0)\}\}$
   $\Rightarrow \delta > Max\{f(x_0), f(y_0)\}$
   $\Rightarrow \delta > f(x_0)$ and $\delta > f(y_0)$
   $\Rightarrow x_0, y_0 \in f_\delta$
   $\therefore x_0 + y_0 \notin f_\delta$ and $x_0, y_0 \in f_\delta$
   This is a contradiction to $f_\delta$ is an ideal of $\mathcal{N}$
   Then our assumption is wrong.
   Hence $f(x+y) \leq \text{Max}\{f(x), f(y)\}$, $\forall\ x, y \in \mathcal{N}$

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2. Let $x, y \in \mathcal{N}$
   If possible, let there exists $x_0, y_0 \in \mathcal{N}$ such that
   $f(y_0 + x_0 - y_0) > f(x_0)$
   Let $\delta = \frac{1}{2}\{f(y_0 + x_0 - y_0) + f(x_0)\}$
   Then $\delta < \frac{1}{2}\{2f(y_0 + x_0 - y_0)\}$ and $\delta > \frac{1}{2}\{2f(x_0)\}$
   $\Rightarrow \delta < f(y_0 + x_0 - y_0)$ and $\delta > f(x_0)$
   $\Rightarrow y_0 + x_0 - y_0 \notin f_\delta$ and $x_0 \in f_\delta$
   This is a contradiction to $f_\delta$ is an ideal of $\mathcal{N}$
   Then our assumption is wrong and hence $f(y + x - y) \leq f(x)$,
   $\forall\, x, y \in \mathcal{N}$
3. Let $x, a, b \in \mathcal{N}$ and $\alpha \in \Gamma$
   If possible, let there exists $x_0, a_0, b_0 \in \mathcal{N}$ and $\alpha \in \Gamma$ such that
   $f(a_0\alpha(x_0 + b_0) - a_0\alpha b_0) > f(x_0)$
   $Let\ \ \delta = \frac{1}{2}\{f(a_0\alpha(x_0 + b_0) - a_0\alpha b_0) + f(x_0)\}$
   Then $\delta < \frac{1}{2}\{2f(a_0\alpha(x_0 + b_0) - a_0\alpha b_0)\}$ $and$ $\delta > \frac{1}{2}\{2f(x_0)\}$
   $\Rightarrow \delta < f(a_0\alpha(x_0 + b_0) - a_0\alpha b_0)$ and $\delta > f(x_0)$
   $\Rightarrow a_0\alpha(x_0 + b_0) - a_0\alpha b_0 \notin f_\delta$ and $x_0 \in f_\delta$
   This is a contradiction to $f_\delta$ is an ideal of $\mathcal{N}$
   Then our assumption is wrong and hence
   $f(a\alpha(x + b) - a\alpha b) \leq f(x)$ ,$\forall\, x, a, b \in \mathcal{N}$ and $\alpha \in \Gamma$.
   Then $f$ is a co-fuzzy left ideal of a finite Γ-near ring $(\mathcal{N}, +, \Gamma)$.
4. Let $x, a \in \mathcal{N}$ and $\alpha \in \Gamma$
   If possible, let there exists $x_0, a_0 \in \mathcal{N}$ and $\alpha \in \Gamma$ such that
   $f(x_0\alpha a_0) > f(x_0)$
   Let $\delta = \frac{1}{2}\{f(x_0\alpha a_0) + f(x_0)\}$
   Then $\delta < f(x_0\alpha a_0)$ and $\delta > f(x_0)$
   $\Rightarrow x_0\alpha a_0 \notin f_\delta$ and $x_0 \in f_\delta$
   This is a contradiction to $f_\delta$ is an ideal of $\mathcal{N}$:
   Then our assumption is wrong and hence $f(x\alpha a) \leq f(x)$ ,$\forall\, x, a \in \mathcal{N}$ and $\alpha \in \Gamma$
   Then $f$ is a co- fuzzy right ideal of a finite Γ-near ring $(\mathcal{N}, +, \Gamma)$
   Hence $f$ is a co-fuzzy ideal of a finite Γ-near ring $(\mathcal{N}, +, \Gamma)$.

**Theorem 3.13:** Let $S(\neq \phi)$ be a non empty sub set of a finite Γ-near ring $(\mathcal{N}, +, \Gamma)$. Then the fuzzy set $f_S$: $\mathcal{N} \to [0,1]$ defined by $f_S(x) = \begin{cases} 0 & if\ x \in S \\ 1 & if\ x \notin S \end{cases}$ is a co-fuzzy ideal of $\mathcal{N}$ if and only if $S$ is an ideal of $\mathcal{N}$.

**Proof**: Let $S(\neq \phi)$ be a non empty sub set of a finite Γ-near ring $(\mathcal{N}, +, \Gamma)$
Define $f_S$: $\mathcal{N} \to [0,1]$ such that $f_S(x) = \begin{cases} 0 & if\ x \in S \\ 1 & if\ x \notin S \end{cases}$
Let $f_S$ be a co-fuzzy ideal of a finite Γ-near ring $(\mathcal{N}, +, \Gamma)$

Now we prove that $S$ is an ideal of $\mathcal{N}$

1. Let $x, y \in S$
   Then $f_S(x) = 0$ and $f_S(y) = 0$
   Now $f_S(x + y) \leq \text{Max}\{f_S(x), f_S(y)\} = 0$
   $\therefore f_S(x + y) = 0$
   $\Rightarrow x + y \in S$

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2. $x \in S$ and y $\in \mathcal{N}$
   Then $f_S(x) = 0$
   Now $f_S(y + x - y) \leq f_S(x) = 0$
   $\therefore f_S(y + x - y) = 0$
   $\Rightarrow y + x - y \in S$
3. Let $x \in S,\ a, b \in \mathcal{N}$ and $\alpha \in \Gamma$
   Then $f_S(x) = 0$
   Now $f_S(a\alpha(x + b) - a\alpha b) \leq f_S(x) = 0$
   $\therefore f_S(a\alpha(x + b) - a\alpha b) = 0$
   $\Rightarrow a\alpha(x + b) - a\alpha b \in S$
   Then $S$ is a left ideal of $\mathcal{N}$
4. Let $x \in S,\ a \in \mathcal{N}$ and $\alpha \in \Gamma$
   Then $f_S(x) = 0$
   We have $f_S(x\alpha a) \leq f_S(x) = 0$
   $\therefore f_S(x\alpha a) \leq 0$
   $\Rightarrow f_S(x\alpha a) = 0$
   $\Rightarrow x\alpha a \in S$
   Then $S$ is a right ideal of $\mathcal{N}$
   Hence $S$ is an ideal of $\mathcal{N}$

Conversely assume that $S$ is an ideal of $\mathcal{N}$

We prove that $f_S$ is a co-fuzzy ideal of a finite Γ-near ring $(\mathcal{N}, +, \Gamma)$

1. Let $x, y \in \mathcal{N}$

   $(i)$ *Let* $x, y \in S$

   *Then* $f_s(x) = 0$ *and* $f_s(y) = 0$ *and* $x + y \in S$

   $\Rightarrow f_s(x + y) = 0 \leq \max\{f_s(x), f_s(y)\}$

   $\therefore f_s(x + y) \leq \max\{f_s(x), f_s(y)\}$

   $(ii)$ *Let* $x, y \notin S$ *and* $x + y \in S$

   *Then* $f_s(x) = f_s(y) = 1$ *and* $f_s(x + y) = 0$

   *Now* $f_s(x + y) = 0 \leq \max\{f_s(x), f_s(y)\}$

   $\therefore f_s(x + y) \leq \max\{f_s(x), f_s(y)\}$

   $(iii)$ *Let* $x, y \notin S$ *and* $x + y \notin S$

   *Then* $f_s(x) = f_s(y) = f_s(x + y) = 1$

   *Now* $f_s(x + y) = 1 \leq \max\{f_s(x), f_s(y)\}$

   $\therefore f_s(x + y) \leq \max\{f_s(x), f_s(y)\}$

2. Let $x, y \in \mathcal{N}$

   (i) Let $x \in S$ and $y \in \mathcal{N}$
   Then $f_s(x) = 0$ and $y + x - y \in S$
   $\Rightarrow f_S(y + x - y) = 0 \leq f_S(x)$
   $\therefore f_S(y + x - y) \leq f_S(x)$

   (ii) Let $x \notin S$ and $y \in \mathcal{N}$
   Then $f_S(x) = 1$
   Now $f_S(y + x - y) \leq 1 \leq f_S(x)$
   $\therefore f_S(y + x - y) \leq f_S(x)$

3. Let $x, a, b \in \mathcal{N}$ and $\alpha \in \Gamma$

   (i) Let $x \in S, a, b \in \mathcal{N}$ and $\alpha \in \Gamma$
   Then $f_S(x) = 0$ and $a\alpha(x + b) - a\alpha b \in S$
   $\Rightarrow f_S(a\alpha(x + b) - a\alpha b) = 0$
   Now $f_S(a\alpha(x + b) - a\alpha b) = 0 \leq f_S(x)$
   $\therefore f_S(a\alpha(x + b) - a\alpha b) \leq f_S(x)$

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(ii) Let $x \notin S$, $a, b \in \mathcal{N}$ and $\alpha \in \Gamma$
Then $f_S(x) = 1$
Now $f_S(a\alpha(x+b) - a\alpha b) \leq 1 = f_S(x)$
$\therefore f_S(a\alpha(x+b) - a\alpha b) \leq f_S(x)$
Thus $f_S$ is a co-fuzzy left ideal of a finite Γ-near ring $(\mathcal{N}, +, \Gamma)$

4. Let $x, a \in \mathcal{N}$ and $\alpha \in \Gamma$

(i) Let $x \in S$, $a \in \mathcal{N}$ and $\alpha \in \Gamma$
Then $f_S(x) = 0$ and $x\alpha a \in S$
$\Rightarrow f_S(x\alpha a) = 0$
Now $f_S(x\alpha a) = 0 \leq f_S(x)$
$\therefore f_S(x\alpha a) \leq f_S(x)$

(ii) Let $x \notin S$, $a \in \mathcal{N}$ and $\alpha \in \Gamma$
Then $f_S(x) = 1$
Now $f_S(x\alpha a) \leq 1 \leq f_S(x)$
$\therefore f_S(x\alpha a) \leq f_S(x)$

Thus $f_S$ is a co-fuzzy right ideal of a finite Γ-near ring $(\mathcal{N}, +, \Gamma)$

Hence $f_S$ is a co-fuzzy ideal of a finite Γ-near ring $(\mathcal{N}, +, \Gamma)$

**Theorem 3.14:** If $f$ is a co-fuzzy ideal of a finite Γ-near ring $(\mathcal{N}, +, \Gamma)$ then the set $S = \{x \in \mathcal{N} / f(x) = f(0)\}$ is an ideal of $\mathcal{N}$

**Proof:** Let $f$ is a co-fuzzy ideal of a finite Γ-near ring $(\mathcal{N}, +, \Gamma)$
Given that $S = \{x \in \mathcal{N} / f(x) = f(0)\}$
We know that $f(0) \leq f(x)$, $\forall x \in \mathcal{N}$
Now we prove that $S$ is an ideal of $\mathcal{N}$

1. Let $x, y \in S$
Then $f(x) = f(0)$ and $f(y) = f(0)$
Since $f$ is a fuzzy ideal, $f(x+y) \leq \text{Max}\{f(x), f(y)\} = f(0)$
$f(x+y) \leq f(0)$
$\Rightarrow f(x+y) = f(0)$
$\Rightarrow x + y \in S$
2. Let $x \in S$ and $y \in \mathcal{N}$
Then $f(x) = f(0)$
Since $f$ is a fuzzy ideal, $f(y+x-y) \leq f(x) = f(0)$
$\therefore f(y+x-y) \leq f(0)$
$\Rightarrow f(y+x-y) = f(0)$
$\Rightarrow y + x - y \in S$
3. Let $x \in S, a, b \in \mathcal{N}$ and $\alpha \in \Gamma$
Then $f(x) = f(0)$
Since $f$ is a fuzzy left ideal, $f(a\alpha(x+b) - a\alpha b) \leq f(x) = f(0)$
$\therefore f(a\alpha(x+b) - a\alpha b) \leq f(0)$
$\Rightarrow f(a\alpha(x+b) - a\alpha b) = f(0)$
$\Rightarrow a\alpha(x+b) - a\alpha b \in S$
Thus $S$ is a left ideal of $\mathcal{N}$.
4. Let $x \in S$, $a \in \mathcal{N}$ and $\alpha \in \Gamma$
Then $f(x) = f(0)$
Since $f$ is a fuzzy right ideal, $f(x\alpha a) \leq f(x) = f(0)$
$\therefore f(x\alpha a) \leq f(0)$
$\Rightarrow f(x\alpha a) = f(0)$
$\Rightarrow x\alpha a \in S$
Thus $S$ is a right ideal of $\mathcal{N}$.
Hence $S$ is an ideal of a finite Γ-near ring $(\mathcal{N}, +, \Gamma)$.

**Theorem 3.15:** Let $S(\neq \phi)$ is an ideal of a finite Γ-near ring $(\mathcal{N}, +, \Gamma)$. Then for all $t \in (0, 1]$ there exists a co-fuzzy ideal $f$ of $\mathcal{N}$ Such that $\mathcal{N}_f = S$, Where $\mathcal{N}_f = \{x \in \mathcal{N} / f(x) = f(0)\}$.

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**Proof:** Given that $S(\neq \phi)$ is an ideal of $\mathcal{N}$.Define $f$: $\mathcal{N} \to [0,1]$ such that $f(x) = \begin{cases} 0 & if\ x \in S \\ t & if\ x \notin S \end{cases}$

We prove that $f$ is a co-fuzzy ideal of a finite Γ-near ring $(\mathcal{N}, +, \Gamma)$

1. Let $x, y \in \mathcal{N}$
   (i) Let $x, y \in S$
   Then $f(x) = f(y) = 0$
   Since $S$ is an ideal of $\mathcal{N}$, $x + y \in S$
   $\Rightarrow f(x + y) = 0$
   $\Rightarrow f(x + y) = 0 \leq \text{Max}\{f(x), f(y)\}$
   $\therefore f(x + y) \leq \text{Max}\{f(x), f(y)\}$
   (ii) Let $x, y \notin S$ and $x + y \in S$
   Then $f(x) = f(y) = t$ and $f(x + y) = 0$
   Now $f(x + y) = 0 \leq \text{Max}\{f(x), f(y)\}$
   $\therefore f(x + y) \leq \text{Max}\{f(x), f(y)\}$
   (iii) Let $x, y \notin S$ and $x + y \notin S$
   Then $f(x) = f(y) = t$ and $f(x + y) = t$
   Now $f(x + y) = t \leq \text{Max}\{f(x), f(y)\}$
   $\therefore f(x + y) \leq \text{Max}\{f(x), f(y)\}$
2. Let $x, y \in \mathcal{N}$
   (i) Let $x \in S$ and $y \in \mathcal{N}$
   Then $f(x) = 0$
   Since $S$ is an ideal of $\mathcal{N}$, $y + x - y \in S$
   $\Rightarrow f(y + x - y) = 0 \leq f(x)$
   $\Rightarrow f(y + x - y) \leq f(x)$
   (ii) Let $x \notin S$ and $y \in \mathcal{N}$
   Then $f(x) = t$ and $y + x - y \notin S$
   $\Rightarrow f(y + x - y) = t \leq f(x)$
   $\Rightarrow f(y + x - y) \leq f(x)$
3. Let $x, a, b \in \mathcal{N}$ and $\alpha \in \Gamma$
   (i) Let $x \in S$, $a, b \in \mathcal{N}$ and $\alpha \in \Gamma$
   Then $f(x) = 0$ and $a\alpha(x + b) - a\alpha b \in S$
   $\Rightarrow f(a\alpha(x + b) - a\alpha b) = 0 \leq f(x)$
   $\Rightarrow f(a\alpha(x + b) - a\alpha b) \leq f(x)$
   (ii) Let $x \notin S$ and $a\alpha(x + b) - a\alpha b \in S$
   Then $f(x) = t$ and $f(a\alpha(x + b) - a\alpha b) = 0$
   $\Rightarrow f(a\alpha(x + b) - a\alpha b) = 0 \leq t = f(x)$
   $\Rightarrow f(a\alpha(x + b) - a\alpha b) \leq f(x)$
   (iii) Let $x \notin S$ and $a\alpha(x + b) - a\alpha b \notin S$
   Then $f(x) = t$ and $f(a\alpha(x + b) - a\alpha b) = t$
   $\Rightarrow f(a\alpha(x + b) - a\alpha b) = t = f(x)$
   $\Rightarrow f(a\alpha(x + b) - a\alpha b) \leq f(x)$
   Thus $f$ is a co-fuzzy left ideal of a finite Γ-near ring $(\mathcal{N}, +, \Gamma)$.
4. Let $x, a \in \mathcal{N}$ and $\alpha \in \Gamma$
   (i) Let $x \in S$, $a \in \mathcal{N}$ and $\alpha \in \Gamma$
   Then $f(x) = 0$ and $x\alpha a \in S$
   $\Rightarrow f(x\alpha a) = 0$
   $\Rightarrow f(x\alpha a) = 0 \leq f(x)$
   $\Rightarrow f(x\alpha a) \leq f(x)$
   (ii) Let $x \notin S$ and $x\alpha a \in S$
   Then $f(x) = t$ and $f(x\alpha a) = 0$
   $\Rightarrow f(x\alpha a) = 0 \leq t = f(x)$
   $\Rightarrow f(x\alpha a) \leq f(x)$
   (iii) Let $x \notin S$ and $x\alpha a \notin S$
   Then $f(x) = t$ and $f(x\alpha a) = t$
   $\Rightarrow f(x\alpha a) = t = f(x)$
   $\Rightarrow f(x\alpha a) \leq f(x)$
   Thus $f$ is a co-fuzzy right ideal of a finite Γ-near ring $(\mathcal{N}, +, \Gamma)$.
   Hence $f$ is a co-fuzzy ideal of a finite Γ-near ring $(\mathcal{N}, +, \Gamma)$.

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Finally, $\mathcal{N}_f = \{x \in \mathcal{N} / f(x) = f(0)\}$
$= \{x \in \mathcal{N} / f(x) = 0\}$
$= S$
$\therefore \mathcal{N}_f = S$

**Theorem 3.16:** If $f$ and $g$ are two co-fuzzy ideals of a finite Γ-near ring $(\mathcal{N}, +, \Gamma)$, then their intersection $(f \cap g)$ is also co- fuzzy ideal of $\mathcal{N}$.

**Proof:** Given that $f$ and $g$ are two co-fuzzy ideals of a finite Γ-near ring $(\mathcal{N}, +, \Gamma)$

Now we prove that $(f \cap g)$ is co-fuzzy ideal of $\mathcal{N}$.

Let $x, y, a, b \in \mathcal{N}$ and $\alpha \in \Gamma$

1. $(f \cap g)(x+y) = Min\{f(x+y), g(x+y)\}$
$\leq Min\{\text{Max}\{f(x), f(y)\}, \text{Max}\{g(x), g(y)\}\}$
$\leq Max\{\text{Min}\{f(x), g(x)\}, \text{Min}\{f(y), g(y)\}\}$
$= Max\{(f \cap g)(x), (f \cap g)(y)\}$
$\therefore (f \cap g)(x+y) \leq Max\{(f \cap g)(x), (f \cap g)(y)\}$
2. $(f \cap g)(y+x-y) = Min\{f(y+x-y), g(y+x-y)\}$
$\leq Min\{f(x), g(x)\}$
$= (f \cap g)(x)$
$\therefore (f \cap g)(y+x-y) \leq (f \cap g)(x)$
3. $(f \cap g)(a\alpha(x+b) - a\alpha b) = Min\{f(a\alpha(x+b) - a\alpha b), g(a\alpha(x+b) - a\alpha b)\}$
$\leq Min\{f(x), g(x)\}$
$= (f \cap g)(x)$
$\therefore (f \cap g)(a\alpha(x+b) - a\alpha b) \leq (f \cap g)(x)$
Thus $(f \cap g)$ is a co-fuzzy left ideal of $\mathcal{N}$
4. $(f \cap g)(x\alpha a) = Min\{f(x\alpha a), g(x\alpha a)\}$
$\leq Min\{f(x), g(x)\}$
$= (f \cap g)(x)$
$\therefore (f \cap g)(x\alpha a) \leq (f \cap g)(x)$
Thus $(f \cap g)$ is a co-fuzzy right ideal of $\mathcal{N}$.
Hence $(f \cap g)$ is a co-fuzzy ideal of $\mathcal{N}$.

**Remark 3.17:** The union of two co-fuzzy ideals of a finite Γ-near ring $(\mathcal{N}, +, \Gamma)$ need not be a co-fuzzy ideal of $\mathcal{N}$. Now, we prove a sufficient condition for the union of two co-fuzzy ideals of a finite Γ-near ring $(\mathcal{N}, +, \Gamma)$ to be a co-fuzzy ideal of $\mathcal{N}$.

**Theorem 3.18:** If $f$ and $g$ are two co-fuzzy ideals of a finite Γ-near ring $(\mathcal{N}, +, \Gamma)$, then their union$(f \cup g)$ is fuzzy ideal of $\mathcal{N}$ if $f \subseteq g$ or $g \subseteq f$.

**Proof:** Given that $f$ and $g$ are two co-fuzzy ideals of a finite Γ-near ring $(\mathcal{N}, +, \Gamma)$ such that $f \subseteq g$ or $g \subseteq f$, Without loss of generality, We assume that $f \subseteq g$
Now we prove that $(f \cup g)$ is co-fuzzy ideal of $\mathcal{N}$.
Let $x, y, a, b \in \mathcal{N}$ and $\alpha \in \Gamma$

1. $(f \cup g)(x+y) = Max\{f(x+y), g(x+y)\}$
$\leq Max\{\text{Max}\{f(x), f(y)\}, \text{Max}\{g(x), g(y)\}\}$
$\leq Max\{\text{Max}\{f(x), g(x)\}, \text{Max}\{f(y), g(y)\}\}$
$= Max\{(f \cup g)(x), (f \cup g)(y)\}$
$\therefore (f \cup g)(x+y) \leq Max\{(f \cup g)(x), (f \cup g)(y)\}$
2. $(f \cup g)(y+x-y) = Max\{f(y+x-y), g(y+x-y)\}$
$\leq Max\{f(x), g(x)\}$
$= (f \cup g)(x)$
$\therefore (f \cup g)(y+x-y) \leq (f \cup g)(x)$
3. $(f \cup g)(a\alpha(x+b) - a\alpha b) = Max\{f(a\alpha(x+b) - a\alpha b), g(a\alpha(x+b) - a\alpha b)\}$
$\leq Max\{f(x), g(x)\}$
$= (f \cup g)(x)$
$\therefore (f \cup g)(a\alpha(x+b) - a\alpha b) \leq (f \cup g)(x)$
Thus $(f \cup g)$ is a co-fuzzy left ideal of $\mathcal{N}$

4. $(f \cup g)(x\alpha a) = Max\{f(x\alpha a), g(x\alpha a)\}$
$\leq Max\{f(x), g(x)\}$
$= (f \cup g)(x)$
$\therefore (f \cup g)(x\alpha a) \leq (f \cup g)(x)$
Thus $(f \cup g)$ is a co-fuzzy right ideal of $\mathcal{N}$
Hence $(f \cup g)$ is a co-fuzzy ideal of $\mathcal{N}$

**Remark 3.19:** The converse of the above theorem need not be true. i.e, even if $(f \cup g)$ is a co-fuzzy ideal of a finite Γ-near ring, either one may not contained in other.

**Example:** Let $S = \{1,2,3,4\}$ and $\mathcal{N} = P(S)$, Where $P(S)$ is the power set of $S$.
Then $(\mathcal{N}, \Delta, \cap)$ is a finite near ring.
Let us take $\Gamma = \{\{1\},\{1,2,3\}\}$, then $(\mathcal{N}, \Delta, \Gamma)$ is a finite Γ-near ring.
Define $f$: $\mathcal{N} \to [0,1]$ such that $f(A) = \begin{cases} 0.6 & if\ A \neq \phi \\ 0.3 & if\ A = \phi \end{cases}$
and define $g$: $\mathcal{N} \to [0,1]$ such that $g(A) = \begin{cases} 0.7 & if\ A \neq \phi \\ 0.2 & if\ A = \phi \end{cases}$

Then $(f \cup g)$: $\mathcal{N} \to [0,1]$ such that $(f \cup g)(A) = \begin{cases} 0.7 & if\ A \neq \phi \\ 0.3 & if\ A = \phi \end{cases}$ is a co-fuzzy ideal of a finite Γ-near ring $(\mathcal{N}, \Delta, \Gamma)$. But $f \not\subseteq g$ and $g \not\subseteq f$.

## 4. CO-FUZZY HOMOMORPHISM OF FINITE Γ-NEAR RINGS

In this section, we define co-fuzzy homomorphism between two finite Γ-near rings and we prove that the homomorphic image of co-fuzzy ideal is a co-fuzzy ideal and inverse image of a co-fuzzy ideal is also a co-fuzzy ideal.

**Definition 4.1:** Let $(\mathcal{N}_1, +, \Gamma)$ and $(\mathcal{N}_2, +, \Gamma)$ be two finite Γ-near rings. Then the function $f$: $\mathcal{N}_1 \to \mathcal{N}_2$ is said to be a homomorphism from $\mathcal{N}_1$ to $\mathcal{N}_2$ if

1. $f(a+b) = f(a) + f(b)$
2. $f(a\alpha b) = f(a)\alpha f(b),\ \forall\ a, b \in \mathcal{N}_1$ and $\alpha \in \Gamma$

**Definition 4.2:** Let $(\mathcal{N}_1, +, \Gamma_1)$ be a finite $\Gamma_1$-near ring and $(\mathcal{N}_2, +, \Gamma_2)$ be a finite $\Gamma_2$-near ring, and $f$: $\mathcal{N}_1 \to \mathcal{N}_2$ and $g$: $\Gamma_1 \to \Gamma_2$ be two functions. Then the pair $(f, g)$ is said to be a homomorphism from $\mathcal{N}_1$ to $\mathcal{N}_2$ if

1. $f(a+b) = f(a) + f(b)$
2. $f(a\alpha b) = f(a)g(\alpha)f(b), \forall\ a, b \in \mathcal{N}_1$ and $\alpha \in \Gamma_1$

**Definition 4.3:** Let $(\mathcal{N}_1, +, \Gamma)$ and $(\mathcal{N}_2, +, \Gamma)$ be two finite Γ-near rings and $f$: $\mathcal{N}_1 \to \mathcal{N}_2$ is a homomorphism from $\mathcal{N}_1$ to $\mathcal{N}_2$. If $\mu$ is a fuzzy sub set of $\mathcal{N}_1$ then its image $f(\mu)$ is a fuzzy sub set of $\mathcal{N}_2$ is defined by

$$\big(f(u)\big)(y) = \begin{cases} \inf_{z \in f^{-1}(y)} \mu(z) & if \quad f^{-1}(y) \neq \phi \\ 0 & if \quad f^{-1}(y) = \phi \end{cases} \quad \forall y \in N_2$$

**Definition 4.4:** Let $(\mathcal{N}_1, +, \Gamma)$ and $(\mathcal{N}_2, +, \Gamma)$ be two finite Γ-near rings. The function $f$: $\mathcal{N}_1 \to \mathcal{N}_2$ is a homomorphism from $\mathcal{N}_1$ to $\mathcal{N}_2$. If $\sigma$ is a co-fuzzy sub set of $\mathcal{N}_2$ then its inverse image $f^{-1}(\sigma)$ is a fuzzy sub set of $\mathcal{N}_1$ defined by $\big(f^{-1}(\sigma)\big)(x) = \sigma\big(f(x)\big),\ \forall\ x \in \mathcal{N}_1$.

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**Theorem 4.5:** Let $\left(\mathcal{N}_1,+,\Gamma\right)$ and $\left(\mathcal{N}_2,+,\Gamma\right)$ be two finite Γ-near rings. The function $f$: $\mathcal{N}_1 \to \mathcal{N}_2$ is a homomorphism from $\mathcal{N}_1$ to $\mathcal{N}_2$. If $\sigma$ is a co-fuzzy ideal of $\mathcal{N}_2$ then its inverse image $f^{-1}(\sigma)$ is a co-fuzzy ideal of $\mathcal{N}_1$.

**Proof:** Let $f$: $\mathcal{N}_1 \to \mathcal{N}_2$ is a homomorphism from the finite Γ-near rings $\left(\mathcal{N}_1,+,\Gamma\right)$ to $\left(\mathcal{N}_2,+,\Gamma\right)$ and $\sigma$: $\mathcal{N}_2 \to [0,1]$ is a co-fuzzy sub set of $\mathcal{N}_2$.

Let $\sigma$ be a co-fuzzy ideal of $\mathcal{N}_2$

Now we prove that $f^{-1}(\sigma)$ is a co-fuzzy ideal of $\mathcal{N}_1$

Let $x, y, a, b \in \mathcal{N}_1$ and $\alpha \in \Gamma$

1. $$\begin{aligned}\left(f^{-1}(\sigma)\right)(x+y) &= \sigma\left(f(x+y)\right)\\ &= \sigma\left(f(x)+f(y)\right)\\ &\le Max\left\{\sigma\left(f(x)\right),\sigma\left(f(y)\right)\right\}\\ &= Max\left\{\left(f^{-1}(\sigma)\right)(x),\left(f^{-1}(\sigma)\right)(y)\right\}\end{aligned}$$
$$\therefore \left(f^{-1}(\sigma)\right)(x+y) \le Max\left\{\left(f^{-1}(\sigma)\right)(x),\left(f^{-1}(\sigma)\right)(y)\right\}$$

2. $$\begin{aligned}\left(f^{-1}(\sigma)\right)(y+x-y) &= \sigma\left(f(y+x-y)\right)\\ &= \sigma\left(f(y)+f(x)-f(y)\right)\\ &\le \sigma(f(x))\\ &= \left(f^{-1}(\sigma)\right)(x)\end{aligned}$$
$$\therefore \left(f^{-1}(\sigma)\right)(y+x-y) \le \left(f^{-1}(\sigma)\right)(x)$$

3. $$\begin{aligned}\left(f^{-1}(\sigma)\right)(a\alpha(x+b)-a\alpha b) &= \sigma\left(f(a\alpha(x+b)-a\alpha b)\right)\\ &= \sigma\left(f(a)\alpha\left(f(x)+f(b)\right)-f(a)\alpha f(b)\right)\\ &\le \sigma(f(x))\\ &= \left(f^{-1}(\sigma)\right)(x)\end{aligned}$$
$$\therefore \left(f^{-1}(\sigma)\right)(a\alpha(x+b)-a\alpha b) \le \left(f^{-1}(\sigma)\right)(x)$$

Thus $\left(f^{-1}(\sigma)\right)$ is a co-fuzzy left ideal of $\mathcal{N}_1$

4. $$\begin{aligned}\left(f^{-1}(\sigma)\right)(x\alpha a) &= \sigma\left(f(x\alpha a)\right)\\ &= \sigma\left(f(x)\alpha f(a)\right)\\ &\le \sigma(f(x))\\ &= \left(f^{-1}(\sigma)\right)(x)\end{aligned}$$
$$\therefore \left(f^{-1}(\sigma)\right)(x\alpha a) \le \left(f^{-1}(\sigma)\right)(x)$$

Thus $\left(f^{-1}(\sigma)\right)$ is a co-fuzzy right ideal of $\mathcal{N}_1$

Hence $\left(f^{-1}(\sigma)\right)$ is a co-fuzzy ideal of $\mathcal{N}_1$.

**Theorem 4.6:** Let $\left(\mathcal{N}_1,+,\Gamma\right)$ and $\left(\mathcal{N}_2,+,\Gamma\right)$ be two finite Γ-near rings. The function $f$: $\mathcal{N}_1 \to \mathcal{N}_2$ is a onto homomorphism from $\mathcal{N}_1$ to $\mathcal{N}_2$. If $\mu$ is a co-fuzzy ideal of $\mathcal{N}_1$ then its image $f(\mu)$ is a co-fuzzy ideal of $\mathcal{N}_2$.

**Proof:** Let $f$: $\mathcal{N}_1 \to \mathcal{N}_2$ is an onto homomorphism from the finite Γ-near rings $\left(\mathcal{N}_1,+,\Gamma\right)$ to $\left(\mathcal{N}_2,+,\Gamma\right)$ and $\mu$: $\mathcal{N}_1 \to [0,1]$ is a fuzzy sub set of $\mathcal{N}_1$

Let $\mu$ be a co-fuzzy ideal of $\mathcal{N}_1$

Now we prove that $f(\mu)$ is a co-fuzzy ideal of $\mathcal{N}_2$

We have

$$\left(f(u)\right)(y) = \begin{cases}\inf_{z\in f^{-1}(y)}\ \mu(z) & if \quad f^{-1}(y) \neq \phi\\ 0 & if \quad f^{-1}(y) = \phi\end{cases} \quad \forall y \in N_2$$

Let $x, y, a, b \in \mathcal{N}_2$ and $\alpha \in \Gamma$

Since $f$ is onto from $\mathcal{N}_1$ to $\mathcal{N}_2$ then there exists $x_0, y_0, a_0, b_0 \in \mathcal{N}_1$ such that

$f(x_0) = x, f(y_0) = y, f(a_0) = a$ and $f(b_0) = b$

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1. $\big(f(\mu)\big)(x+y) = \text{Inf}_{z\in f^{-1}(x+y)}\,\mu(z)$ (1)

Let $\mu(x_0) = \text{Inf}_{z\in f^{-1}(x)}\,\mu(z)$ and $\mu(y_0) = \text{Inf}_{z\in f^{-1}(y)}\,\mu(z)$

$\Rightarrow f(x_0) = x$ and $f(y_0) = y$

Now $f(x_0 + y_0) = f(x_0) + f(y_0) = x + y$

$\Rightarrow x_0 + y_0 \in f^{-1}(x+y)$

From equation (1), $\big(f(\mu)\big)(x+y) = \text{Inf}_{z\in f^{-1}(x+y)}\,\mu(z)$

$\leq \mu(x_0 + y_0)$

$\leq Max\,\{\mu(x_0), \mu(y_0)\}$

$= Max\,\{\text{Inf}_{z\in f^{-1}(x)}\,\mu(z)\,, \text{Inf}_{z\in f^{-1}(y)}\,\mu(z)\}$

$= Max\,\{\big(f(\mu)\big)(x), \big(f(\mu)\big)(y)\}$

$\therefore (f(\mu))(x+y) \leq Max\,\{(f(\mu))(x), (f(\mu))(y)\}$

2. $\big(f(\mu)\big)(y+x-y) = \text{Inf}_{z\in f^{-1}(y+x-y)}\,\mu(z)$ (2)

Now $f(y_0 + x_0 - y_0) = f(y_0) + f(x_0) - f(y_0) = y + x - y$

$\therefore y_0 + x_0 - y_0 \in f^{-1}(y+x-y)$

From equation (2), $\big(f(\mu)\big)(y+x-y) = \text{Inf}_{z\in f^{-1}(y+x-y)}\,\mu(z)$

$\leq \mu\,(y_0 + x_0 - y_0)$

$\leq \mu(x_0)$

$= \text{Inf}_{z\in f^{-1}(x)}\,\mu(z)$

$= \big(f(\mu)\big)(x)$

$\therefore (f(\mu))(y+x-y) \leq (f(\mu))(x)$

3. $\big(f(\mu)\big)(a\alpha(x+b) - a\alpha b) = \text{Inf}_{z\in f^{-1}(a\alpha(x+b)-a\alpha b)}\,\mu(z)$ (3)

Now $f(a_0\alpha(x_0 + b_0) - a_0\alpha b_0) = f(a_0)\alpha\big(f(x_0) + f(b_0)\big) - f(a_0)\alpha f(b_0)$

$= a\alpha(x+b) - a\alpha b$

$\therefore a_0\alpha(x_0 + b_0) - a_0\alpha b_0 \in f^{-1}(a\alpha(x+b) - a\alpha b)$

From equation (3), $\big(f(\mu)\big)(a\alpha(x+b) - a\alpha b) = \text{Inf}_{z\in f^{-1}(a\alpha(x+b)-a\alpha b)}\,\mu(z)$

$\leq \mu(a_0\alpha(x_0 + b_0) - a_0\alpha b_0)$

$\leq \mu(x_0)$

$= \text{Inf}_{z\in f^{-1}(x)}\,\mu(z)$

$= \big(f(\mu)\big)(x)$

$\therefore (f(\mu))(a\alpha(x+b) - a\alpha b) \leq (f(\mu))(x)$

Thus $\big(f(\mu)\big)$: $N_2 \to [0,1]$ is a co-fuzzy left ideal of $\mathcal{N}_2$

4. $\big(f(\mu)\big)(x\alpha a) = \text{Inf}_{z\in f^{-1}(x\alpha a)}\,\mu(z)$ (4)

Now $f(x_0\alpha a_0) = f(x_0)\alpha f(a_0) = x\alpha a$

$\therefore x_0\alpha a_0 \in f^{-1}(x\alpha a)$

From equation (4), $\big(f(\mu)\big)(x\alpha a) = \text{Inf}_{z\in f^{-1}(x\alpha a)}\,\mu(z)$

$\leq \mu(x_0\alpha a_0)$

$\leq \mu(x_0)$

$= \text{Inf}_{z\in f^{-1}(x)}\,\mu(z)$

$= \big(f(\mu)\big)(x)$

$\therefore (f(\mu))(x\alpha a) \leq (f(\mu))(x)$

Then $\big(f(\mu)\big)$: $\mathcal{N}_2 \to [0,1]$ is a co-fuzzy right ideal of $\mathcal{N}_2$

Hence $\big(f(\mu)\big)$: $\mathcal{N}_2 \to [0,1]$ is a co-fuzzy ideal of $\mathcal{N}_2$.

## 5. CONCLUSION

In this article, we inspected the idea of co-fuzzy ideals of a finite $\Gamma$ – near ring. We proved some necessary and sufficient conditions for a fuzzy subset of finite $\Gamma$ – near ring to be co-fuzzy ideal of the ring. The intersection and union of co-fuzzy ideals and homomorphism theorems have been proved. This concept may be extended to Bipolar co-fuzzy ideals in finite $\Gamma$ – near rings.

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# Phytochemical Profile, Free Radical Scavenging and Anti-Inflammatory Properties of *Acalypha Indica* Root Extract: Evidence from In Vitro and In Vivo Studies

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**Abstract:** In our in vitro and in vivo studies, we used *Acalypha indica* root methanolic extract (AIRME), and investigated their free radical scavenging/antioxidant and anti-inflammatory properties. Primarily, phytochemical analysis showed rich content of phenols (70.92 mg of gallic acid/g) and flavonoids (16.01 mg of rutin/g) in AIRME. We then performed HR-LC-MS and GC-MS analyses, and identified 101 and 14 phytochemical compounds, respectively. Among them, ramipril glucuronide (1.563%), antimycin A (1.324%), swietenine (1.134%), quinone (1.152%), oxprenolol (1.118%), choline (0.847%), bumetanide (0.847%) and fenofibrate (0.711%) are the predominant phytomolecules. Evidence from in vitro studies revealed that AIRME scavenges DPPH and hydroxyl radicals in a concentration dependent manner (10–50 µg/mL). Similarly, hydrogen peroxide and lipid peroxidation were also remarkably inhibited by AIRME as concentration increases (20–100 µg/mL). In vitro antioxidant activity of AIRME was comparable to ascorbic acid treatment. For in vivo studies, carrageenan (1%, sub-plantar) was injected to rats to induce localized inflammation. Acute inflammation was represented by paw-edema, and significantly elevated ($p < 0.05$) WBC, platelets and C-reactive protein (CRP). However, AIRME pretreatment (150/300 mg/kg bodyweight) significantly ($p < 0.05$) decreased edema volume. This was accompanied by a significant ($p < 0.05$) reduction of WBC, platelets and CRP with both doses of AIRME. The decreased activities of superoxide dismutase, catalase, glutathione reductase and glutathione peroxidase in paw tissue were restored ($p < 0.05$ / $p < 0.01$) with AIRME in a dose-dependent manner. Furthermore, AIRME attenuated carrageenan-induced neutrophil infiltrations and vascular dilation in paw tissue. For the first time, our findings demonstrated the potent antioxidant and anti-inflammatory properties of AIRME, which could be considered to develop novel anti-inflammatory drugs.

**Keywords:** C-reactive protein; edema; free radical scavengers; phytochemicals; Indian Acalypha

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## 1. Introduction

Inflammation is a complex biological immune response to harmful stimuli of irritant chemicals, pathogens and damaged local injury cells in the tissue. Inflammatory system plays an important role in life-threatening diseases including COVID-19, cancer, diabetes and cardiovascular dysfunction [1,2]. Leukocyte activation such as macrophages, neutrophils, eosinophils and monocytes may occur during inflammation in order to protect the tissue, and simultaneously trigger the production of reactive oxygen species (ROS) or free radicals [3]. These ROS, include superoxide anion ($O_2^-$), hydrogen peroxide ($H_2O_2$), and hydroxyl radical ($^{\bullet}OH$) are highly reactive in nature, which counteract with adjacent

polyunsaturated fatty acids, proteins and DNA, and leading to cause lipid peroxidation, protein degradation, and DNA damage, respectively [4,5]. In order to combat this oxidative stress, cells are equipped with endogenous antioxidant enzymes and non-enzymatic defense systems. The antioxidant enzymes, mainly superoxide dismutase (SOD), catalase (CAT), glutathione reductase (GR) and glutathione peroxidase (GPx) however reach insufficient during inflammation and/or oxidative stress [4,6]. C-reactive protein is an acute phase inflammatory marker that remarkably elevates in various inflammatory diseases, including COVID-19, cancer, cardiovascular diseases (CVDs) and diabetes [7,8]. Oxidative stress can trigger various genes involved in inflammatory pathways, including nuclear factor kappa B (NF-κB), and intrinsically involved in the progression of chronic diseases [2,4]. It is therefore necessary to supplement anti-inflammatory and/or antioxidant compounds to assist the impaired immune and antioxidant defense systems.

Various plant-derived or synthetic antioxidant and anti-inflammatory compounds have been used to treat oxidative insult and inflammation, as these substances are capable in scavenging of ROS and inflammatory mediators [9,10]. However, the synthetic compounds have been claimed to cause mild to severe adverse effects. On the other hand, usage of herbal medication has been increased over the past three decades, and ~80% of the world's population living in the developing nations are rely on plant-based medicinal products as the primary source of healthcare [11]. Although several herbal compounds have been widely used as antioxidant or anti-inflammatory substances, many of them are yet to be investigated and their molecular mechanism needs to be disclosed. Therefore, identification of novel and effective therapeutic substances from medicinal plants with low or no side effects became prioritized research. The phenolic compounds and flavonoids are a family of bioactive constituents have been demonstrated as promising source for new medications to treat inflammation and related chronic painful diseases [12]. Phytol, a diterpene constituent of chlorophyll has been shown to suppress pro-inflammatory cytokines release through downregulation of NF-κB signalling pathway [13]. Methanolic extracts *Sideritis bilgeriana* reported to suppress tumour necrosis factor alpha (TNF-α), interleukin-1β (IL-1β) and leukocyte migration in carrageenan-induced pleurisy model. These pharmacological effects are due to the presence of phenolic and flavonoids content detected by HPLC-DAD-UV analysis [14].

*Acalypha indica* also known as 'Indian copperleaf' or 'Indian mercury' is a medicinal plant that belongs to *Euphorbiaceae* family. *A. indica* is widely distributed throughout the Asia and Africa. In folk medicine, the whole plant and leaves of *A. indica* have been used to treat asthma, pneumonia, stomach discomforts, skin injuries and snake bites [15,16]. Leaves of *A. indica* have been scientifically tested for their anti-bacterial [17], anti-inflammatory [18] and antioxidant [19] properties. Few studies isolated and identified the phytochemical constituents from the leaf extracts of *A. indica* [16,19]. Stems of *A. indica* are also reported to have antioxidant, glucose lowering and hepato-protective properties in experimental diabetic rats [20].

Nevertheless, the pharmacological properties of *A. indica* root methanolic extract (AIRME) have not been demonstrated. Furthermore, isolation and characterization of phytochemical compounds in AIRME is yet to be performed. We assume that roots of *A. indica* may also contain various phytochemical constituents that could exhibits pharmacological efficacies. Therefore, we aimed to perform HR-LC-MS and GC-MS techniques to identify the bioactive compounds in AIRME. In vitro studies were performed to investigate the free radical scavenging activity of AIRME. Subsequently, in vivo studies were conducted on rats to evaluate the antioxidant and anti-inflammatory activities of AIRME in carrageenan-induced acute inflammatory model.

## 2. Results

### *2.1. Phytochemicals in A. indica Root Extract*

Qualitative estimation of phytochemicals based on color intensity in the AIRME revealed that it has several phytochemical compounds such as phenols, flavonoids, saponins,

tannins, reducing sugars, alkaloids, terpenoids, coumarins, anthraquinones and anthocyanins. We then quantified major phytochemicals, phenols and flavonoids based on qualitative analysis, which aided in further fractionation, isolation and biological assessment. Quantitative estimations revealed total phenolic content in AIRME was 70.92 mg of gallic acid equivalent/g extract, and flavonoids content was 16.01 mg of rutin/g extract.

### *2.2. Phytochemical Profile of A. indica Root Methanolic Extract*

After quantification of phytochemicals, the AIRME was subjected to GC-MS and HR-LC-MS for profiling their individual chemical constituents. GC-MS analysis revealed that the extract contains a significant amount of lipid soluble constituents (volatile) and their metabolites. To be specific, GC-MS results showed 14 volatile compounds whereas HR-LC-MS explored 101 semi volatile and non-volatile phytochemicals in AIRME. The details of each phytochemical constituent, including molecular formula, mass, PubChem CID and percentage were presented in Table 1. The predominant phytomolecules in AIRME through HR-LC-MS were, retusoquinone (1.694%), ramipril glucuronide (1.563%), antimycin A (1.324%), propionylglycine methyl ester (1.18%), swietenine (1.134%), quinone (1.152%), oxprenolol (1.118%), choline (0.847%), bumetanide (0.847%) and fenofibrate (0.711%). Similarly, the major phytochemical constituents by GC-MS were piperidine-2,5-dione (3.73%), cephalotaxine, 3-deoxy-3,11-epoxy-,(3a,11a)- (2.66%) and octadecanoic acid (2.053%). Most of these compounds displayed a higher number of hydrogen bond donor/acceptor counts. The chromatograms obtained from GC-MS and HR-LC-MS analyses (Supplementary Materials Figures S1 and S2) and chemical structures of all compounds identified in AIRME (Figures S3 and S4) were provided as Supplementary Materials.

Computational calculations for the adverse effect descriptors of AIRME compounds showed that many compounds may not possess mutagenicity, tumorigenicity, reproductive toxicity and irritation (Table 1). These predictive non-toxic effects of the compounds need to be further confirmed through laboratory studies.

### *2.3. A. indica Root Extract Scavenges DPPH and Hydroxyl Radicals*

In vitro free radical scavenging activity of AIRME was determined by measuring the inhibition of DPPH and $^{\bullet}$OH. The results revealed that AIRME (10–50 µg/mL) significantly scavenges the DPPH radical in a concentration dependent manner with a $IC_{50}$ of 15.85 µg/mL, whereas the $IC_{50}$ with ascorbic acid treatment was 5.71 µg/mL (Table 2). Hydroxyl radical-induced deoxyribose sugar damage was significantly decreased by AIRME in a concentration-dependent manner with $IC_{50}$ of 14.74 µg/mL (Table 2). These findings signify the potent free radical scavenging activity of AIRME.

### *2.4. A. indica Root Extract Suppress Hydrogen Peroxide and Lipid Peroxidation In Vitro*

We found that the AIRME (20–100 µg/mL) effectively converted the hydrogen peroxide into water with $IC_{50}$ value of 65.40 µg/mL whereas ascorbic acid converted at $IC_{50}$ of 33.31 µg/mL. Furthermore, anti-lipid peroxidation activity of AIRME (20–100 µg/mL) was evidenced by a substantial suppression of lipid peroxides in egg homogenate. Inhibition of lipid peroxidation was proportionate with AIRME concentrations, and $IC_{50}$ was 79.70 µg/mL. The efficacy of AIRME against hydrogen peroxide and lipid peroxidation propagation was comparable to the potency of ascorbic acid (Table 2).

**Table 1.** Phytochemical profile of AIRME using chromatography techniques (HR-LC-MS and GC-MS), antioxidant descriptors (Hbds—Hydrogen bond donor count and Hbas—Hydrogen bond acceptors count) and adverse properties (Mut—mutagenicity, Tum—tumarogenicity, Irri—irritant and RepTox—reproductive toxicology) predicted using Marvin sketch, a computational tool.

| No | Compounds Identified by HR-LC-MS | RT | Formula | Mass | Hbds | Hbas | Mut | Tum | Irri | RepTox | PubChem CID | Percentage |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Oxtriphylline | 0.42 | $C_{12}H_{22}N_5O_3$ | 284.1715 | 1 | 4 | No | No | No | No | 656652 | 0.677 |
| 2 | Choline | 0.501 | $C_5H_{14}NO$ | 104.1074 | 1 | 2 | No | No | No | No | 6209 | 0.847 |
| 3 | Bumetanide | 0.612 | $C_{17}H_{20}N_2O_5S$ | 364.1112 | 3 | 7 | No | No | Yes | No | 2471 | 0.847 |
| 4 | Indospicine | 0.612 | $C_7H_{15}N_3O_2$ | 173.1165 | 4 | 4 | No | No | Yes | No | 108010 | 0.776 |
| 5 | 10-Hydroxy-2*E*,8E-Decadiene-4,6-diynoic acid | 0.613 | $C_{10}H_{12}O_3$ | 180.0772 | 2 | 2 | No | No | Yes | No | 9543616 | 0.745 |
| 6 | 2,6-Piperidinedicarboxylic acid | 0.615 | $C_7H_{11}NO_4$ | 173.069 | 2 | 4 | No | No | No | Yes | 557515 | 0.881 |
| 7 | Ala Ser His | 0.616 | $C_{12}H_{19}N_5O_5$ | 313.1392 | 6 | 7 | No | No | No | No | - | 0.644 |
| 8 | Arg Pro | 0.656 | $C_{11}H_{21}N_5O_3$ | 271.1652 | 5 | 7 | No | No | No | No | - | 0.677 |
| 9 | His Gly Val | 0.658 | $C_{13}H_{21}N_5O_4$ | 311.1577 | 5 | 6 | No | No | No | No | - | 0.627 |
| 10 | Pro Ile | 0.662 | $C_{11}H_{20}N_2O_3$ | 228.1459 | 4 | 4 | No | No | No | No | - | 0.661 |
| 11 | Fenofibrate | 0.669 | $C_{20}H_{21}ClO_4$ | 360.116 | 0 | 3 | No | No | No | No | 3339 | 0.711 |
| 12 | Mycophenolic Acid | 0.671 | $C_{17}H_{20}O_6$ | 320.1239 | 2 | 5 | No | No | No | No | 446541 | 0.881 |
| 13 | Mimosine | 0.673 | $C_8H_{10}N_2O_4$ | 198.0642 | 3 | 6 | low | No | No | No | 440473 | 0.911 |
| 14 | Dimethylglycine | 0.684 | $C_4H_9NO_2$ | 103.0634 | 1 | 3 | No | No | No | No | 673 | 0.640 |
| 15 | 3,7-Epoxycaryophyllan-6-one | 0.688 | $C_{15}H_{24}O_2$ | 236.1759 | 0 | 2 | No | No | No | No | 4330530 | 0.745 |
| 16 | L-2-Aminoadipic acid | 0.778 | $C_6H_{11}NO_4$ | 161.0686 | 3 | 5 | No | No | No | No | 92136 | 0.474 |
| 17 | *Trans*-4-Hydroxy-L-proline | 0.869 | $C_5H_9NO_3$ | 131.058 | 3 | 4 | No | No | No | No | 5810 | 0.372 |
| 18 | *N*2-Succinylglutamic acid | 0.883 | $C_9H_{13}NO_7$ | 247.0694 | 4 | 7 | No | No | No | No | 25244383 | 0.406 |
| 19 | Mucronulatol((+/−)) | 1.157 | $C_{17}H_{18}O_5$ | 302.111 | 2 | 5 | No | No | No | Yes | 442811 | 0.372 |
| 20 | Propionylglycine methyl ester | 1.698 | $C_6H_{11}NO_3$ | 145.0738 | 1 | 2 | No | No | No | No | - | 1.186 |
| 21 | Ile Tyr | 1.744 | $C_{15}H_{22}N_2O_4$ | 294.1575 | 4 | 6 | No | No | No | No | - | 0.847 |
| 22 | Phendimetrazine | 1.855 | $C_{12}H_{17}NO$ | 191.131 | 0 | 2 | No | No | No | No | 30487 | 1.016 |
| 23 | 4-(2-Hydroxy-3-isopropylaminopropyl)benzoic acid | 2.163 | $C_{13}H_{19}NO_4$ | 253.1313 | 3 | 5 | No | No | No | No | - | 0.406 |
| 24 | Mexiletine | 2.219 | $C_{11}H_{17}NO$ | 179.1309 | 0 | 1 | No | No | Yes | No | 4178 | 0.406 |
| 25 | *N*-(3-Oxo-octanoyl)homoserine lactone | 2.753 | $C_{12}H_{19}NO_4$ | 241.1335 | 1 | 3 | No | No | Yes | No | 127293 | 0.474 |
| 26 | Retusoquinone | 3.071 | $C_{11}H_{12}O$ | 160.0872 | 0 | 1 | No | No | No | No | 6111564 | 1.694 |
| 27 | Peucenin | 3.385 | $C_{15}H_{16}O_4$ | 260.103 | 2 | 4 | No | No | No | No | 68477 | 0.949 |
| 28 | Dehydrovariabilin | 3.494 | $C_{17}H_{14}O_4$ | 282.0845 | 0 | 3 | No | No | No | Yes | 624785 | 1.050 |
| 29 | Normeperidine | 3.598 | $C_{14}H_{19}NO_2$ | 233.1414 | 1 | 2 | No | No | No | No | 32414 | 0.881 |
| 30 | Thr Ala Ser | 3.605 | $C_{10}H_{19}N_3O_6$ | 277.1311 | 6 | 7 | No | No | No | No | - | 1.016 |
| 31 | Diethyl Oxalpropionate | 3.711 | $C_9H_{14}O_5$ | 202.0842 | 0 | 3 | No | No | No | No | 97750 | 0.881 |
| 32 | 3-*O*-Methylrimiterol | 3.763 | $C_{13}H_{19}NO_3$ | 237.1366 | 3 | 4 | No | No | No | No | - | 1.118 |
| 33 | Citrulline *n*-butyl ester | 4.092 | $C_{10}H_{21}N_3O_3$ | 231.1582 | 3 | 3 | No | No | Yes | No | 6426971 | 0.542 |
| 34 | 2(Benzylmethylamino)Ethanol *N*-Oxide | 4.126 | $C_{10}H_{15}NO_2$ | 181.1102 | 1 | 2 | No | No | No | No | 264996 | 0.372 |

**Table 1.** *Cont.*

| No | Compounds Identified by HR-LC-MS | RT | Formula | Mass | Hbds | Hbas | Mut | Tum | Irri | RepTox | PubChem CID | Percentage |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 35 | Chloramphenicol alcohol | 4.177 | $C_{11}H_{14}N_2O_6$ | 270.0845 | 4 | 6 | Yes | No | No | No | 10107147 | 0.406 |
| 36 | 12-Aminododecanoic acid | 4.41 | $C_{12}H_{25}NO_2$ | 215.1891 | 2 | 3 | No | No | No | No | 69661 | 0.745 |
| 37 | 3-Oxa-9azoniatricyclo[3.3.1.02,4]non ane, 9-ethyl-9-methyl-7[(phenylacetyl)oxy] | 4.522 | $C_{18}H_{24}NO_3$ | 302.1757 | 1 | 4 | No | No | No | No | - | 0.542 |
| 38 | 3,11-Dihydroxy myristoic acid | 4.835 | $C_{14}H_{28}O_4$ | 260.2002 | 3 | 4 | No | No | No | No | 5282923 | 0.881 |
| 39 | Avocadene acetate | 4.835 | $C_{19}H_{36}O_4$ | 328.2622 | 2 | 3 | No | No | Yes | No | 3624980 | 0.881 |
| 40 | Sulindac sulfide | 4.881 | $C_{20}H_{17}FO_2S$ | 340.0902 | 1 | 2 | No | No | No | No | 5352624 | 1.013 |
| 41 | 6-Methoxyquinoline | 4.928 | $C_{10}H_9NO$ | 159.0686 | 0 | 2 | Yes | No | No | No | 14860 | 1.288 |
| 42 | Edrophonium | 4.928 | $C_{10}H_{16}NO$ | 166.1233 | 1 | 1 | No | No | No | No | 3202 | 1.220 |
| 43 | Quinine | 4.939 | $C_{20}H_{24}N_2O_2$ | 324.1837 | 1 | 4 | No | No | No | No | 3034034 | 1.152 |
| 44 | 3-[2(Dimethylamino)ethoxy]phen ylmethyl]-4-methyl-phenol | 5.11 | $C_{18}H_{23}NO_2$ | 285.173 | 1 | 3 | No | No | No | No | - | 1.050 |
| 45 | Metyrapol | 5.301 | $C_{14}H_{16}N_2O$ | 228.1292 | 1 | 3 | No | No | No | No | 161210 | 0.949 |
| 46 | Oxprenolol | 5.322 | $C_{15}H_{23}NO_3$ | 265.1682 | 2 | 7 | No | No | Yes | No | 4631 | 1.118 |
| 47 | Oxyphencyclimine | 5.541 | $C_{20}H_{28}N_2O_3$ | 344.2094 | 1 | 6 | No | No | No | No | 4642 | 0.986 |
| 48 | Oxycodone | 6.166 | $C_{18}H_{21}NO_4$ | 315.1486 | 1 | 9 | No | No | No | No | 5284603 | 0.406 |
| 49 | Ergoline-8-methanol, 10-methoxy-1,6-dimethyl | 6.279 | $C_{18}H_{24}N_2O_2$ | 300.1858 | 1 | 3 | No | No | No | Yes | - | 0.847 |
| 50 | *Evoxine* | 6.332 | $C_{18}H_{21}NO_6$ | 347.136 | 2 | 10 | No | No | No | No | 73416 | 0.542 |
| 51 | 2-Hydroxytrimipramine | 6.339 | $C_{20}H_{26}N_2O$ | 310.2038 | 1 | 3 | No | No | No | No | 160610 | 0.474 |
| 52 | Penbutolol | 6.575 | $C_{18}H_{29}NO_2$ | 291.2196 | 2 | 5 | Yes | No | No | No | 37464 | 1.152 |
| 53 | Ala Lys Ile | 6.581 | $C_{15}H_{30}N_4O_4$ | 330.23 | 7 | 10 | No | No | No | No | - | 1.322 |
| 54 | Oxymorphone | 6.76 | $C_{17}H_{19}NO_4$ | 301.131 | 2 | 9 | No | No | No | No | 5284604 | 0.334 |
| 55 | Diamorphine (heroin) | 6.762 | $C_{21}H_{23}NO_5$ | 369.1566 | 0 | 7 | No | No | No | Yes | 5462328 | 0.406 |
| 56 | Terbinafine metabolite | 6.911 | $C_{19}H_{23}NO_3$ | 313.1672 | 3 | 5 | No | No | No | No | - | 1.098 |
| 57 | Strychnine | 6.912 | $C_{21}H_{22}N_2O_2$ | 334.1672 | 0 | 5 | No | No | No | No | 441071 | 1.050 |
| 58 | Hydrolysis product of bussein | 7.021 | $C_{32}H_{40}O_{14}$ | 648.241 | 8 | 26 | No | No | low | No | 54699399 | 1.145 |
| 59 | Ambelline | 7.026 | $C_{18}H_{21}NO_5$ | 331.1412 | 0 | 9 | Yes | No | No | No | 25092366 | 1.321 |
| 60 | 2-Pyrrolidinone, 4-(2aminoethyl)-1-ethyl-3,3diphenyl-(AHR 5904) | 7.039 | $C_{20}H_{24}N_2O$ | 308.1882 | 2 | 3 | No | No | No | No | 164917 | 1.023 |
| 61 | Glu Val Asp | 7.221 | $C_{14}H_{23}N_3O_8$ | 361.1518 | 7 | 17 | No | No | No | No | - | 0.953 |
| 62 | 10-Nitro,9Z,12Zoctadecadienoic acid | 7.339 | $C_{18}H_{31}NO_4$ | 325.2246 | 1 | 8 | No | No | No | No | 5282259 | 0.994 |
| 63 | 5β-Chol-2-en-24oic Acid | 7.397 | $C_{24}H_{38}O_2$ | 358.2954 | 1 | 4 | No | No | No | No | - | 0.912 |
| 64 | 5α-Cholan-24oic Acid | 7.733 | $C_{24}H_{40}O_2$ | 360.311 | 1 | 4 | No | No | No | No | 5283802 | 0.832 |
| 65 | Etioporphyrin III | 7.793 | $C_{32}H_{38}N_4$ | 478.317 | 2 | 4 | No | No | No | No | 141310 | 0.814 |
| 66 | Coproporphyrin II | 8.066 | $C_{36}H_{38}N_4O_8$ | 654.2548 | 6 | 10 | No | No | No | No | 165072 | 0.964 |

**Table 1.** *Cont.*

| No | Compounds Identified by HR-LC-MS | RT | Formula | Mass | Hbds | Hbas | Mut | Tum | Irri | RepTox | PubChem CID | Percentage |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 67 | Arg Ala Arg | 8.473 | $C_{15}H_{31}N_9O_4$ | 401.2552 | 15 | 15 | No | No | No | No | - | 0.456 |
| 68 | (5*Z*)-4,4-difluoro1alpha,25-dihydroxyvitamin D3/(5Z)-4,4-difluoro1alpha, 25dihydroxycholecalcifer | 8.766 | $C_{27}H4_2F_2O_3$ | 452.304 | 3 | 6 | No | No | No | No | - | 0.754 |
| 69 | Arg Val Pro | 8.887 | $C_{16}H_{30}N_6O_4$ | 370.2321 | 8 | 12 | No | No | No | No | - | 1.101 |
| 70 | Dihydrodeoxystreptomycin | 9.017 | $C_{21}H_{41}N_7O_{11}$ | 567.2862 | 16 | 29 | No | No | No | No | 11953824 | 1.021 |
| 71 | Swietenine | 9.019 | $C_{32}H_{40}O_9$ | 568.2704 | 1 | 10 | No | No | No | No | 76327465 | 1.134 |
| 72 | C16 Sphinganine | 9.686 | $C_{16}H_{35}NO_2$ | 273.266 | 3 | 3 | No | No | No | No | 5283572 | 0.786 |
| 73 | (*Z*)-*N*-(2hydroxyethyl)hexadec-7- | 11.085 | | 297.2658 | 2 | 2 | No | No | No | No | - | 0.354 |
| 74 | *N*-Hexadecyl-L-hydroxyproline | 11.684 | $C_{21}H_{41}NO_3$ | 355.307 | 3 | 4 | No | No | No | No | 66690736 | 0.834 |
| 75 | Trihexyphenidyl *N*-oxide | 12.227 | $C_{20}H_{31}NO_2$ | 317.2342 | 1 | 2 | No | No | No | No | 129318457 | 0.965 |
| 76 | Zearalenone | 12.772 | $C_{18}H_{22}O_5$ | 318.1478 | 2 | 4 | No | No | No | No | 5281576 | 0.236 |
| 77 | GPEtn(10:0/11:0)[U] | 12.813 | $C_{26}H_{52}NO_8P$ | 537.3399 | 2 | 4 | No | No | No | No | - | 0.875 |
| 78 | 25-Hydroxycholesterol(d3) | 12.829 | $C_{27}H_{43}D_3O_2$ | 405.3607 | 2 | 2 | No | No | low | No | - | 0.823 |
| 79 | Disopyramide | 13.729 | $C_{21}H_{29}N_3O$ | 339.2395 | 1 | 3 | No | No | No | No | 3114 | 0.787 |
| 80 | 12-Hydroxy-10octadecynoic acid | 13.763 | $C_{18}H_{32}O_3$ | 296.2341 | 2 | 3 | No | No | No | No | - | 0.867 |
| 81 | Anandamide (18:3, *n*-6) | 14.295 | $C_{20}H_{35}NO_2$ | 321.2652 | 2 | 2 | No | No | No | No | 5283445 | 0.564 |
| 82 | 9-Hydroxy-12-oxo10-octadecenoic acid | 14.4 | $C_{18}H_{32}O_4$ | 312.2287 | 2 | 4 | No | No | No | No | 5282968 | 0.753 |
| 83 | 13-OxoODE | 14.417 | $C_{18}H_{30}O_3$ | 294.2184 | 1 | 3 | No | No | Yes | No | 5283012 | 0.700 |
| 84 | 2*R*-hydroxy9*Z*,12*Z*,15*Z*-octadecatrienoic acid | 14.648 | $C_{18}H_{30}O_3$ | 294.2188 | 2 | 3 | No | No | No | No | 16061058 | 1.032 |
| 85 | Lactone of PGFMUM | 14.85 | $C_{16}H_{24}O_5$ | 296.1612 | 1 | 4 | No | No | No | No | - | 0.854 |
| 86 | *N* Acetylsphingosine | 15.403 | $C_{20}H_{39}NO_3$ | 341.2915 | 3 | 3 | No | No | No | No | 5497136 | 1.132 |
| 87 | Phytosphingosine | 16.285 | $C_{18}H_{39}NO_3$ | 317.2918 | 4 | 4 | No | No | No | No | 122121 | 0.126 |
| 88 | Dihydroceramide C2 | 16.767 | $C_{20}H_{41}NO_3$ | 343.3073 | 3 | 3 | No | No | No | No | 6610273 | 0.453 |
| 89 | 3-Deacetyl Khivorin | 16.926 | $C_{30}H_{40}O_9$ | 544.2667 | 1 | 5 | No | No | No | No | 46878892 | 0.763 |
| 90 | Harderoporphyrin | 17.931 | $C_{35}H_{36}N_4O_6$ | 608.2594 | 5 | 8 | No | No | No | No | 3081462 | 0.998 |
| 91 | His Arg Val | 18.001 | $C_{17}H_{30}N_8O_4$ | 410.2411 | 8 | 9 | No | No | No | No | - | 0.324 |
| 92 | Harderoporphyrinogen | 18.177 | $C_{35}H_{42}N_4O_6$ | 614.3115 | 4 | 9 | No | No | Yes | No | 193825 | 0.231 |
| 93 | Ramipril glucuronide | 18.404 | $C_{29}H_{40}N_2O_{11}$ | 592.2643 | 5 | 10 | No | No | No | No | - | 1.563 |
| 94 | Deoxykhivorin | 18.791 | $C_{32}H_{42}O_9$ | 570.282 | 0 | 4 | No | No | No | No | 6708722 | 0.232 |
| 95 | Antimycin A (A1 shown) | 19.021 | $C_{27}H_{38}N_2O_9$ | 534.2592 | 3 | 6 | No | No | Yes | No | 12550 | 1.324 |
| 96 | *N*-(2hydroxyethyl)icosanamide | 19.051 | $C_{22}H_{45}NO_2$ | 355.3432 | 2 | 2 | No | No | No | No | 3787294 | 1.021 |
| 97 | 9,14,19,19,19Pentadeuterio-1α,25dihydroxyprevitamin D3 / 9,14,19,19,19-pentadeuterio1alpha,25 | 19.24 | $C_{27}H_{39}D_5O_3$ | 421.355 | 1 | 1 | No | No | low | No | - | 1.240 |
| 98 | 2Tricosanamidoethanesulfonic acid | 19.241 | $C_{25}H_{51}NO_4S$ | 461.3489 | 2 | 4 | No | No | No | No | - | 1.200 |

**Table 1.** *Cont.*

| No | Compounds Identified by HR-LC-MS | RT | Formula | Mass | Hbds | Hbas | Mut | Tum | Irri | RepTox | PubChem CID | Percentage |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 99 | Trandolapril glucuronide | 20.16 | $C_{30}H_{42}N_2O_{11}$ | 606.2793 | 5 | 10 | No | No | No | No | 92023960 | 0.932 |
| 100 | 2,4,6-Trimethyl-2,15tetracosadienoic acid | 20.184 | $C_{27}H_{50}O_2$ | 406.3821 | 1 | 2 | No | No | No | No | - | 0.901 |
| 101 | 3β,6α,7αTrihydroxy-5β-cholan-24oic Acid | 20.754 | $C_{24}H_{40}O_5$ | 408.2845 | 4 | 5 | No | No | No | No | - | 0.875 |
| | **Compounds Identified by GC-MS** | | | | | | | | | | | |
| 1 | Piperidine-2,5-dione | 8.97 | $C_5H_7NO_2$ | 113.047 | 1 | 2 | No | No | No | No | 533930 | 3.733 |
| 2 | Phenol, 2,4-bis(1,1-dimethylethyl)- | 12.53 | $C_{14}H_{22}O$ | 206.167 | 1 | 1 | No | No | No | No | 528937 | 1.333 |
| 3 | Tridecanoic acid,12-methyl-, methyl ester | 14.92 | $C_{15}H_{30}O_2$ | 242.224 | 0 | 1 | No | No | No | No | 21204 | 1.200 |
| 4 | 1-Oxacyclopentadecan-2-one,15,15-dimethyl | 15.63 | $C_{16}H_{30}O_2$ | 254.224 | 0 | 1 | No | No | No | No | - | 0.800 |
| 5 | 11-Hexadecenoic acid, methyl ester | 16.88 | $C_{17}H_{32}O_2$ | 268.24 | 0 | 1 | No | No | No | No | 5364696 | 1.040 |
| 6 | Pentadecanoic acid, 14-methyl-, methyl ester | 17.08 | $C_{17}H_{34}O_2$ | 270.255 | 0 | 1 | No | No | No | No | 21205 | 1.493 |
| 7 | Octadecanoic acid | 17.78 | $C_{19}H_{38}O_2$ | 298.287 | 0 | 1 | No | No | No | No | 5281 | 2.053 |
| 8 | 13-Hexyloxacyclotridec-10-en-2-one | 18.52 | $C_{18}H_{30}O_2$ | 278.224 | 0 | 1 | No | No | No | No | 5369119 | 1.066 |
| 9 | 10-Octadecenoic acid,methyl ester | 18.82 | $C_{19}H_{36}O_2$ | 296.271 | 0 | 1 | No | No | No | No | 5364425 | 1.954 |
| 10 | Octadecanoic acid,methyl ester | 19.05 | $C_{19}H_{38}O_2$ | 298.287 | 0 | 1 | No | No | No | No | 8201 | 0.956 |
| 11 | Dasycarpidan-1-methanol,acetate (ester) | 20.37 | $C_{20}H_{26}N_2O_2$ | 326.44 | 1 | 2 | No | No | No | No | 550072 | 0.543 |
| 12 | Aspidospermidine-3-carboxylic acid, 2,3-didehydro-,methyl ester,[5a,12a,19a]- | 20.65 | $C_{21}H_{26}N_2O_2$ | 338.199 | 1 | 3 | No | No | No | No | - | 2.123 |
| 13 | Cephalotaxine, 3-deoxy-3,11-epoxy-, (3a,11a)- | 22.96 | $C_{18}H_{19}NO_4$ | 313.131 | 0 | 5 | No | No | No | No | - | 2.666 |
| 14 | 4-*H*-1-Benzopyran-4-one, 7-(acetyloxy)-2-(4-(acetyloxy)phenyl)-5-methoxy- | 25.6 | $C_{19}H_{14}O_7$ | 354.073 | 1 | 5 | Yes | No | No | Yes | - | 2.456 |

**Table 2.** In vitro free radical scavenging activity of AIRME. The results were compared with ascorbic acid and values represented as mean ± SD ($n$ = 3).

| Conc. (µg/mL) | Scavenging of DPPH Radical (%) | | Scavenging of Hydroxyl Radical (%) | | Conc. (µg/mL) | Inhibition of Hydrogen Peroxide (%) | | Inhibition of Lipid Peroxidation (%) | |
|---|---|---|---|---|---|---|---|---|---|
| | AIRME | Ascorbic Acid | AIRME | Ascorbic Acid | | AIRME | Ascorbic Acid | AIRME | Ascorbic Acid |
| 10 | 41.02 ± 0.58 | 50.38 ± 0.40 | 46.17 ± 0.77 | 53.81 ± 0.85 | 20 | 22.53 ± 1.41 | 42.68 ± 0.76 | 20.68 ± 1.72 | 33.06 ± 2.85 |
| 20 | 56.92 ± 1.15 | 61.46 ± 0.66 | 53.82 ± 1.13 | 61.88 ± 1.19 | 40 | 41.73 ± 0.70 | 55.88 ± 1.13 | 31.03 ± 2.97 | 43.34 ± 2.65 |
| 30 | 62.82 ± 0.59 | 70.36 ± 0.99 | 60.74 ± 1.61 | 68.48 ± 0.86 | 60 | 51.00 ± 1.17 | 59.44 ± 0.83 | 40.80 ± 2.10 | 50.77 ± 1.98 |
| 40 | 66.02 ± 0.80 | 77.04 ± 1.21 | 64.69 ± 1.30 | 82.36 ± 1.04 | 80 | 58.31 ± 1.09 | 62.49 ± 0.80 | 52.58 ± 1,87 | 58.66 ± 2.10 |
| 50 | 68.46 ± 0.70 | 78.88 ± 1.65 | 71.48 ± 0.63 | 84.41 ± 1.61 | 100 | 63.20 ± 1.20 | 68.85 ± 0.68 | 57.75 ± 2.06 | 65.25 ± 3.06 |
| $IC_{50}$ | 15.85 | 5.71 | 14.74 | 5.28 | $IC_{50}$ | 65.40 | 33.31 | 79.70 | 59.45 |

### 2.5. *A. indica* Root Extract Decreases Paw Edema Volume in Rats

Carrageenan induced acute inflammation was evidenced by the appearance of paw edema in rats. Carrageenan-induced rat paw edema is a well-established animal model to evaluate the anti-inflammatory properly of phytochemicals [10,21]. The edema volume was sharply increased 1 h after injection (38%) and reached maximum size by 5/6 h (52%) (Figure 1). However, edema volume was significantly decreased with ARIME (150 and 300 mg/kg b.w.) pretreatment. Although both doses of AIRME significantly inhibited the edema growth against carrageenan, the high-dose of AIRME (300 mg/kg b.w.) is more effective in inhibiting ($p < 0.05$) the edema development. The edema volume with AIRME high-dose at 1, 2, 3, 4, 5 and 6 h after injection was 24, 32, 34, 29, 21 and 7%, respectively, which is significantly lower compared to carrageenan group at all time points (Figure 1). Our results further emphasized that the decreased edema volume with AIRME was parallel with the standard anti-inflammatory drug, diclofenac treatment. Physical observations of paw further revealed that carrageenan-induced inflammatory edema was smaller in AIRME pretreated rats than that of their disease controls (Figure 2).

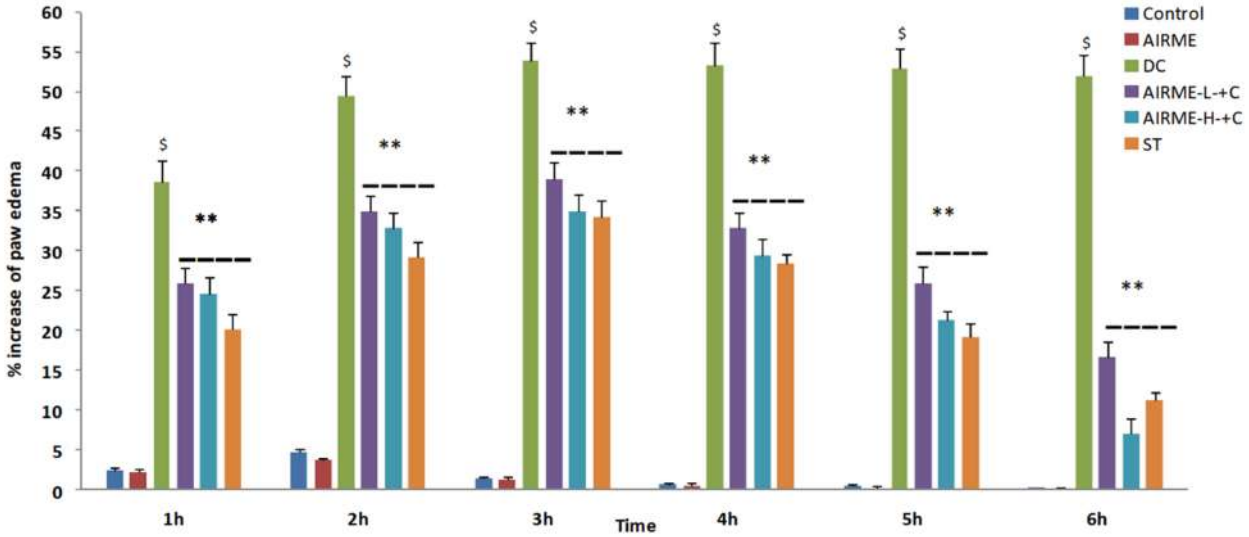



**Figure 1.** Percent changes in paw volume during the time course of 6 h after carrageenan injection (acute inflammation) in control and AIRME pretreated groups. Values are significant compared with control (\$ $p < 0.05$) and compared with carrageenan-injected group (** $p < 0.01$). NC, normal control; DC, disease control; AIRME, *A. indica* root methanolic extract; AIRME-L+C, AIRME-low-dose plus carrageenan; AIRME-H+C, AIRME-high-dose plus carrageenan; ST, standard treatment.

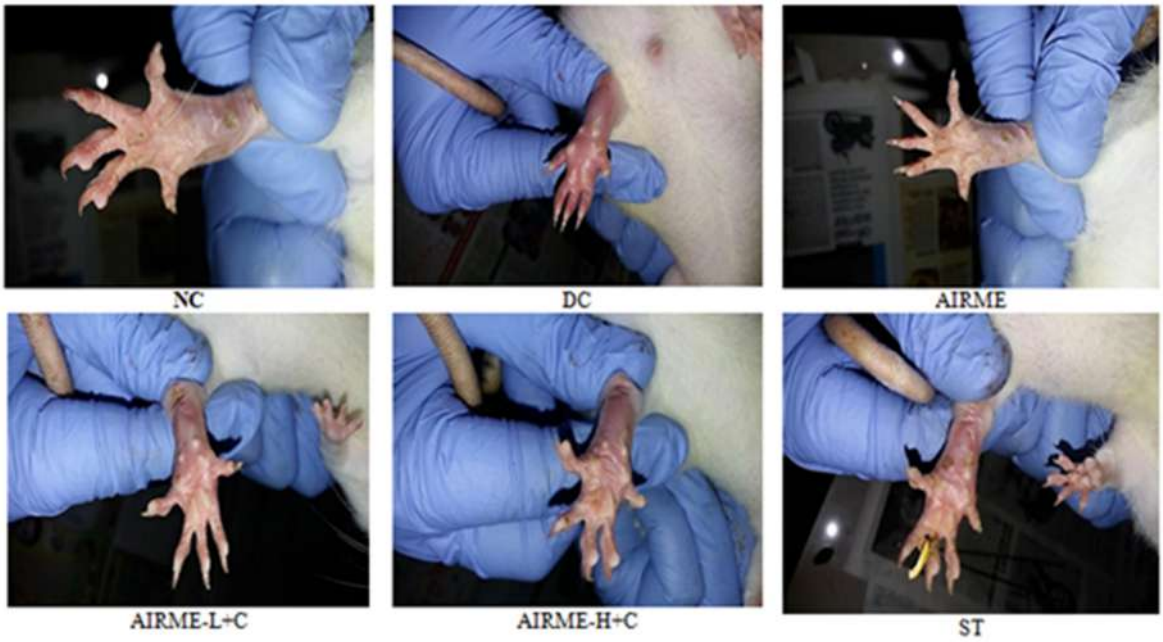



**Figure 2.** Physiological changes in rat paw tissue following carrageenan injection (1%) in different groups with or without AIRME 150. mg/kg), AIRME-H+C (300 mg/kg) and diclofenac (ST) pretreated rats. NC, normal control; DC, disease control; AIRME, *A. indica* root methanolic extract; AIRME-L+C, AIRME-low-dose plus carrageenan; AIRME-H+C, AIRME-high-dose plus carrageenan; ST, standard treatment.

### *2.6. A. indica Root Extract Attenuates Acute Inflammatory Response in Rats*

Hematological analyses showed a significant rise in white blood cells and platelets in carrageenan injected group compared with normal control ($p < 0.05$), which indicates acute inflammation in rats. The surge in WBC count and platelets in inflammatory rats was not seen in AIRME pretreated rats. This was represented by a remarkably less number of WBC and platelets with low-dose (150 mg/kg; $p < 0.05$) and high-dose (300 mg/kg; $p < 0.01$) of AIRME treatment (Table 3). Similarly, elevated CRP level (55.94 ± 4.86 ng/mL) with carrageenan injection was substantially decreased in AIRME treated groups (low-dose 36.98 ± 3.24; high-dose 31.84 ± 3.09 ng/mL). The dose-dependent decrease of CRP with AIRME was statistically significant ($p < 0.05$ and $p < 0.01$) compared with disease control group (Table 3).

**Table 3.** Effect of AIRME on white blood cells (WBC) and platelets count, and changes in serum C-reactive protein (CRP) in rats. Values represented as mean ± SD ($n = 6$). $ denotes significant at $p < 0.05$ compared with normal control (NC). Results are significant at $p < 0.05$ (*) and $p < 0.01$ (**) compared with disease control (DC).

| Groups | WBC ($10^9$/L) | Platelets ($10^9$/L) | CRP (ng/mL) |
|---|---|---|---|
| NC | 3.95 ± 2.06 | 320 ± 4.94 | 28.93 ± 2.95 |
| DC | 14.48 ± 4.76 $ | 1025 ± 8.67 $ | 55.94 ± 4.86 $ |
| AIRME | 4.02 ± 2.14 | 343 ± 5.07 | 30.32 ± 3.06 |
| AIRME-L+C | 9.76 ± 2.75 * | 765 ± 6.06 * | 36.98 ± 3.24 * |
| AIRME-H+C | 4.89 ± 2.43 ** | 366 ± 5.51 ** | 31.84 ± 3.095 ** |
| ST | 4.37 ± 2.14 ** | 337 ± 5.06 ** | 30.94 ± 3.065 ** |

NC—normal control; DC—disease control (carrageenan); AIRME—*Acalypha indica* roots methanolic extract; AIRME-L+C—AIRME-low dose plus carrageenan; AIRME-H+C—AIRME-high dose plus carrageenan and ST—standard treatment (diclofenac).

### *2.7. A. indica Root Extract Restores Antioxidant Enzyme Activities in Paw Tissue*

We then studied the response of antioxidant system with AIRME treatment against acute inflammation. Carrageenan-induced impaired antioxidant homeostasis in paw

tissue was represented by a significant reduction ($p < 0.05$) of SOD, CAT, GR and GPx enzyme activities. It is worth to note that carrageenan-induced loss of antioxidant enzyme activities was not seen in AIRME pretreated groups (150 and 300 mg/kg body weight). The dose-dependent preservation of antioxidant enzyme activities with AIRME was significant compared to the disease control group. To be specific, antioxidant property of the high-dose of AIRME is more effective ($p < 0.01$) and almost similar to the standard anti-inflammatory drug, diclofenac (Figure 3).

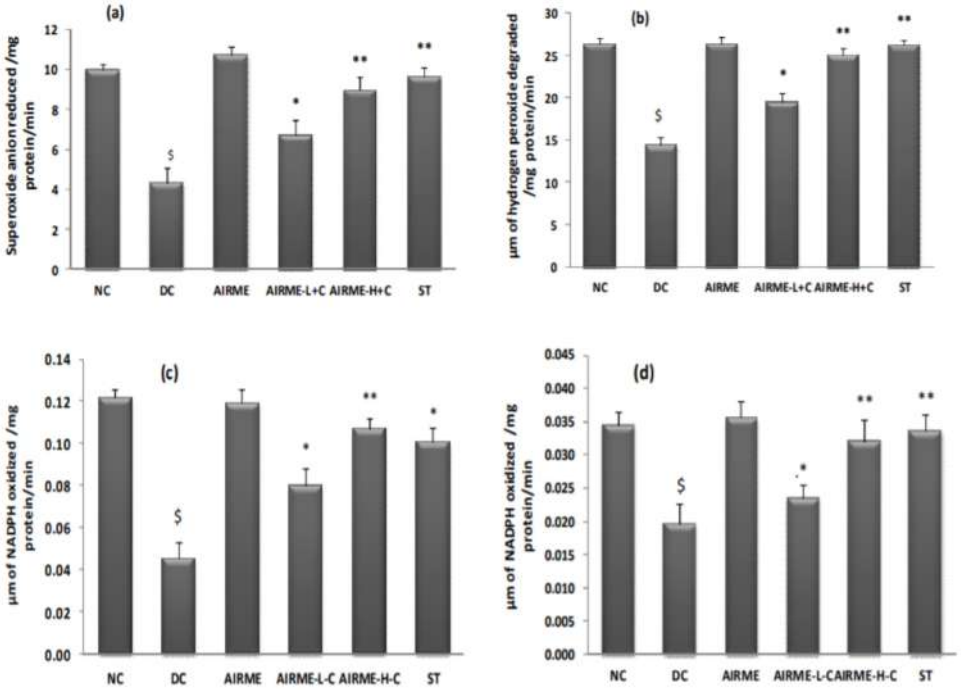



**Figure 3.** Changes in antioxidant enzyme (superoxide dismutase (**a**), catalase (**b**), glutathione reductase (**c**), glutathione peroxidase (**d**)) activities in paw tissues of different groups of rats. NC, normal control; DC, disease control (carrageenan); AIRME, *Acalypha indica* root methanolic extract; AIRME-L+C (AIRME low dose plus carrageenan); AIRME-H+C (AIRME high dose plus carrageenan), and ST (standard treatment, diclofenac). All values represented as mean ± SD ($n = 6$). $ indicates significant ($p < 0.05$) difference with NC. * ($p < 0.05$) and ** ($p < 0.01$) indicates significant difference with DC.

### *2.8. A. indica Root Extract Prevent Tissue Architectural Damage*

Tissue architectural derangements that occurred upon carrageenan injection, and tissue protective effects with AIRME pretreatment against inflammatory damage were examined through histopathological studies. Images from normal control and AIRME control groups showed normal architecture of the paw tissue with normal muscle around decalcified bone (DB) without vascular dilation and neutrophil infiltration. Carrageenan-induced acute inflammation was visualized by redness and swelling of paw, and tissue derangements were represented by edema, vascular dilation and accumulation of neutrophil infiltration in disease control group (Figure 4). Nevertheless, AIRME pretreatment (150 and 300 mg/kg b.w.) confined the paw tissue architectural damage through preventing the neutrophil infiltration, vascular dilation and suppressing edema (Figure 4). The anti-edematous activity of AIRME against acute localized inflammation was comparable with diclofenac treatment.

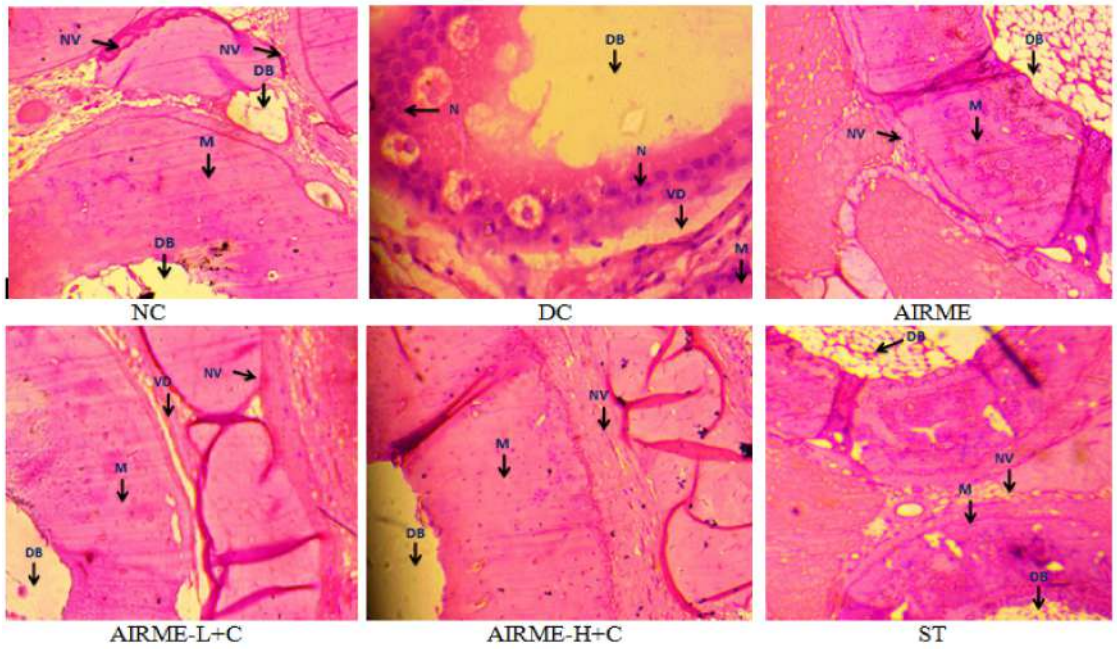



**Figure 4.** Histopathological study of inflamed paw tissue treated with AIRME. Paw tissue in NC and AIRME groups showed normal appearance of muscle (M) around the decalcified bone (DB), no vascular dilation (NV) and no infiltrate.

## 3. Discussion

Previous studies have shown the antioxidant, anti-inflammatory and tissue protective properties of *A. indica* leaf and stem extracts [18–20], but not the root extract. Besides, no study has identified the phytochemical constituents in *A. indica* root methanolic extract (AIRME) yet. For the first time, we screened the phytochemical constituents in AIRME, and reported 101 and 14 compounds from HR-LC-MS and GC-MS techniques, respectively. The major phytomolecules in AIRME were ramipril glucuronide (1.563%), antimycin A (1.324%), swietenine (1.134%), quinone (1.152%), oxprenolol (1.118%) choline (0.847%), bumetanide (0.847%) and fenofibrate (0.711%). Then, we demonstrated the antioxidant and anti-inflammatory properties of AIRME through in vitro and in vivo studies. In vitro free radical scavenging activity of AIRME was evidenced by a potent inhibition of DPPH and $^{\bullet}$OH radicals and substantial suppression of $H_2O_2$ and lipid peroxidation. Evidence from in vivo studies revealed that carrageenan-induced paw edema was significantly decreased (volume) in AIRME pretreated rats. The surge in WBC and platelets with response to acute inflammation was significantly suppressed in AIRME pretreated groups. Furthermore, elevated CRP levels with carrageenan injection were not seen in AIRME pretreated rats, which indicates potent anti-inflammatory activity of AIRME. Most importantly carrageenan-induced impaired antioxidant homeostasis in paw tissue was attenuated with AIRME treatment. This was represented by a significant conservation of SOD, CAT, GPx and GR activities against carrageenan-induced loss. Histopathological studies further emphasize the tissue protective effect of AIRME against carrageen-induced tissue derangements, accumulation of neutrophil infiltration and vascular dilation.

Oxidative stress is an imbalance between pro-oxidants and antioxidants that is typically involved in the progression of many diseases, including cancer, CVDs, diabetes and atherosclerosis [22]. Natural antioxidant compounds, such as plant-based phenols and flavonoids can give protection against oxidative stress by scavenging the highly reactive free radicals, and inhibiting the lipid peroxidation [23]. In this study, naturally occurred large quantities of phenols (70.92 mg of gallic acid/g) and flavonoids (16.01 mg of rutin/g) in AIRME could potentially scavenge the free radicals, and thereby prevent the oxidative stress. HR-LC-MS is a chromatography technique that examines the polar (phenols and flavonoids) and semi-polar compounds in plant extract [19]. Furthermore, GC-MS analysis

reported 14 compounds wherein non-polar/volatile phytochemicals are found in the root extract. Hydroxyl groups play an important role as a donor of hydrogen bonds, which is necessary for free radical scavenging, reduction of metals and molecular interaction with biomolecules [24]. In this study, we counted the hydrogen bond donors for all the identified phytochemicals through HR-LC-MS and GC-MS. The results showed that the majority of the compounds identified by HR-LC-MS exhibited these groups; while the number of compounds identified by GC-MS was lower (Table 1). These findings revealed that AIRME is a good source of antioxidant compounds, which could effectively eradicate the free radicals and/or prevent the oxidative stress.

Free radicals, and free radical source $H_2O_2$, is a well-known weak oxidizing agent, rapidly cross the cell membrane, reacts with ions such as $Fe^{2+}/Cu^{2+}$ and resulting in the generation of highly toxic hydroxyl radicals [25]. The cellular antioxidant defense system plays a significant role in quenching the toxic free radicals, and thereby protects the biomolecules from oxidative modification. In addition to the cellular antioxidant mechanism, the exogenous antioxidants from natural medicinal plants can enhance the protection against disease or stress [26,27]. The free radical scavenging activity of AIRME in this study was revealed by efficient scavenging of $H_2O_2$, $^{\bullet}OH$ and DPPH radicals, which is comparable to the scavenging ability of the standard ascorbic acid (Table 2). The existence of phenols and flavonoids with HBDC, such as Bumetanide, Bussein's hydrolysis product, Coproporphyrin II, Dihydrodeoxystreptomycin, Ramipril glucuronide and Trandolapril glucuronide further strengthen the free radical scavenging or antioxidant activity of AIRME.

Identification and developing of natural medicinal compounds without adverse effects is critical for pharmaceutical companies in order to promote the medicinal values and to gain final marketing approval. Toxicity evaluation of the plant compounds is typically a laborious process with several complexities, and includes the requirement of animal models, cell lines, expenditure, man power and a long duration of time. To overcome these difficulties, computational calculation is an alternative approach to assess the adverse effects of newly identified plant compounds [28]. Therefore, we used computational calculation, and measured the potential adverse effects, such as mutagenicity, tumorigenicity, irritant and reproductive toxicity of the compounds that were identified in AIRME. The predictions showed that most of the compounds in AIRME may not have mutagenicity, tumorigenicity, irritant and reproductive toxicity. These toxicity assessments are predictive, and laboratory studies are necessary to confirm the toxicity of individual phytomolecules of AIRME.

Acute inflammatory response is mainly represented by an increased vascular permeability and neutrophil infiltration, which leads to edema formation. In the cellular events, extravasation of fluids and proteins is accompanied with excessive accumulation of leukocytes at the inflammatory site [29,30]. Carrageenan, a highly sulfated polysaccharide is widely used as food additive due to its capability to enhance the food structure [31]. Carrageenan (non-antigenic phlogistic agent)-induced rat paw edema is a well-established and widely used model to evaluate the anti-inflammatory properly of plant and synthetic compounds [10,21]. Carrageenan-induced edema development is a biphasic acute inflammatory response [29]. In the first phase from 0 to 2.5 h, carrageenan triggers the release of acute phase mediators, mainly serotonin, histamine and kinins, which influence the vascular permeability [32]. Then, prostaglandins are the key players in the second phase of inflammation that occurs around 3 h after carrageenan injection [33]. These events provoke the release of several pro-inflammatory mediators, where inhibition terminates the inflammatory process [34]. Local inflammation is associated with oxidative burst and increased production of pro-inflammatory cytokines, such as TNF-$\alpha$, IL-1$\beta$, IL-6 and nitric oxide [35].

The carrageenan-induced inflammation in our study was witnessed by increased CRP levels and elevated WBC and platelet count. Platelets usually gathered at the injured site, adhere to the WBCs and release cytokines and chemokines that are chemotactic

for neutrophils and monocytes. These events subsequently increase inflammation [36]. CRP is an acute phase inflammatory marker that increases rapidly and dramatically in response to acute inflammation [37]. It has been shown that CRP can enhance the platelet-activating factor (PAF)-induced inflammation via binding to PAF and its precursor [38]. One of our key findings is that AIRME received rats exhibited lower levels of CRP as well as decreased WBC and platelet count, which implies potent anti-inflammatory activity. In the phytochemical screening, we reported several pharmacological compounds, like oxtriphylline (0.677%), choline (0.847%), bumetanide (0.847%), swietenine (1.13%) and fenofibrate (0.711%) in the root extract. A previous study has shown that choline and aspirin together can suppress the pro-inflammatory mediators against acute inflammation induced by carrageenan and lipopolysaccharide [39]. Other phytochemicals, bumetanide [40], fenofibrate [41] and swietenine [42] are also reported to possess anti-inflammatory activity via downregulation of pro-inflammatory cytokines. Another study documented that methanolic extract *Sideritis bilgeriana* suppressed TNF-α, IL-1β and leukocyte migration in carrageenan-induced pleurisy model, which is due to the presence of f phenolic and flavonoids content [14]. It is persuaded that existence of these pharmacological compounds in AIRME could act as anti-inflammatory agents, and thereby suppress inflammation and edema in carrageenan-injected rats. The anti-inflammatory property of AIRME was comparable to the diclofenac, a nonselective non-steroidal anti-inflammatory drug.

ROS or free radicals at low concentrations act as signaling molecules; however, they are deleterious to cells at high concentrations. Due to their highly reactive nature, ROS reacts with vital biomolecules, proteins, lipids and DNA and can cause irreversible damage. To prevent such oxidative damage, cells have evolved an array of defense systems, including antioxidant enzymes that scavenge excessive ROS. Cells experienced oxidative stress when the balance tipped between antioxidants and free radicals [4,5]. All antioxidant enzymes, including SOD, CAT, GPx and GR estimated in paw edema were significantly decreased after carrageenan injection, which reflects impaired antioxidant homeostasis and state of oxidative stress. Carrageenan injection has been reported to trigger intracellular ROS production, decrease antioxidant capacity and cause inflammation [31,43]. Excessive production of oxygen free radicals in the extracellular space and relatively low activities of SOD and CAT in the inflammatory state increase the vulnerability of extracellular components to ROS and stimulate chemotaxis for other inflammatory cells [44].

However, pretreatment of AIRME restored the SOD, CAT, GPx and GR activities against carrageenan-induced loss. In vivo antioxidant property of AIRME is corroborates with in vitro DPPH radical scavenging activity, and suppressed $H_2O_2$ and lipid peroxidation. Similar to our findings, oral administration of amiodarone, an anti-arrhythmic agent to carrageenan-injected rats has been shown to decrease the paw edema volume and inflammation in association with increased antioxidant enzyme activities [45]. The anti-inflammatory property of *Pistacia lentiscus* fruit oil is accompanied by the increased activities of SOD, CAT and GPx and decreased lipid peroxidation in rat paw tissue after carrageenan injection [46]. Another study showed that cashew nuts supplementation ameliorated the carrageenan-induced diminution of SOD and CAT activities and GSH concentrations. Cashew nuts further suppressed the release of pro-inflammatory cytokines and prevent the oxidative stress [47]. These findings imply that the anti-inflammatory property of natural compounds is associated with antioxidant property against carrageenan-induced oxidative stress. The increased antioxidant enzyme activity or free radical scavenging capacity of AIRME in our study might be due to the presence of various phytochemicals in the root extract. AIRME phytochemical screening represented with high HBDC and HBAC, including ramipril glucuronide (1.563%), antimycin A (1.324%), dihydrodeoxystreptomycin (1.021%), swietenine (1.134%), hydrolysis product of bussein (1.145%), terbinafine metabolite (1.098), oxprenolol (1.118%) and 3-*O*-methylrimiterol (1.118%).

The antioxidant activity of AIRME was further confirmed by tissue protective effect against carrageenan-induced architectural damage to paw tissue. From the histopathological studies, it is visible that the inflamed area appears with edema, congestion, vascular

dilation and neutrophil infiltration. These morphological changes in paw tissue are the typical events of local inflammation caused by carrageenan injection. However, AIRME treatment prior to carrageenan injection decreased edema and prevented vascular dilation and a surge in neutrophil infiltration, which reveals an anti-inflammatory property. Suppressed paw edema and neutrophil recruitment in paw tissue have been reported as a key anti-inflammatory property of crocin (an active constituent of saffron) against histamine injection in rats [48]. Naik and colleagues reported that pathological changes, including hepatic steatosis with severe swelling of hepatocytes and fat accumulation in obese rats were partially attenuated with *A. indica* leaf extracts. However, this study not revealed the phytochemical composition in the leaf extracts of *A. indica* [49]. Another study showed that quinone alkaloid pretreatment significantly inhibited carrageenan-induced paw edema in rats [50]. Astragalin, a naturally existing flavonoid in plants alleviated epithelial hyperplasia, severe leukocyte infiltration and sub epidermal edema induced by carrageenan injection [51]. AIRME also possesses flavonoids, quinine, phenols and other active ingredients which may contribute for the tissue protective effects. To our knowledge, this is the first evidence to demonstrate the tissue protective effect of AIRME against carrageenan-induced tissue damage.

## 4. Materials and Methods

### *4.1. Chemicals*

The chemicals used in this research were obtained from the following scientific companies: Sigma (St. Louis, MO, USA), TCI (Shanghai, China), Merck (Mumbai, India), SRL (New Delhi, India) and Fisher (Pittsburgh, PA, USA).

### *4.2. Collection and Preparation of A. indica Root Extract*

*A. indica* whole plant was collected from the campus garden of Sri Venkateswara University, Tirupati, India. Plant specimen was authenticated by the Taxonomist, Department of Botany, Sri Venkateswara University, Tirupati and herbarium was deposited with a voucher no: SVU-BOT-926. The roots were separated from the plant, and washed with running tap water to remove soil, then washed again with fresh water and shade dried. The dried root material was powdered using blender, and 100 g of the powder was transferred into amber color bottle containing 500 mL of methanol (1:5). The mixture was incubated with occasional stirring for 3 days, and the solvent was filtered with non-absorbent cotton, muslin cloth and Whatman no 1 filter paper finally. The filtrate was concentrated in rotary evaporator (BUCHI 036576, Roskilde, Denmark) and lyophilized (VIRTIS:Model BT4KZL-105, Midland, Canada) to obtain *A. indica* root methanolic extract (AIRME).

### *4.3. Qualitative Estimation of Phytochemicals*

We have primarily tested for the phytochemicals of phenols, flavonoids, saponins, tannins, reducing sugars, alkaloids, terpenoids, coumarins anthraquinones and anthocyanins in the AIRME according to the protocols stated by Shukla and colleagues [52].

### *4.4. Quantitative Estimation of Phytochemicals*

#### 4.4.1. Determination of Total Phenolic Content

According to Gutierrez and Navarro [53], the total phenolic content of AIRME was measured using the Folin Ciocalteu (FC) method. Briefly, 0.5 mL (5 mg) of extract at different concentrations (5–50 µg/mL) and same concentrations of standard gallic acid was added to 1 mL of FC (10%) reagent. For this reaction, 2.5 mL of sodium carbonate solution was added and incubated at room temperature for 30 min. Using a UV-Vis spectrophotometer (Shimadzu UV-1800, Kyoto, Japan) the resulting reaction was measured at 760 nm. The gallic acid standard graph was used to calculate the phenolic content of the extract, and expressed as mg of gallic acid equivalent per g of extract.

#### 4.4.2. Determination of Total Flavonoids Content

Total flavonoid content in AIRME was quantified by following aluminum chloride method [54]. Briefly, 1.0 mL of extract (10 mg/mL) was added to 4 mL of distilled water. To this, 0.3 mL of 5% $NaNO_2$ and 0.3 mL of 10% aluminum chloride ($AlCl_3$) solutions were added and incubate for 6 min. Then, 2 mL of 1 M NaOH solution was added and made up to 10 mL with distilled water. The reaction mixture was incubated for another 15 min and the flavonoid content was measured at 510 nm. Rutin was used as standard for calculating flavonoid content in AIRME, and content was expressed as mg of rutin equivalent per g of extract.

#### 4.4.3. Phytochemical Profiling and Gas Chromatography-Mass Spectrometry (GC-MS) analysis of AIRME

GC-MS analysis for AIRME was achieved by JEOL GC MATE II (GC model, Agilent Technologies 6890N Network GC system, Santa Clara, CA, USA) equipped with HP 5 MS column. High pure helium as carrier gas at a constant flow rate of 1 mL/min was used for GC separation. Injector temperature was set at 220 °C and oven temperature was set as 50 °C raised to 250 °C at 10 °C/min. Total GC running time was 30 min. A highly sensitive quadruple double focusing mass analyzer was used and equipped with photon multiplier tube as the detector; mass range of 50 to 600 amu; and ionization voltage (Electron impact ionization) 70 eV was used. This protocol was also explained in our previous study [19]. Mass of each peak was obtained from mass spectroscopy while the proposed structures of compounds were predicted from the screening library of National Institute of Standard and Technology (NIST, Gaithersburg, MD, USA).

#### 4.4.4. Phytochemicals Profiling and HR-LC-MS Analysis of AIRME

The AIRME was then analyzed in HR-LC-MS (Model: Agilent 1290 Infinity UHPLC System, Santa Clara, CA, USA) in order to identify the finger prints of other hidden phyto moieties. For this assessment we followed procedure described by Ravi et al., [19]. Briefly, an auto sampler injected a 3 µL volume of the sample into a C18 column (ZORBAX 2.1 9. 50 mm 1.8 Micron). The auto sampler has a 100 µL/mL auxiliary pull and ejects the sample quickly. Two binary pumps (G4220B) are integrated in one housin and deliver desired mobile phase gradient ratios (solvent A: 0.1% Formic Acid (FA) in water and B: 90% Acetonitrile + 10% $H_2O$ + 0.1% FA). The total run time was 30 min, during which the solvent A-95% + B-5% was initiated at 2 min, the solvent A gradient ratio changed to 5% at 20 min, and the solvent A 95% was maintained from 26 to 30 min. The binary pump pressure was kept stable at 1200 bar, and the flow rate was 0.300 mL/min. The Mass Hunter workstation program was used to gain an edge in identifying correct MS and MS/MS for the extract's LC profile.

#### 4.4.5. Computational Calculations for the Identified Phytochemicals

The resulted phytochemicals from analytical techniques were structurally drawn and their chemical descriptors, such as hydrogen bond donor count (HBDC) and hydrogen bond acceptor count (HBAC) were predicted using Marvin Sketch 16.3.21 version (https://chemaxon.com/products/marvin, (accessed on 8 June 2021)), a chemo informatics tool. In addition, the pharmacological properties of these compounds include tumorigenic, mutagenic, irritant and reproductive effects were assessed using DataWarrior V4.7.2 software (http://www.openmolecules.org/datawarrior/, (accessed on 8 June 2021)).

### *4.5. In Vitro Studies*

Free Radical Scavenging and Anti-Lipid Peroxidation Activities of AIRME

In vitro free radical scavenging activity of AIRME was carried out by incubating different concentrations of extract (10–50 µg/mL) with 0.6 mM DPPH. The resulting reaction optical density (OD) was read at 517 nm against ethanol blank [55]. Hydroxyl radical ($^{\bullet}OH$) scavenging ability of AIRME was assayed by adopting the deoxyribose

method as described by Nagai et al., [56]. The •OH radicals of Fentons reagent degrade the deoxyribose sugar, whereas prevention of such degradation of sugar by AIRME was studied with different concentrations (10–50 µg/mL). The OD of samples was read at 520 nm against blank containing total reaction mixture with absence of AIRME.

The hydrogen peroxide ($H_2O_2$) inhibition/reduction property of AIRME was carried out by incubating different concentration of extract (20–100 µg/mL) with $H_2O_2$ for 30 min. Retained $H_2O_2$ after incubation was read at 230 nm against phosphate buffer blank [57] in UV-VIS spectrophotometer (Shimadzu UV-1800, Kyoto, Japan). Next, anti-lipid peroxidation property of AIRME was determined using egg homogenate treated with Fentons reagent for 1 h incubation as described by Upadhyay et al. [58]. Prevention of lipid peroxidation by various concentrations of AIRME (20–100 µg/mL) was read at 532 nm using total reaction without extract as a blank.

### *4.6. In Vivo Studies*

#### 4.6.1. Experimental Design and Treatment

Anti-inflammatory and antioxidant activity of AIRME was studied in 1% carrageenan induced paw edema in rats. Thirty-six male adult rats of Wistar strain were purchased from the Indian Institute of Science (IISc), Bangalore. Rats were kept in cages, allowed to acclimatize for a week with conditions of 25–28 °C temperature, 50–55% humidity, with regular light/dark cycle (7:00 AM to 7:00 PM). Strict ethical guidelines for the maintenance and care of experimental animals were followed. The entire study design and protocols used in this study were reviewed and approved by the Institutional Animal Ethics Committee (09/(i)/a/CPCSEA/IAEC/SVU/ZOOL/KSR/Dt.08/07/2012) of Sri Venkateswara University, Tirupati, India. After acclimatization, rats (190 gm ± 10 gm bodyweight) were divided into six experimental groups with six rats in each as mentioned below:

- Group I—Normal control (NC): Rats in this group received 50 µL normal saline by sub-plantar injection (SPI);
- Group II—Disease control (DC): Carrageenan (1%, 100 µL) was injected (SPI) into the rat paw to induce acute localized inflammation;
- Group III—AIRME control (AIRME): Rats in this group received only AIRME (300 mg/kg bodyweight) by oral gavage;
- Group IV—AIRME low-dose plus carrageenan (AIRME-L+C): Rats were orally administered with low dose of AIRME (150 mg/kg body weight) through oral gavage 1 h prior to carrageenan injection.;
- Group V—AIRME high-dose plus carrageenan (AIRME-H+C): Rats in this group received high dose of AIRME (300 mg/kg body weight) 1 h prior to carrageenan injection, as described in group IV;
- Group VI—Standard treatment (ST): Rats in this group received diclofenac (20 mg/kg body weight) by oral gavage one hour before carrageenan injection.

Carrageenan-induced rat paw edema is a well-established and widely used model to evaluate the anti-inflammatory properly of plant and synthetic compounds [10,21,59]. The AIRME doses (150 and 300 mg/kg body weight) used in this study were based on our preliminary dose-dependent studies, where we found various doses of AIRME (100, 150, 200, 250 and 300 mg/kg bodyweight) did not produce any physiological or behavioral changes in normal rats. Besides Sathya and colleagues documented no adverse with different doses of *A. indica* ethanolic extracts ranges from 5 to 2000 mg/kg b.w. [60].

#### 4.6.2. Measurement of Paw Volume

The perimeter of the inflamed and AIRME treated paws of experimental animals was measured using digital screw gauge (model: Insize-3109-25s-digital outside micrometer) as described by Killari and team (2019) [61]. The paw volume was measured for every

hour until 6 h following carrageenan injection. The percent increase in paw thickness was calculated using the formula (Equation (1)):

$$\frac{Y_t - Y_0}{Y_0 x \times 100} \quad (1)$$

where:

- $Y_t$—thickness of paw at different time intervals (1, 2, 3, 4, 5 and 6 h) (after carrageenan induction);
- $Y_0$—thickness of paw at 0 h (before injection of carrageenan).

Resulted final value for every group at every hour was obtained through calculated mean.

#### 4.6.3. Blood Collection and Analyses

After treatment period, rats were subjected to chloroform anesthesia and sacrificed with cervical dislocation. On the experiment day, the blood samples (approximately 5 mL) were immediately collected through heart puncture into tubes that contain anti-coagulant (EDTA). In blood, white blood cells (WBC) and platelets were counted using a haemogram. For the CRP assay, blood samples were centrifuged at 4000× *g* rpm for 15 min, and serum was collected. Then C-reactive protein (CRP) levels were measured in the serum using kit provided by Aspen Laboratories (Himachal Pradesh, India). The changes in CRP in different groups were expressed as ng/mL. The blood collection procedures and assay protocols were approved Institutional Animal Ethics Committee.

#### 4.6.4. Determination of Antioxidant Enzyme Activities in Paw Tissue

Paw tissue was separated, cleaned with normal saline and stored at −40 °C for further biochemical analysis. Antioxidant status of paw tissue was measured by assessing the primary antioxidant enzyme activities. The activity of superoxide dismutase (SOD) in the paw homogenates was measured using the Misra and Fridovich [62] method at 480 nm for 4 min on a Shimadzu UV-1800 spectrophotometer. The activity was measured as the quantity of enzyme that prevents epinephrine from being oxidized by 50%, which was equal to 1 U per mg of protein. Catalase (CAT) activity was evaluated using Aebi, [63] procedure, and the sample's absorbance was recorded using a UV spectrophotometer at 240 nm for 1 min. The moles of hydrogen peroxide (0.066 M) decomposed per mg of protein each minute equals to one unit activity. The GR activity was measured at 340 nm for 3 min in spectrophotometer. The GR activity was expressed in micromoles of NADPH oxidized per mg of protein per minute [64]. GPx activity of paw tissue was measured using a reaction mixture composed of GSH (0.01 M), 12 mM *t*-butyl-hyroperoxide, 1.5 mM NADPH, and GR (0.24 units). The mM of NADPH oxidized/mg protein/min was measured at 340 nm for 180 s to determine enzyme activity [65].

#### 4.6.5. Histopathology

The paw tissue biopsy of rats from all experimental groups were taken and fixed in 10% formalin to prevent autolysis, which permanently cross-links and stabilizes their proteins. Then, the paw tissue was decalcified with weak formic acid before trimming to acquire the proper size and orientation of tissue (10%). The tissue sample was also infiltrated with paraffin to obtain its water content before being embedded in paraffin. Then the tissue embedded in paraffin was sliced into 6–8 µm section cuttings in a microtome as described by Slaoui and Fiette [66]. Further, tissue sections were stained with hematoxylin and eosin (H&E) on glass slide. The histopathological changes in paw tissue sections were observed under the microscope (Trinocular BX53, Olympus, Singapore) and the changes were recorded at 40× magnification.

### *4.7. Statistical Analysis*

We used SPSS (Version 15, SPSS Inc., Chicago, IL, USA) and Excel for statistical analyses. The data expressed as means ± standard deviation (SD). One-way analysis of variance (ANOVA), followed by Duncan's multiple comparison tests were performed for group comparison and significance. Statistical significance was set at $p < 0.05$.

## 5. Conclusions

For the first time, we demonstrated that *A. indica* root extract is rich in various phytochemical constituents without adverse effect descriptors. The major phytomolecules are ramipril glucuronide, antimycin A, swietenine, quinone, oxprenolol, choline, bumetanide and fenofibrate. AIRME showed potent free radical scavenging activity (DPPH and $^{\bullet}$OH) and inhibition of lipid peroxidation ability. AIRME pretreatment diminished carrageenan-induced paw edema, and decreased WBC, platelets and CRP levels in rats. Improved antioxidant status with AIRME was further confirmed by its tissue protective effects against acute inflammatory damage. Owing to the potent antioxidant and anti-inflammatory properties of AIRME, our findings suggest considering of AIRME in developing and preparation of novel anti-inflammatory drugs. However, further studies are necessary to explore in-depth molecular mechanism with specific known compounds of *A. indica* root extract.

**Supplementary Materials:** The following are available online, Figure S1: Chromatogram obtained for AIRME from HR-LC-MS, Figure S2: Chromatogram obtained for AIRME from GC-MS and Figure S3: Chemical structures of AIRME obtained from both HR-LC-MS and GC-MS.

**Author Contributions:** Conceptualization, R.S., S.R.K. and M.K.; methodology and analyses, R.S., J.P., S.B. and V.S.G.; data curation and visualization, S.K.R., W.Y. and R.S.; writing—original draft preparation, R.S. and J.P.; writing—review, editing and finalizing, S.R.K., W.Y. and M.K.; supervision, S.R.K. and M.K.; project administration and funding acquisition, R.S. and S.R.K. All authors have read and agreed to the published version of the manuscript.

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**Institutional Review Board Statement:** This study was performed in accordance with the institutional animal care and use committee, Sri Venkateswara University, India. The study design and protocols used in this study were reviewed and approved by the Institutional Animal Ethical Committee (09/(i)/a/CPCSEA/IAEC/SVU/ ZOOL/KSR/Dt.08/07/2012).

**Data Availability Statement:** The data presented in this study are available from the corresponding authors on request.

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**Conflicts of Interest:** All authors declared that there are no conflict of interest.

**Sample Availability:** Samples of the plant extract with phytochemical composition are available from the authors.

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**REVIEW ARTICLE**

# Medicinal Plants and Bioactive Compounds for Diabetes Management: Important Advances in Drug Discovery

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**Abstract:** ***Background*:** Diabetes is a major public health problem in the world. It affects each and every part of the human body and also leads to organ failure. Hence, great progress is made in the field of herbal medicine and diabetic research.

***Objectives*:** Our review will focus on the effect of bioactive compounds of medicinal plants which are used to treat diabetes in India and other countries.

***Methods*:** Information regarding diabetes, oxidative stress, medicinal plants and bioactive compounds was collected from different search engines like Science direct, Springer, Wiley online library, Taylor and francis, Bentham Science, Pubmed and Google scholar. Data was analyzed and summarized in the review.

***Results*:** Anti-diabetic drugs that are in use have many side effects on vital organs like heart, liver, kidney and brain. There is an urgent need for alternative medicine to treat diabetes and their disorders. In India and other countries, herbal medicine was used to treat diabetes. Many herbal plants have antidiabetic effects. The plants like ginger, phyllanthus, gymnea, aswagandha, aloe, hibiscus and curcuma showed significant anti-hyperglycemic activities in experimental models and humans. The bioactive compounds like Allicin, azadirachtin, cajanin, curcumin, querceitin, gingerol possess anti-diabetic, antioxidant and other pharmacological properties. This review focuses on the role of bioactive compounds of medicinal plants in the prevention and management of diabetes.

***Conclusion*:** Moreover, our review suggests that bioactive compounds have the therapeutic potential against diabetes. However, further *in vitro* and *in vivo* studies are needed to validate these findings.

**Keywords:** Diabetes, medicinal plants, bioactive compounds, drug discovery.

## 1. INTRODUCTION

Diabetes is the single most important endocrine disorder, widely recognized as one of the leading causes of death and disability in the world. Diabetes is a metabolic syndrome which affects more than 15% of the population in the world, which could jump up to 55% by 2035. It is predicted that by 2030, India, China and the United States will have the largest number of diabetic peoples [1] (Fig. **1**).

The prevalence of diabetes is expected to increase to 9.9% by the year 2045. Diabetes causes about 5% of all deaths globally each year, and diabetic deaths are likely to increase by more than 50% in the next 10 years. Therefore, developing novel drugs or new therapies to combat diabetes has become an urgent need.

The World Health Organization (WHO) estimated the global prevalence of diabetes among adults over 18 years of age was 8.5% in 2014. In India, there are about 69.2 million cases of diabetes in the adult population. The prevalence in urban areas ranges between 10.9% and 14.2% and prevalence in rural India was 3.0-7.8% among the population aged 20 years and above with a much higher prevalence among individuals aged over 50 years (INDIAB Study). The prevalence of diabetes in India has remained at 11.8% in the last four years (Fig. **2**).

Statistical projections for India suggest that the number will rise from 19.4 million in 1995 to 65.1 million in the year 2035, making India the country with the highest number of diabetics in the world. One in six people with diabetes in the world is from India. China is in second place by having 16 million peoples in 1995 and more than 38 million peoples by 2025. India is at the top of the table [2]. The diabetes burden in India results from various factors like sedentary life, dietary habits, lack of physical activity, lifestyle habits, obesity, hypertension all together contribute to the rapid rise of diabetes in India (Table **1**).

Diabetes mellitus, the most common metabolic disease in the world, is a group of disorders characterized by hyperglycemia, which results from defects in insulin secretion or insulin action. Diabetic complications include retinopathy, nephropathy, micropathy, cardiomyopathy, renal deterioration and cerebrovascular diseases [3]. The control and treatment of diabetes and its complications mainly depend on the chemical or biochemical agents, pharmacological compounds or diet therapy.

Therefore, understanding the mechanisms and the biological consequence of diabetes is essential for the development of novel therapeutic drugs. Cellular senescence may be one mechanism contributing to diabetes.

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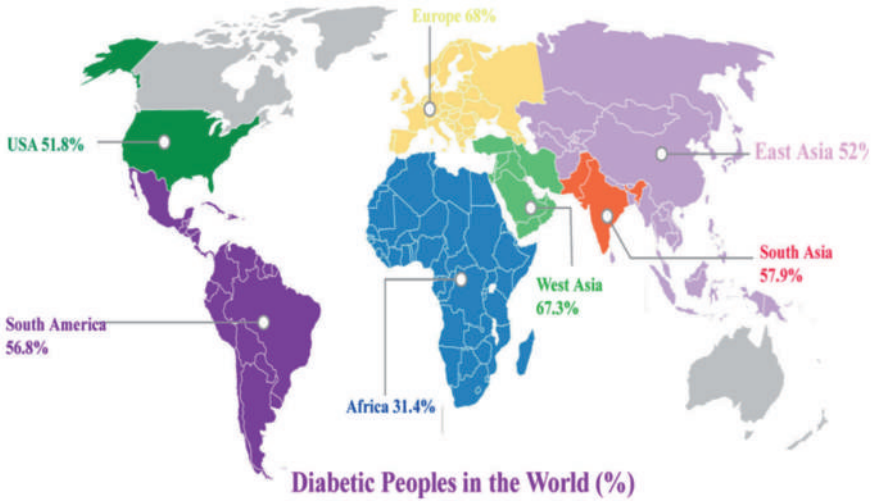



**Fig. (1).** Diabetic Peoples in the world. (*A higher resolution/colour version of this figure is available in the electronic copy of the article*).

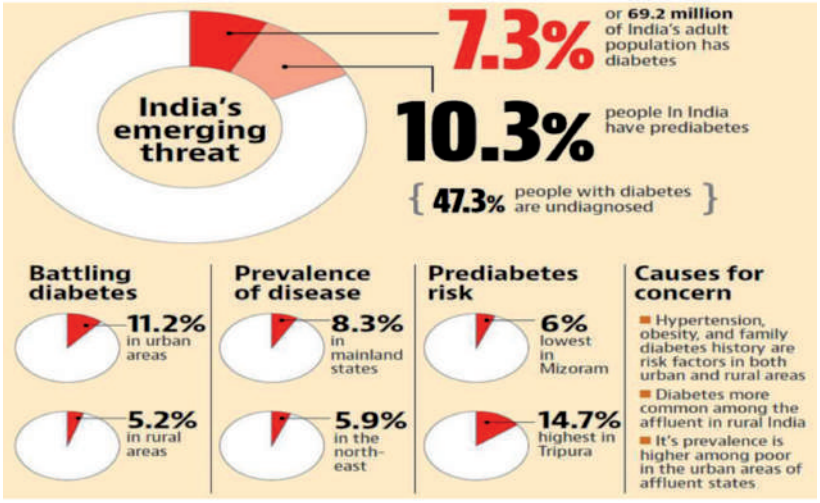



**Fig. (2).** Diabetic peoples in India. (*A higher resolution/colour version of this figure is available in the electronic copy of the article*).

**Table 1. Top ten countries for estimated number of Adults with diabetes in 1995 and 2025 and 2035. (King *et al*. [2]).**

| Rank | Country | 1995 (Millions) | Rank | Country | 2025 (Millions) | Rank | Country | 2035 (Millions) |
|---|---|---|---|---|---|---|---|---|
| 1. | India | 19.4 | 1 | India | 57.2 | 1 | China | 98.4 |
| 2. | China | 16.0 | 2 | China | 37.6 | 2 | India | 65.1 |
| 3. | USA | 13.9 | 3 | USA | 21.6 | 3 | USA | 24.4 |
| 4. | Russia | 8.9 | 4 | Pakistan | 14.5 | 4 | Brazil | 11.9 |
| 5. | Japan | 6.3 | 5 | Indonesia | 12.4 | 5 | Russia | 10.9 |
| 6. | Brazil | 4.9 | 6 | Russia | 12.2 | 6 | Mexico | 8.7 |
| 7 | Indonesia | 4.5 | 7 | Mexico | 11.7 | 7 | Indonesia | 8.5 |
| 8. | Pakistan | 4.3 | 8 | Brazil | 11.6 | 8 | Germany | 7.6 |
| 9. | Mexico | 3.8 | 9 | Egypt | 8.8 | 9 | Egypt | 7.5 |
| 10. | Ukraine | 3.6 | 10 | Japan | 8.5 | 10 | Japan | 7.2 |
| | All other countries | 49.7 | - | - | 103.6 | - | - | 253.5 |
| | **Total** | **135.3** | | | **300.0** | | | **486** |

**Table 2. Types of diabetes.**

| Type 1 Diabetes | Type 2 Diabetes | Type 3 Diabetes |
|---|---|---|
| **1) Typically Associated with** Children to Young adult | **Typically Associated with** Adults | **Typically Associated with** Pregnant women |
| **2) Risk Factors** Generic/Environmental | **Risk Factors** Obesity, old age, family Obesity, family of prehistory | **Risk Factors** Obesity, old age, family of prehistory |
| **3) Treatment** Insulin | **Treatment** Diet/drugs/Insulin | **Treatment** Diet & drugs/Insulin |
| **4) % of Populations** 5% of cases (2 Millions) | **% of Populations** 90-95% of diabetic cases (414 Million) | **% of Populations** up to 6 to 13% pregnant cases (6 Millions) |

## 2. OXIDATIVE STRESS AND DIABETES

Diabetes is one of the stress related disorders. Diabetes mellitus has been shown to be a state of increased free radical formation. The existence of oxidative stress resulting from increased free radicals has been postulated in diabetes. Oxidative stress induced by chronic hyperglycemia has been associated with dysfunction and apoptosis of several cell types, including pancreatic β cells, endothelial cells, neurons and glial cells. These evidences indicate that hyperglycemia and oxidative stress promote the progression and complications of diabetes [4]. (Table **2**).

Oxidative stress results from overproduction of reactive oxygen species (ROS) coupled with insufficient antioxidant capacity. Oxidative stress is currently suggested as one of the mechanisms underlying diabetes mellitus, which affects carbohydrate, lipid and protein metabolism. Several alterations in diabetic individuals are oxidative in nature and may depend on increased oxidative stress. Glycation and hyperglycemic pseudohypoxia can generate a redox imbalance inside the cells, especially in the liver. Furthermore, lipid peroxidation plays a role in the production of free radicals and oxidative stress during diabetes [5, 6].

In a diabetic condition, mitochondria play an important role in the production of toxic free radicals. During oxidative metabolism in mitochondria, a component of the utilized oxygen is reduced to water, and the remaining oxygen is transformed into oxygen free radical (OFR), which is an important reactive oxygen species that is converted to other reactive species such as hydroxyl radical, hydrogen peroxide [7]. Insulin signaling is modulated by reactive oxygen species and reactive nitrogen species (RNS) in two ways. On one side, in response to insulin, the ROS/RNS are produced to exert its full physiological function and on the other side, the ROS and RNS have got negative regulation on insulin signaling, interpreting them to develop insulin resistance, which is a risk factor for diabetes [8].

Under normal conditions, reactive oxygen species are neutralized by the antioxidative defense system, which, however, is severely altered during the diabetic condition. Antioxidant enzymes are proteins involved in the catalytic transformation of reactive oxygen species and their byproducts into stable, nontoxic molecules, therefore representing the most important defense mechanism against oxidative stress induced cell damage. A precise balance between ROS concentrations and antioxidants must be maintained inside the cells and tissues to ensure a proper redox state that guarantees the required control of metabolism and organic homeostasis. Antioxidant enzymes catalyze mainly three different reaction mechanisms: dismutation, peroxidise reactions and thiol reductions.

Antioxidant enzymes such as Superoxide dismutase (SOD), Catalase (CAT), Glutathione peroxidase (GPx), Glutathione reductase (GR), Glutathione –s– transferase (GST) activities and Glutathione (GSH) levels are decreased in liver, heart, kidney and brain of diabetic subjects [3, 4]. Lipid peroxidation levels increased in diabetic subjects. Oxidative stress is proposed to be a potential contributor to the development of complications in diabetes. Increased free radical production or decreased antioxidant defense system enzymes may give rise to increased oxidative stress. Consequences of oxidative stress are cell injury, *i.e*., alteration in antioxidant enzyme system, disruption in cellular homeostasis and accumulation of damaged molecules. The observed decrease in SOD activity in diabetic rats could result from the inactivation of $H_2O_2$ and inefficient scavenging of reactive oxygen species, which might be implicated in oxidative inactivation of enzymes and especially the deleterious effects due to the accumulation of superoxide radicals in diabetic subjects. Reduced activity of CAT has been observed in diabetic rats and this may result in a number of deleterious effects due to the accumulation of $H_2O_2$ [3, 4].

Decreased activities of GPx have been well documented in STZ-induced diabetic rats. The activity of GPx is also responsible for metabolizing lipid peroxides. Many reports reported the GPx activity was decreased in diabetic rats due to the action of GPx on lipid hydroperoxidases [3, 4]. The decrease in GR activity may reflect the decline in the production and availability of GSH to overcome $H_2O_2$. A decrease in GST activity in diabetic rats might indicate reduced detoxification or free radical scavenging capacity in diabetes. This decrease in GST activity may result from decreased enzyme production or enzyme inactivation. Many investigations reported that GSH levels are reduced in diabetic rats. Depletion of tissue GSH levels enhances cellular damage caused by oxidative stress. Significant depletion of GSH in diabetic rats suggests its increased utilization against reactive oxygen species. The depletion of GSH in the tissue of diabetic subjects may be due to the utilization of GSH enzyme by two antioxidant enzymes, GPx and GST. Increased lipid peroxidation under diabetic conditions can be due to increased oxidative stress in the cell as a result of the depletion of antioxidant enzymes [3, 4].

The coordination and synchronized activities of SOD, catalase, and glutathione metabolism enzymes avoid the production of the highly reactive hydroxyl radical and peroxynitrite (ONOO-), therefore preventing cell damage in diabetic conditions.

Nuclear Factor-kβ (NF-kβ), Transforming Growth Factor β (T-GF-β), Poly ADP-Ribose Polymerase (PARP), İnterleukin-6 (IL-6), İnterleukin-1beta (IL-1β), Mitogen-Activated Protein Kinase (MAPK), Vascular Endothelial Growth Factor (VEGF) play a crucial role in the progression of diabetic complications [9]. Untreated diabetes is an important risk factor for macrovascular complications such as heart attack and stroke as well as common microvascular complications such as retinopathy, nephropathy, neuropathy and amputations [10, 11].

In spite of having all the advanced treatments in allopathic medicine, diabetes remains one of the prominent causes of death in the world. Drugs that increase insulin production by the pancreas are chlorpropamide, glimepiride, glipizide, glyburide, nateglinide,

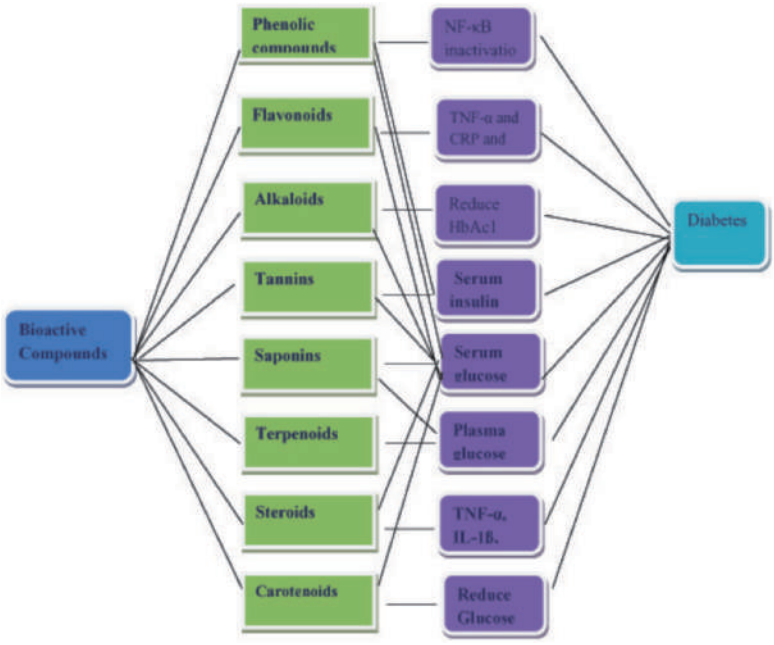



**Fig. (3).** Effect of bioactive compounds on diabetic subjects. (*A higher resolution/colour version of this figure is available in the electronic copy of the article*).

repaglinide. The drug that decreases sugar production by the liver and improves insulin resistance is metformin. Drugs that increase insulin production by the pancreas or its blood levels and reduce sugar production from the liver are galogliptin, dulaglutide, exenatide, linagliptin, liraglutide, lixisenatide, saxagliptin, semaglutide and sitgliptin. Drugs that block the reabsorption of glucose by the kidney and increase glucose excretions in urine are called sodium-glucose co-transporter 2 (SGLT2) inhibitors. They also trigger weight loss, which helps bring blood sugars back to normal; they are canaglifozin, dapagliflozin, empagliflozin, and ertugliflozin. These drugs have been used as monotherapy or in combination to treat diabetes. Continuous usage of these anti-diabetic drugs damages the kidney, liver, eyes, heart and brain. Thus, there is a need for search and investigation for more effective and safer treatment for diabetes. This leads to the origin of hypoglycemic agents from plant sources called herbal drugs [12].

## 3. MEDICINAL PLANTS AND THEIR BIOACTIVE COMPOUNDS

The earliest description of the curative properties of medicinal plants is found in Rigveda (2500 - 1800 BC). Charaka Samhita and Sushruta Samhita give an extensive description of various medicinal plants. Information on medicinal plants in India has been systematically organized. The World Health Organization also recommended that traditional methods for the treatment of diabetes should be further investigated. Medicinal plants and their active constituents play a role in the prevention and treatment of diabetes. Over 7500 plant species have been reported to be used to treat diabetes in the Indian traditional systems. A number of pharmacological studies of medicinal plants have been used to treat diabetes because of their antidiabetic, antioxidant and anti-insulin properties [3]. Several laboratories in India and across the globe are involved in isolating new herbal drugs from plants.

Bioactive substances are compounds that can modulate specific metabolic processes, providing health benefits and a positive impact on the function of the human body. Bioactive compounds have many pharmacological properties like antioxidant, antidiabetic, anti-cancer, antimicrobial, antiviral, antiulcer and anti bacterial activities. These bioactive compounds play a key role in clinical investigations. These bioactive compounds include phenolic compounds, flavonoids, alkaloids, tannins, saponins, terpenoids, glycosides, steroids, chalcones, carotenoids, peptides, lipids, glycopeptides, iridoids, ursolic acid and imidazoline. These bioactive compounds found in fruits, vegetables, herbs, tea, soy and spices are used to treat diabetes [13] (Fig. **3**).

### 3.1. Phenolic Compounds

Phenolic compounds are one of the most widely distributed groups of phytochemicals. They exhibit a great diversity of structures, ranging from simple phenolic molecules with one aromatic ring to larger and complex polymerized molecules such as lignans, coumarins, anthraquinones, tannins and flavonoids.

Phenols are present in several vegetables (cabbage, cauliflower), spices (ginger, garlic), herbs (terminalia, cassia), berries, grape, citrus fruits, and mango. The interest in phenols is mainly attributed to their contribution to human health through multiple biological effects, which include antioxidant, anti-inflammatory, anti mutagenic and anti-carcinogenic activities. Their physiological and pharmacological functions may originate from their free radical scavenging properties and functions of regulating detoxifying enzymes. Phenolic compounds may reduce the risk of development of several diseases due to their antioxidant power [14] (Table **3**).

Phenolic acids include hydroxybenzoic acids (*e.g.*, gallic acid, p-hydroxybenzoic acid, protocatechuic acid, vanillic acid, and syringic acid) and hydroxycinnamic acids (*e.g.*, ferulic acid, caffeic acid, p-coumaric acid, chlorogenic acid), and bioactive compounds like Curcumin, Eugenol, Carvacrol and many more compounds (Table **4**).

**Table 3. Medicinal plants which are used to treat Diabetes.**

| Sr. No. | Botanical Name | Common Name | Parts Used | References |
|---|---|---|---|---|
| 1. | *Acalypha indica* | Indian Copperleaf | Stem, Leaf | Priya & BhaskaraRao [55] |
| 2. | *Aerva lanata* | Wool Plant | Leaf | Akanji *et al.* [56] |
| 3. | *Allium cepa* | Onion | Bulb | Ribeiro *et al.* [57] |
| 4. | *Allium sativum* | Garlic | Bulb | Pantoja*et al.* [58] |
| 5. | *Aloe vera* | Indian Aloe | Whole plant | Al-Awadi *et al.* [59] |
| 6. | *Ananas comosus* | Pineapple | Root | Sripanidkulchai *et al.* [60] |
| 7. | *Arachis hypogaea* | Groundnut | Seed | Bilbis *et al.* [61] |
| 8. | *Argania spinosa* | Argan | Seeds | Hebi *et al.* [62] |
| 9. | *Artemisia pallens* | Wormwood | Fruits | Subramoniam *et al*. [63] |
| 10. | *Asparagus racemosus* | Shatavari, or Shatamull | Whole Plant | Ramachandran *et al.* [64] |
| 11. | *Azadirachta indica* | Nim or Neem | Leaf, Stem | Khosla *et al.* [65] |
| 12. | *Beta vulgaris* | Garden beet | Root | Tunali *et al.* [66] |
| 13. | *Bombax ceiba* | Cotton Tree | Leaves | Saleem *et al.* [67] |
| 14. | *Bouganville aspectabilis* | Great bougainvillea | Leaves | Chauhan *et al.* [68] |
| 15. | *Brassica oleracea* | Brassica | Leaves, Whole Plant | Kataya *et al.* [69] |
| 16. | *Cajanus cajan* | Red gram | Seeds | Amalraj & Ignacimuthu [70] |
| 17. | *Capsicum annuum* | Bell pepper | Seeds | Sanati *et al.* [71] |
| 18. | *Carica papaya* | Papaya | Root | Sripanidkulchai *et al.* [60] |
| 19. | *Carissa edulisVahl* | Natal Plum | Root | Nedi *et al.* [72] |
| 20. | *Catharanthus roseus* | Cape periwinkle Plant | Leaves | Nammi *et al.* [73] |
| 21. | *Cinnamomum zeylanicum* | Cinnamon | Bark | Ranasinghe *et al.* [74] |
| 22. | *Citrus limonum* | Risso Lemon | Fruit | Ribeiro *et al.* [57] |
| 23. | *Coccinia indica* | Kanduri | Whole plant | Hossain, *et al.* [75] |
| 24. | *Commiphora mukul* | Guggal | Whole plant | Sotoudeh *et al.* [76] |
| 25. | *Coriandrum sativum* | Coriander | Seed | Udupihille & Jiffry [77] |
| 26. | *Curcuma longa* | Curcumin | Whole Plant | Srinivasan *et al.* [78] |
| 27. | *Cymbopogon citrates* | Lemon grass | Root | Sripanidkulchai *et al.* [60] |
| 28. | *Cyperus esculentus* | Nut Sedge | Seeds | Oluwajuyitan *et al.* [79] |
| 29. | *Digitalis purpurea* | Common foxglove | Fruit | Navarro *et al.* [80] |
| 30. | *Emblica officinalis* | Indian gooseberry | Fruit | Variya *et al.* [81] |
| 31. | *Eucalyptus globules* | Safeda tree | Leaves | Gray & Flatt [82] |
| 32. | *Eugenia jambolana* | Jamun | Fruit, Seed | Achrekar *et al.* [83] |
| 33. | *Ficus bengalenesis* | Indian Banyan tree | Bark, Leaves | Augusti *et al.* [84] |
| 34. | *Ficus racemosa* | Indian fig tree | Bark | Sophia & Manoharan [85] |
| 35. | *Garcinia mangostana* | AsamGelugur | Leaves | Karim *et al.* [64] |
| 36. | *Ginkgo biloba* | Ginkgo | Whole Plant | Tian *et al.* [86] |
| 37. | *Glycine max* | Soybean | Seeds | Oluwajuyitan *et al.* [79] |
| 38. | *Gymnema sylvestre* | Gudmar or Merasingi | Leaves | Shanmugasundaram *et al.* [87] |
| 39. | *Hibiscus rosa-sinesis* | Rose Plant | Leaves, | DehghanShahreza [88] |
| 40. | *Hyptis verticillata* | Hyptis | Seeds | Ogar *et al.* [89] |
| 41. | *Lepidium latifolium* | Pepperweed | Seed | Maghrani *et al.* [90] |
| 42. | *Mangifera indica* | Mango | Leaves | Saleem *et al.* [91] |
| 43. | *Momordica charantia* | Bitter gourd | Fruits | Pugazhenthi & Murthy [92] |
| 44. | *Moringa oleifera Lam.* | Horseradish Bark | Leaf | Caceres *et al.* [93] |
| 45. | *Murraya koenigi* | Curry leaf | Leaves | Iyer & Mani [94] |
| 46. | *Musa sapientum* | Banana | Leaf | Ribeiro *et al.* [57] |
| 47. | *Nigella sativa* | Blackseed cumin | Seeds | Mohebbati *et al.* [95] |
| 48. | *Ocimum sanctum* | Tulasi Plant | Whole Plant | Husain *et al.* [96] |
| 49. | *Olea europaea* | Olive | Leaf | Somova *et al.* [97] |
| 50. | *Opuntia ficus-indica Mill.* | Cactus pear, | Fruit | Galati *et al.* [98] |
| 51. | *Panax ginseng* | Asian ginseng | Whole Plant | Amin *et al.* [99] |
| 52. | *Persea gratissima Gaertn.* | Avocado | Leaf | Ribeiro *et al.* [26] |
| 53. | *Phlebodium aureum* | Cabbage | Root | Cáceres etal [93] |
| 54. | *Phyllanthus amarus* | Bhuiamla | Whole Plant | Srividya & Periwal [100] |
| 55. | *Phyllanthus niruri* | Stonebreaker plant | Whole plant | Giribabu et [101] |

| Sr. No. | Botanical Name | Common Name | Parts Used | References |
|---|---|---|---|---|
| 56. | *Pimpinella tirupatiensis* | Forest coriander | Leaves | Saddala *et al.* [102] |
| 57. | *Piper betle* | Betel leaf | Leaf | Santhakumari *et al.* [103] |
| 58. | *Psidium guajava* | Guava | Fruit, Leaves | Shen *et al.* [104] |
| 59. | *Pterocarpus marsupium* Roxb | Indian kino tree | Wood | Manickam *et al.* [105] |
| 60. | *Pterocarpus santalinus* | Red sandalwood | Bark, Leaf | Kondeti *et al.* [106] |
| 61. | *Punica granatum* | Pomegranate | Leaf | Banihani *et al.* [107] |
| 62. | *Raphanus sativus* | Radish | Bark | Vargas *et al.* [108] |
| 63. | *Saccharum officinarum* | Sugarcane | Leaf | Ribeiro *et al.* [57] |
| 64. | *Salacia prenoids* | Saptrangi | Leaves and Stem | Vyas *et al.* [109] |
| 65. | *Solanum lycopersicum* | Tomoto | Leaves | Banihani [110] |
| 66. | *Solanum muricatum* | Sweet potato | Whole plant | Hsu *et al.* [111] |
| 67. | *Solanum nigrum* | Blackberry | Fruit | Umamageswari *et al.* [112] |
| 68. | *Syzygium cumini* | Black Plum | Bark | Perera *et al.* [113] |
| 69. | *Taraxacum officinale* | Weber Dandelion | Root | Hook *et al.* [114] |
| 70. | *Terminalia chebula* | Chebulic Myrobalan | Leaves, Seeds | Nalamolu *et al.* [115] |
| 71. | *Tinospora cordifolia* | Giloya | Stem | Sharma *et al.* [116] |
| 72. | *Tribulus terrestris* | Caltrop, | Leaf | Al Ali *et al.* [117] |
| 73. | *Tridax procumbens* | Coat buttons Plant | Whole Plant | Petchi *et al.* [118] |
| 74. | *Trigonella foenumgraecum* | Fenugreek | Seeds | Gupta *et al.* [119] |
| 75. | *Vernonia polyanthes* Less. | Chamarrita | Leaf | Ribeiro *et al.* [54] |
| 76. | *Vinca rosea* | Sadaphuli | Leaves | Ahmed *et al.* [120] |
| 77. | *Vitexagnus-castus* | Vitex | Whole Plant | Ahangarpour *et al.* [121] |
| 78. | *Vitis vinifera* | Grape | Leaves | Zunino [122] |
| 79. | *Withania somnifera* | Ashwagandha | Root | Andallu & Radhika [123] |
| 80. | *Zea mays* | Corn | Stigmata | Al Ali *et al.* [117] |
| 81. | *Zizyphus zujuba* | Common jujube | Seeds | Elbashir *et al.* [124] |
| 82. | *Zingiber officinale* | Ginger | Rhizome | Shanmugam *et al.* [3] |

Curcumin is a bioactive compound found in *Curcuma longa* L. and it shows anti-oxidant, anti-inflammatory, anti-diabetic, anti-viral, anti-bacterial, anti-fungal, and anti-cancer activities [15]. These modes of action are mediated by the regulation of various transcription factors, growth factors, inflammatory cytokines, protein kinases, and other enzymes. A recent study highlighted the ability of curcumin to modulate the destruction of β-cells by key immune cells. The mechanism of curcumin included reduction of oxidative stress, NF-κB inactivation, and increased SCF/Kit expression in STZ-treated rats. Curcumin also depleted pancreatic lipid peroxidation and serum TNF-a1β in diabetic subjects [16]. Al-Ali *et al.* [17] also reported that in diabetic rats, curcumin decreased the glucose concentrations, lipid profiles, enhanced insulin, and lowered the leptin, adiponectin, IL-6 (Table **3**).

Eugenol is a major bioactive compound found in Ocimum. It is used as a flavoring agent in various food and cosmetic industries. Several studies have shown the beneficial biological properties of eugenol, including antimicrobial, antifungal, antioxidant, anti-inflammatory, anti-diabetic antiviral, anticancer, analgesic, and antispasmodic activities [18, 19] (Table **4**).

### 3.2. Flavonoids

Flavonoids are the largest group of phenolic compounds present in almost all fruits and vegetables. Flavonoids are used in Chinese and Ayurvedic medicine. Flavonoids have different subclasses, including flavones, flavonols, flavanones, isoflavones, flavan-3-ols, tannins, anthocyanins, quercitin, luteolin, apigenin, kaempferol, trichostatin and resveratrol. It has skin protection, hypoglycemic, antioxidant, anti-diabetic and anti-inflammatory properties.

Quercetin is a bioactive compound found in vegetables, tea, apples, berries, broccoli, red onions and capers [20]. Inflammatory mediators can activate a number of receptors, which subsequently result in pancreatic β-cell dysfunction, insulin signaling impairment, endothelial dysfunction and altered vascular flow that lead to diabetic vascular complications. Quercetin administration protects against diabetes-induced exaggerated vasoconstriction. Quercetin treatment in diabetic subjects showed a reduction in serum levels of both TNF-α and CRP and inhibition of aortic NF-kβ [21].

Epicatechin is a bioactive compound found in cocoa, tea (*Camellia sinensis*), Phyllanthus, peanuts, apples, rapes and berries. Epicatechin is a flavonoid and it has diverse biological properties, out of which the major biological properties that they possess antioxidant, antimicrobial, anti-inflammatory, anti-diabetic, antitumor and cardioprotective activity [22]. Eng *et al.* [23] reported that dietary supplementation of Epicatechin (200 mg/kg diet) increased body weight and ameliorated insulin sensitivity in high fat-fed mice. In addition, Epicatechin (2-20 mg/kg of body weight) treatment elevated body weights, improvement in glucose tolerance and insulin sensitivity and lipid profiles in high fat-fed C57BL/6J mice and high-fructose fed rats. These results suggest that the capacity of Epicatechin improves insulin sensitivity in rodent models (Table **4**).

Resveratrol is a flavonoid isolated from several fruits, including berries, grapes and peanuts [24, 25]. In recent years, the use of Resveratrol has gained attention because of its therapeutic effects. This natural polyphenol has numerous pharmacological impacts, including anti-diabetic [26, 27], antioxidant [28], anti-inflammatory,

**Table 4. Activities of Bioactive compounds of Medicinal plants.**

| Sr. No. | Name of the Medicinal Plant | Bioactive compounds | Activity |
|---|---|---|---|
| 1. | *Allium cepa* | Quercetin,Cycloalliin, Alliuocide A | Antidiabetic, Antioxidant |
| 2. | *Allium sativum* | Allicin, Alliin, Ajoene, Allyl sulfide | Antidiabetic, Antibacterial |
| 3. | *Aloe vera* | Aloin, Lupeol, Acemannan | Antiseptic, Antidiabetic |
| 4. | *Azadirachta indica* | Azadirachtin, Nimbin, Nimbolide | Antiviral, Antidiabetic |
| 5. | *Beta vulgaris* | Betanin, β-carotene, Lutein | Anti-hypertensive Antidiabetic |
| 6. | *Bombax ceiba* | Bergenin, Lupeol, Vicenin 2, Linarin | Antioxidant, Antidiabetic |
| 7.. | *Cajanus cajan* | Cajanin, Cajanol, Pinostrobin | Antidiabetic |
| 8. | *Coriandrum sativum* | Quercetin, Kaempferol, Rhamnetin | Antibactetial, Antidiabetic |
| 9. | *Carica papaya* | Ascorbic Acid, Riboflavin, Lycopene | Anti- arthritis, Antidiabetic |
| 10. | *Curcuma longa* | Curcumin, Curlone, Curcuphenol | Anti-cancer, Antidiabetic |
| 11. | *Digitalis purpurea* | Digitoxin, Digitoxigenin, Gitoxigenin | Cardiovascular, Antidiabetic |
| 12. | *Emblica officinalis* | Chebulagic acid, Emblicanin A | Antipyretic, Antidiabetic |
| 13. | *Ficus benghalensis* | Kaempferol, Catechin, Rutin | Antioxidant, Antidiabetic |
| 14. | *Ginkgo biloba* | Ginkgolides, Bilolabide | Anti-inflammatory, Antidiabetic |
| 15. | *Lepidium latifolium* | Andrographolide, Berberine | Antidiabetic |
| 16. | *Momordica charantia* | Momordicines I, Momordicines II | Antibacterial |
| 17. | *Nigella sativa* | Nigellicine, Thymol, Thymoquinone | Antifungal, Antidiabetic |
| 18. | *Ocimum sanctum* | Carvacrol, Eugenol,Linalool | Antidiabetic, Antibactetial |
| 19. | *Olea europaea* | Catechin, p-Coumaric acid | Antioxidant, Antidiabetic |
| 20. | *Opuntia ficus-indica* | Betacyanins, Indicaxanthin | Antidiabetic |
| 21. | *Piper betle* | Chavibetol, Eugenol | Anti-malaria, Antidiabetic |
| 22. | *Phyllanthus amarus* | Phyllanthin, Catechin | Antidiabetic |
| 23. | *Phyllanthus niruri* | Epicatechin, Ellagic acid | Anti-tumor, Antidiabetic |
| 24. | *Pterocarpus santalinus* | Santalin, Lupeol, Pterocarpin | Antidiabetic |
| 25. | *Raphanus sativus* | Khellin, Visnagin, Luteolin | Antidiabetic, Antimicrobial |
| 26. | *Syzygium cumini* | Jambosine, Friedelin, Quercetin | Cardioprotective, Antidiabetic |
| 27. | *Tribulus terrestris* | Harmine, Oleic acid, Kaempferol | Antidiabetic |
| 28. | *Trigonella* | Trigonelline, Isoorientin, Pinitol | Antioxidant, Antidiabetic |
| 29. | *Withania somnifera* | Withanone, Withaferin A | Anti-inflammatory, Antidiabetic |
| 30. | *Zingiber officinale* | 6-Gingerol, Shogaols, Zingiberene | Anti-cancer, Antidiabetic |

cardioprotective and hypolipidemic properties. Resveratrol has been shown that it protects the β cell of the pancreas [29, 30]. These therapeutical effects are mainly due to its antioxidant effect.

Resveratrol has anti-diabetic properties and its treatments have been studied using different animal models. This compound was found to be effective in rodents with diabetes induced by streptozotocin. Many reports indicate that resveratrol ameliorates symptoms of diabetes induced by a high-energy diet [31]. This action is largely associated with the anti-inflammatory properties of resveratrol. This compound was shown to downregulate proinflammatory genes and proteins, such as TNF-α, IL-1β, interleukin 6 (IL-6), interleukin 4 (IL-4), interleukin 17 (IL-17), cyclooxygenase 2 (COX-2), intracellular adhesion molecule 1 (ICAM) and vascular cell adhesion protein 1 (VCAM-1) [31]. The therapeutic potential of resveratrol was also demonstrated in humans with type 2 diabetes. Results of many studies and clinical trials indicate that resveratrol may be useful to diabetes related therapies [32].

Kaempferol is a natural flavonol, relatively abundant in grape, tea, beans, spinach, broccoli, cruciferous vegetables and some edible berries [33]. Numerous preclinical studies have shown that kaempferol has many pharmacological activities like antioxidant, antidiabetic, anticancer, antiinflammatory, and antimicrobial activities. Kaempferol reduced IL-1β, TNF-α and also reported to significantly decrease the fasting blood glucose and improve insulin resistance. Anti-inflammatory and anti-diabetic effects of kaempferol are mediated by AMPK activation [34].

### 3.3. Tannins

Tannins are the polyphenolic biomolecules having a high molecular weight and are widely distributed in many species of plants, like coffee, tea, grapes, apricots, barley, peaches, dry fruits, mint, basil, rosemary, pomegranate, strawberries, amla, clove, rice, oat, rye *etc* [35]. Nowadays, tannins have gained more attention because of the health benefits associated with their antioxidant properties. Tannins have anti-bacterial [36], anti-viral [37] anti-diabetic [38], anti- hypercholesterolemic [39] activities. Tannins bind and precipitate proteins and various other organic compounds, including amino acids and alkaloids (Table **3**).

### 3.4. Terpenoids

Terpenoids are commonly found in many plants. This class of compounds includes oleanolic acid, glycyrrhizin, glycyrrhetinic acid, ursolic acid, betulin, betulinic acid, lupeol, *etc*. These compounds have multiple biological activities that act on glucose absorption, glucose uptake, and insulin secretion.

Linalool is an enantiomer of the natural bioactive compound present in Ocimum, Citrus and Coriandrum. It is aromatic monoterpene alcohol [40, 41]. Linalool exhibits antimicrobial, anti-inflammatory, antileishmanial, anti-atherogenic, anti-diabetic, antioxidant and anti-depressant effects [42-44] (Table **4**).

Carvacrol is a monoterpenoid compound that is found in essential oils of aromatic plants like Ocimum, Rose. It has a characteris-

tic odor and exhibits numerous biological and pharmacological activities, including anti-inflammatory, antioxidant, antidiabetic, antibacterial, antifungal, anticancer and vasorelaxant, both *in vitro* and *in vivo* [45]. It has been reported that diabetic rats showed a slight reduction in blood glucose levels and a marked reduction in total cholesterol, alanine aminotransferase, aspartate aminotransferase and lactate dehydrogenase levels after oral administration of carvacrol [46] (Table **3**).

### 3.5. Anthocyanins

Anthocyanins have gained the attention of the scientific community mostly due to their vast range of possible applications. Anthocyanins are natural pigments belonging to the flavonoid family. They are naturally occurring pigments in Blueberry, Raspberry, Black rice, Apples, Peaches [47]. Anthocyanins are polyhydroxy and polymethoxy derivatives of flavylium salt, possessing a characteristic C3–C6–C3 carbon structure. Anthocyanins have also gained considerable attention due to their purported health benefits and potent antioxidant, anti-diabetic properties [48].

### 3.6. Saponins

Saponins are phytochemicals which can be found in most of the plants like peas, soybeans, *Momordica, Garcinia, Solanum terminalia, Trigonella foenum-graecum*, saoproot, soapbark and soapberry. Studies have illustrated the beneficial effects on blood cholesterol levels, cancer, bone health and stimulation of the immune system. Saponins have antioxidant, anti-diabetic and immunity boosting activities. Saponin has been reported to possess antioxidant properties in both *in vivo* and *in vitro* models. The presence of many OH groups in the structure of saponin is responsible for the enhancement of antioxidant activity and this property is responsible for the prevention of ROS formation in diabetes [49, 50] (Table **3**).

Saponins capture free radicals and stimulate antioxidant enzymes. Saponins decrease blood glucose levels, augmenting serum insulin and glycogen contents by regulating PI3K/PKB pathways [51]. Saponins have insulin mimicking property [52].

### 3.7. Alkaloids

Alkaloids are a class of naturally occurring organic compounds that contain basic nitrogen atoms. Alkaloids are mostly found in Artocarpus, *Morus alba, Psium sativum, Desmodium gangeticum, Berberis vulgaris, Trigonella foenumgraecum*. 80% of alkaloids' are derived from amino acids. Alkaloids have diverse and important physiological effects on humans and other animals. Well-known alkaloids include morphine, strychnine, quinine, ephedrine, and nicotine. Alkaloids have a wide range of pharmacological activities, including antimalarial (*e.g.*, quinine), anticancer (*e.g.*, homoharringtonine), cholinomimetic (*e.g.*, galantamine), vasodilatory (*e.g.*, vincamine), antiarrhythmic (*e.g.*, quinidine) and antidiabetic [53]. Some are already in clinical trials to test their potential to lower plasma glucose concentration, reduction of serum HbAc1 levels and anti-dyslipidemia in diabetic subjects. Berberine and trigonelline have anti-diabetic potential against diabetic subjects [54]. There are so many outstanding contributions to therapeutics of plant origin. Hence, the role of medicinal plants in human life is immense (Table **3**).

## CONCLUSION

Diabetes alters carbohydrate, fat, protein, antioxidant enzymes metabolism and it diminished the production of insulin and its action. In India and other countries, medicinal plants and their drugs are used to treat diabetes. Scientific information regarding medicinal plants has proved that they reduce glucose levels and elevate insulin levels in diabetic subjects. The current review is intended to provide an overview of the current knowledge about herbal medicines and their bioactive compounds to treat diabetes. In this review, we reported 82 medicinal plants, their bioactive compounds and anti-diabetic effects. From the available research reports on their potential effectiveness against diabetes, it is assumed that the herbal medicine has a major role to play in the management of diabetes, which needs further exploration for the necessary development of anti-diabetic drugs. Many herbal drugs used today have not undergone careful scientific assessment and validation. Hence, there is a need to identify and elucidate the clinical applications of medicinal plants against diabetes.

## AUTHORS' CONTRIBUTION

The first and second authors played an important role in data collection, interpretation of the data, analysis of the data and preparation of the review. The other co-authors contributed their roles excellently in fine tuning of the review. The corresponding author is critically responsible for the revision of the review.

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## CONFLICT OF INTEREST

The authors declare no conflict of interest, financial or otherwise.

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Research Article

# Effect of Sodium Fluoride (NaF) Exposure on Heart: Protective Effect of Eugenol with Reference to the Lipid Metabolic Profiles

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**ABSTRACT**

The aim of our study is to investigate the anti-hyperlipidemic effect of eugenol, a bioactive compound of *Ocimum sanctum* in the NaF intoxicated fluorosis induced albino male rats of wistar strain albino rats. *Ocimum sanctum* (OS) has been used in the Indian system of traditional medicine for the treatment of diabetes, liver disorders and heart problems. However, the bioactive compound of *Ocimum sanctum*, eugenol with reference to fluorosis was not carried out till date. Male rats were administered with eugenol for 60 days. The lipid metabolic profiles like MDA, TC, TG, LDL, VLDL and HDL are estimated in the plasma of all groups. The fluorosis markers calcium and phosphorus are also estimated. MDA, TC, TG, LDL, VLDL levels are elevated while HDL levels are depleted in NaF treated rats. Calcium levels decreased and phosphorus levels increased in NaF administered rats. However, eugenol supplementation for 60 days normalized all the lipid metabolic profiles in NaF rats. The fluorosis markers also came to near normalcy in eugenol treated rats. This shows the anti-lipidemic properties of eugenol.

**Keywords:** NaF, eugenol, lipids, rats.

**QUICK RESPONSE CODE →**

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## INTRODUCTION

Currently, fluoride pollution is a worldwide problem as the fluoride levels in drinking water above the tolerable limit in several countries such as China, Sri Lanka, West Indies, Holland, Italy, and India.[1]In India, fluoride levels in drinking water are also above the permissible limit in wide areas of the states of Andhra Pradesh, Tamil Nadu, Karnataka, Punjab, Bihar, Haryana, Kerala and West Bengal.[2] The international standard of permissible limit of fluoride in drinking water has been established at 1.[3] Fluoride is a common element in our daily life as it is natural mineral component of drinking water, tea, meat, beverages. It is often added to dental products because of its ability to prevent dental caries or cavities. However, excess intake of fluoride can result in fluorosis that causes not only dental and skeletal damage but also problems in the central nervous system such as brain damage, Alzheimer syndrome, thyroid disorder, DNA damage, gastro-intestinal irritation, and kidney function disorder.[4]

The most common manifestations that have been reported arising from chronic exposure of fluorides are skeletal, dental fluorosis, arthritic pain, osteosclerosis, and crippling fluorosis.[5] Fluoride intoxication results in neurologic damage, primarily in the impairment of both cognition and memory.[6] Fluoride intoxication also results in metabolic disorders, hepatitis, renal toxicity, muscular atrophy, decalcification and fragility of bone, and reproductive disorders.[7-9]

Numerous medicinal plants have been identified that exhibit anti-oxidative and anti-hyperglycemic activities. Among them, *Ocimum sanctum* L. has got paramount importance in folklore and traditional medicinal practices such as Ayurveda, Siddha and Unani. OS has been recommended for the treatment of a number of diseases.[10] Therapeutic value of *Ocimum sanctum* L. to treat a number of diseases including bronchitis, diarrhea and dysentery. OS has antioxidant, antibiotic, hypocholesterolemia, and hypoglycemic as well as hypotensive activities. [11]

The objective of the study was to investigate the anti-fluorosis, anti-lipidemic activity of eugenol, a bioactive compound of *Ocimum sanctum* in NaF induced fluorosis rats. This is the first reported data on the effect of eugenol in fluorosis induced rats.

## MATERIALS AND METHODS

### Chemicals and reagents

All chemicals used were of analytical grade and purchased from Sigma–Aldrich, Merck, India. All chemicals and reagents were used without further purification.



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### Selection and collection of plant material

Leaves of OS were collected from Seshachalam hills of Tirupati, Andhra Pradesh, India and identified by the Dr. Madhav Chetty, Department of Botany, SV University, Tirupati. Voucher specimen of *Ocimum sanctum* No 1183 was deposited in the Botany department.

### Extraction of Eugenol from *Ocimum sanctum*

The extraction of eugenol was carried out with batch extraction setup. It consists of a 500 ml reactor in which extraction is to be carried out; a turbine type four blade agitator connected with motor (REMI, maximum speed of 1200 rpm) was used.

### Grouping of Animals

The study design was approved by the animal ethical committee (Resolution No.10/08/a/CPCSCA/IAEC/SVU/09-10/ZOOL/KRS/Dt.25.09.2009). After 7 days of acclimatization, the rats were divided into five groups of six rats in each group and treated as follows.

**Group I – Normal Control (NC):** Six rats received saline via orogastric tube for a period of 60 days.

**Group II – Eugenol Control (EGt):** Six rats received *Ocimum sanctum* bioactive compound (10mg/kgBW) for 60 days.

**Group III – NaF treatment (Na F):** Six rats received the sodium fluoride (10mg/kgBW) dissolved in water for 60 days.

**Group IV – NaF + Ocimum treatment (NaF+EGt):** Six rats received fluoride and eugenol as described in group 3 and group 2for a period of 60 days.

**Group V –Na F+ Vitamin E treatment (NaF+VitE)**: Six rats received fluoride and Vitamin E for a period of 60 days.

The animals were sacrificed by cervical dislocation and the blood was collected for biochemical investigations after completion of 60 days of treatment and with a 24 hrs. of brief time lapse of the last treatment.

### Estimations of Lipid metabolic profiles

Blood was collected from the abdominal vein to determine lipid profile parameters such as total cholesterol (TC), triglyceride (TG), low-density lipoprotein cholesterol (LDL), very low-density lipoprotein cholesterol (VLDL) and high-density lipoprotein cholesterol (HDL). Fluorosis markers like calcium and phosphorus levels are estimated in the plasma all the groups of rats.

### Statistical analysis

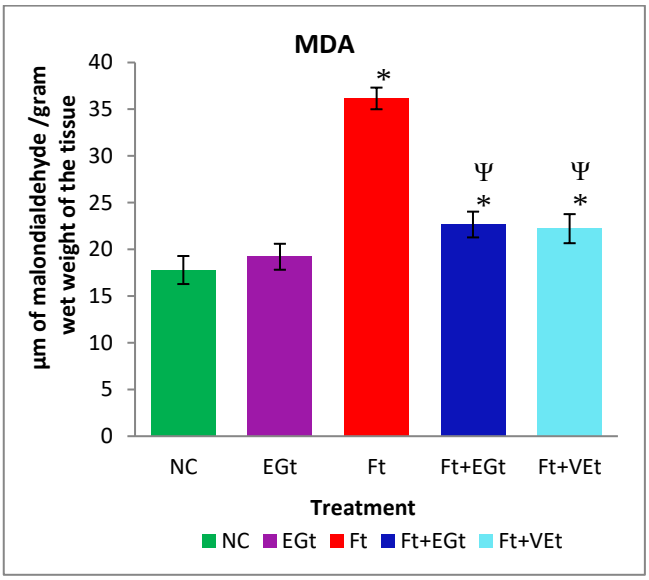
The data are expressed as mean values with their Standard Deviation (SD). Readings of the five different groups were compared using one-way ANOVA analysis with Dunnett's multiple comparison Test. Statistical analysis was performed using SPSS (Version 13.5; SPSS Inc., Chicago, IL, USA). Using M.S. Office, excel software. The data has been analyzed for the significance of the main effects (factors) and treatments along with their interactions. Differences were considered significant at $p < 0.001$.

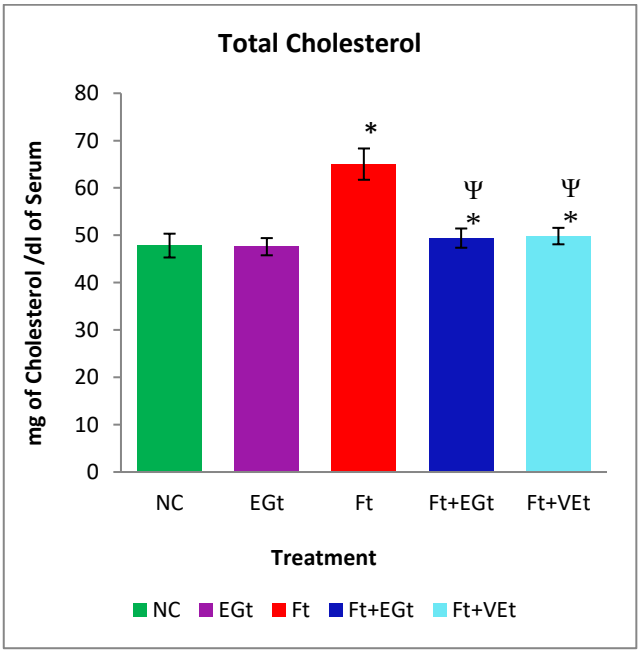
## RESULTS

### Effect of Eugenol on Lipid metabolic profiles in Sodium Fluoride intoxicated rats

In the present investigation, MDA, TC, TG, LDL, VLDL levels are significantly increased and HDL levels are decreased in Na F intoxicated rats, but eugenol supplementation could decrease all these lipid metabolic profiles except HDL cholesterol. This shows the anti-hyperlipidemic effect of eugenol (Figure 1).

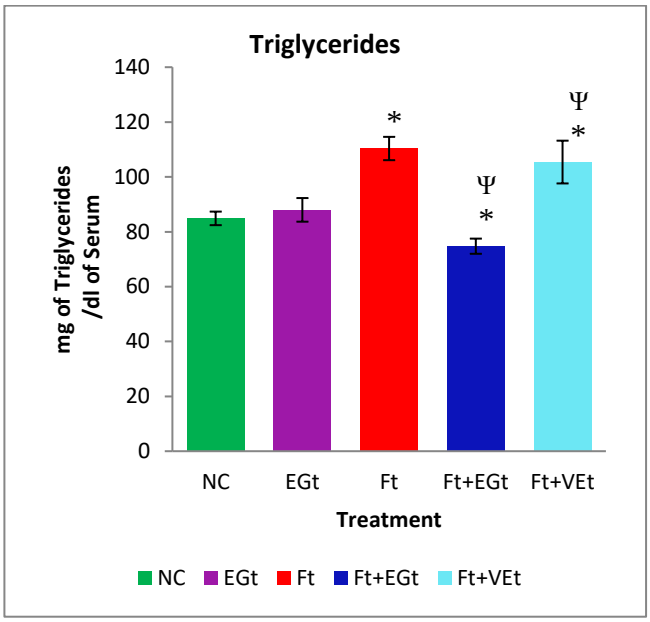
**Figure 1:** The Impact of Eugenol on Lipid metabolic profiles in NaF intoxicated rats. Data are expressed as means ± SD (n = 6). * The values are significant compared to the following: control (* p < 0.001), Fluorosis (Ψp < 0.01) (Dunnett's multiple comparison tests).

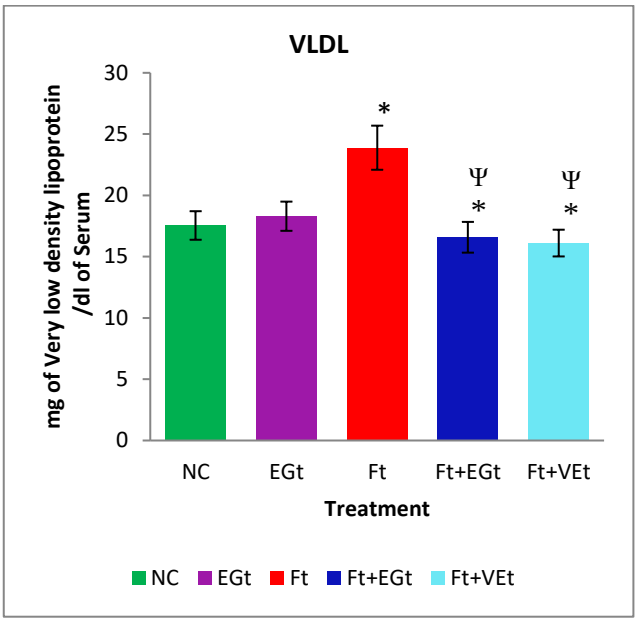


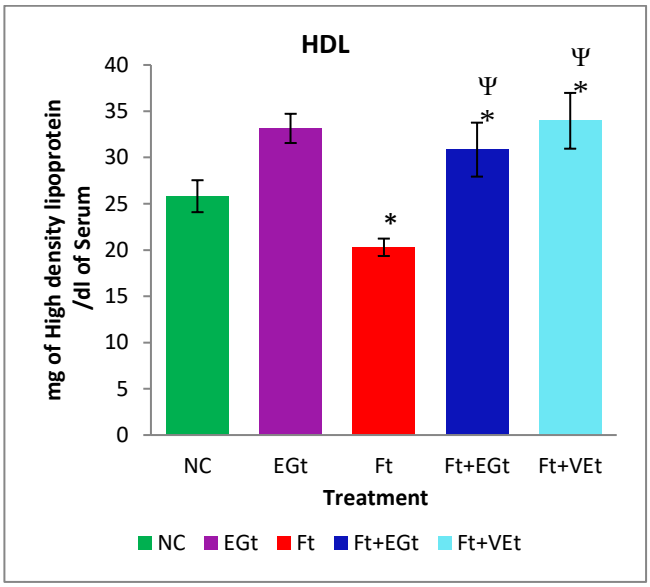



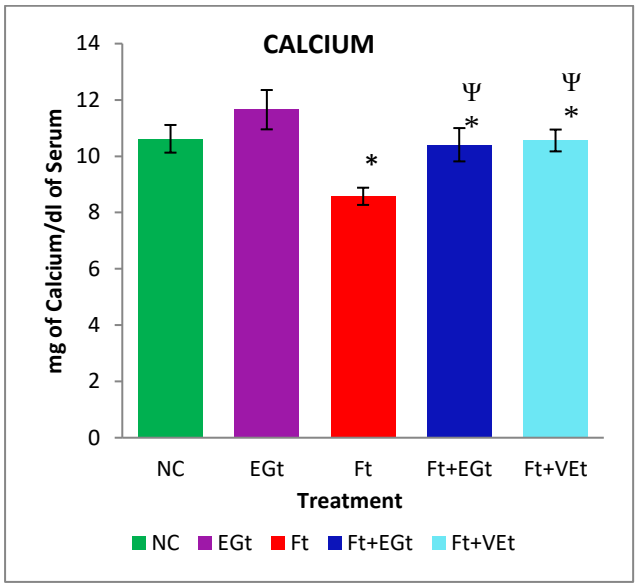


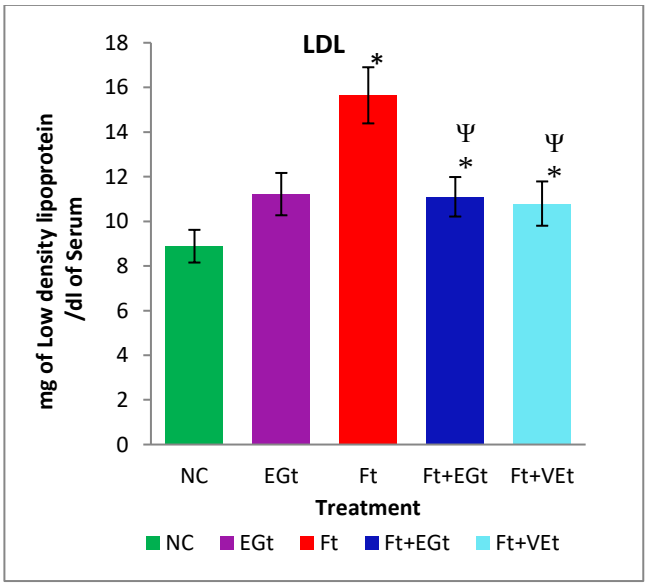
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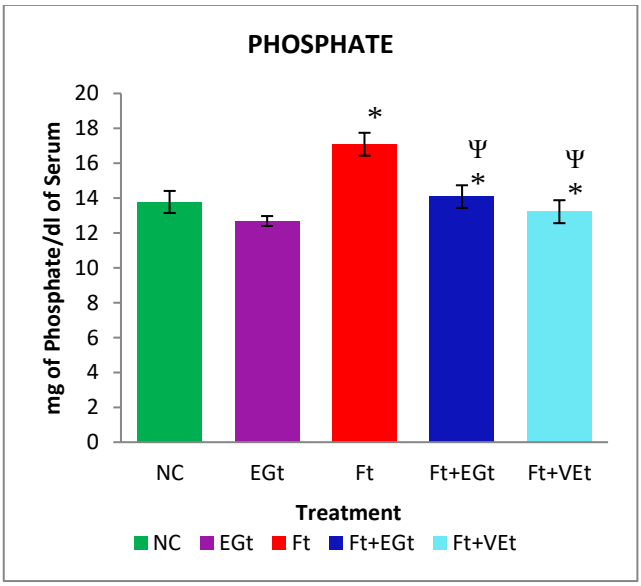




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**Effect of Eugenolon fluorosis markers in NaFintoxicated rats**

In the current study, we observed that calcium levels are depleted and phosphorus levels are elevated influoride intoxicated rats. However, with eugenol treatment for 60 days modulated the fluorosis markers in all experimental treated rats.

## DISCUSSION

The present study was done to know the pharmacological action of eugenol in NaF intoxicated rats. Bioactive compounds of *Ocimum sanctum* reported to possess antitussive, hypoglycemic, antioxidant, antistress, anti-ulcerative, anti-inflammatory, antiasthmatic, immune stimulatory and neuroprotective effects.

Sufficient evidence has demonstrated that fluoride produces deleterious effects in skeletal, dental and soft tissues. There are documentary evidences concerned with the mechanism of bone and dentalfluorosis.[12] But it is not clear of how fluoride interferes with soft tissues. However, some of the following viewpoints may be very helpful for us to understand the mechanism of fluorosis in soft tissues.

Lipid related abnormalities are most common in toxicity subjects. Alterations in lipid metabolism have been reported in NaF intoxicated rats. In this study, we observed elevated levels of MDA, total cholesterol, LDL cholesterol, VLDL cholesterol, triglycerides in NaF rats. This may be due to the lipid peroxidation process that occur in plasma membrane, microsomes and mitochondrial membranes in fluorosis subjects.[13]Several studies declared that increased production of ROS is an important mechanism in fluoride-induced toxicity in experimental animals.

Exposure to fluoride has been reported to induce oxidative stress in vivo and in vitro. Oxidative stress is considered to play an important role in the pathogenesis of fluorosis and excess ROS production liberated from peroxisomes and mitochondria can directly inflict direct damage to structural polar lipid molecules of various cellular membranes. MDA, end product of lipid peroxidation in tissues, is also an indicator of oxidative stress. Lipid peroxidation is a free radical-mediated process that occurs following oxidative stress. Alterations in lipid metabolism maybe responsible for the altered MDA, TC and TG levels in fluorosis condition. It appears that enzymes inhibited by fluoride, such as triglyceride lipase, unspecific esterase and pyrophosphates. Also, the obtained results of hyperlipidemia may be attributed to an increase in the synthesis of fatty acids in the liver or possibility due to incidence of liver cholestasis 2000.[14]

Many reports suggested that the abnormal activities of lipase enzymes seem to be one of the chief factors responsible for the rise in plasma triglycerides and total cholesterol. However, with eugenol supplementation, TG an TC levels are depleted in NaF treated rats by preventing lipid peroxidation. This is attributed to the anti-lipidemic property and free radical scavenging activity of eugenol.

In our study, we reported that LDL, VLDL are elevated and HDL levels are depleted in NaF treated rats when compared to control. This dyslipidemia manifestations are due to decreased activity of lipoprotein lipase. Increased VLDL levels in NaF rats are due to increased concentration of free fatty acids.

Lipid disorders, most often encountered in fluorosis diseases also include increased levels of LDL and VLDL.[15] Eugenol supplementation may elevate the activity of lipoprotein lipase and decrease in LDL, VLDL in NaF treated rats. Moreover, with eugenol treatment HDL levels are increased in NaF rats. It could be understood rise in levels of lipoprotein lipase and HDL prevents the formation of coronary artery plaques and cardiac ischemia.[16]Hence, eugenol may be considered as a candidate for prevention of cardiovascular disorders since it promotes anti-lipidemic factors like HDL and LDL. In conclusion, our results revealed the hypolipidemic effect of (−)-eugenol that was evidenced by all the lipid metabolic profiles MDA, TC, TG, LDL, VLDL, HDL return to normalcy with eugenol supplementation in fluorosis rats.[15] (Figure 1).

In our study, we reported that calcium levels decreased and phosphorus levels increased in NaF rats. This may be due to alterations in metabolism of calcium and phosphorus. The calcium in the blood is transported to the intercellular fluid after which it is deposited in bones and teeth. However, with eugenol treatment for 60 days, these fluorosis markers normalized to near normal levels.

In our study, we reported that eugenol ameliorated the lipid metabolic profiles in sodium fluoride induced toxicity rats. Hence, we concluded that eugenol of *Ocimum sanctum* can be used as anti-lipid agents in many diseases.

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# CARDIO PROTECTIVE PROPERTY OF NATURAL COMPOUND EUGENOL IN FLUORIDE INTOXICATED MALE RATS WITH RESPECT TO ANTIOXIDANT ENZYMES

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## ABSTRACT

Eugenol is a medicinally important antioxidant phenolic compound. This plant compound has been used as ameliorative agent against variety of severe ailments. The aim of this research was to see whether the Eugenol has any cardio protective property. We tested eugenol on male albino rat's cardiac tissue suffering from fluoride toxicity with reference to antioxidant enzymes. The results showed that antioxidant enzymes such SOD, CAT, GPx and GR levels were considerably higher in the eugenol treated fluoride intoxicated group, but they were lower in the fluoride alone rat group. In conclusion, eugenol displays cardio protective effects in the cardiac tissue via boosting endogenous antioxidant enzymes. Future clinical study into the mechanism of action of eugenol under fluoride intoxication will confirm the current findings.

**KEYWORDS:** Antioxidant enzymes, cardio protective, fluoride intoxication, eugenol

## INTRODUCTION

Fluorine is an element that does not occur in the elemental state in nature because of its high reactivity. Many studies revealed that the long-term fluoride intake has damaging effects on the heart. Association between fluoride endemicity and prevalence of cardiac complications has been observed among adult males (Amini et.al.,2011). Diastolic dysfunction due to chronic fluoride exposure was observed in fluoride endemic areas and also noticed in elevation of the risk of heart failure (Varol et.al.,2010). Oxidative stress is known to be a key factor to heart failure and ischemic heart disease (Kiyuna et.al., 2018). Fluoride interacts with cellular systems and induce oxidative stress by induce the production of reactive oxygen species (ROS) and by modulating intracellular redox homeostasis, lipid peroxidation, and alteration of gene expressions were studied (Chattopadhyay et. al., 2011).

Eugenol (4-allyl-2-methoxy-phenol), the principle bioactive compound *of Syzygium aromaticum, Ocimum sanctum, Pimenta racemose* is an antioxidant, used as a food-flavouring agent and as an analgesic. Eugenol, a methoxyphenol with a short hydrocarbon chain, found in bay leaves, allspice, and the oil of cloves that originate from the Syzygium species (Kollmannsberger and Nitz, 1994). Eugenol antioxidant activity has been evidenced by the DPPH assay (Teresa *et.al.*, 2006). Eugenol possesses the antioxidant property by virtue of its phenolic hydroxyl group that donates electrons to quench free radicals. Hence it could preserve the enzymatic and nonenzymatic antioxidant systems in the myocardium and prevent lipid peroxidation. Eugenol could prevent electrophysical alterations and electrolyte imbalances and restore QT interval to normal (Binu *et.al.*,2017). Eugenol has attenuated isoproterenol-induced cardiac apoptosis by increasing intracellular calcium and oxidative stress (Choudhary *et.al.*,2006). Eugenol compounds have a methoxy phenolic structure

similar to capsaicinoids, inhibited iron-mediated lipid peroxidation and copper dependent LDL oxidation. The antioxidant action of eugenol compounds was analysed by its radical-scavenging activity and on the basis of the protective effect on metal-mediated lipid peroxidation. (Ito *et.al*.,2005). The antioxidant activity of eugenol was either equal to or better than the activities of TBHQ and BH. The presence of the 4-0H group in eugenol may be responsible for the antioxidant activity. Eugenol has shown good antioxidant activity at 10-μM concentration (Kelm *et.al*., 2000). Based on literature review, we aimed at identification of antioxidant activity of eugenol under fluoride intoxication, in the present study.

## MATERIAL AND METHODS

### Care and Maintenance of Experimental Albino Rats:

Thirty healthy adult male Wister strain albino rats (weighing 200±20g) were purchased from M/s. Sri Venkateswara Enterprises, Bangalore, India. The animals were kept in cages made up of Polypropylene with top stainless-steel grill. Six rats were accommodated in each cage and maintained under controlled laboratory conditions (Photoperiod of 12 hours light/ 12 hours dark cycle and Temperature 25±2 $^{0}$C). The rats were given a standard pellet diet (Purchased from Lipton Animal feed Ltd. Pune, India) and provided drinking water ad libitum during the complete experimental period. All the experiments were carried out according to the guidelines of the Institutional Animal Ethical Committee. (Resolution No: 09/ (i)/a/CPCSEA/IAEC/SVU/ZOOL/KSR/Dt. 08-07-2012).

### Selection of Age Group:

Based on the growth and physiology of the animal, four (4) months aged male Wister albino rats were considered as "Adults" and selected for the present experiment. A definite table regarding the age and life expectancy of various strains of laboratory animals was published in the book, entitled "International care and treatment of rabbits, mice, rats, guinea pigs and hamsters" by W.B. Saunders Co., Philadelphia, USA. Age-related changes in 2 weeks, 2.5, 10 and 23 months of Wistar strain rats were clearly explained by Jang.*et al*., (2001).

### Procurement of Chemicals:

All the chemicals used in the experiments were Analar Grade (AR) and purchased from Sigma Aldrich Corporation (St. Louise, Missouri, USA) Merck (Mumbai, India), Ranbaxy (New Delhi, India). "Barnstead Thermolyne" water purification plant was used to get nano-pure water. "Remi cooling high speed centrifuge" was used for centrifugation of the tissue homogenate. Shimadzu UV-1800 Spectrophotometer was used for measuring the optical density values and obtained results.

### Grouping of Animals:

The rats of same age were selected and segregated randomly into five groups of six rats and given treatment as follows:

**1.Group I**: **Normal Control (NC)**: Six rats received saline (0.9% NaCl) through orogastric tube for 60 days.

**2. Group II**: **Ocimum-Bio active compound, Eugenol Control (EGt)**: Six rats received Eugenol (10 mg/kg BW) for 60 days.

**3. Group III**: **Na F treatment (Ft)**: Six rats received the sodium fluoride (NaF) (10 mg/kg BW) dissolved in drinking water for 60 days.

**4. Group IV: NaF + Ocimum Bioactive compound (Eugenol) (Ft + EGt)**: Six rats received NaF (10 mg/kgBW) dissolved in drinking water and Eugenol (10 mg/kgBW) for 60 days.

**5. Group V**: **NaF + Vitamin E treatment (NaF + VEt)**: Six rats received NaF and Vitamin E (200 mg/kgBW) for 60 days.

### Isolation of heart:

After 60 days of treatment period was over, the animals were sacrificed by cervical dislocation. The heart tissue was excised and washed with ice-cold normal saline and stored in deep freezer at -80$^{0}$C for biochemical assay of antioxidant enzymes.

**Estimation of Antioxidant enzymes in Cardiac tissue:**

Superoxide dismutase (SOD) activity was evaluated by the method of Misra and Fridovich (1972) at 30$^0$C. The heart tissue was homogenized in chilled 50 mM phosphate buffer (pH 7.0) containing 0.1 mM EDTA to give 5% homogenate (w/v). The homogenates were centrifuged at 10,000 rpm for 10 min at -4$^o$C in cooling high-speed centrifuge. The supernatant part was segregated and used for enzyme assay in both standard and experimental tubes. 200µl of tissue sample was added to 1760µl of 0.05 M carbonate buffer which contains 0.1 mM EDTA at pH 10.2 at which SOD inhibits autooxidation of epinephrine. Then 40 µl of 30 mM epinephrine (in 0.05% acetic acid) was added to the above mixture and measured the OD values at 480 nm for 4 min on a Shimadzu UV-1800 Spectrophotometer. Activity expressed in terms of units and the amount of enzyme that inhibits the oxidation of epinephrine by 50%, which is equal to 1 unit.

Catalase activity was estimated by applying the method of Aebi (1984), with slight modifications. 5% homogenate (weight/volume) of cardiac tissue was prepared in ice cold 50 mM phosphate buffer (pH 7.0) containing 0.1 mM EDTA. The homogenates were centrifuged at 10,000 rpm for 10 min at -4 $^0$C. The supernatant part was separated and used as enzyme source. 200 µl of tissue homogenate was taken into a test tube and 20 µl of 100% Ethyl alcohol was added to it. The reaction mixture was kept in an ice bath for 30 minutes. Then the tubes were kept at room temperature till the reaction mixture attain normal room temperature and added 20 µl of Triton X-100 RS. In a cuvette containing 400µl of phosphate buffer and 100 µl of tissue extract was added 0.5 ml of 0.066 M Hydrogen Peroxide (in phosphate buffer) and decreases in optical density measured at 240 nm for 60s in a UV-Vis Double beam spectrophotometer. The molar extinction coefficient of 43.6 M cm-1 was used to determine the Catalase activity. One unit of activity is equal to the moles of $H_2O_2$ degraded / mg protein/min.

Se-dependant Glutathione peroxidase (Se-GSH-Px) activity was measured by the modified method of Flohe and Gunzler (1984). 5% (w/v) of cardiac tissue homogenate was prepared in 50 mM phosphate buffer (pH 7.0) containing 0.1 mM EDTA. The homogenate was centrifuged at 10,000 rpm for 10 min at -4 $^0$C in cooling high-speed centrifuge. The supernatant was used as an enzyme source. The reaction mixture contains of 0.5 ml of phosphate buffer, 0.1 ml of 0.01 MGSH (reduced form), 0.1 ml of 1.5 mM NADPH and 0.1 ml of glutathione reductase (0.24 units). 0.1 ml of tissue homogenate was added to the reaction mixture and incubated at 37 $^0$C for 10 min. Then 50 µl of 12 mM t-butyl hydroperoxide was added to 0.45 ml of the tissue reaction mixture and measured at 340 nm for 3 min. The molar extinction coefficient of 6.22 X $10^3$ M $cm^{-1}$ used to determine the activity of glutathione peroxidase. One unit of activity is equal to the mM of NADPH oxidized / mg protein / min. The activity of the enzyme was expressed in µ moles of NADPH oxidized / mg protein / min.

Glutathione reductase (GR) activity was assayed by the method of Carlberg and Mannervik (1985) with slight modifications. The cardiac tissue was homogenized (5% w/v) in 50 mM phosphate buffer (pH 7.0) containing 0.1 mM EDTA. The homogenates were centrifuged at 10,000 rpm for 10 min at -4$^0$C in cooling high speed centrifuge. The separated supernatant part was used as enzyme source. NADPH (50 µl, 2 mM) in 10 mM Tris buffer (pH 7.0) was added to the cuvette containing 50 µl of GSSG (20 mM) in phosphate buffer (0.5 M, pH 7.0 containing 0.1 mM EDTA) and 0.8 ml of phosphate buffer. The tissue extract (0.1 ml) was added to the NADPH – GSSG buffered solution and take OD values at 340 nm of 3 min. The molar extinction coefficient of 6.22 X $10^3$ M cm $^{-1}$ was used to determine glutathione reductase activity is equal to the mM of NADPH oxidized / mg protein / min. The activity of the enzyme was expressed in µ moles of NADPH oxidized / mg protein / min.

The data obtained was expressed as Mean values with their SD. Readings of the six different groups were compared using one-way ANOVA analysis with Dunnett's multiple comparison tests. Statistical analysis was performed using SPSS (Version 13.5; SPSS Inc., Chicago, IL, USA). Using M.S. Office, Excel Software the data has been analyzed for the significance of the main effects (factors) and treatments along with their interactions.

**RESULTS AND DISCUSSION**

In the present research work, SOD activity levels were measured in experimental animal rats. SOD levels were significantly lower in the Ft group than NC, while SOD levels were significantly higher in Ft+Egt rats when compare to Ft (Fig.1). Treatment of Eugenol to flouride rats confirmed a greater enhancement in SOD activity relative to Flouride intoxicated group and a slight decrement when compared to standard Vitamin E treatment. When compared to NC, there were no changes in the Egt group.

SOD plays a critical role in the body's antioxidant defense in contradiction of oxidative stress. The enzyme is an effective treatment for illnesses caused by reactive ROS by converting superoxide anion free radical (O2-) into oxygen and hydrogen peroxide (Kangralkar et al., 2010; Yasui and Baba, 2006). It was found that oxidative stress is linked to numerous cardiac disorders, including myocardial infarction, peripheral vascular disease, and stroke, while, these conditions were get normal with supplementation of antioxidants (Farías et al., 2017). These radicals target the cardiac antioxidant system as well as biomolecules (carbohydrates, lipids, proteins, and DNA), causing cardiac tissue damage. Generally, superoxide radical is produced in the heart tissue from the mitochondrial electron transport chain. To decrease reactivity, antioxidants in the mitochondria, such as SOD and glutathione are quickly breakdown or sequester superoxide radicals. High numbers of mitochondria in cardiac tissue are required for proper function, but cardiac dysfunction can arise from a reduction in mitochondrial antioxidant ability (Sánchez-Villamil et al., 2016; Rathore et al 2008).

In this study, fluoride intoxicated rats have been exhibited the reduced activity of SOD in heart tissue. Fluoride supplemented pigs had lower levels of SOD in their hepatic tissue in a previous research. In a separate research, mice given fluoride had a detrimental effect on the testes and epididymis via decreasing SOD levels (Zhan et al., 2006; Sun et al 2018). Wistar strain male albino rats exposed to high fluoride levels in their drinking water for two generations enhanced oxidative stress via lowering SOD levels in cardiac tissue (Basha et al 2011). Hence, fluoride is toxic in inducing oxidative stress by reducing SOD activity. Present study results also correlate with the all previous studies.

Increased levels of SOD were detected in the Ft+Egt experimental group of this study, compared to fluoride-intoxicated rats that eugenol compound treatment to the fluoride rats increased the SOD activity. It was discovered that rising quantities of free radicals reduce the antioxidant enzyme system in the body, but free radical scavengers reduce radicals, allowing the antioxidant enzyme system to increase. In an *in vitro* ABTS test, eugenol decreased free radical-induced lipid peroxidation and protected liver tissue against lipid peroxidation in CCl4-induced hepatotoxicity (Nagababu et al., 2010). It is obvious that eugenol reduces the number of free radicals in the body during sickness. Similarly, eugenol may scavenge free radicals generated by fluoride in the current research, therefore increasing the SOD activity. Similar results were observed in a study, cisplatin caused oxidative stress in the testicular tissue, which reduced SOD enzyme activity, but raised SOD levels in the cisplatin group when administered with eugenol (Ekinci Akdemir et al., 2019). In the same manner, Kumaravelu et al. (1996) discovered that eugenol has antioxidant action in CCl4-induced erythrocyte damage *in vivo*, and that eugenol enhanced SOD activity in red blood cells whereas CCl4 lowered it. Eugenol activity was somewhat lower than the standard vitamin E, in this study because vitamin E is potential antioxidant agent. It was proven by huge scientific reports (Rizvi et al 2014). It is positive entity that eugenol acted SOD acceleration property which is very near to the vitamin E.

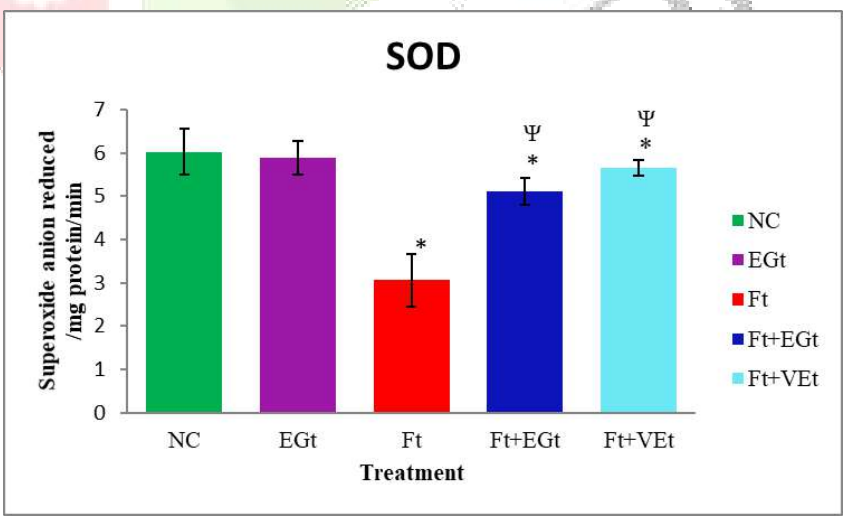



Fig.1. Effect of eugenol on SOD activity in the cardiac tissue of male albino rats. The values are significant compared with normal control (*p<0.05).

In addition to SOD, CAT activity levels were measured in experimental animal groups. CAT levels were significantly lower in the Ft group than NC, while CAT levels were significantly higher in Ft+Egt rats when compare to Ft (Fig.2). Treatment of Eugenol to fluoride rats confirmed a greater enhancement in CAT activity relative to fluoride intoxicated group and a slight decrement when compared to standard Vitamin E treatment. When compared to NC, there were no significant changes have been observed in the Egt group.

A variety of inhibitors including sulfide, hydroxyl amine, fluoride, cyanide, azide and acetate are decrease catalase's enzymatic activity. These chemicals are thought to substitute an aquo ligand in the prosthetic group that inhibits hydrogen peroxide catalysis (Schonbaum and Chance, 1976). Fluoride inhibited catalase activity *in vitro* at 1 mg/L, according to a Clark-type oxygen electrode sensor research (Stein and Hain, 1995). When ingested in abundance, fluoride is known for causing harm to key organs and systems, including the cardiac tissue, in addition to dental and skeletal fluorosis (Cicek et al., 2005). Fluoride interferes with soft tissues by blocking a variety of enzymes, ultimately resulting in the formation of free radicals. In the present study also, fluoride ingested rats exhibited changes in antioxidant enzyme CAT in heart tissue. Our findings were also consistent with a previous study that rat puffs exposed to 200 ppm NaF by the mother's milk throughout lactation and directly exposed through fluoride water in the post-suckling time frame for 3 months had lower antioxidant activity and decreased catalase enzyme in heart tissue (Basha and Sujitha, 2011).

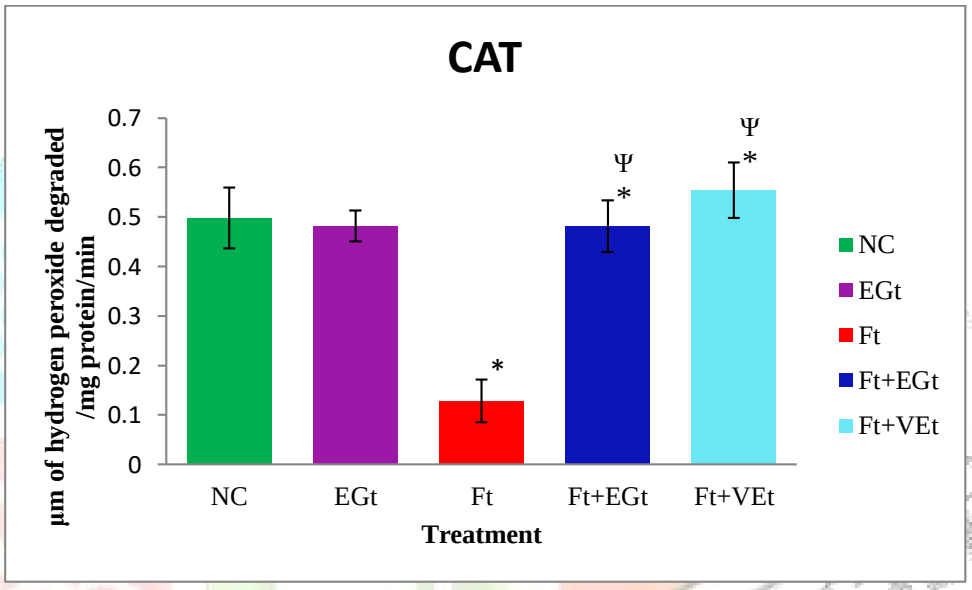



Fig.2. Effect of eugenol on the CAT under fluoride intoxicated condition. The values are significant compared with normal control (*p<0.05).

In the current study, CAT activity in cardiac tissues was significantly increased when sodium fluoride intoxicated rats were given eugenol. Treatment with eugenol for 21 days enhanced the antioxidant enzyme CAT activity of liver in carrageenan-induced arthritis, according to a previous study (Adefegha et al 2018). Rauscher et al (2001) were identified that antioxidant enzyme CAT enhancing capacity of isoeugenol in the tissue such as brain, kidney, heart and liver of streptozotocin induced diabetes Sprague-Dawley rats. As per Oroojan et al (2020), eugenol has an antioxidant impact on oxidative stress that caused by H2O2 in male mice islets of Langerhans via boosting catalytic activity of CAT. Furthermore, eugenol showed antioxidant activity *in vitro* by scavenging hydrogen peroxide produced by the fentons reaction and preventing the development of lipid peroxidation (Nagababu et al 2010). In another *in vitro* free radical scavenging activity assay, eugenol potentially scavenged the hydrogen peroxide on dose dependent manner. Hence it is clear that eugenol has potential hydrogen peroxide scavenging activity in *in vitro* and CAT enhancing capacity in *in vivo*. More importantly, eugenol rich leaf extract of *oscimum* sanctum (250 mg/kg) nullified the oxidative stress caused by sodium fluoride in swiss albino mice by increasing CAT enzyme activity (Prakash et al 2018). At the same time, eugenol exhibited the cardio protective role in rats under doxorubicin toxicity (Fouad and Yacoubi, 2011). Gathering all, due to free radical scavenging property and CAT enhancing capacity, eugenol protected the heart tissue under sodium fluoride toxicity induced oxidative stress, in this study.

Further, GPx levels were significantly lower in the Ft group than NC, while GPx levels were significantly higher in Ft+Egt rats when compare to Ft (Fig.3). Treatment of Eugenol to fluoride rats confirmed a greater enhancement in GPx activity relative to fluoride intoxicated group and a slight decrement when compared to standard Vitamin E treatment. When compared to NC, there were no significant changes have been observed in the Egt group.

GPx activity was significantly decreased in the fluoride intoxicated rats, in the present study. The similar results have been observed in Chauhan and colleagues (2013) conducted an experiment, in which female Sprague Dawley rats at the age of 6 and 18 month old were subjected to sodium fluoride. The results revealed that increased oxidative stress reduced glutathione peroxidase activity. In another study, fluoride intoxication for 25 days to adult female rats also found that decreased levels of glutathione reductase activity due to oxidative stress in the liver tissue (Błaszczyk et al 2011). It was also observed that fluoride poisoning reduces glutathione peroxidase enzyme activity in the brain, kidney, liver, plasma, and testis of 8 week old male Wistar rats, according to Inkielewicz-Stepniak and Krechniak (2004). Furthermore, prolonged exposure to sodium fluoride through drinking water for 60 days causes oxidative damage in wistar strain rats' kidney and liver tissues through lowering glutathione peroxidase enzyme activity. Sodium fluoride was also induced the hypertension and oxidative stress causing cardiac damage in heart tissue male albino rats on dose dependent manner (Oyagbemi et al 2016). Hence it is thought that sodium fluoride increased the oxidative stress in different tissues including heart, while in the same manner antioxidant enzyme GPx was decreased in the present study.

In the current research, GPx activity levels were significantly increased in the eugenol treated fluoride intoxicated rats. Similarly, eugenol was decreased the oxidative stress by increasing the glutathione peroxidase activity in liver tissue of rat under arthritis induced by carrageenan (Adefegha et al 2018). A research on the effects of eugenol on glutathione peroxidase in bovine ovarian cortical secondary follicles grown *in vitro* found that eugenol enhanced glutathione peroxidase enzyme activity m-RNA expression levels. Additionally, eugenol prevents cisplatin-induced testicular damage via boosting antioxidant capacity by raising glutathione peroxidase enzyme activity, which was dramatically reduced in the cisplatin-induced rat group (Ekinci Akdemir et al 2019). Moreover, eugenol protected male rats against carbon tetra chloride-induced oxidative stress by boosting glutathione peroxidase enzyme activity, whereas this enzyme activity was dramatically reduced in the carbon tetra chloride toxicity rat group (Kumaravelu et al 1996). In BRL-3A normal rat hepatocytes *in vitro*, another eugenol analogue, aspirin eugenol ester, prevented the paraquat producing oxidative stress caused liver damage by boosting antioxidant enzyme glutathione peroxidase enzyme activity (Zhang et al 2016). The antioxidant enzyme glutathione peroxidase was increased in the Arsenic Trioxide group supplemented with eugenol where it prevented the oxidative stress assisted renal injury in wistar rats, while this enzyme was lowered in the Arsenic Trioxide alone group (Binu et al 2017). Hence, gathering all, it is very clear that eugenol has antioxidant potentiality that correlated with increased antioxidant enzyme glutathione peroxidase enzyme in both previous studies and in the present study.

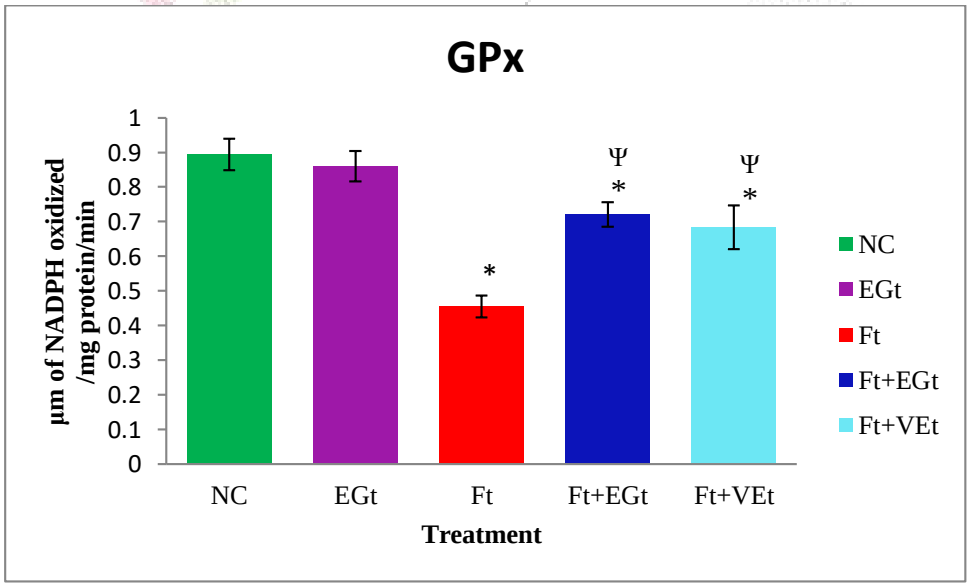



Fig.3. Effect of eugenol on the GPX under fluoride intoxicated condition. The values are significant compared with normal control (*p<0.05).

Finally, when compared to NC, there was slight GR changes have been observed in the Egt group. While, GR levels were significantly lower in the Ft group than NC, further GR levels were significantly higher in Ft+Egt rats when compare to Ft (Fig.4). Treatment of Eugenol to fluoride rats confirmed a greater enhancement in GR activity relative to fluoride intoxicated group and a slight increment when compared to standard Vitamin E treatment.

The obtained results in the present study were revealed that decreased levels of GR observed in the fluoride intoxicated rat heart tissue. Similar results were observed by Bharti and Srivastava (2009) in the rat brain. They have been administered fluoride orally at a dose of 150 mg/L for 28 days to rats which causing oxidative stress in the brain. Under fluoride-induced oxidative stress, glutathione reductase enzyme levels were shown to be lower. On other hand, Chauhan and colleagues (2013) conducted an experiment, in which female Sprague Dawley rats at the age of 6 and 18 month old were subjected to sodium fluoride. The results revealed that increased oxidative stress reduced glutathione reductase activity. Fluoride consumption of adult female rats for 25 days resulted in reduced glutathione reductase activity owing to oxidative stress in the liver tissue, according to another study (Błaszczyk et al 2011). It was found that sodium fluoride was induced the hypertension and oxidative stress, causing cardiac damage in heart tissue of male albino rats on dose dependent manner (Oyagbemi et al 2016). In addition, female wistar strain rats were given 150 ppm sodium fluoride in their drinking water. Sodium fluoride caused oxidative stress in numerous tissues such the heart, liver, and kidneys by inhibiting antioxidant enzyme like glutathione reductase (Bharti et al 2014). Fluoride has a detrimental influence on the antioxidant system through changing antioxidant enzymes such as glutathione reductase, as evidenced by all prior findings. It also validates the findings of the current study, which show that fluoride inhibits the glutathione reductase enzyme in heart tissue.

Increased glutathione reductase activity was observed in the fluoride intoxicated rats supplemented with eugenol natural compound. It was found that eugenol has the antioxidant activity that reduces the oxidative stress under illness. In a study, eugenol protected male rats against carbon tetra chloride-induced oxidative stress by boosting glutathione reductase enzyme activity, whereas this enzyme activity was dramatically reduced in the carbon tetra chloride toxicity rat group (Kumaravelu et al 1996). In a study, sub-acute administration of antioxidant compound isoeugenol in 30-day streptozotocin-induced diabetic Sprague-Dawley strain rats was studied by Rauscher and his colleagues in the year 2001. Eugenol enhanced glutathione reductase activity in the hepatic, renal, brain, and cardiac tissues, but this enzyme activity was lowered in the organs examined. Eugenol enhanced antioxidant capacity by raising glutathione reductase activity levels in concanavalin-A assisted T-cell-mediated acute hepatitis, but its levels were lowered in the hepatitis state. It was also found that eugenol rich extract of clove significantly decreased the oxidative stress in liver cirrhosis by increasing glutathione reductase activity, while glutathione reductase activity was significantly decreased in liver cirrhosis (Ali et al 2014).

Glutathione reductase activity involves conversion of oxidized glutathione into reduced form. While, reduced glutathione is very essential for the glutathione peroxidase enzyme. By utilizing reduced glutathione, glutathione peroxidase enzyme converts hydrogen peroxide into water, where hydrogen peroxide is very toxic to the cell. At the same time increased levels of glutathione peroxidase enzyme in the eugenol treated fluoride intoxicated rats, in the present study also support the increased levels of glutathione reductase activity. It is very clear the both glutathione peroxidase and glutathione reductase activities are interdependent. Hence, it is very clear that eugenol has antioxidant property due to its role in increasing levels of antioxidant enzymes such as glutathione reductase and glutathione peroxidase.

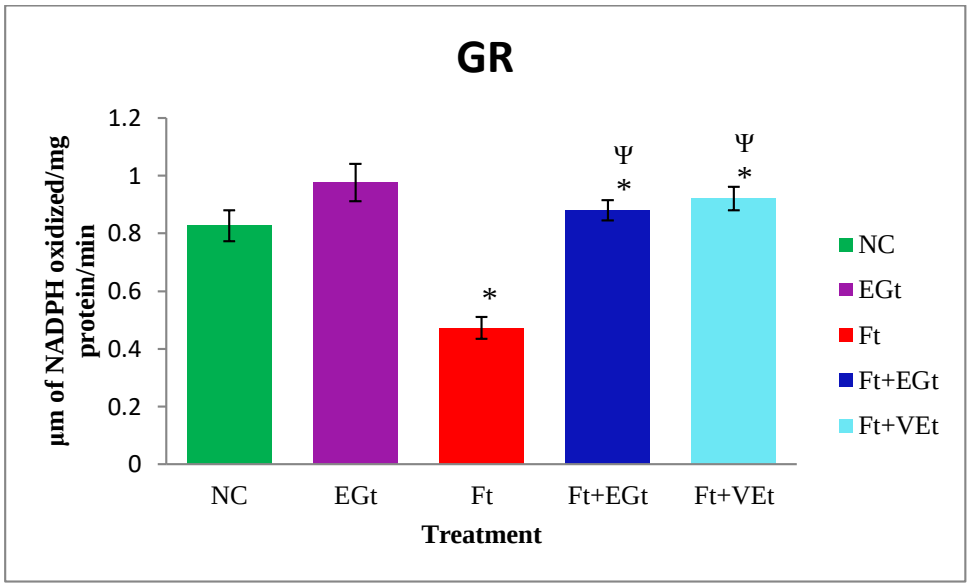



Fig.4. Effect of eugenol on the GR under fluoride intoxicated condition. The values are significant compared with normal control (*p<0.05).

## CONCLUSION

The findings of this study reveal that the eugenol can protect cardiac tissue under oxidative stress caused by fluoride by enhancing antioxidant enzyme. In future, clinical studies on the action of eugenol must be determined in fluoride intoxicated people.

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## CONFLICT OF INTEREST

All authors declare that there is no conflict of interest.

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Research Article

# Hepatoprotective Property of *Phyllanthus amarus* Alkaloid-Rich Fraction with Respect to Oxidative Stress Marker Enzymes

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**ABSTRACT**

A disruption in the equilibrium between the generation of reactive oxygen species and antioxidant defense enzymes is referred to as oxidative stress. In the present study, we planned to identify the hepatoprotective effect of *Phyllanthus amarus* alkaloid rich fraction in wistar strain albino male rats. The hepatic damage was induced by the D-galactosamine and ameliorative effect was tested with alkaloid rich fraction of *P. amarus* by measuring oxidative stress markers such as G6PDH, LDH, SDH, MDH and GDH in the liver tissue. Activity levels of G6PDH, SDH, MDH and GDH were significantly decreased in D-galactosamine induced hepatitis rats when compare to normal control rat group, while their activities were significantly increased in hepatitis rat group that supplemented with alkaloid rich fraction of *P. amarus*. In contrast, LDH enzyme activity of liver was significantly increased in the hepatitis rat group when compare to normal control rats, while its activity was significantly decreased in hepatitis rats treated with alkaloid fraction. In conclusion, it is very clear that alkaloid fraction of *P. amarus* has hepatoprotective property with respect of decreasing oxidative stress by regulating oxidative stress marker enzymes. The isolation and identification of specific alkaloid compounds with hepatoprotective properties and anti-oxidative stress will require much further research.

**Keywords:** *Phyllanthus amarus*, oxidative stress, alkaloid rich fraction, hepatoprotective, medicinal plants.

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## INTRODUCTION

*Phyllanthus amarus* is medicinally important medicinal plant, belongs to the family *Euphorbiaceae.* It has been proved to treat many deadly diseases traditionally and pharmaceutically. In traditional herbal system, *P. amarus* has been used hugely in various regions around world to treat many adverse effects. In India, especially, this plant being used traditionally to treat anemia, appetizer, asthma, astringent, bronchitis, conjunctivitis, cough, diabetes, diarrhoea, diuretic, dropsy, dysentery, dyspepsia, eye disorders, fevers,, genitourinary disorders, gonorrhea, hepatitis, itchness, jaundice, leucorrhea, menorrhagia, oligogalactia, ringworm, scabies, skin ulcers, sores, stomachic, swelling, thirst, tuberculosis, tumor (abdomen), urogenital tract infections, and warts.[1] In addition, pharmaceutically this plant has been proved as antiamnesic, antibacterial, anticancer, antifungal, anti-diarrhoeal, gastroprotective, antiulcer, analgesic, anti-inflammatory, anti-allodynic, anti-oedematogenic, antinociceptic, antioxidant, antiplasmodial and antiviral.[1]

Alkaloids are indeed organic molecules which mostly contain basic nitrogen atoms, those abundantly available in nature in the tissues of plants and others. This group also contains certain associated neutral molecules and weakly acidic constituents also present. Allo-securine, dihydrosecurinine, epibubbialine, isobubbialine, nor-securinine, phyllanthine,

Securinine, securinol and tetrahydrosecurinine alkaloids were isolated from the *P. amarus* through chromatographic methods.[2,3] In addition to that alkaloids Foo and Wong, were isolated 4-hydrosecurinine, 4-methoxy-nor-securinine, 4-methoxy dihydrosecurinine and 4-methoxytetrahydrosecurinine.[4] Hence, the present research paper design to separate alkaloids fraction from *P.amarus* and the same was tested for hepatoprotective activity with reference to oxidative stress enzymes.

G6PDH is a cytoplasmic enzyme present all organisms, a part in pentose phosphate pathway which produces NADPH (nicotinamide adenine dinucleotide phosphate) that is necessary for elimination of free radicals such as reactive oxygen species produced in cell.[5] This NADPH helps to protect the cells from oxidative stress caused by substances like $H_2O_2$ by maintaining the level of glutathione in these cells and also maintains glucose through pentose phosphate pathway.[6] LDH is abbreviated as lactate dehydrogenase enzyme present in virtually most living tissue/cells. Generally, a dehydrogenase is a molecule-to-molecule hydride exchange enzyme. It is a biomarker of severe ailments and diseases since it is


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produced after tissue injury.[7] LDH mediates the rearrangement of pyruvate and lactate, as well as NAD+ and NADH, at the same time. Whenever $O_2$ is missing or in scarcity, it transforms pyruvate, the end result of glycolysis, to lactate, and it reverses the process during the Cori cycle in the hepatic tissue.[8] Succinate dehydrogenase, also known as respiratory complex II, is an enzyme complex present in the inner mitochondrial membrane of eukaryotic and several bacterial cells. In the TCA cycle, this enzyme transforms succinate to fumarate catalytically, and in the electron transport chain, it converts ubiquinone to ubiquinol.[9] SDH receives electrons and transfers them through its four subunits, SDH-A, SDH-B, SDH-C, and SDH-D, before continuing the electron transfer to electron transport chain's complex II. Further, the electrons of FADH2 following SDH catalysis and ubiquinone are subsequently transported to complex III of electron transport chain, where they are used to continue the synthesis of the cell's energy moiety, adenosine triphosphate.[10] The MDH2 gene encodes malate dehydrogenase (MDH), which is found in mitochondria and is also known as malate dehydrogenase 2 in humans. Malate dehydrogenase uses the NAD/NADH cofactor complex in the TCA cycle of carbohydrate metabolism to catalyze the bidirectional oxidation of malate to oxaloacetate. MDH is indeed active in gluconeogenesis, or the conversion of simpler compounds into glucose.[11] Glutamate dehydrogenase (GDH) enzyme present in the mitochondrial matrix made up of six identical monomers that form hexameric forms. This enzyme catalyzes the reversible oxidative deamination of glutamate to alpha-ketoglutarate with the release of free ammonia as a by-product. This enzyme uses either NAD or NADP as a co-factor to complete this reaction.[12]

## MATERIAL AND METHODS

### Collection of plant material

*P. amarus* plant was collected in Tirupati, Andhra Pradesh, India in the month of August and September 2017. Botany taxonomist Dr. Madhava Chetty, Department of Botany, S. V. University has identified and authenticated it. The Department of Botany, S. V. University, Tirupati has held a voucher specimen No.2151 in the herbarium lab. Further, the plant material was washed with water and rinsed with sterile distilled water. It was subjected to shade dry after washing and powdered with a mechanical grinder. This material was further used for extraction of alkaloid rich fraction.

### Preparation of alkaloids rich fraction from *P.amarus*

Alkaloids rich fraction was prepared by the method of general acid–base extraction as described by Houghton and Raman, 1998[13]. Briefly, the dried plant powder of *P.amarus* soaked in methanol for 24 h with occasional stirring. After soaking, the mixture was filtered using Whatman No. 1 filter paper. The filtrate collected had been concentrated under reduced pressure using rotary evaporator. The concentrated crude extract has been combined with 1 M Hcl and purified for any precipitate removal. 2N NaOH was gradually applied to this filtrate to produce an off-white precipitate. Now the precipitate was divided into equal quantities of water and dichloromethane (DCM) layers. Separated, evaporated and measured the DCM layer contained alkaloids. Dragendorff 's reagent (5 % bismuth nitrate, 4 % acetic acid, and 2 % potassium iodide) tested the separated alkaloids from crude. The rich alkaloid fraction yield was approximately 5 % (w/w).

### Animals and maintenance:

Indian Institute of Science (IISc), Bangalore provided male Wistar rats weighing 180± 200 g. The animals were kept under standard laboratory conditions by maintaining temperature 27 ± 2ºC, natural light dark cycle such as photoperiod of 12 h light and 12 h, and humidity about 55–60%. The rats were maintained by providing regular pellet diet that was supplied by M / s Hindustan Lever Ltd., Mumbai and water ad libitum. Animal ethical committee approved the design of this study (Resolution No.10/08/a/CPCSCA/IAEC/SVU/09-10/ZOOL/KRS/ Dt.25.09.2009). Animals were divided into five groups of six rats each, after 7 days of acclimatization.

### Grouping of animals:

**Group I- Normal Control (NC)**: Rats received saline for 21 days and served as normal control.

**Group II- Alkaloid rich Fraction control (AF)**: Rats were given alkaloid rich fraction of *P. amarus* (100mg/kg b/w**)** for 21 days.

**Group III- Hepatitis Control (H)**: A single injection of D-galactosamine hydrochloride (800mg/kg b/w) was given intraperitoneally for the induction of hepatitis 48 hours before sacrifice.

**Group IV- Hepatitis + Alkaloid rich Fraction treatment (H+AF)**: Pre-treatment of alkaloid rich fraction of *P. amarus* (100mg/kg b/w**)** orally for 21 days and a single injection D-galactosamine hydrochloride (800mg/kg b/w) 48 hours before sacrifice.

**Group V- Hepatitis + Silymarin treatment (H+S):** Pre-treatment of standard drug silymarin (100 mg/kg b/w) orally for 21 days and a single injection D-galactosamine hydrochloride (800mg/kg b/w) 48 hours before sacrifice.

### Glucose-6-Phosphate dehydrogenase (G-6-PDH)

The behavior of glucose-6-posphate dehydrogenase was assessed using the Mastanaiah et. al. (1978) method.[17] 10% (W / V) of homogeneous tissue was prepared in ice cold sucrose solution (0.25 M), centrifuged at 1000 g at $4^0$C for 15 minutes, and supernatant used as an enzyme source. The 2 ml reaction mix comprises 2 µ moles of INT, 100 µ moles of sodium phosphate buffer (pH 7.4), 0.3 µ mole of NADP and 20 µ moles of glucose-6-phosphate. The reaction was started by adding 0.5 ml of homogenous tissue containing 50 mg as an enzyme extract. The incubation was done at $37^0$C for 30 minutes, and the


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reaction was then halted by adding 5 ml of glacial acetic acid. The developed formazan was extracted into toluene in 5 ml at $5^0$C. The color intensity was read at 495 nm versus the blank toluene. The G-6-PDH activity was represented as µ moles of formazan formed/mg protein/hour.

**Lactate dehydrogenase (LDH)**

The activity of Lactate Dehydrogenase was determined by the Nachlas et. al., (1960),[14] and with minor modifications as suggested by Prameelamma and Swami (1975).[15] 10% (W / V) homogeneous liver tissue was prepared in an ice cold solution of 0.25 M sucrose, centrifuged for 15 minutes at 40C at 1000 g and supernatant used as enzyme source. The final 2 ml reaction mixture contained 40 µ moles of sodium lactate, 100 µ moles of phosphate buffer (pH 7.4), 0.1 µ mole of NAD and 4 µ moles of INT. The reaction was started by adding 0.2 ml of homogeneous 20 mg tissue as an enzyme resource and incubated at 37°C for 30 minutes, and the reaction was halted by adding 5 ml of glacial acetic acid. Zero time controls were retained by adding 5 ml of glacial acetic acid to the incubation solution led to the advent of the source enzyme. At 50C, the formazan developed was extracted into 5 ml of toluene overnight. The color formed was analyzed against the blank toluene at 495 nm in a Spectrophotometer. The activity of the enzyme was represented in µ moles of formazan formed / mg protein / hour.

**Succinate dehydrogenase (SDH)**

The activity of SDH was determined by the Nachlas et. al., (1960),[14] and with minor modifications as suggested by Prameelamma and Swami (1975).[15] 10% (W / V) homogeneous liver tissue was prepared in an ice cold solution of 0.25 M sucrose, centrifuged at 1000 g at 40C for 15 minutes and obtained supernatant used as enzyme resource. The 2 ml reaction mix comprises 4 µ moles of INT, 100 µ moles of phosphate buffer (pH 7.0) and 40 µ moles of sodium succinate. The incubation was done at 370C for 15 minutes, and the reaction was then halted by adding 5 ml of glacial acetic acid. The following stages were followed same as designated for LDH. The SDH activity was represented in µ moles of formazan formed / mg protein / hour.

**Malate dehydrogenase (MDH)**

The activity of MDH was determined by the Nachlas et. al., (1960),[14] and with minor modifications as suggested by Prameelamma and Swami (1975).[15] 10% (W / V) homogeneous liver tissue was prepared in an ice cold solution of 0.25 M sucrose, centrifuged at 1000 g at 40C for 15 minutes and obtained supernatant used as enzyme resource. The 2 ml reaction mix comprises 4 µ moles of INT, 100 µ moles of phosphate buffer (pH 7.0), 0.1 µ mole of NAD and 40 µ moles of sodium malate. The reaction was started by adding 0.2 ml of homogenous tissue containing 20 mg as an enzyme extract. The incubation was done at 370C for 15 minutes, and the reaction was then halted by adding 5 ml of glacial acetic acid. The following stages were followed same as designated for LDH. The MDH activity was represented in µ moles of formazan formed / mg protein / hour.

**Glutamate dehydrogenase (GDH)**

Activity of glutamate dehydrogenase (GDH) was assessed using the Lee and Lardy (1965) procedure.[16] 5% (W / V) of homogeneous tissue was prepared in ice cold sucrose solution (0.25 M), centrifuged at 1000 g at 40C for 15 minutes, and supernatant used as an enzyme source. The 2 ml reaction mix comprises 2 µ moles of INT, 100 µ moles of phosphate buffer (pH 7.0), 0.1 µ mole of NAD and 40 µ moles of sodium glutamate. The reaction was started by adding 0.2 ml of homogenous tissue containing 10 mg as an enzyme extract. The incubation was done at 370C for 15 minutes, and the reaction was then halted by adding 5 ml of glacial acetic acid. The developed formazan was extracted into toluene in 5 ml. The color intensity was read at 495 nm versus the blank toluene. The GDH activity was represented as µ moles of formazan formed/mg protein/hour.

## RESULTS AND DISCUSSION

In the present study, the activity levels of G6PDH in alkaloid fraction treated hepatitis animals were recovered as compared to normal control rats. The G6PDH of the hepatitis control rat group was considerably lower than that of the other groups studied. Normal control rats given the alkaloid fraction, on the other hand, showed very minor increasing changes in G6PDH when compared to the normal control group. In hepatitis rats, silymerin, a widely available plant-derived medicine, was shown to be somewhat greater efficient than the alkaloid fraction in increasing G6PDH activity (Figure 1)

D-galactosamine is a hepatotoxin which induces the hepatic tissue damage by producing oxidative stress such as reactive oxygen species and reactive nitrogen species. In the oxidative stress, reactive oxygen species like superoxide radicals are generated through mitochondria which in turn converted into the hydrogen peroxide by the enzyme superoxide dismutase.[18] Further, these superoxide radicals converted into most dangerous hydroxyl radials. D-galactosamine, on the other hand, causes liver damage in rats, which is linked to induction of lower levels of G6PDH by the hepatotoxin in rats. Due to lower activity of G6PDH, increased levels of oxidative stress were observed in hepatic tissue.[19] Alternatively, the functionality of G6PDH was reduced in the hepatic tissue of the current study's hepatitis rats. This implies that reduced conversion of glucose-6-phosophate to 6-phosphogluconate causes NADPH production in the HMP shunt to be diminished. Intern, the glycolytic and krebs cycle paths are harmed by this process as an alternative source of energy. When oxidoreductases in the mitochondria are inhibited, the energy supply for regular metabolic processes is reduced. The decreased amount of NADP might potentially be a factor in Dgalactosamine's inhibition of G6PDH.[20] Many research studies found that a toxin that induces the liver


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toxicity causes the decline of G6PDH.[21] Similarity, in the present study, D-galactosamine also induced the hepatic damage and reduction levels of G6PDH.

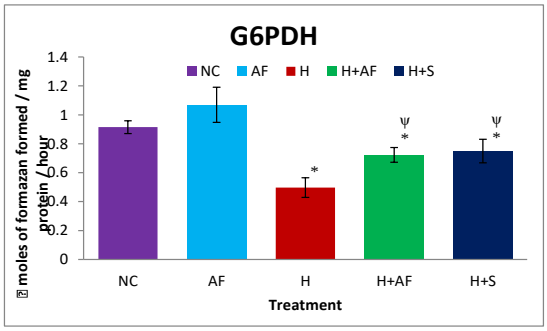



**Figure 1:** Effect of Alkaloid rich fraction on Glucose-6-Phosphate Dehydrogenase (G-6-PDH) activity in the hepatic tissue of male albino rats.

A research found that an alkaloid-rich extract of *Litsea glutinosa* bark enhanced the activity of G6PDH in diabetic mice's liver.[22] The restoration of decreased GSH is the primary function of NADPH generated by G6PDH within liver. This protects liver tissue by detoxifying hydroxyl radicals, and hydrogen peroxide which are oxygen radicals generated in the liver.[23] Likewise, in the current study, an alkaloid-rich fraction and silymerin enhanced the activity of G6PDH in the hepatitis liver. At the same time, alkaloids from plant species also showed free radical scavenging activity.[24] On whole G6PDH reduction resulting free radicals were might also scavenged by the alkaloids of *P.amarus,* in the present study. Hence it is hypothesized that alkaloid rich fraction increased the G6PDH activity in the liver tissue by scavenging free radicals such as hydrogen peroxide and hydroxyl radicals.

LDH levels in the hepatitis group were considerably higher than NC, but LDH levels in alkaloid-rich fraction treated hepatitis rats were substantially lower than Hepatitis (Figure 2). Treatment of hepatitis rats with alkaloid-rich fraction resulted in a larger decrease in LDH activity compared to hepatitis groups, as well as a substantial decrease compared to standard medication Silymarin treatment. There were no significant differences in the AF group as compared to the NC group.

The livers plays a significant role in regulating the metabolism of carbohydrates by keeping glucose levels within a normal range and express a series of enzymes that are turned on alternatively or off probably depends on if the blood sugar levels take up or down. Especially, glycolysis of glucose in liver cells takes place in the cytosol under aerobic and anaerobic conditions.[25] In muscle and liver, during aerobic respiration, glucose in the cytosol is transformed to pyruvate, which then enters mitochondria for high energy generation, but during anaerobic respiration, pyruvate in the cytosol is transformed to lactic acid by the enzyme LDH, which then transforms NADH to NAD.[26] Again, to improve aerobic respiration, lactic acid is formed and enters the liver, where it is converted to glucose through a process known as the cori cycle by LDH. Hence liver is a main organ for the regeneration of glucose under hypoxia.[27] Furthermore, liver failure has been linked to an increase in macrophage content, which causes endothelial cell destruction in sinusoids either direct or indirect through the production of cytokines. Hypoxia liver injury, commonly known as hepatitis, is a condition in which the liver's normal function is disrupted and the level of hypoxia-sensitive enzymes such as LDH rises.[28] Another reason is that hypoxia inducible fctor-1 is a gene found in the liver that causes increased hypoxia in liver disorders such as cirrhosis, tumors, and fibrosis, and others.[29]

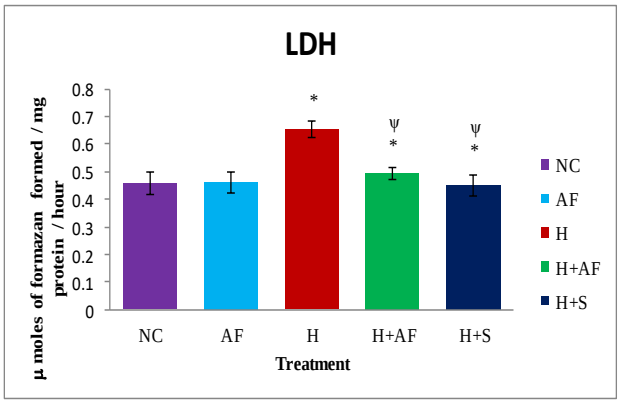



**Figure 2:** Effect of Alkaloid rich fraction of *P. amarus* on Lactate Dehydrogenase (LDH) activity in the hepatic tissue of male albino rats.

When compared to the normal control rats, the D-Galactosamine induced hepatitis rat group had higher levels of LDH in this research. Our findings are consistent with a recent study that after two injections of D-Galactosamine, LDH levels in liver fibrosis rats increased dramatically as compared to normal rats.[30] In a similar manner, CCL4-induced hepatic damage in Kunming mice produced the same effects, such as an increase in LDH levels.[31] In this research work, D-galactosamine-induced hepatitis rats treated with an alkaloid fraction obtained from the *p.amarus*, on the other hand, had lower LDH activity levels in rats when compare to hepatitis group. Similar results were reported in previous study that, *Acanthus ilicifolius* plant contained *alkaloid Acanthus ilicifolius* alkaloid A synthesized and tested for hepatoprotective activity in CCl4 induced hepatic damage in rats. Where they found that a decreased level of LDH was observed in alkaloid treated rats, an indication that alkaloid protected the liver cell from the hepatotoxin.[31] Our results correspond those of another study, which found that an alkaloid fraction extracted from *Hygrophila auriculata* leaves protected liver tissue against CCL4 toxicity by lowering LDH levels at various doses.[32] Based on the findings and their agreement with prior research, it is clear that the alkaloid-rich fraction of *P. amarus* is an excellent source of hepatoprotective alkaloids. Furthermore, it is believed that *P. amarus* alkaloids protected liver tissue by lowering hypoxia levels and reducing the expression of the hypoxia inducible fctor-1 gene and LDH in the liver.


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SDH levels in the hepatitis group were considerably lower than NC, but SDH levels in alkaloid-rich fraction treated hepatitis rats were substantially higher than Hepatitis (Figure 3). Treatment of hepatitis rats with alkaloid-rich fraction resulted in a larger increase in SDH activity compared to hepatitis groups, as well as a little bit decrease compared to standard medication Silymarin treatment. There were no significant differences in the AF group as compared to the NC group.

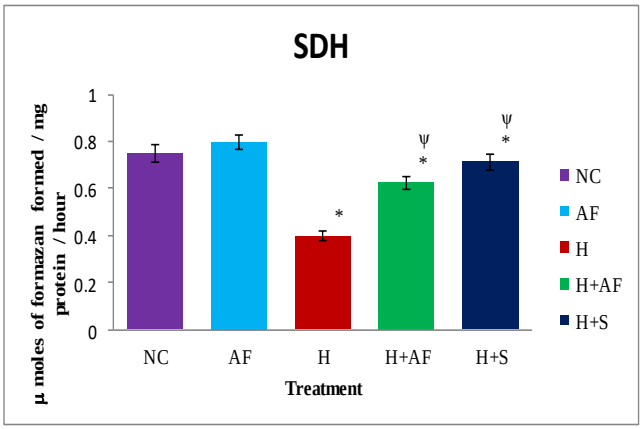



**Figure 3:** Effect of Alkaloid rich fraction of *P. amarus* on Succinate dehydrogenase (SDH) activity in the hepatic tissue of male albino rats

Studies on the worm *Caenorhabditis elegans* supported the theory that perhaps the SDH performs a particular role in mitochondrial oxygen management. An oxygen-hypersensitivite worm was found to have a particular SDH mutation instead of a complete class of mitochondrial respiratory mutants.[33] Mutations in any of the SDH genes cause the complex II to breakdown completely in humans. Complex II can thus be ignored as a cause of further superoxide generation because it is not present. As a result, scientists believe that superoxide excessive production, which has been linked to carcinogenesis in humans and hypersensitivity to oxygen in mutant worms, is due to the SDH's inability to appropriately diminish the UQ pool, which is required to withstand oxidative stress.[34] The deficiency of SDH activity would not only lead to lower ATP production–a situation that may also be caused by a severe Complex I or Complex IV defect–but it will also deprive the Reaction Center of the only dehydrogenase activity capable of keeping the Ubiquitin pool at a high reduction status. This might lead to a decrease of the respiratory chain's anti-oxidant ability, as well as oxidative stress.[34] On other hand, Succinate, a tricarboxylic acid cycle intermediary involved in mitochondrial ATP production, has been identified as a key signaling molecule in a number of diseases. When succinate concentrations are high, the major ROS generating site in Complex II, FAD in SDHA, is unable to produce ROS. The mechanism of succinate-mediated suppression of ROS generation at FAD is that succinate may prevent FAD from receiving oxygen.[35] The stimulation of human GPR91, which really is accountable for liver damage, is induced by succinate. Furthermore, succinate is a substrate for the SDH enzyme, which is diminished in many liver disorders, resulting in an increase in ROS, which leads to liver damage.[36] Similarly, decreased SDH levels were observed in the liver cancer.[37] In the present study, D-galactosamine induced hepatitis rats exhibited decreased levels.

In contrast, plant compounds such as phenols, flavonoids and alkaloids are pharmaceutically active in reducing liver diseases by inducing increase levels of SDH. SDH levels were found to be higher in the alkaloid-rich fraction obtained from *Phyllanthus amarus* treated hepatitis rats in the current investigation. Our results were correlated with a study that the hydroalcoholic extract of *Chrysanthemum balsamita, Calendula officinalis* herbs were increased the SDH activity in the CCl4 induced heptotoxicity in the albino rats. These herbs were contained rich amount of alkaloids.[38] Along with, the similar results were observed in another study that a single dosage of 120 mg/kg of monocrotaline, a pyrrolizidine alkaloid, induced the increased levels of SDH in rats after 12 days.[39] Hence, it is hypothesize that alkaloid fraction of this study protected the liver tissue from the D-galactosamine induce hepatotoxicity by inducing SDH, decreasing oxidative stress.

MDH levels in the hepatitis group were considerably lower than NC, but MDH levels in alkaloid-rich fraction treated hepatitis rats were substantially higher than Hepatitis (Figure 4). Treatment of hepatitis rats with alkaloid-rich fraction resulted in a larger increase in MDH activity compared to hepatitis groups, as well as a somewhat lower when compared to standard medication Silymarin treatment. There were slight differences in the AF group was observed as compared to the NC group.

It has been reported that mitochondrial destruction is an initial and distinctive hallmark of alcohol liver diseases, and that it plays a role in liver damage etiology. Distended mitochondria with disoriented cristae have been seen in electron microscopy investigations, and experimental animal research have indicated that giving high amounts of ethanol to rats reduces the functional capacities of hepatic mitochondria by a modest but substantial amount.[40] Decrease levels of hepatic enzymes, notably the mitochondrial enzyme MDH, are commonly observed in alcoholics, even when steatosis is the sole histopathological abnormalities and this has supported the idea of mitochondrial damage.[41] It was well understood that higher amounts of free radicals cause mitochondrial damage. Reduced levels of mitochondrial enzymes have been linked to mitochondrial damage in liver disorders. In the same manner, decreased activity levels of MDH have been found in D-galactosamine induced hepatitis rats because of D-galactosamine induces the liver damage by increasing free radicals.[42] In the current investigation, reduced levels of MDH were detected in the D-galactosamine induced hepatitis rat group, which was consistent with previous findings.


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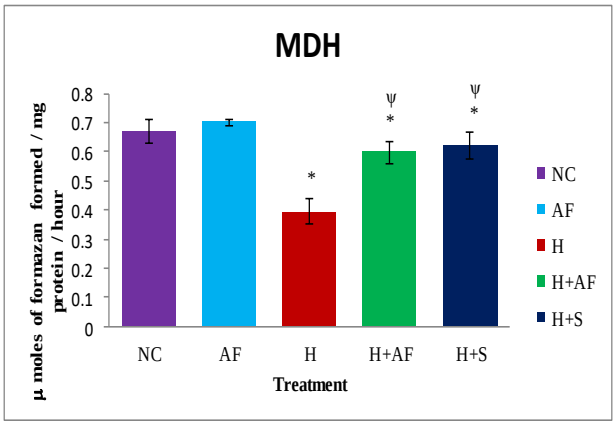



**Figure 4:** Effect of Alkaloid rich fraction of *P. amarus* on Malate dehydrogenase (MDH) activity in the hepatic tissue of male albino rats

Phytochemical secondary metabolites are abundant in medicinal plants. Phenols, flavonoids, and alkaloids are among the most commonly used medicinal formulations. Several investigations have discovered that plant alkaloids and alkaloid fractions protect liver tissue against chemically induced liver damage. The alkaloid fractions isolated from *Murraya koenigii* leaves ethanol extract protected liver tissue infected with chemicals like paracetamol and CCl4.[43] In another study, *Sarcococca saligna* plant alkaloids such as alkaloid-C, holaphylline and sarcovagine-D were reported to exhibit hepatoprotective properties in CCl4-induced hepatotoxicity.[44] The alkaloid fraction isolated from *p. amarus* also protected the hepatic tissue of male albino rats infected with D-galactosamine hepatitis in the current study. Furthermore, plant alkaloids have a number of significant pharmacological characteristics, one of which is free radical scavenging or antioxidant activity. In a study, fangchinoline and Cepharanthine from the *Stephania rotunda* plant scavenge free radicals such as DPPH, ABTS, and superoxide radicals *in vitro* antioxidant assays.[45] Hence, it is very clear that alkaloid fraction of this study also might be scavenges the free radicals in hepatitis rats. At the same time alkaloid fraction protected liver tissue under the hepatitis by increasing the MDH levels in this study. Furthermore, silymarin also exhibited highest hepatoprotective property by increasing MDH leaves. Hence, alkaloid fraction from *Phyllanthus amarus* is protected liver tissue by preventing free radicals, mitochondria damage and increasing MDH.

GDH levels in the hepatitis group were significantly lower than NC, but GDH levels in alkaloid-rich fraction treated hepatitis rats were substantially higher than Hepatitis (Figure 5). Treatment of hepatitis rats with alkaloid-rich fraction resulted in a larger increase in GDH activity compared to hepatitis groups, as well as a somewhat lower when compared to standard medication Silymarin treatment. There were slight differences in the AF group was observed as compared to the NC group.

The current study indicates that in hepatitis rats, GDH activity was significantly reduced. The reduction in GDH function is due to the enzyme's inactivation by higher ammonia levels (product-inhibitor), which reduces the enzyme's kinetic effectiveness.[46] Drug injuries, ischemia injuries, metabolic illness, toxins and viral infections, are some of the causes of hepatic necrosis. Liver necrosis induced the damage of mitochondria which induce the release of mitochondrial enzymes. In the present study, increased mitochondrial membrane fluidity and subsequent mitochondrial enlargement may affect the activity of the mitochondrial enzyme GDH, which in turn may affect the state of mitochondrial NAD depletion in hepatitis. The reduction in GDH activity implies that during the hepatitis condition, the mechanisms of deamination and amination that regulate ammonia toxicity in the kidney are also disrupted.[47] In GDH knockout mice, however, a lack of GDH in liver leads to greater in circulatory ammonia and a reduction in the detoxification mechanism into urea, altering ammonia metabolism. The same study discovered that a lack of GDH in the liver causes metabolic changes such as changes in gluconeogenesis, the use of lipids instead of carbohydrates for energy generation, and an influence on food intake circadian rhytms.[48] Hence it is very supportive to the present investigation that decreased levels of GDH in hepatitis rats may induces the all the above said alterations in rats body.

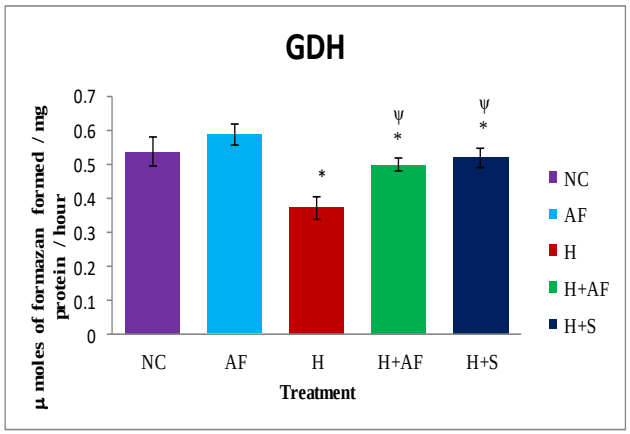



**Figure 5:** Effect of Alkaloid rich fraction of *P. amarus* on Glutamate dehydrogenase (GDH) activity in the hepatic tissue of male albino rats.

Alterations in GDH activity is caused by ethanol exposure to progressive mitochondrial modification and degradation. The reduction in GDH activity is due to the enzyme's inactivation by higher ammonia levels, which reduces the enzyme's functional effectiveness. Besides, high ammonia and lactate levels, according to another study, inhibit GDH function.[46] The elevated LDH seen in this study is consistent with the fact that lactate limits GDH action. Means hepatitis rats exhibited elevated LDH which intern increase lactate, such lactate inhibits the GDH.

Many medicinal plants have been studied in vitro and *in vivo* for their hepatoprotective efficacy against CCl4, d-galactosamine, paracetamol-induced liver damage, and viral-infected hepatitis. These plants have been prevented


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hepatic damage by inhibiting oxidative stress caused by chemicals and virus. plants with antioxidant property is major agent in reducing oxidative stress whereas this property is associated with phenols, flavonoids, terpenoids, alkaloids and may other plant secondary metabolites.[49] Plant extracts, separated fractions and isolated compounds protects the liver damage from chemicals and others. In this connection, plants having liver protection by increasing MDH also studied. For example, *phyllanthus niruri, Croton hypoleucus, Vicia calcarata Desf* have been protected liver damage by reducing oxidative stress and increasing MDH in animal models.[50] Similarly, alkaloid rich fraction isolated from *P. amarus* and silymerin, in this study, were also protected the liver tissue from oxidative stress by increasing MDH levels. Hence, these fraction and compounds are suggestive agents to treat hepatitis associated with oxidative stress.

## CONCLUSION

The findings of this study reveal that the alkaloid fraction of *P. amarus* is a rich source of oxidative stress relievers which enhance oxidative stress marker enzymes in hepatic tissue under hepatitis conditions. In future, the mechanism of action of the alkaloid fraction must be determined, as well as the isolation of individual alkaloid compounds is necessary to be done.

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Dr.V.Sailaja has been working and contributing to the field of organic farming, & environmental science related to bio-diversity and aquaculture. She has 31 years of teaching and Research experience. She was awarded Gold medal in M.Sc Zoology by Sri Venkateswara University, Tirupathi. She has 58 research publications in reputed highly scopus national and international journals and presented more than 50 papers in various National and International seminars and conferences. She attended 25 national and International workshops. She attended more than 50 online seminars and workshops. She has received many honourary awards. Some of the important awards are Best women award-2011, State Best Citizen of Andhra Pradesh Award -2011, International Women of Distinction Award in Sciences -2016, Bharath Vikas National Award -2016, Outstanding Educator and Scholar Award-2017, National Distinguished scholar and Icon -2017, Exemplary Teacher Award -2018, Outstanding National Science service Award -2019, National Distinct Women Educator and Scholar award-2021. She has organized three National Seminars, one National Symposium, one National Workshop, one National webinar, one International Webinar and one training programme on skill development. Two PhD's were awarded under her able guidance. Presently she is guiding three Ph.D students. She Worked as Co-Ordinator, Eco-AIR Project, A.P State science centre, Amaravathi. This project was sanctioned by DST, New Delhi.She has done minor research project on "Ecological Study of Mangroves at Chippaleru Estuary Lakshmipuram Village Thummalapenta, Kavali, SPSR Nellore". She has published 15 books and her biodata was published in books The Magnificience of Humbles and Imminent Researcher and Scholar Icon 2017. She held different positions like In-charge for Central Instrumentation Facilities scheme under UGC Programme in J.B Degree and p.g college, Kavali, worked as HOD, Dept of Biotechnology, J.B. Degree and P.G. College, Kavali, worked as Head In-charge, Department of Zoology, and presently working as Head In-charge, Department of Botany, Vikrama Simhapuri University Post Graduate Centre, Kavali. She acted as paper setter for different Colleges and various Universities. She worked as In-charge for Biotechnology Park at Jawahar Bharathi College, Kavali performing various activities like 'Spirulina Cultivation', 'Mushroom Cultivation', 'Green House and Shady House maintenance', 'Vermicompost and Biopesticide preparation'. She is an Associate fellow of A.P Academy of Sciences. She worked as Co-ordinator, Eco-AIR Project, AP State Science Centre, Vijayawada. She is an Editorial Board Member and reviewer for various reputed journals. She is a life member in Association of Biotechnology and pharmacy, ISCAP, Indian Science Congress and All India Association for Educational Research.

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# THE IMPORTANCE OF NATURAL PRODUCTS IN THE MODERN DRUG DISCOVERY AND DEVELOPMENT

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Running title : Natural products and drug discovery

## Abstract

Natural products have a long history of clinical use and are rich source of bioactive compounds. The development of tools and techniques for identifying and analyzing NP bioactive compounds to ensure their quality and discover new drugs is thus very important and still in demand. The developmental prospects in bio-medical, health, nutrition, and other interrelated sciences along with some of the emerging trends in the subject area are also discussed as part of the current review of the basic and core developments, innovation in techniques, advances in methodology, and possible applications with their effects on the sciences in general and natural products chemistry in particular. The present study showed that the in-depth analysis of the drug relationships extracted from the literature-based network sheds new light on drug discovery research. The results also suggested that certain drugs could be purposed for treatment of various ailments.

**Keywords:** Natural products, Drug discovery

## Introduction

Natural products are the source of active ingredients in most of the drugs. The current era has witnessed an ever changing role in modern drug discovery. Natural product based medicines also flourished in the Orient. Charaka Samhita, the first treatise devoted to the concepts and practice of Indian Ayurveda, was written around 900 BC and contains 341 plant derived medicines. The Sushruta Samhita (Circa 600 BC) was mainly devoted to surgical practices, but also described 395 medicinal plants and 57 animal derived products (Dev, 1999).

Historically, natural products served as important drug leads against a wide array of human diseases. From 1981 to 2014, among all of the 1211 approved small-molecule therapeutic agents, natural product related drugs could account for almost 65% of the marketed drugs, which were either used unaltered or developed based on the naturally occurring structures. (Newman & Cragg 2016).

Natural extracts can be sourced in huge number of plants materials and includes primary and secondary metabolites as proteins, fats and oils, dietary fibers, sugars, antioxidants, essential oils and aromas, and colors. They are largely used as ingredients in the food processing industry for their texturing, reservative or coloproperties, and as active compounds in cosmetics or pharmaceuticals. Conventionally, such extracts are obtained using solid-liquid ring extraction considered as a unit operation. Extraction process is composed of several unit operations such as pre-treatment of plant material (drying, grinding…) and post-treatment of liquid extract (filtration, concentration, purification). The most crucial unit operation in the process is solid-liquid extraction, particularly when it is not optimized, is often time and energy consuming, induces the use of huge amount of water or petroleum solvents harmful for environment and users and generates large quantity of waste. Moreover, resulting extract is not always safe as it may contain residual solvents, contaminants from raw material, or denatured compounds due to drastic extraction conditions.

Natural medicines have been extensively used for thousands of years in many regions of the world, including China, India, USA, Russia etc. These medicines have gained increasing popularity in many western countries in recent years due to their reliable therapeutic effects. (Hu et al 2012; vikram et al., 2014). In the past 30 years, the percentage of use of natural products for the treatment of different diseases has risen to 50%. With increasingly extensive application of natural medicines and their bioactive ingredients for disease treatment, therapeutic responses need to be clearly identified to ensure their therapeutic efficacy and safety.(De Gorter et al., 2012;Patridge et al., 2016).

Recent scientific findings, concerning the medicinal applications of bioactive substances from plant extracts, have sparked more interest for further development of novel plant-based pharmaceuticals (Verpoorte 2009). This initiative might be very important for more than 80% of the world's population, who are still largely reliant on plant-based medicines and natural products as a primary source of treatment (Beyene et al., 2016). About 500 various herbal species have been used in modern medicine to treat various illnesses based on anti-inflammatory antioxidant properties of plant derived drug-like substances. The last decade

has witnessed an unprecedented growth of herbal medicine all over the world (Barnes et al., 2007; Pathak & Das 2013).

The chemical methods adopted for the discovery of the molecules have also undergone changes leading to the development of technologies such as combinatorial chemistry (combichem), microwave assisted organic synthesis (MAOS) and high-throughput (HTS) biological screening. These new technologies have enabled medicinal scientists to accelerate the discovery process. Drugs are designed, synthesised and purified as the first stage of the development process. The medicinal chemist leverages knowledge of synthetic chemistry, medicinal chemistry and biology to achieve the lead molecule for further clinical development.

The contribution of chemistry is not confined just to the discovery stage. It carries its purpose along the entire spectrum of clinical development. Each and every stage of clinical development involves surplus amounts of formulated drugs for studying potential benefits in human trials. All drugs are manufactured under strict Good Manufacturing Practices (GMP) standards to ensure they meet the compliance requirements drafted by regulatory bodies. Drug developers leverage on the analytical chemical testing and process development for meeting the regulatory compliances. It is estimated that about 50% of the analytical chemistry services are outsourced. The majority of these support services are now being rendered by Contract Research Organisations such as Charles River Laboratory, Covance, Quintiles, PPD, Eurofins, SGS Life Sciences, Wuxi AppTech, etc. Analytical methods and instrumentation are regularly used in the preclinical testing, toxicity testing, ADME analysis, product release testing, formulation and quality control.

In short, chemistry remains the most invaluable science and plays the most critical role in the drug development process. It serves as the backbone to framework the drug discovery and bolstering the growth of the pharmaceutical industry.

Many chemists and biologists have attempted to explain the puzzle of why so many compounds in nature have biological effects in humans and other species. One explanation that has been widely accepted is that it is the result of long term coevolution within biological communities: interacting organisms that evolved in close proximity to one another developed compounds that could influence the biological processes of neighboring species. As these compounds proved to be advantageous, they became a trait on which natural selection could act, and were retained and improved throughout the course of evolution. Given the similarities between aspects of human physiology and that of other animals, it is not

surprising that such molecules can also exert biological effects in humans. For example, many chemicals that plants evolved to defend themselves against herbivores are now used as laxatives, emetics, cardiotonics or muscle relaxants in humans. In addition, humans have taken advantage of some of the discovered properties of natural compounds: those that are able to interact with or suppress the growth of bacteria, for example, are now used as antimicrobial drugs in medicine.

Drug discovery and development is one of the most complex and expensive activities within the framework of the pharmaceutical industry. It encompasses a wide array of end-to-end activities with a plethora of supply chain and support services. It is estimated that the average cost to research and develop each successful drug is between $800 million to $1billion (Paul et al., 2010). Drug discovery and development can be classified into discovery phase, preclinical phase and early stage development, mid stage development and late stage development. Drug discovery has undergone many changes over the years but the goal has remained same: to uncover safer medicines for all diseases. Drug discovery and development is driven by the knowledge of chemistry of the molecules and their association with life process.

Historically, drugs were discovered through identifying the active ingredient from traditional remedies or by serendipitous discovery. Later chemical libraries of synthetic small molecules, natural products or extracts were screened in intact cells or whole organisms to identify substances that have a desirable therapeutic effect in a process known as classical pharmacology. (Takenaka 2001; Lee et al., 2012). Since sequencing of the human genome which allowed rapid cloning and synthesis of large quantities of purified proteins, it has become common practice to use high throughput screening of large compounds libraries against isolated biological targets which are hypothesized to be disease modifying in a process known as reverse pharmacology. Hits from these screens are then tested in cells and then in animals for efficacy.

Drug discovery has changed over the years but the goal remains the same: to find safer medicines for the deadliest diseases. Traditionally, the discovery of new drugs has arisen from observations that various plant extracts possess interesting biological effects. However, early users of such plant extracts did not understand or realize which components in the material were responsible for achieving these therapeutic benefits. The main difference between modern and age-old medicine is identifying the composition of matter, or the active form, within the medicine itself. This modern drug discovery and development is mostly a

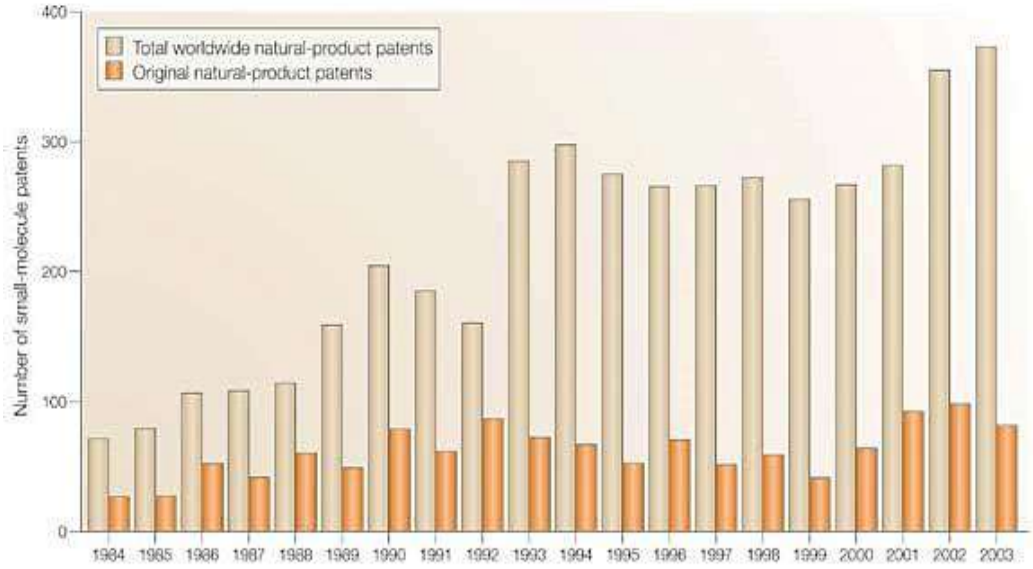
complex, expensive, time consuming and market-driven process with very few novel drug candidates actually making it through the Food and Drug Administration (FDA) for approval. Discovery and development of new drugs does not rely so much on miracles or serendipity anymore, but instead utilizes highly planned processes involving cutting edge technologies. The previous era of modern drug discovery was dominated by chemistry, whereas now a more rational approach is employed where knowledge about enzymes and receptors has required a unique dialogue between chemists and biologists.

Modern drug discovery involves the identification of screening hits, medicinal chemistry and optimization of those hits to increase the affinity, selectivity (to reduce the potential of side effects), efficacy/potency, metabolic stability (to increase the half-life), and oral bioavailability. Once a compound that fulfills all of these requirements has been identified, it will begin the process of drug development prior to clinical trials. One or more of these steps may, but not necessarily, involve computer-aided drug design. Modern drug discovery is thus usually a capital-intensive process that involves large investments by pharmaceutical industry corporations as well as national governments (who provide grants and loan guarantees). Despite advances in technology and understanding of biological systems, drug discovery is still a lengthy, "expensive, difficult, and inefficient process" with low rate of new therapeutic discovery. In 2010, the research and development cost of each new molecular entity was about US$1.8 billion. Drug discovery is done by pharmaceutical companies, with research assistance from universities. The "final product" of drug discovery is a patent on the potential drug. The drug requires very expensive Phase I, II and III clinical trials, and most of them fail. Small companies have a critical role, often then selling the rights to larger companies that have the resources to run the clinical trials.

Finding viable drug targets (the so-called biological approach) (Overington et al., 2006) has become increasingly used in recent decades with the advancements in the field of genomics and proteomics. A medicinal chemist uses this information to seek out relevant targets capable of being affected by the addition of compounds. These specifically synthesized drug molecules are proposed, synthesized and tested for direct action on these protein targets in order to effectively treat a wide variety of illnesses. In previous times, “classical medicinal chemists” would modify the existing bio-active molecules from natural products. These natural products were the source of most of the active ingredients in most medicine (Newman & Cragg 2007). With the help of molecular biology in combination with computer-assisted drug design, medicinal chemists can now rationally design new drug

molecules with known targets in mind. These compounds would have computational data encouraging the intended results even before they screen. This saves time and allows for a more comprehensive understanding of the drug-target interplay. To succeed in the discovery process medicinal chemists have to perform these initial important tasks: i) identification of lead molecules which have the desired biological activity using new technologies such as HTS and combinatorial chemistry ii) the lead modification or optimization which could be done by employing structure-activity analysis (SAR) in order to improve the desired pharmacological properties by considering absorption, distribution, metabolism, and excretion (ADME) profile, and iii) scale-up of the optimized lead for further drug development process and efficacy testing.

Figure 1 shows worldwide pharmaceutical small-molecule natural-product patents granted in the years 1984–2003.




The chart shows a period of increasing patent activity through the 1980s, a flattening or even slight decline from 1990 to 1999, and a pickup of activity between 2000–2003. In the context of worldwide pharmaceutical R&D spending, which essentially tripled from roughly US $10 billion to US $30 billion over the same period, the overall trend in the 1990s can be viewed as a relative decline.

Fig. 2.Natural products have already made extensive contributions to society. The finding that the chemical space they occupy is largely bounded paradoxically reveals substantial opportunity for future impact.

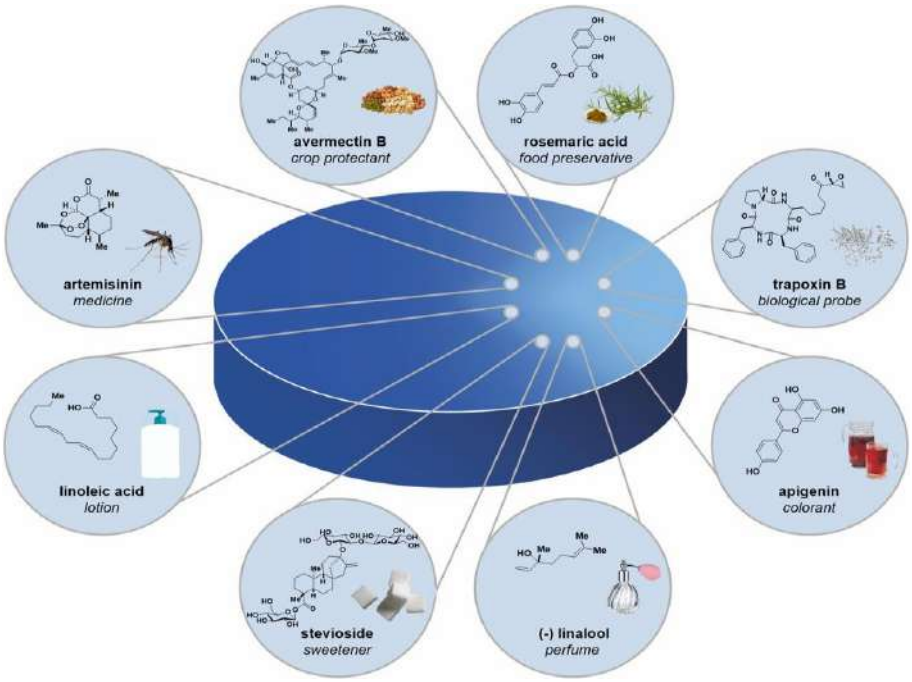



Figure 3: Drug discovery cycle

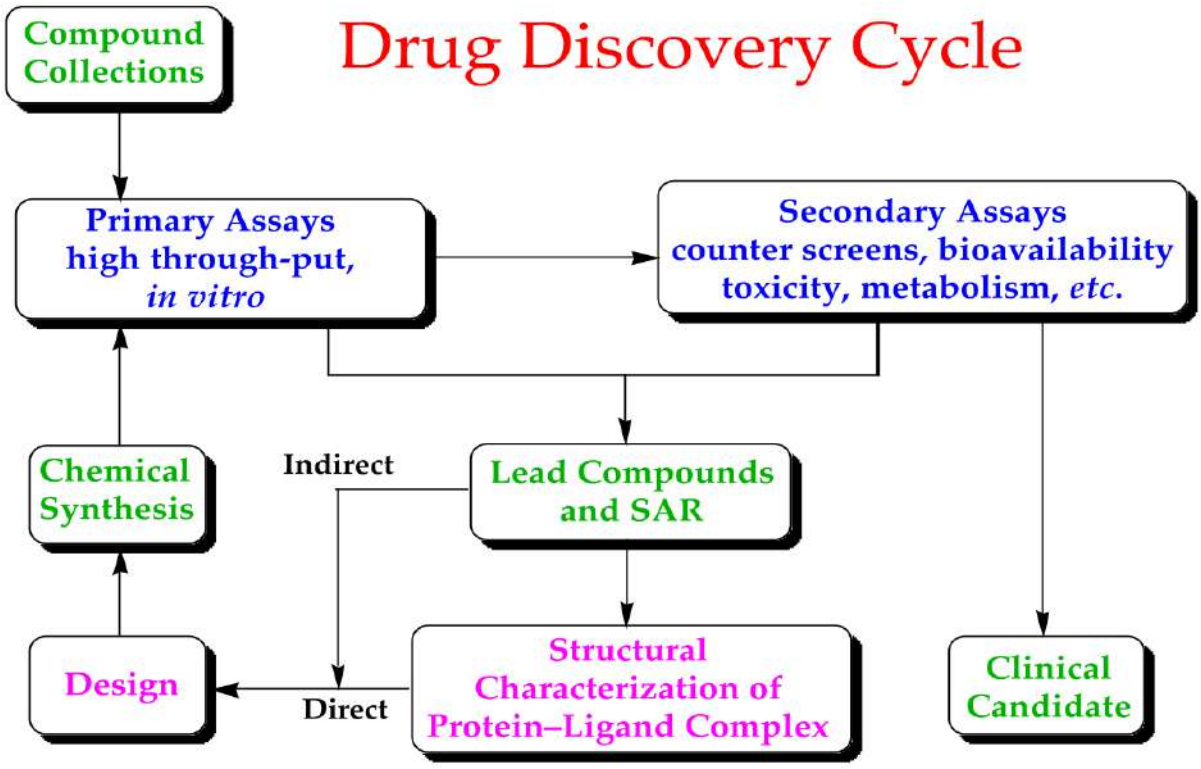
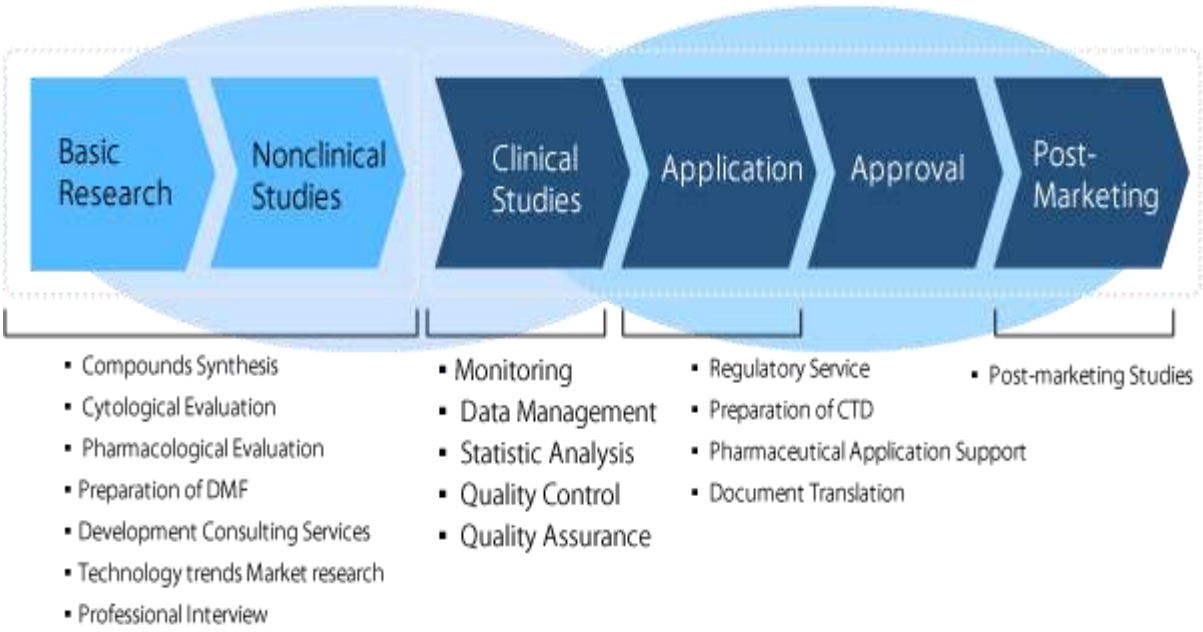



Figure 4 : Stages in the dug discovery




**Conclusion:**

In summary, new biological targets, methodologies and advanced computing have improved modern drug discovery and have given medicinal chemists and biologist a more profound skill set and toolkit to grasp the nuances of disease pathophysiology.

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# NANOSCIENCE IN THE CELL

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## ABSTRACT

This study is aimed at presenting the existing nanoscience in the cell. Nature itself is an excellent nanotechnologist. Nature provides us with a range of fine particles. Cell is the structural and functional unit of life. Any living body in general and the cell in particular is considered as an museum for nanoscience. It is amazing to note that all living organisms consist of a variety of nano structures. It is the basal metabolism, environmental influence that transforms certain structures into nano structures by evolution. In this paper a review is presented in a novel way integrating the nanoscience with cell and cell organelle

**Keywords**: Nano Science, Human Body, Organ system

## INTRODUCTION

Each biological activity whether catabolic or anabolic is tailored from the nanoscience. In all the living being the activities are performed at a nano level, the cumulative effect of these nano actions result in any of the life processes. Nature itself is an excellent nano technologist, there are a number of natural processes were the application of nanoscience is seen. In day to day activities all the living beings are completely associated with the manifestations of nanoscience. If we consider the theory of evolution the manifestation of nanoscience is flavored. Nanoparticles are peculiar and unique in their properties and nature. Nanoscale materials have far larger surface areas than similar masses of large scale materials. As surface area per mass of a material increases, a greater amount of the material can come into contact with surrounding materials, thus affecting reactivity. One benefit of greater surface area and improved reactivity in nanostructured materials is that they have helped create better catalysis. As a result, catalysis by engineered nanostructured materials already impacts 1/3 of catalyst market. Large surface area also makes nanostructured membranes and materials ideal candidates for water treatment and desalination, among other uses.

## REVIEW OF LITERATURE

Literature review was done to explore the nanoscience, nanotechnology in biological activities. Most of the literature is on nanotechnology and its applications in industry

and agriculture and human health care. These concepts were considered and implied to the metabolic activities of the cell. One medical example of nanotechnology is the bio barcode assay, a relatively low-cost method of detecting disease-specific biomarkers in the blood. The bio –barcode assay has proven to be considerably more sensitive that conventional assays for the same target biomarkers, and it can be adapted to detect almost any molecular target.

## DISCUSSION

Globally nanotechnology and its diverse products are omnipresent and form an integral part of our life style. Nature itself is a skilled nanotechnologist, with numerous examples of common nano materials in the living organisms, indeed life revolves around cells which themselves are microscopic in size and metabolize molecules which are pico to nano in size, precipitation, oxidation, reduction are the natural processes involving the nanoparticales . It is estimated that there are more that 100 million living species on the earth today. Each living organism consumes free energy to create and maintain its organization; this free energy drives complex system of chemical processes at nano level.

Cell is an unique entity where there are no of cell organelle with a specific boundary the cell membrane . If we look into the basic structure of the cell the main components are cell membrane, cytoplasm and cell organelle. These components are interlinked and integrated at nanolevel. Cell membrane or Plasma membrane is a biological membrane which formed by the assembly of biomolecules i.e., proteins and lipds at nano scale. This nanonature of the cell wall is responsible for its unique properties of selective permeability a rare phenomenon in the biological systems. If we go deep into this phenomenon of selective permeability, transport across the membrane the manifestation of nanotechnology can be visualized. There is nothing in the living organisms, but with certain chemicals for its own, obeys the physical laws. However the chemistry of cell is very unique. There is 70 % of water in the cell, which recalls water is the medium for the life supporting chemical reactions. Matter is made of combination of elements, likewise the cells too. However the characteristic feature of the cell is the way in which the atoms are linked together in groups to form molecules. Atoms are so small that it is hard to imagine their size, for example the carbon atom is roughly 0.2 nanometer in diameter. There are 89 naturally occurring elements, each differing form the other. Living organisms, however are made of only a small selction of these elements .i.e,., carbon 0.2 nm radius (C) , Hydrogen 0.12 nm radius (H), Nitrogen 0.15 nm radius (N), and oxygen 0.14 nm radius (O) , make up 95 % of organic weight. Water accounts for 70% of a cell's weight, and most intracellular reactions occur in an aqueous environment. Life on the Earth began in the ocean, and conditions in that primeval environment put a permanent stamp on the chemistry of living things. Life therefore depends mostly on the properties of water. Most of the biological activities are based on the reactions of the elements H and O. Similarly C also plays an important role as an element in the living organisms (Table: 1 )

| Sl No | Building blocks of life at Nanolevel | Large Units of life |
|---|---|---|
| 01 | Monosaccharide- sugars (1 nm) | Polysaccharides |
| 02 | Fatty Acids (4-200 nm) | Fats, Lipids and Membranes |
| 03 | Amino acids (0.1 -1 nm) | Proteins |
| 04 | Nucleotides (0.33 nm) | Nucleic Acids |

Table: 1, Size of bimolecules at Nano level

## CONCLUSION

Life is an autocatalytic process, where the nano particles of nucleotides, amnioacids, provide the information. With the above discussion it may be concluded that the nano particles are the basis of life process. Nanotechnology is entering many industry sectors including plastic, energy, electronics, and aerospaceResearch is going on the nanotechnology imply with the life processes. These studies pave way for the improvement of human health. Nanomaterials are playing very important role in generating environmental friendly and treating pollutants effectively. The environment is protected by using nanomaterials in Fuel cells and solar cells which gives long lasting power which can be used in all electrical, mechanical, agricultural and electronic devices instead of burning fuels eliminating pollutants. Nanotechnology has the potential to generate radically new food products, and this technology is increasingly employed in the areas of food production and packaging.

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# SUSTAINING QUALITY IN HIGHER EDUCATION

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**ABTRACT:**

Quality assurance in higher education is the need of the hour in Indian scenario. Quality of any higher education institution is measured by carefully devised bench marking. Indian Higher education has developed by leaps and bounds since independence, but quality is questionable. Many challenges need to be addressed. This paper critically examines the challenges faced by Indian Higher education in brief and the steps to be taken to sustain and assure quality.

**Key words** : Quality, Quality Assurance, Higher Education

***"Excellence in thinking and action is the foundation for any mission. Excellence is not by accident. It is a process, where an individual or organization or nation continuously strives to better oneself"***

***-Dr. APJ Abdul Kalam***

Higher education of any country is an enabler to attain economic growth, a vehicle for wealth generation and technological progress. Ancient India was a centre of excellence, as detailed in the chronicles. British invasion transformed Indian education to their colonial needs. At the time of independence, only 20 universities and 500 colleges were existing. There were about 2.1 lakh students pursuing different courses in higher education. After independence, there has been an asymptomatic growth of Indian Higher Education. There is a growth of 47.9 times in the case of the Degree awarding Universities, 82.02 times in the case of Colleges. The students enrolment has increased to over 174.49 times in the system of higher education in comparison to the times of Independence. With more than 990 universities, 40000 colleges and 5000 technical institutions, India has the second biggest higher education system in the world. This is quite enchanting. But the other side of the coin portrays a gloomy outlook. Poor student –teacher ratio, exclusivity, lack of research culture integrating institute and industry are the main short comings.

The challenges faced by higher education in India include -

- Gross enrollment ratio is still less than 30%
- Mere degree holders are being produced, not intellectuals
- Degrading environment consciousness, values & ethics among youth
- Insufficient global competitiveness and employability in Indian youth
- Higher education is not still inclusive, not extended to the masses

- Competent faculty are not being attracted to work in this arena
- Lacking world class institutions and research facilities at higher education level
- Quality of academic research is poor
- Applied research is not upto the global bench mark
- Lack of innovation culture
- Higher education institutions are not able to get a place in global rankings
- Industry-institution interaction is very poor

Amidst these challenges, 'quality' is a big question mark. Though the National Assessment and Accreditation Council (NAAC) has been instrumental in generating a quality consciousness and quality culture among the Higher Education Institutions in India, still many are out of NAAC framework. According to the British Standards Institution, "the totality of features and characteristics of a product or service that bearon its ability to satisfy stated or implied needs". The concept and culture of quality is essential for accountability, credibility, visibility, image and brand value of any institution. It is also required for getting through the competition and maintain standards. In the light of the challenges mentioned above, there is a dire need to expand the accreditation frame work to include more and more Higher education institutions. Since its institution in 1994, NAAC has instilled quality culture in Indian Higher education, while travelling through the path of resistance to acceptance, acceptance to appreciation and appreciation to enlightenment.

In the context of higher education, Quality assurance is a "systematic management and assessment procedures adopted by a higher education institution or system to monitor performance and to ensure achievement of quality outputs or improved quality". Quality assurance aims at giving stakeholders confidence about the management of quality and the outcomes achieved. Quality Assurance indicators framework and benchmarking is effectively devised by NAAC on par with global standards. As afore said, NAAC is successful in motivating Higher Education Institutions to volunteer for assessment, quality sustenance is questionable due to the challenges faced by our higher education system. The following may help sustain quality.

**Steps to sustain Quality:**

1. Steps shall be taken to improve the graduate outcomes. At the minimum, 50% of students should secure employment or pursue higher education
2. Curriculum shall be framed in such a way that at least 60% of the Under graduate students engage themselves in socially productive nd economically viable activites during the period of their study.
3. Students pursuing UG courses shall be trained in soft/life skills that lead them to be better citizens in the changing global scenario
4. Vacancies of teaching positions shall be filled from time to time and all the teachers must be trained in their respective domains and methodologies to carry out teaching-learning transaction effectively
5. All institutions shall get NAAC accreditation within a prescribed time limit.

6. Outcome based curriculum shall be implemented immediately.
7. There should be continuous evaluation of learning outcomes, with a combination of formative, interim and summative evaluation.
8. Faculty should be given professional enrichment continuously by way of awareness programmes about emerging trends and empowered technologically in assisting teaching technologies.
9. All educational administrators must be given leadership training to realize national educational goals.
10. Higher educational institutions shall be connected to local communities and industries.
11. While research is promoted, the same should be integrated with community well being in particular and national well being at large. Quality research should be encouraged.

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# THE IMPACT OF COVID - 19 ON CANCER CARE

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ABSTRACT:

Emergence of novel corona virus (SARS-CoV-2) in 2019 has marked the third major event after Severe Acute Respiratory Syndrome Corona virus (SARS-CoV) in 2002 and the Middle East Respiratory Syndrome Coronavirus (MERS-CoV) that introduced pathogenic coronavirus into human populations on a global scale. The disease caused by SARS-CoV2 is named Corona Virus Disease (COVID-19). This pandemic spread over 205 countries including India and has become a public health emergency. As on 06th April 2020, 3577 cases are reported in India, out of which 83 died. While the Govt. of India is taking all the measures including lock down, to control the pandemic, efforts have been intensified to device low-cost indigenous testing kits and discover potential therapeutic agents to combat the pandemic successfully. The present paper reviews the impact of COVID-19 on cancer patients suggests measures needed to help in this emergency.

**Key Words:** COVID-19; Corona virus; Lock down; Health emergency; Public health

## INTRODUCTION:

The outbreak of novel corona virus - 2019 was first reported on December 31, 2019 from Wuhan city of Hubei province in China[1]. The outbreak started as a cluster of pneumonia cases, caused by a new Corona virus[2]. Number of new cases are reported all over the world, including India. On 30th January 2020, the World Health Organization (WHO) declared global Public Health Emergency[3]. There have been many remedial measures taken by government of various countries across the world, which include travel restriction, awareness campaigns, timely release of guidelines & health bulletins by authorities and even lock down.

## CORONA VIRUSES:

Corona viruses are positive sense RNA viruses, having spike like projections on the surface which render them a crown like appearance[4]. In the past, two major outbreaks of coronavirus infection caused much damage. In 2002, Severe Acute Respiratory Syndrome (SARS) coronavirus[5] and in 2012 Middle East Respiratory Syndrome coronavirus (MERS-CoV)[6] emerged causing potentially life-threatening respiratory tract infections[7].

## NOVEL CORONA VIRUS-2019 AND ITS TRANSMISSION:

The novel corona virus responsible for COVID-19 also belong to β-genera of corona viruses. This belongs to the subgenus *sarbecovirus*, subfamily

orthocoronavirinae[8] and is named as SARS-CoV-2, by the Corona Virus Group (CSG) of the International Committee on Taxonomy of Viruses[9]. The genome of the SARS-CoV-2 was sequenced[10], and it is found to have 79 % similarity with the genome of SARS-CoV and 96.2% similarity to a bat CoV RaTG13[11]. As per the availability of data as on the date of writing this paper, it is assumed that the SARS-CoV-2 might have transmitted from bats, which are the most likely reservoirs, to human beings, employing an unknown intermediate host[12,13]. Studies reveal that the new virus emerged as solitary species jump from possibly a mammalian intermediary host[14]. It is established by now that the SARS-CoV-2 infects humans utilizing the angiotensin converting enzyme 2 (ACE 2) as the receptor[11]. Probably the bat coronavirus and novel corona virus might have emerged from same ancestor [15].

The basic reproduction number (Ro) of the novel corona virus is estimated to be about 2.2[16] or even more. Evidences of pneumonia cases indicate the human-to-human transmission of this virus[17], possibly through a mammalian intermediary host[14]. SARS-CoV-2 has 10-20 times higher affinity towards humans than SARS-CoV[1]. The transmission is taking place at alarming rates. Nosocomial infection among healthcare workers and patients, contact-transmission among family members and droplet infection in crowded areas are of critical concern at this juncture.

## COVID-19 CLINICAL SYMPTOMS:

The common clinical symptoms of COVID-19 infection include cough, tiredness, production of phlegm, sore throat, headache, fever and shortness of breath [18]. Fever and cough are dominant, while diarrhoea and vomiting seem less common [19]. Manifestation of the disease suggests that viral tropism differs among SARS-CoV-2[20], SARS CoV[21], MERS-CoV[22] and influenza[23]. While a few of the patients were quite asymptomatic, few others developed acute respiratory distress syndrome, septic shock, multi organ dysfunction and metabolic acidosis that was difficult to correct[24]. Disease progression is associated with high levels of inflammatory cytokines[25]. While majority of the patients exhibit lymphocytopenia[26,27], severely affected patients showed renal involvement [28]. Elderly male patients, who have comorbidities showed higher death rate and risk as well[29]. The overall fatality rate is apparently less, between 2-3%[30], but the absolute numbers are very high. Neonates and elderly people must be taken care of to reduce the death rates due to COVID-19. Therapies aiming to disturb virus entry into host may prove good to combat the disease [31].

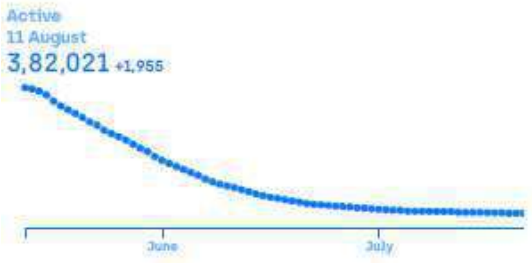
## COVID -19 IN INDIA:

The first COVID-19 case in India was recorded in Kerala state on30th January 2020[32]. By 2nd February 2020 two more cases were recorded. Then there was a brief pause, and by 07th March 2020 the number of cases raised to 34. There has been a steady increase in the number of cases. On 06th April 2020, at 16.58pm, the number of cases all over India raised to 4067 (Image 1) as per the announcement of Ministry of Health and Family Welfare, Govt of India (GOI)[32]. There has been a steady raise in the number of cases, and the situation is alarming, as it is globally.

The Govt. of India has taken good measures to contain COVID - 19 transmission including the lockdown imposed on 23rd March 2020, after a one-day Janata curfew call given by the Prime Minister of India. GOI has taken a number of good initiatives including regular announcements, awareness programmes on use of sanitisers, social distancing & home quarantines, and issue of advisories and release of various guidelines for management of the disease outbreak and related issues from time to time. As of 05th April 2020, India is classified as being in local transmission stage by World Health organization (WHO)[33]. The second wave badly hit India in the month of March 2021, with the COVID-19 spreading to the nook and corners of the country. Many causalities happened, and people in the age group of 21-45 were even affected worst.

Gradually the curve was flattened among hue and cry of a possible third wave. As on 12th August 2021, at 8.00 am IST, there were 3,87,987 active cases reported with a net positivity rate of 1.2%[34].

Image 1: Spread of COVID-19 in India as on 12th Aug 2021




(Source:, https://www.covid19india.org/ accessed on 12.08.2021; 11:35 am)

IMPACT OF COVID ON CANCER PATIENTS:

With the spread of COVID-19, governments have taken various measures from limited restrictions to lockdowns across Indian states. Mobility of people was curtailed. Transborder movement of people was affected. Many decisions had to be taken to safeguard public health at large, sacrificing economic interests. People suffered a lot due to lack of timely access to amenities, resources, health care services. Mass migrations of people were witnessed.

Healthcare providers strived hard to meet the demands. Many people restrained themselves from routine clinical investigations, screening, diagnosis and treatment for non-COVID 19 diseases. So also, people suffering from various cancers could not access health care facilities. The impact of COVID-19 on cancer patients is of concern.

Cancer is characterized by uncontrolled cell growth and their spread to other parts of the body[35]. It is a set of is a set of diseases and the prognosis is influenced by the timing of diagnosis and intervention[36]. There has been an unprecedented competition for health-care facilities during the COVID-19 outbreak, and oncology professionals have had to protect the most vulnerable from a potentially fatal pandemic. The general principle of risk-to-benefit ruled the prioritization of utilization of health-care facilities[37]. Since the onset of pandemic, there is a steep drop in cancer diagnosis across the world[36]. Studies show there has been a decline in the number of tests to screen for cervical, breast and colon cancer by 85 per cent or more after the first Covid-19 cases were diagnosed in India[38].

A drop-in diagnosis and reported number of cases does not necessarily reflect a drop-in incidence of the disease. Many surgeries were cancelled during the pandemic period. Delays in cancer screening and treatment is expected to cause 10000 more deaths over the next decade[39]. Not only cancer care, but also research was impacted much during the time. The vulnerable population of cancer patients suffered a lot due to reduction in the number of outpatient clinics, elective procedures, and from discharging patients from inpatient services[40,41].

In spite of the above, there have been certain positive effects. People accessed diagnostic and therapeutics nearby, avoiding journey. This led to a diversified approach in treating cancer patients. Three tired approach of giving health care to low, medium and high priority regimens is developed[40]. Telehealth and virtual medicine are more utilized.

## CONCLUSION:

Fighting against COVID-19 is no mean to a world war. Fight against the spread of this disease is almost a war without weapons. In these times, a coherent effort from all the stakeholders – policy makers, health care professionals, scientists, educationists and the general public is the need of the hour to contain the pandemic.

Since cancer patients are vulnerable and prone to many an illness, it is time to revisit the priorities of providing health care during the pandemic times. A congenial way of balancing the provision of cancer care while minimizing exposure risk to COVID-19 must be developed.

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# Pharmacological evaluation of *Strychnos colubrina* L., an endangered medicinal plant

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**Abstract**
Plants have been used since ancient times to cure diseases and to improve health and wellbeing of the populations. Plant diversity is a great source of medicines, while it provides direct economic benefits in the form of timber, food, fibre, industrial enzymes, flavours, cosmetics, emulsifiers, dyes, plant growth regulators, bio-pesticides and biofertilizers etc. The secondary metabolites, alkaloids, saponins, quinones, indoles, anthraquinones, terpenoids, flavonoids, phenolic compounds and amino acids are localised in cells. These have therapeutic properties and responsible for phytochemical markers to identify the genuine drug. *Strychnos colubrina* L. was screened for the presence of secondary metabolites using standard protocols as given by Harborne (1973),Gibbs(1974), Kokate (2001)and Khandelwal (2006), followed by pharmacological evaluation. Methanolic leaf extracts are tested for antioxidant and antimicrobial activities. The results were expressed as standard ± mean deviation (SD) of five replicates. Where ever applicable, the data were subjected to one-way and 2-way ANOVA and differences between samples were determined by with Scheffe's post hoc test, Dunnet's test using the program Statistical Analysis System (SASS V25). P Values < 0.05 were regarded as significant. In the preliminary phytochemical studies, the tannins, phenolic compounds, Alkaloids, flavonoids, Saponins, fats, oils, terpenoids have *shown positive test in Strychnos colubrina.* Glycosides, Lignins, Quinones, Anthraquinones, Anthocyanides, Coumarins, Carbohydrates, reducing sugars and Aminoacids are found to be absent. Sterols are absent in *Strychnos colubrina.* Administration of methanolic leaf extracts of *Strychnos colubrine* (200mg/kg) to have significant detrimental effect on one of 3 bacterial strains used i.e, *Staphylococcus aureus* and it has no effect on other 3 microbes namely, *Bacillus subtilis, Pseudomonas aeruginosa* and a fungal strain namely *Candida albicans.* Methanolic extract of plant leaves of *Strychnos colubrina* has not earlier been reported to have anti-microbial activity. The statistical analysis of the DPPH and $NO_3$ free radical tests with the *Strychnos colubrina* methanol extract has shown significant difference in results with the control groups in both the comparisons. The extracts solution exhibited significant anti-oxidant properties in the both tests Present study is significant and fills the gap in the ethno-medico-botanical repository of Andhra Pradesh.

**Keywords:** methanolic extract, snake wood tree, phytochemicals, antioxidant, antimicrobial, scheffe's post hoc test, dunnet's test

## Introduction

Plants have been used since ancient times to heal and cure diseases and to improve the health and the wellbeing of the populations. Products made out plants for therapeutic or other human health benefits contain either raw or processed ingredients from one or more plants, is the focus of this research. The plant diversity is a great source of medicines, provides direct economic benefits in the form of timber, food, fibre, industrial enzymes, flavours, fragrance, cosmetics, emulsifiers, dyes, plant growth regulators, bio-pesticides and biofertilizers. The biochemicals present in vast majority of the plant species are the great reservoirs of new and potential drugs. They can be used for monitoring the environmental changes. They are the key resources for new genes and biotechnological valuable compounds (Marotrao Dalvi, 2010). Parts of any plant that are used for therapeutic purpose or used a precursor for making a useful drug. This makes it possible to differentiate between medicinal plants whose therapeutic properties and constituents have been established scientifically, and plants that are considered as medicinal but which have not yet been subjected to a thorough scientific study (Sofowora *et al.,* 2013). Medicinal plants are important constitute of flora and are widely distributed in India. The importance of medicinal plants and traditional health systems to solve healthcare problems of the world is gaining increasing attention. Because of this resurgent interest, the research on plants of medicinal importance is growing phenomenally across the world, often to the detriment of natural habitats and mother populations in the countries of origin. In most of the developing countries traditional medical practices have adopted as an integral part of their culture. Medicinal plants form an important pool for the identification of novel drug leads which have proven their value as a source of molecules with therapeutic potential since ancient time (Atanasov *et al.,* 2015). According to Harshberger (1896) the study on ethnobotany has now become a critical need of time.

### India-An 'Emporium of Ethnomedicinal Plants'.

India has been one of the oldest countries having well-orchestrated medical practices based on plant resources. So

far on the globe about 4, 80, 000 plant species are discovered. India is known as an 'Emporium of Medicinal Plants' due to occurrence of more than 48,000 plant taxa, of which 18,000 are flowering plants, among these 10,000 plant species are estimated to be used by 4635 ethenic communities for human and veterinary health care.

The plant materials and recipes from herbs used traditionally by various human societies is a challenging field of research in ethnobotanical studies. The indigenous systems of medicine have their roots in folk medicine still practiced in remote tribal and rural areas and aboriginal societies where modern civilization has not yet made in roads. There are some miraculous medicines known to the tribals and rural folk and much acquired knowledge through experience of ages is usually passed on from one generation to other generation as a guarded secret of certain families. Recent studies have shown that groups having common or similar climate and environments but different ethnic and /or religion backgrounds have a very different knowledge and use of medicinal plant. It is not yet clear what factors influence this diversity in utilization.



**Fig 1:** Strychnos colubrina Plant

## Materials and Methods

Leaves of *Strychnos colubrina* were collected from Penchalakona forest of Nellore district Andhrapradesh, India. The plants were identified by comparing with herbarium specimens. The plant material was purified with distilled water and was shade dried for one month. Leaf sample of the material was ground into fine powder and stored in air tight containers at room temperature. The powdered material was then extracted using solvent, methanol in the ratio 1:10 using Soxhlet apparatus. (Khan *et al*., 1988). The solvent was evaporated under reduced pressure in rotatory evaporator to get methanol and ethanol extracts. After extracting all colouring material, the solvent was removed by evaporating in a water bath, which gave rise to a solid isolate of extract used for antimicrobial and antioxidant activities along with phytochemical analysis.

**I. Phytochemical analysis:** The phytochemical analysis of the leaves was done to find out the presence of bioactive compounds with the help of standard qualitative protocols. (Harborne, 1973 and Gibbs, 1974, Kokate, 2002.)

**Tests performed for the presence of phytochemicals**

**A. Tests for Flavonoids**

- **Shinoda test (Magnesium hydrochloride reduction test):** To the test solution few fragments of magnesium ribbon and concentrated hydrochloric acid were added drop wise and reddish to pink colour was resulted.
- **Zinc Hydrochloride reduction test:** To test the sample solution for the flavonoids added a mixture of zinc dust and concentrated hydrochloric acid results in red colour.
- **Lead acetate test:** When aqueous basic lead acetate was added to test sample produces reddish brown precipitate.

**Ferric chloride test:** To few ml of test samples taken separately, few drops of ferric chloride were added which resulted in the formation of blackish red precipitate.

- **Alkaline reagent test**: To detect the presence of flavonoids, sodium hydroxide solution is added to turn the test sample solution green. When few drops of diluted acid is added the solution turns colourless to indicate the presence of flavonoids.

**B. Tests for Saponins**

- Foam test: 5ml of extract was vigorously shaken to obtain a stable froth, which was added with olive oil (3 drops). Presence of emulsion indicates the existence of saponins.

**C. Tests for Glycosides**

- **Kellar Kiliani test:** 1ml of concentrated sulphuric acid was taken in a test tube then 5ml of extract and 2ml of glacial acetic acid and ferric chloride (one drop) and observed for blue color formation.
- **Raymond's test:** Test solution when treated with dinitrobenzene in hot methanolic alkali giving a violet colour.
- **Molisch test:** Alpha naphthol with conc.H2SO4 when added to test sample gives reddish violet ring at the junction of 2 layers.
- **Conc.H2SO4 test:** Conc.H2SO4 was added to test sample which resulted in appearance of reddish colour.
- Legal's test: The test samples when treated with pyridine and sodium nitroprusside solution blood red colour will be developed.
- **Bromine water test:** When bromine solution is added the test solution gives yellow precipitate.

**Tests for Alkaloids**

- **Dragendorff's test:** 1 ml of the sample solution is taken in a test tube, and few drops of potassium bismuth iodide solution (Dragendorff's reagent) was added. The presence of alkaloids was determined by the appearance of reddish-brown precipitate.
- **Meyer's test:** 1ml of the sample solution is added with few drops of potassium mercuric chloride solution (Meyer's reagent). A creamy white precipitate was formed indicating the presence of alkaloids.
- **Hager's test:** To 1 ml of each of the sample few drops of Hager's reagent (Picric acid) was added. Yellow precipitate was formed reacting positively for alkaloids.
- **Tannic acid test:** When few ml of 10% Tannic acid was added to 1ml of each sample, a buff colour precipitate was formed giving positive result for alkaloids.

- **FeCl 3 test:** One drop of FeCl 3solution was added to each of the test sample, formation of yellow precipitate was resulted reacting positively for alkaloids.

**D. Tests for Sterols**

- **Libermann-Buchard test:** When few drops of acetic anhydride and few drops of concentrated sulphuric acid were added to the test samples if a brown ring shows up at the junction of two layers, it indicates presences of steroids. 2. Salkowski test: The presence of sterols can be detected by adding few drops of concentrated sulphuric acid to the test samples in chloroform, the lower layers of solution turns green on sterols presence.

**E. Tests for Tannins and Phenolic Compounds**

- **Gelatin test:** When gelatine and water were added to test samples formation of white precipitate was resulted.
- **Lead acetate:** Few ml of test samples were taken in different test tubes followed by the addition of aqueous basic lead acetate. It results in the formation of reddish brown bulky preceipitate.
- **Alkaline reagent:** The test solution will give a yellowish red precipitate when sodium hydroxide solution was added.
- **Ellagic acid test:** Presence of phenols in the test solution can be detected by adding 5% each of glacial acetic acid and Sodium Nitrite. If the solution turn Niger brown colour, it indicates phenols in solution.

**F. Tests for Fats and Oils**

- **Stain test:** when we a small quantity of extract between two filter papers, the stain on filter papers gives the presence of the oils.
- **Saponification test:** Added a few drops of 0.5N alcoholic potassium hydroxide to various extracts with a drop of phenolphthalein separately and heat on water bath for 1-2hours. If the solution produces soap or partial neutralization of alkali, it's a sign of presence of oils and fats.

**G. Tests for Lignins**

- **Labat test:** The test sample turns olive green colour on addition of gallic acid when lignins are present.
- **Furfuraldehyde test:** The test sample turns red colour on addition of fur furaldehyde when lignins are present.

**H. Tests for Quinones**

- **Alcoholic KOH test:** When alcoholic KOH was added to the test samples red to blue colour appears reacting positively for quinones.

**I. Terpenoids and steroids test**

- 50% $H_2SO_4$ is added along the sides of the test tube containing a mixture of methanolic HCl and acetic anhydride. If there is any change in color, from green to blue-green (sometimes via red or blue) indicates the presence of terpenoids and steroids Anthraquinones test
- 5 g plant powder was shaken with 20 ml of benzene and filtered. To the filtrate 5 ml of 10% ammonium hydroxide solution was added and shaken well. Presence of pink red or violet color, in the ammonical phase indicates the presence of free anthroquinones (Fransworth, 1966).

**J. Anthocyanidin test**

- To the plant extract was added equal volume of methanolic HCl. Appearance of red or purple color indicates the presence of anthocyanidins.

**K. Coumarin test**

- When few drops of sodium hydroxide are added to the methanolic extracted test solution, if the solutions turning yellow indicates presence of coumarins.

**L. Proteins test (Millions test)**

- 2 ml of methanolic extract was boiled with a few drops of Million's reagent (Millions reagent is a solution of mercuric nitrate in nitric acid) results in the formation of red color indicates the presence of proteins.

**M. Carbohydrate test (Molish test)**

- To the methanolic extract, c-naphthol solution (1gm dissolved in 100 ml of ethanol w/v) was added. Then conc. $H_2SO_4$ is added gently along the walls of the inclined test tube. Appearance of a red to violet color at the interface is taken as a positive reaction.

**N. Indole test**

- If a violet color was developed on adding Ehrlich reagent to the alcoholic extract, it is considered as a positive reaction for indoles.

**O. Test for reducing sugars**

- To the 5 ml of methanolic extract, 5 ml of Benedict's reagent was added in a boiling test tube. The test tubes were incubated in boiling on water bath for 15-30 minutes. The formation of an orange red precipitate indicated the presence of reducing sugars.

**P. Test for amino acids**

- To the methanolic extract, was added few drops of Ninhydrin solution and boiled. The formation of violet colour indicates the presence of amino acids.

**Determination of In vitro Antioxidant Activity of *Strychnos colubrina* methanolic leaf extracts Using DPPH Scavenging Method, Nitric oxide radical scavenging method.**

**A. DPPH (1, 1-Diphenyl-2picrylhydrazyl) free radical scavenging activity**:(**Blois, 1958)**

1. The ability of the sample to scavenge DPPH radicals were determined
2. 0.5 ml of aliquot of test at different concentrations (100 µg/ml and 200 µg/ml) in methanol was taken and to this, 100mM methanolic solution (0.5 ml) of 1, 1-Diphenyl-2picryl hydrazyl (DPPH) was added.
3. The mixture was incubated for 30 min in darkness and at ambient temperature.
4. Absorbance was recorded at 517 nm.

**B. Nitric oxide radical scavenging activity: (Ganesh *et al*., 2004).**

- The standard used here was Ascorbic acid. 100 µg/ml and 200 µg/ml solution of standard in methanol and ethanol were used for assay.
- Sample solution was prepared by dissolving the sample in methanol and ethanol

- 10 mg of each extract were dissolved in methanol and ethanol and solutions of 100 µg/ml and 200 µg/ml concentrations were prepared.
- In this assay 0.5 ml of Sodium nitro prusside (Ganesh *et al*., 2004). (5 mmol) in phosphate buffered saline pH 7.4, was mixed with different concentration of the sample and incubated at 25°C for 3 hrs.
- A control without the test compound, but an equivalent amount of methanol and ethanol were taken. Buffer solution containing tube is acted as control.
- Then 1.5 ml of Griess reagent (1% sulphonyl amide, 2% phosphoric acid and 0.1% N-1-naphthyl ethylene diamine dihydrochloride) was added and incubated for 30 minutes.
- The absorbance of the chromophore formed during diazotization of nitrite ions with suphanilic acid and its subsequent coupling with Napthyl ethyl enediamine was read at 546 nm. The experiment was repeated in triplicate.
- Absorbance was measured at 546 nm and the percentage scavenging activity was measured.

$$\text{Percentage inhibition} = \frac{\text{Absorbance of Control} - \text{Absorbance of Test X } 100}{\text{Absorbance of Control}}$$

- The percentage of inhibition for each reaction was then calculated, and EC50 values (µg/mL) were calculated from the linear equation from the curve between the percentage of inhibition and the solution's concentration. Each experiment was conducted in triplicate. The EC50 value of each extract was expressed as the mean˘SD. The assays were performed as previously described.

**Determination of Antibacterial Activity activity of *Strychnos colubrina* methanolic leaf extracts using Disc Diffusion Assay**

Kirby-Bauer method (Bauer *et al* 1966) was followed to perform sensitivity test using disc diffusion with standard antibiotics. The assessment of antimicrobial activity was done based on the measure of diameter of inhibition zones, Sensitivity tests were performed by disc diffusion (*NCCLS, 1998*). The assays were performed against three clinically pathogenic bacteria *Bacillus subtilis MTCC 441, Staphylococcus aureus MTCC 737, Pseudomonas aeruginosa MTCC 1035* and a fungal pathogen *Candida albicans MTCC 3018.* Each extract was dissolved in 95% Methanol or sterile water at different concentrations (250, 500 and 1000 mg/mL). Then each solution was impregnated on to a small disc of filter paper and placed on the top of agar containing 100 µL of bacterial solution at a concentration of 1.5ˆ108 CFU/mL per plate (adjusted by comparing to 0.5 McFarland). In the same manner each plate has carried a blank disk by keeping solvent control only in the centre, and antibiotic discs (6mm diam) of 20 µg/ml, Streptomycin sulphate (for bacteria) and Nystatin 20 µg/ml, (for fungal) were used as positive control. All of the plates were incubated at 37°C for 18 hours for bacteria and at 28°C for 48 hours for fungi. The zones of growth inhibition around the discs were measured after 18 hours of in incubation at 37°C for bacteria and 48 hours for fungi at 28°C, respectively. The size of inhibitory zone is taken as a measure of sensitivity of micro-organism to the plant extract.

**Statistical Analysis**

Each test is conducted in three sets. The average value is calculated duly following statistical methods. Experimental results were expressed as standard ± mean deviation (SD) of five replicates.

Where ever applicable, the data were subjected to one-way analysis of variance (ANOVA), 2-way analysis of variance (ANOVA) methods and differences between samples were determined by with Scheffe's post hoc test, Dunnett's post hoc test using the Statistical Analysis System (SAS, 1999) programme. P Values < 0.05 were regarded as significant.

## Results

**Phytochemical studies**

**Table 1:** Analysis of Phytochemicals from methanolic leaf extracts of *Strychnos colubrina.*

| S. NO. | Name of the phytochemical | Name of the test | Methanolic leaf extract of *Strychnos columbrina* |
|---|---|---|---|
| 1. | Flavonoids | Shinoda test | + |
| | | Zn-HCl reduction test | + |
| | | Lead acetate test | - |
| | | $Fecl_3$ test | + |
| | | Alkaline reagent test | + |
| 2 | Saponins | Frothing test/Foam test | + |
| 3 | Glycosides | Keller-Kilianii test | - |
| | | Raymond's test | - |
| | | Molisch test | - |
| | | Conc.$H_2SO_4$ test | - |
| | | Legal's test | - |
| | | Bromine water test | - |
| 4 | Alkaloids | Dragendorff test | + |
| | | Mayer's test | - |
| | | Wagner's test | + |
| | | Hager's test | - |
| | | Tanicacid test | + |
| | | $Fecl_3$ test | + |
| 5 | Sterols | Lieberman Burchardt test | + |
| | | Salkowski test | + |

| | | | |
|---|---|---|---|
| 6 | Tannins and Phenolic Compounds | $FeCl_3$ test | + |
| | | Gelatin test | - |
| | | Lead acetate test | + |
| | | Alkaline reagent test | - |
| | | Mitchell's test | + |
| | | Elagic acid test | + |
| 7 | Fats and Oils | Stain test | + |
| | | Saponification test | + |
| 8 | Lignins | Labat test | - |
| | | Lignin(furfuraldehyde) test | - |
| 9 | Quinones | Alcoholic KOH test | - |
| 10 | Terpenoids | 50% $H_2SO_4$ Test | + |
| 11 | Anthraquinones | Benzene+ammonium hydroxide test | - |
| 12 | Anthocyanides | Methanolic HCl test | - |
| 13 | Coumarins | Alcoholic Sodium hydroxide | - |
| 14 | Proteins | Million's test | - |
| 15 | Carbohydrate test | Molish test | - |
| 16 | Indole test | Ehrlich reagent +alcoholic extract | - |
| 17 | Reducing sugars | Benedict's reagent test | - |
| 18 | Aminoacids | Ninhydrin test | - |

'+' Present, '--' Absent

## Anti-oxidant properties of *Strychnos colubrine*

### DPPH Method

**Table 2:** DPPH Mean values for Anti-oxidant properties of *Strychnos colubrine*

| Treatments | Concentration (µg/ml) | Absorbance at 517 nm | % Absorbance at 517 nm |
|---|---|---|---|
| Control | - | 1.68 ± 0.03 | 0.00% |
| Standard(Ascorbic acid) | 100 | 0.78 ± 0.03 | 53.57% |
| | 200 | 0.47 ± 0.06 | 72.02% |
| Methanolic Leaf extract of *Strychnos columbrina* | 100 | 0.82 ± 0.03 | 51.19% |
| | 200 | 0.57 ± 0.03 | 66.07% |

**Table 3:** One-way Anova of DPPH for Anti-oxidant property of *Strychnos colubrine*

| ANOVA | | | | | |
|---|---|---|---|---|---|
| Absorbance Value | | | | | |
| | **Sum of Squares** | **df** | **Mean Square** | **F** | **Sig.** |
| Between Groups | 2.734 | 4 | .684 | 490.579 | .000 |
| Within Groups | .014 | 10 | .001 | | |
| Total | 2.748 | 14 | | | |

**Table 4:** Dunnett's Post Hoc Test Analysis for DPPH of *Strychnos colubrine*

| Multiple Comparisons | | | | | |
|---|---|---|---|---|---|
| Dependent Variable: Absorbance Value | | | | | |
| Dunnett t (<control)[a] | | | | | |
| **(I) Treatment** | **(J) Treatment** | **Mean Difference (I-J)** | **Std. Error** | **Sig.** | **95% Confidence Interval** |
| | | | | | **Upper Bound** |
| Standard (Absrobic Acid ) 100 | Control - DPPH solution | -.89667* | .03048 | .000 | -.8215 |
| Standard (Absrobic Acid ) 200 | Control - DPPH solution | -1.20667* | .03048 | .000 | -1.1315 |
| strychnos columbrina 100 mg | Control - DPPH solution | -.86000* | .03048 | .000 | -.7849 |
| strychnos columbrina 200 mg | Control - DPPH solution | -1.10667* | .03048 | .000 | -1.0315 |
| *. The mean difference is significant at the 0.05 level. | | | | | |
| a. Dunnett t-tests treat one group as a control, and compare all other groups against it. | | | | | |

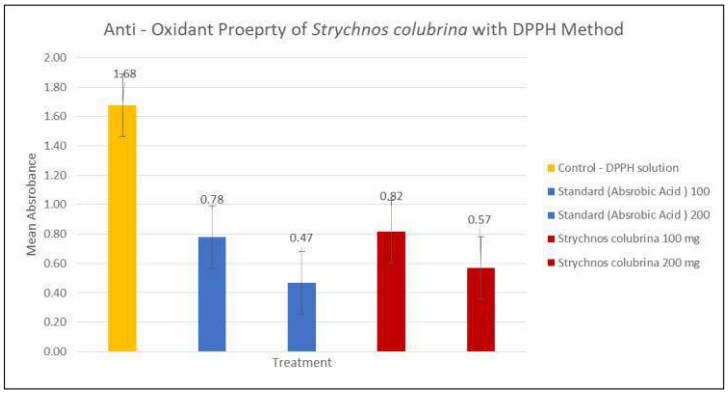



**Fig 2:** For DPPH method for Anti-oxidant property of *Strychnos colubrina*

### Nitric Oxide ($NO_3$) free radicals absorption method

**Table 5:** Mean values for $NO_3$ Free radical scavenging of *Strychnos colubrine*

| Treatments | Concentration (µg/ml) | Absorbance at 546 nm | % Absorbance at 546 nm |
|---|---|---|---|
| Control | - | 1.5 ± 0.03 | 0.00% |
| Standard (Ascorbic acid) | 100 | 0.63 ± 0.06 | 58.00% |
| | 200 | 0.34 ± 0.04 | 77.33% |
| Methanolic Leaf extract of *Strychnos columbrina* | 100 | 0.66 ± 0.06 | 56.00% |
| | 200 | 0.42 ± 0.04 | 72.00% |

**Table 6:** Anova of NO3 free radical scavenging test of *Strychnos colubrine*

| ANOVA | | | | | |
|---|---|---|---|---|---|
| Absorbance Value | | | | | |
| | **Sum of Squares** | **df** | **Mean Square** | **F** | **Sig.** |
| Between Groups | 2.550 | 4 | .638 | 289.829 | .000 |
| Within Groups | .022 | 10 | .002 | | |
| Total | 2.572 | 14 | | | |

**Table 7:** Dunnett's Post Hoc Analysis of NO3 test of *Strychnos colubrine*

| Multiple Comparisons | | | | | |
|---|---|---|---|---|---|
| Dependent Variable: Absorbance Value | | | | | |
| Dunnett t (<control)[a] | | | | | |
| **(I) Treatment** | **(J) Treatment** | **Mean Difference (I-J)** | **Std. Error** | **Sig.** | **95% Confidence Interval** |
| | | | | | **Upper Bound** |
| Standard (Absrobic Acid ) 100 | Control -nitric oxide | -.87333* | .03830 | .000 | -.7789 |
| Standard (Absrobic Acid ) 200 | Control -nitric oxide | -1.15667* | .03830 | .000 | -1.0622 |
| strychnos columbrina 100 mg | Control -nitric oxide | -.84000* | .03830 | .000 | -.7456 |
| strychnos columbrina 200 mg | Control -nitric oxide | -1.07667* | .03830 | .000 | -.9822 |
| *. The mean difference is significant at the 0.05 level. | | | | | |
| a. Dunnett t-tests treat one group as a control, and compare all other groups against it. | | | | | |

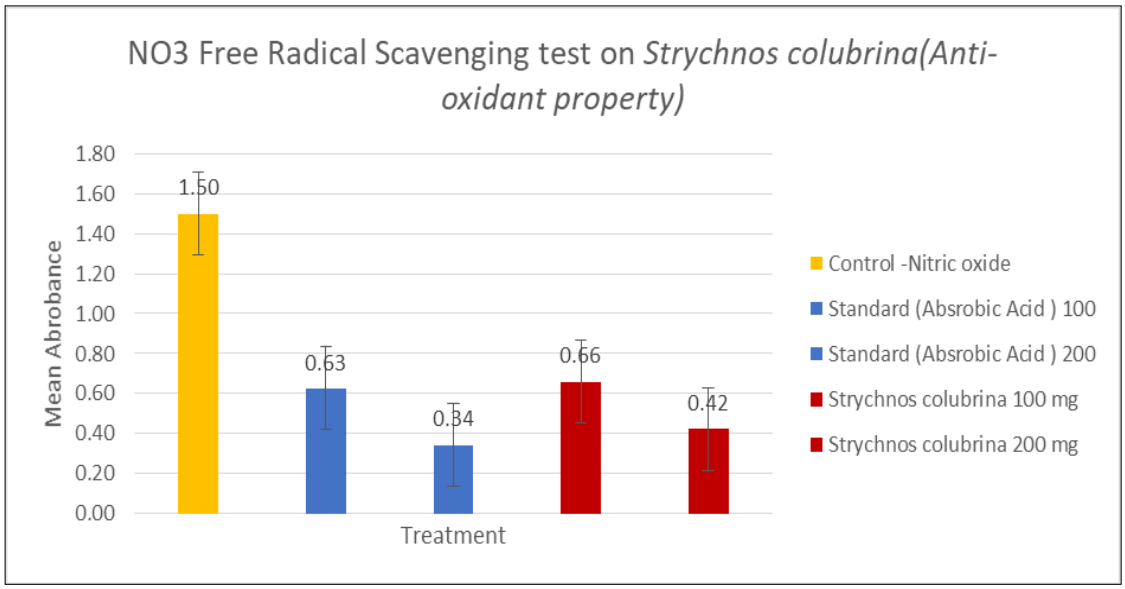



**Fig 3:** For NO3 Free Radical scavenging test of *Strychnos colubrina*

### Anti-microbial activity of and *Strychnos Columbrina*

**Table 8:** Anti-microbial property of *Strychnos Colubrina*

| Solvent extracts | Zone of inhibition in mm | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Names of microbes | | | | | | | | | | | |
| | ***Bacillus subtilis* (MTCC 441)** | ***Staphylococcus Aureus* (MTCC 737)** | ***Pseudomonas aeruginosa* (MTCC 1035)** | | | | | | | ***Candida albicans*** | | |
| Quantity (Micrograms) | 1000 | 500 | 250 | 1000 | 500 | 250 | 1000 | 500 | 250 | 1000 | 500 | 250 |
| Methanolic extract of *Strychnos Columbrina* | -N- | -N- | -N- | 17.7 ± 1.2 | 16.5 ± 0.5 | 15.5 ± 0.4 | -N- | -N- | -N- | -N- | -N- | -N- |

**Table 9:** 2-way Anova of Anti-microbial property of *Strychnos Colubrina*

| Tests of Between-Subjects Effects | | | | | |
|---|---|---|---|---|---|
| Dependent Variable: Zone of Inhibition in mm | | | | | |
| **Source** | **Type III Sum of Squares** | **df** | **Mean Square** | **F** | **Sig.** |
| Corrected Model | 1867.310[a] | 11 | 169.755 | 1055.474 | .000 |
| Intercept | 620.010 | 1 | 620.010 | 3854.984 | .000 |
| Dosage | 1.820 | 2 | .910 | 5.658 | .010 |
| Microbe | 1860.030 | 3 | 620.010 | 3854.984 | .000 |
| dosage * microbe | 5.460 | 6 | .910 | 5.658 | .001 |
| Error | 3.860 | 24 | .161 | | |
| Total | 2491.180 | 36 | | | |
| Corrected Total | 1871.170 | 35 | | | |
| a. R Squared =. 998 (Adjusted R Squared =. 997) | | | | | |

**Table 10:** 2-Scheffe's Post Hoc analysis of Anti-microbial property of *Strychnos Colubrina*

| Multiple Comparisons | | | | | | |
|---|---|---|---|---|---|---|
| Dependent Variable: Zone of Inhibition in mm | | | | | | |
| Scheffe | | | | | | |
| **(I) microbe** | **(J) microbe** | **Mean Difference (I-J)** | **Std. Error** | **Sig.** | **95% Confidence Interval** | |
| | | | | | **Lower Bound** | **Upper Bound** |
| Bacillus subtilis | Staphylococcus aureus | -16.6000* | .18905 | .000 | -17.1680 | -16.0320 |
| | Pseudomonas aeruginosa | .0000 | .18905 | 1.000 | -.5680 | .5680 |
| | Candida albicans | .0000 | .18905 | 1.000 | -.5680 | .5680 |
| Staphylococcus aureus | Bacillus subtilis | 16.6000* | .18905 | .000 | 16.0320 | 17.1680 |
| | Pseudomonas aeruginosa | 16.6000* | .18905 | .000 | 16.0320 | 17.1680 |
| | Candida albicans | 16.6000* | .18905 | .000 | 16.0320 | 17.1680 |
| Pseudomonas aeruginosa | Bacillus subtilis | .0000 | .18905 | 1.000 | -.5680 | .5680 |
| | Staphylococcus aureus | -16.6000* | .18905 | .000 | -17.1680 | -16.0320 |
| | Candida albicans | .0000 | .18905 | 1.000 | -.5680 | .5680 |
| Candida albicans | Bacillus subtilis | .0000 | .18905 | 1.000 | -.5680 | .5680 |
| | Staphylococcus aureus | -16.6000* | .18905 | .000 | -17.1680 | -16.0320 |
| | Pseudomonas aeruginosa | .0000 | .18905 | 1.000 | -.5680 | .5680 |
| Based on observed means. The error term is Mean Square (Error) =. 161. | | | | | | |
| *. The mean difference is significant at the. 05 level. | | | | | | |

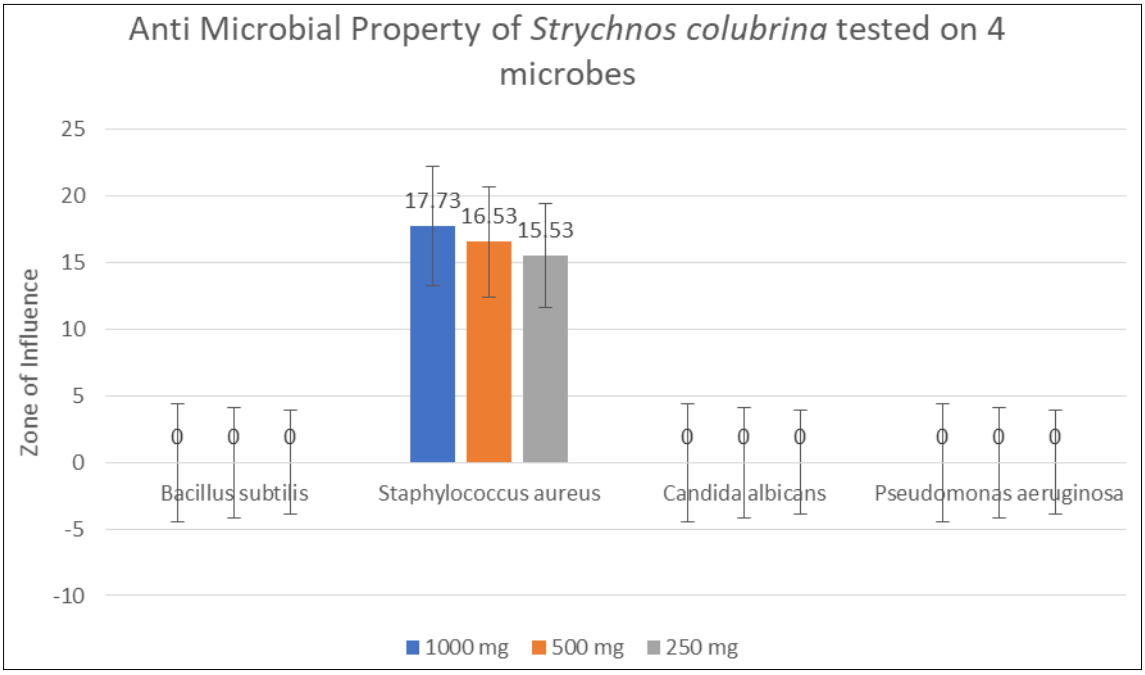



**Fig 4:** Anti-microbial property of *Strychnos Colubrina*

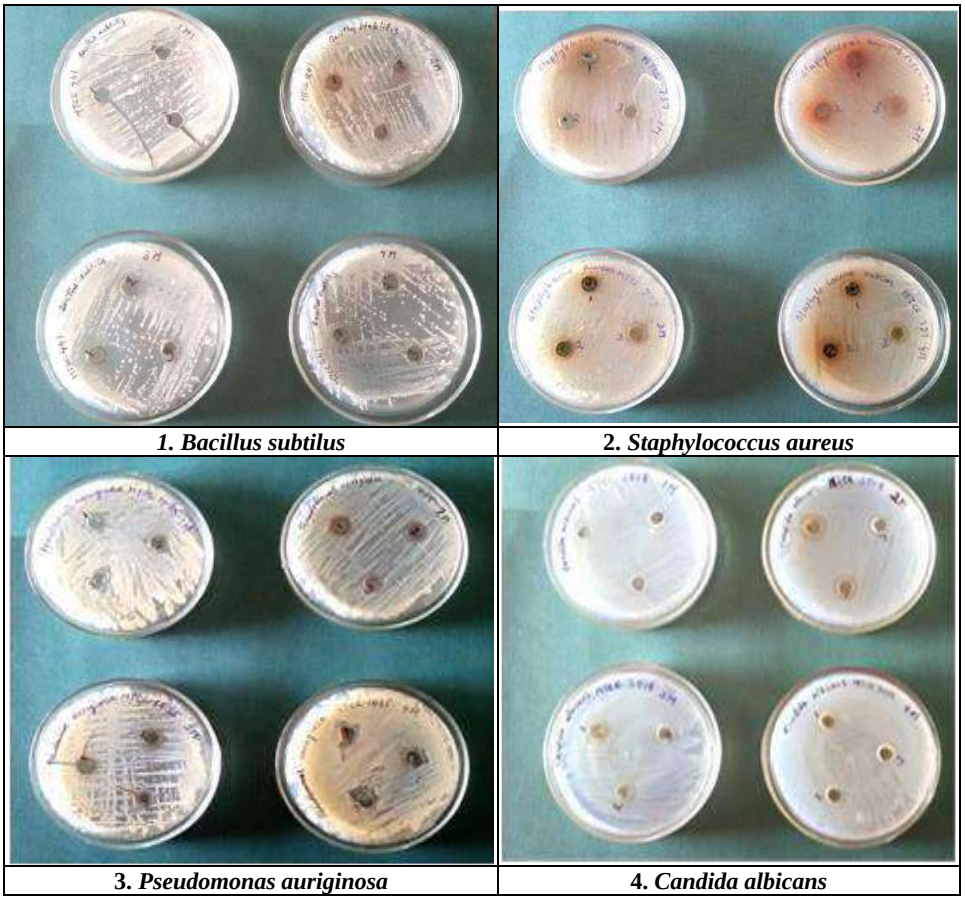



**Fig 5:** Plates with Anti-microbial activity

## Conclusion

**The phytochemical studies:** These studies have been carried out during the present study for preliminary screening of secondary metabolites and qualitative analysis of whether these compounds are present or not in various taxa. These studies act as an identification marker of genuine plant-based drugs. In the preliminary phytochemical studies, the tannins, phenolic compounds, alkaloids, flavonoids, saponins, fats, oils, terpenoids are known to present in *Strychnos colubrina.* Whereas glycosides, lignins, quinones, anthraquinones, anthocyanides, coumarins, carbohydrates, reducing sugars and aminoacids and Sterols are found to be absent in this plant

**The anti-oxidant activity of *Strychnos Colubrina:*** Phytochemical analysis of the extracts has shown the presence of some flavonoids and phenolics. These compounds give antioxidant effect, and this can be used for drug extractions from *Strychnos colubrina* in the future. Quantitative analysis of these bio-active constituents in *Strychnos colubrina* leaves have to be further investigated in the future. They can become potent antioxidants.

**Anti-microbial activity of *Strychnos Colubrina:*** The present study reveals that *Strychnos Colubrina* leaf extracts have significant detrimental effect on one of three bacterial strains used i.e, *Staphylococcus aureus* and it shows no effect on other two bacteria namely, *Bacillus subtilis*, *Pseudomonas aeruginosa* and a fungal strain namely *Candida albicans*. Methanolic plant extract generally contain various potent phytochemicals in mixed form. This may be the reason for the lesser inhibitory effect shown by leaf extract when compared to that exerted by proven antibiotics. For the study of plant extracts, the number of microbial strains was reduced in accordance with their known function as food destroying agents and human pathogens. The methanolic extract of plant leaves of *Strychnos colubrina* has not earlier been reported to have anti-microbial activity.

As discussed above, medicinal plants are at the mainstay in the treatment of diseases for the vast majority of tribal and rural people. As the present study reveals the potential of these medicinal plants, further research can be directed to probe into the structure and mechanism of action of the bioactive therapeutic principles for development of drugs to treat various diseases that affect the mankind. Phytochemical screening of ethno-medico-botanical species indicated the presence of numerous potential chemical constituents which have high therapeutic value. Thus, the phytochemical studies of this species may lead for further investigations to find out drugs of importance. The present study concludes that the plant species with numerous highly effective phytochemical compounds like saponins, alkaloids, terpenoids, steroids, lignins, tannins, indoles, anthroquinones and several types of anthocyanidins, phenolic compounds, flavonoids and lipid compounds having many medicinal applications, used in wide range of formulations, commercial, higher therapeutic and economic values. Biological activity conducted in screening the medicinal properties of selected plant material of methanolic extracts of leaves of *Strychnos colubrina* has proven as antibacterial and anti-oxidant, agent. It is, therefore, implied that the isolation and proper characterization of the active

constituents from the extracts of the select plant species as possible antioxidant, antimicrobial agent is possible. Quantitative analysis of the active compounds in *Strychnos colubrina L.* leaf extracts should be further studied. Hence this report provides insights into the therapeutic potential of the phytomedicine and scope for further research on these drugs. Further investigations must be carried out from this research for the benefit of human welfare. The present screening may also be useful for continuing, future research mainly in the field of pharmaco toxicology.

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# బోయి భీమన్న సాహిత్యం - సమాలోచన

అంతర్జాల అంతర్జాతీయ సదస్సు

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## భావవీణ ప్రత్యేక సంచిక

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మెరినా ఆవరణ, చెన్నై, తమిళనాడు.

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# పాలేరు నాటకం - బోయిభీమన్న సామాజిక స్వప్నం

- డా॥. గోపవరం పద్మప్రియ, తెలుగు అధ్యాపకులు పి.ఆర్. ఆర్ & వి.యస్ ప్రభుత్వ డిగ్రీ కళాశాల, విడవలూరు.

హితేన సహితం సాహిత్యం. ఈ సాహిత్యం ఎవరి హితాన్ని కోరుతుంది? అని ప్రశ్నించుకుంటే ''సామాజిక హితం'' అనే జవాబు దొరుకుతుంది. సమాజంలో ఎవరిమేలును? అని తర్కిస్తే, ఎవరు అన్ని విధాల బాధలను అనుభవిస్తూ అణచివేతకు గురవుతున్నారో వారికి మేలు జరగాలి. మన భారతీయ సమాజంలో వేలాది సంవత్సరాలుగా సాంఘికంగా ఆర్థికంగా అణచి వేతకు గురవుతూ పేదరిక, సామాజిక రేఖకు దిగువన వున్న వారు దళితులే. వీరికే మేలు జరగాలి.

ఆర్థికంగా, రాజకీయంగా అన్ని స్థాయిల వారితో సమానమైన జీవనస్థాయిని వారికి కల్పించాలి. సామాజిక రంగంలో ప్రతిదానిలోను సమానమైన ప్రజాస్వామిక ప్రాతిపదికను వారికందించాలి. సమాజిక వ్యవస్థను సమూలంగా మార్చివేయాలి. దళితుల అభివృద్ధికి ప్రభుత్వాలు, రాజ్యాంగం అనేక పథకాలను రచిస్తున్నా అభివృద్ధి అంతంత మాత్రమే వుంది. దానికి కారణం వాటిని అందుకునే వర్గాలవారికి వాటికి సంబంధించిన సరైన జ్ఞానం లేకపోవడమే. అలాంటి దళితులలో చైతన్యాన్ని పురికొల్పడానికి అనేకమంది సాహితీమూర్తులు సామాజిక చైతన్య ఉద్యమంలో తమవంతు పాత్రను పోషించారు. వారిలో చైతన్యాన్ని నింపడానికి సుంబోధక మైన సాంఘిక నాటక ప్రక్రియను సృజించిన తొలితరం సాంఘిక నాటక రచయితల్లో బోయిభీమన్న ఒకరు. వీరు పేద దళిత వర్గంలో పుట్టి కష్టాలు బాధలు అనుభవించినా నిరంతరం సంతోషంగా జీవించాడు.

నా సుఖాలు, సంతోషాలు
సమస్తమూ సరస్వతీ ప్రీత్యర్థం
నా కష్టాలు, నష్టాలు, దురదృష్టాలు
అన్నీ శివార్పణం - అంటూ జీవించాడు

అవమానాలను ఎదిరిస్తూ కులతత్వాన్ని వివరించి దళితుల సామాజిక చైతన్యానికి మార్గాలను అన్వేషించిన చైతన్యశీలి. ఈయన రచించిన పాలేరు, కూలిరాజు, పడిపోతున్న అడ్డుగోడలు, ప్రగతి, మానవుని మరోమజిలి, అనసూయ ఈ నాటకాలన్నీ ఆనాటి సమకాలిన సామాజిక ప్రతిబింబాలే. సమాజిక శ్రేయస్సే ఆధునిక నాటక ధ్యేయం.

సామాజిక బాధ్యతతో రచనలు చేసే ఏ రచయితకైనా నాలుగు ప్రశ్నలు ఎదురవుతాయని 'జాషువా స్వప్న సందేశం' సిద్ధాంత వ్యాసంలో రాచపాళెం చంద్రశేఖర్ రెడ్డిగారన్నారు అవి ఏమిటంటే?

1. తాను నివశిస్తున్న సమకాలీన సమాజం ఎలావుంది?
2. ఆ సమాజం అలా ఉండడానికి గల కారణాలేవి?
3. ఆ సమాజం ఎలా ఉండాలని రచయిత ఆశిస్తున్నాడు?
4. తాను కలలుగన్న సమాజం ఏర్పడ్డానికి గల పరిష్కారం మార్గాలేమిటి?

ఈ నాలుగు ప్రశ్నలకు రచయితకు దొరికే సమాధానమే రచయిత స్వప్నమవుతుంది. బోయిభీమన్న కూడా ఆనాటి సమాజం ఎలావుందో కళ్ళారా చూచి, అనుభవించారు గనుక దాన్ని ఇతివృత్తంగా స్వీకరించాడు. దానికి గల కారణాలను అన్వేషించి వాటి పరిష్కార మార్గాలను కనుగొన్న ద్రష్ట , స్రష్ట, నవ సమాజ నిర్మాత భీమన్న.

ఏ సమాజమైన వివక్షకు గురవడానికి కారణం అవిద్య, అజ్ఞానం, వీటికి కారణం భారతదేశంలో వేళ్ళూనుకొన్న కులతత్వం. ఈ రెండింటిని భారతీయ సమాజం నుంచి పారద్రోలడానికి బోయిభీమన్న సూచించిన రెండు మార్గాలు.

1. విద్య
2. కులాంతర వివాహాలు

ఈ రెండింటిని తన పాలేరు నాటకంలో ప్రతిపాదించాడు. భీమన్నగారి "కూలిపోతున్న అడ్డుగోడలు" కేవలం కులాంతర వివాహాలకి ప్రాధాన్యమిస్తుంది / ప్రధాన భూమిక వహిస్తుంది. పాలేరు నాటకంలో విద్య, కులాంతర వివాహం అనే ద్విముఖవ్యూహం ద్వారా సాంఘీక విప్లవానికి బోయిభీమన్న అంకురార్పణ గావించారు. భూస్వాములు కామంతో కబళించే దళిత స్త్రీల సమస్యలు సైతం చిత్రిస్తూనే తాను చెప్పదలచుకున్న ప్రధాన సమస్యలపై తన దృష్టిని కేంద్రీకరించి మిగిలిన సమస్యలన్నింటిని పాలేరుతనం చుట్టూ అల్లుకున్న దళిత జీవన విధానాన్ని ఈ నాటకంలో సమర్ధవంతంగా చెప్పగలిగారు.

**ఇతివృత్తం :** "ఇతివృత్తం నాట్యస్య శరీరం పరికల్పితం"

పాలేరు నాటక ఇతివృత్తాన్ని సంక్షిప్తంగా పరిశీలిస్తే గోదావరి తీరంలో కుబేరయ్యే అనే భూస్వామి ఉంటాడు. అతని దగ్గర పుల్లయ్య అనే పాలేరు పనిచేస్తుంటాడు. అతని కొడుకు వెంకన్నను పాలేరుగా నియమిస్తాడు. వెంకన్న తల్లిచనిపోగా పుల్లయ్య భార్య చెల్లెలు సీత వెంకన్న ఆలనా పాలనా చూస్తూవుంటుంది. కుబేరయ్య దగ్గర వీరేశు అనే పాలేరు కూడా వుంటాడు. వాడు భూస్వామి చెప్పిన పనిని తు.చ. తప్పక చేస్తుండేవాడు. వెంకన్న అన్న, అతని చదువు అన్న వీరేశుకు చులకన అదే ఊరిలో సమాజహితం కోరే ఉపకారి మాస్టారు ఉంటాడు. చదువు సమాజాన్ని మారుస్తుందని నమ్మే అభ్యుదయశీలి. అందరిని పాఠశాలకు రమ్మని ప్రభోదిస్తూ వుంటాడు. అదే ఊరిలో సంస్కారవంతమైన సంపన్న కుటుంబానికి చెందిన యువతి వనబాల వెంకన్నను ప్రేమిస్తుంది. వనబాల, ఉపకారి మాస్టారి సహాయంతో వెంకన్న కాకినాడలో అనాధాశ్రమం చేరి అక్కడ సుందరం (వనబాల అన్న) రామంల సహాయంతో చదువును సాగిస్తాడు. వీరేశు, సీత ప్రేమించుకుంటారు. సీతపై భూస్వామి కన్నేశాడని తెలుసుకొని సీతను తీసుకొని వీరేశు పారిపోతాడు. వెంకన్న అనాధ శరణాలయం వారి సహాయంతో బాగాచదువుకొని డిప్యూటి కలెక్టరయి వెంకటేశ్వరరావుగా మారతాడు. వెంకన్న ముందు దోషిగా నిలబడ్డ కుబేర్రావును క్షమిస్తాడు. రామం చేసుకోవాల్సిన వనబాలను, వెంకన్న, వనబాలల ప్రేమ వ్యవహారం తెలుసుకొని రామం, సుందరం వారి వివాహం జరిపిస్తారు. ఇదీ నాటక ఇతివృత్తం.

పాలేరు నాటక ప్రారంభంలోనే.

బానిసతనమును - బావుముురా
భారతభూమికి - భాగ్యము తేరా!
సకల దేశముల - సర్వ మానవుల
సామ్యము - సాధింపుముురా ?
ఒకడు తినుచు - మరియొకడు పస్తుపడి
యుండుట - ధర్మము కాదురా !
కూడూ , గుడ్డ, కొంపయు సమానముగ
కూర్పుముురా లోకమున.
ప్రభువు - సేవకుడు లేని సంఘమును
పదిలముగా నిర్మింపురా !
సౌఖ్యము, సంతోషము మానవులకు
సమకూర్చుముురా ! వీరా ?

ఈ పాట ఆనాటి సమాజాన్ని చిత్రీకరిస్తూ, కవికలగన్న సమాజాన్ని ఆవిష్కరిస్తుంది. పాలితులు పాలకుల మధ్య వ్యత్యాసాలు లేని సమాజం నిర్మాణం చేయమని, అలా చేసేటప్పుడు జాగ్రత్త అవసరమని హెచ్చరిస్తాడు. ఈ ఒక్క గేయం నాటక సారాంశాన్ని, కవి స్వప్నాన్ని ఆవిష్కరిస్తుంది.

ఒకప్పటి హిందూ సమాజ ఆచార వ్యవహారాలు ఈనాడు లేకపోయినప్పటికి, వాటి ప్రభావం ఈ నాటికీ కనిపిస్తూనే వుంది. అస్పృశ్యులుగా గుర్తించబడిన అనేకమంది ఈనాటికి చదువుకు నోచుకోలేదు. ఎన్ని నంక్షేమ కార్యక్రమాలు చేపట్టినా దళితుల్లోని అక్షరాస్యతను ఇతర కులాల అక్షరాస్యతలో పోలిస్తే చాలా తక్కువగానే కనిపిస్తుంది. అనేకమంది దళితపిల్లలు

ఈనాటికి పాలేర్లుగా కార్మికులుగా, కూలీలుగా పని చేయకపోతే గడవని కుటుంబాలు ఈరోజుకు వున్నాయి. ఇలాంటి సామాజిక, ఆర్థిక నేపథ్యంలో చదువు ప్రాధాన్యతను పాలేరు నాటకం వివరిస్తూ.

కన్నబిడ్డ లజ్ఞానాంధకార మందు
ఒకరి నొక్కరు పట్టి కొట్టుకొనుచుండ
విద్య అనియెడు కాగడా వెలుగుజూపి
ఏల రక్షించుకొనరు మీ బాలకులను ?
విద్యలేని మనష్యులు వింత పశువు
లన వినరె? పశుత్వమ్మె మీక మృతమగునె ?
బడికి పంపుడు, విద్యనేర్పుడు, రవంత
ముందునకు బోవనిండు మీ ముద్దుసుతుల

అంటూ పాలేర్లుగా బ్రతుకుతున్న చిన్నారుల జీవితాలను తీర్చిదిద్దాల్సిన తల్లిదండ్రులను చైతన్య వంతం చేస్తూ ఆలపించిన గీతమిది. ఈనాటి బాలకార్మిక వ్యవస్థ 60 సంవత్సరాల స్వాతంత్ర్యం తర్వాత స్వాతంత్ర్యానంతర ఫలశృతిగానే మిగిలిపోయింది. పసి పిల్లల జీవితాన్ని పణంగా పెట్టవద్దని ఉపకారి "పసిబిడ్డ తెచ్చు సంపాదనకాశించి మనుగడ మాపు జనకులారా"! అని తల్లిదండ్రులను మానవత్వం మరచిన మనుషులుగా సంభోదిస్తాడు.

దళిత స్త్రీలలోను విద్యపట్ల ఆసక్తిని కలిగిస్తాడు. స్త్రీల యొక్క విద్యావశ్యకతను ప్రభోదిస్తాడు.

వంటయిల్లోకటె ప్రపంచమ్ముగా చేసి
తనయుల నేర్పించు తల్లులారా
జాతశక్కి విహీనమై చచ్చుచుండ
కన్నులను మూసికొంటిరే గాఢనిద్ర

చిన్నతనంలోనే పసిపిల్లల పెంపకం, ఇంటి చాకిరీ మోసే అమ్మాయి చదువుకోలేక నిరంతర శ్రమలోకి, అంతులేని చాకిరీలోకి తమకు తెలియకుండానే నెట్టివేసే ఆడపిల్లల తల్లుల అమాయకత్వాన్ని చిత్రిస్తూ ఉపకారి పాత్ర ద్వారా జాగృతం చేశాడు.

డిప్యూటీ కలెక్టరు వెంకటేశ్వరరావు తనగ్రామానికి తిరిగివచ్చి ఉపాధ్యాయుడైన ఉపకారితో మీ చలువ వల్లనే నేను ఇంత వాడినయ్యాను. మీరు నాదగ్గర ఉండాలి అని అడిగినప్పుడు.

"అది స్వార్థం అవుతుంది నీ వంటి కలెక్టర్లను ఎంతమందిని తయారు చెయ్యాలో నేను ఈ దళిత సంఘం నుండి ఒక కలెక్టర్ అన్న మాటేమిటి? ఒక్కసారి బడిలో చేరిన వాడు కోరికను బట్టి పట్టుదలను బట్టి ఇంజనీరు, డాక్టరు, ప్రొఫెసర్, లాయరు, జడ్జీ ఏదైనా కావచ్చు. నియమాతిక్రమణ చేయనక్కర్లేదు. న్యాయం కల్గిస్తుంటే చాలు"

ఇక్కడ ఉపకారి ఉపన్యాసం విన్నతర్వాత నేనూ మీ ఉద్యమంలో భాగమవుతానని వెంకటేశ్వరరావు అనడు. ఒక బాధ్యత గల నిజాయితీ ఆఫీసరుగానే చిత్రీకరించ బడ్డాడు. ఇక్కడ బోయిభీమన్న ఎదిగిన దళితుల పట్ల తన అపనమ్మకాన్ని చెప్పి చెప్పక చెప్పాడు. పైకెదిగిన దళితులు క్రిందిస్థాయి దళితుల పట్ల నిర్లక్ష్యాన్ని వ్యక్తం చేస్తున్నారనే వైనాన్ని మౌనంగానే చిత్రీకరించాడు. నేను ఇక్కడ స్పష్టంగా చెప్పదలచిన మాటేమిటంటే దళిత అవకాశాలు పొంది ఉన్నతస్థాయికి వెళ్ళిన దళితులు, దళితాధికారులు వారితోటి పేదరికపు స్థితిలో వున్న దళితుల అభ్యున్నతి కోసం కృషి చేయలేదనడం సత్య దూరం కాదు.

పాలేరు వెంకన్న గ్రాడ్యుయేట్ అయి కలెక్టరయ్యాడు. దళితుల పిల్లలకు పేర్లుండవు. పేర్లున్నా పూర్తి పేరుతో ఏ పాలేరునూ పిలవరూ. అందుకే చదువుకోవడం వల్లనే పాలేరు వెంకన్న వెంకటేశ్వర రావయ్యాడు. ప్రభుత్వం దళితుల కోసం కేటాయించిన పోస్టును అందుకొని డిప్యూటీ కలెక్టరూ అయ్యాడు. ప్రభుత్వం నిర్దేశించిన పథకాలు సఫలం కావాలంటే విద్య తప్పనిసరి అనే అంశాన్ని బోధిస్తుంది. విద్య ద్వారా హోదా, గుర్తింపు పొందిన వెంకన్న లాంటి వాస్తవమూర్తులు ఎవరైనా వున్నారా? ఈ నాటకం ఆశించిన ఫలితాన్ని సాధించిందా అని వితర్కించుకంటే -

ఆ రోజుల్లో ఆంధ్ర రాష్ట్రమంతటా పాలేరు కూలిరాజు, నాటకాలు గ్రామాల్లో ఉర్రూతలూపాయి పాలేరు నాటకాన్ని చూసి, పాలేరుపని మానేసి విద్యనభ్యసించి ఉన్నతోద్యోగాలు సంపాదించిన దళిత ప్రజానీకం అనాడు కోకొల్లలు. నాటక దిక్సూచిలో ముద్రించిన మాజీ ప్రభుత్వ ప్రధాన కార్యదర్శి ఐ.ఏ.ఎస్. ఆఫీసర్ గారి మాటల్ని ఒకసారి పరిశీలిద్దాం. ''నేను పాలేరుని. పాలేరు నాటకం చూసి చదువుకోవాలని అక్షరాలు నేర్చుకొని చదివి కలెక్టరయ్యాను. పాలేరు నాటక ప్రభావం నామీద, నా ప్రజలమీద ఎంతగానో వుంది. ఈ నాటకం రాకపోతే నేను పాలేరుగానే మిగిలిపోయేవాడిని. బోయిభీమన్న ఋణం జన్మజన్మలకు తీర్చుకోలేనిది'' అని ఎన్నో సందర్భాల్లో అన్నారు. ఈ నాటకం సామాజికంగా విప్లవం తీసుకొచ్చిం దనడానికి ఇంతకంటె మరొక నిదర్శనం లేదు.

కవి తనస్వప్నం కోసం నూతన భావాలోచన గలిగిన ఒక పాత్రను ఎన్నుకొన్నాడు. వనబాల మోతుబరి రైతు కులానికి చెందిన అభ్యుదయవాది. అభ్యుదయ నవ సమాజ ఆలోచనపరంపర గలిగిన సోదరుడు సుందరం పాత్రను కవిసృష్టించుకున్నాడు. వారి వాదనకు, వేదనకు, నవసమాజ బోధనకు బ్రహ్మసమాజం వేదికయింది. కులరహిత, మతరహిత, వర్గరహిత సమాజం కోసం బ్రహ్మసమాజం ఏర్పడింది. బ్రహ్మ సమాజ నియమావళిని ఆచరిస్తూ నవ సమాజానికి వెలుగురేఖగా బోయిభీమన్న స్వాప్నిక దర్శనానికి నిదర్శనంగా వనబాల కలెక్టర్ వెంకటేశ్వరరావు వివాహం తరతరాల సంప్రదాయబద్ధమైన ఊరులో బ్రహ్మ సమాజ పద్ధతుల ప్రకారం జరగడం నవసమాజ అభ్యుదయ వేడుక.

అయితే ఇక్కడ కవి ఒక సందేహాన్ని సీతపాత్ర ద్వారా వ్యక్తం చేస్తాడు.

''పైకొచ్చిన వాణ్ణి పై వాళ్ళు పై నుంచే ఎగరేసుకుపోతే,
ఇక మాకు మిగిలిందేమిటండమ్మా''

అప్పుడు వనబాల నేను మీ వాడకీ వచ్చి ఉంటానని నమ్మబలుకుతుంది. ఇక్కడ కవి నేటి వాస్తవిక పరిస్థితిని వివరించినట్లైనది. నేటి సమాజంలో అందరూ వనబాల లాంటి వారు వుండరు కాబట్టి ఈ సందేహాన్ని కవి ఇక్కడ వ్యక్తం చేశాడు. గురజాడ అప్పారావుగారు చెప్పినట్లు దళితులు, అగ్రవర్ణాల వారు వివాహం చేసుకోమన్న భావాన్ని మొదట ఉన్నత దళిత వర్గం పాటిస్తే దళిత సమాజం సమ తౌల్యాన్ని పొందుతుంది. వృద్ధిచెందిన దళితుడు వృద్ధి చెందకుండా ఉన్న అదే దళితవాడకు చెందిన వారితో వివాహాలు కలుపుకుంటే కవి స్వప్నించిన నవసమాజం నిజంగా ఆవిష్కృతమవుతుంది.

రాముడు ఆదర్శమూర్తి. రామతత్వం ప్రజలకు జీవన శుబోధన వ్యక్తం వెంకన్న నవసమాజ రాముడు విద్యా జ్ఞాన ప్రబోధాన్ని తన సమాజానికి అందించి ఉన్నత శిఖరాలకు ఎదగమని ముందు దళిత వర్గాలకు వెన్ను తట్టిన వాడు అభినవ వెంకన్న. పాలేరుతనం నశించినా పాలేరు నాటకం అణచివేత, బానిసత్వం, అస్వతంత్ర్యత ఉన్నంతకాలం నిలచివుంటుంది. కాబట్టి ఇది ఎప్పటికీ క్లాసిక్కే.

❁❁❁

# బోయి భీమన్న సాహిత్యం - సమాలోచన

అంతర్జాల అంతర్జాతీయ సదస్సు – 21 & 22, ఫిబ్రవరి 2022

## భావవీణ ప్రత్యేక సంచిక

Journal of Literary, Culture & Language Studies



భీమన్న గారి సాహిత్యమంతా చదివాను. పాటలను, అందులో వినసొంపులను ఎంచి సిద్ధాంతాలు మొన్న అల్లుకొన్నది. మీసాలని వాళ్ళందాన్ని పంచుకొన్న వాళ్ళనూ వెలుపలికి తరిమేశారా భీమన్న చెప్పిన్న మద్రాసు విశ్వవిద్యాలయం తెలుగు అధ్యాపకులు, రవి, సహచరి, సాహితీమిత్రులు అందరి పక్షాన నిండుదనాన్ని గారవ మహితా అభినందనలు తెలియజేస్తున్నాను.

– డా॥ ఎన్. గోపి



అత్యధిక్యానంతో మొండుకుపోయి అన్యతక్కువ సాహిత్య సృష్టికే సమాజ ప్రయోజనాన్ని అంటి కాకిని బాధ్యతల మీదని మహాకవి దాశ భీమన్న గారి వ్యక్తిత్వం, సాహిత్యం విశ్వం. సామాజిక ప్రయోజనాన్ని అంటి చాటి నిబద్ధతకే ప్రాధాన్యం ఇచ్చిన భీమన్న అభిమాన సాహిత్యాన్ని స్వాగతించిన్న మహోన్నతమైన వ్యక్తి భీమన్న.

– ఆచార్య గుత్తి వీరభద్రుడు



భీమన్న గారు చెప్పినట్లు మనిషి, సాహిత్యం ద్వారా సామాజిక ప్రయోజనం పొందినప్పుడే ఎన్ని గడులు దాటి, ఎన్ని తరాలను ఎంతటి ప్రభావితుల్ని చేసి మంచిని పంచాలనే మాట్లాడిన పరిణామంలో ఉన్నత వ్యక్తులుగా తీర్చుకోవచ్చు. అనుసరణీయ వ్యక్తిత్వంతో మద్రాసు విశ్వవిద్యాలయం తెలుగు శాఖ అందించిన భీమన్న పురస్కారం. భీమన్న పరిశోధన వ్యక్తిత్వం ప్రతిబింబ ద్వారా మెలుగులోకి తీసుకురావడంలో అధ్యాపకులు తెలియజేసే మద్రాసు విశ్వవిద్యాలయం తెలుగు శాఖాధిపతి ఆచార్య పెద్దలి శంకరయ్య గారికి శిష్యురాలిగా, భీమన్న పెంపుదలంలం వారాంతి మనిషిగా రాయించినట్లు...

– డా॥ ఎన్. గోపి వెలిబుచ్చారు


## తెలుగు విభాగం

## మద్రాసు విశ్వవిద్యాలయం

మెరినా ఆవరణ, చెన్నై, తమిళనాడు.

ప్రభుత్వ డిగ్రీ కళాశాల : చేబ్రోలు
NAAC WITH B GRADE
(ఆచార్య నాగార్జున విశ్వవిద్యాలయ అనుబంధ కళాశాల)
చేబ్రోలు, గుంటూరు జిల్లా, ఆంధ్రప్రదేశ్, ఇండియా.

శ్రీ వై.కె.ఆర్ & కె ప్రభుత్వ డిగ్రీ కళాశాల : కోవూరు
(విక్రమ సింహపురి విశ్వవిద్యాలయ అనుబంధ కళాశాల)
కోవూరు, నెల్లూరు జిల్లా, ఆంధ్రప్రదేశ్, ఇండియా.

# భావవీణ ప్రత్యేక సంచిక

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## తెలుగు సాహిత్యం - మహిళ

అంతర్జాల జాతీయ సదస్సు
3-4 మార్చి 2022



నిర్వహణ :
తెలుగు అధ్యయన శాఖ, IQAC మరియు మహిళా సాధికార విభాగాలు
ప్రభుత్వ డిగ్రీ కళాశాల : చేబ్రోలు, గుంటూరు జిల్లా.
శ్రీ వై.కె.ఆర్ & కె ప్రభుత్వ డిగ్రీ కళాశాల : కోవూరు, నెల్లూరు జిల్లా.

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# కార్యనిర్వహణాధికారిగా మార్గదర్శకత్వం వహించగల స్త్రీ మూర్తి తార

– డా॥. గోపవరం పద్మలియ, తెలుగు అధ్యాపకురాలు, పి.ఆర్.ఆర్. & వి.ఎస్. ప్రభుత్వ డిగ్రీ కళాశాల, విడవలూరు, శ్రీ పొట్టి శ్రీరాములు నెల్లూరు జిల్లా.

కూజంతం రామ రామేతి మధురం మదురాక్షరమ్
ఆరుహ్య కవితాశాఖం వందే వాల్మీకి కోకిలం.

వాల్మీకి రామాయణం విశ్వజనీనమైన కావ్యం. ఈ గ్రంథం భారతీయ సంస్కృతినీ, సమగ్ర మానవ జీవన విధానాన్నీ శ్రీరామ చరితం ద్వారా అత్యంత సుందరంగా ఆవిష్కరించింది. దేశ విదేశాల్లో దీనికి కల జనాదరణ అనన్య సామాన్యం. యుగాలు గడిచినా, తరాలు, అభిరుచులు మారినా పాఠకుల్లో రామాయణం పట్ల మక్కువ ఏమాత్రం చెక్కుచెదరలేదు. వివిధ భాషల్లోనూ, విశేషించి తెలుగులోను నేటికి రామాయణం ఆధారంగా అనేక ప్రక్రియలు వెలువడుతున్నాయి. దీనికి కారణం ఆ రచనలో లోకోత్తరమైన శైలి ఉంది. శబ్దాల పోహళింపులో పాఠకుణ్ణి మైమరపించే సొగసు ఉంది. పాత్ర చిత్రణలో అంతులేని సొగసు, నిబద్ధత, ఏకాగ్రత కన్పిస్తుంది.

రామాయణంలోని స్త్రీ పాత్రలన్ని పరిశీలిస్తే అందరిలోను వివేకం, విజ్ఞత, సహనం, భావోద్వేగం, సమయస్ఫూర్తిలో నేటి నారీలోకానికి, సమాజానికి మార్గదర్శకంగా లభిస్తాయి. ఈ లక్షణాలతో పాటు రామాయణంలోని వాలి భార్య కార్యనిర్వహణాధ్యక్షురాలిగా కూడా కన్పిస్తుంది. తార పాత్ర చిత్రణలో మరో ప్రత్యేకత ఉంది. ఈమె మాటల ద్వారా చేతల ద్వారా ఆమె మనస్తత్వం, వ్యక్తిత్వం ప్రస్ఫుటం కావడం సహజమే. అంతకు మించి ఇతరులు ఆమె గురించి మాట్లాడే విధానం ఆమె వ్యక్తిత్వ విశిష్ఠతను బోధపరుస్తుంది.

వాలి సుగ్రీవుల కథ అందరకు విదితమే. వీరి కథలో 'తార' కీలక పాత్ర పోషిస్తుంది. వాలిని సుగ్రీవుడు యుద్ధానికి ఆహ్వానించినప్పుడు ఆమె ఎంతో ముందు చూపును బంధుజనం పట్ల అభిమానాన్ని ప్రదర్శిస్తుంది. వాలిని ''నీ బలం లోకానికతంకూ తెలుసు. నీకు శత్రువులు ఎవరూ లేరు. నిన్ను యుద్ధానికి రమ్మని రెచ్చగొడుతున్నవాడు సుగ్రీవుడే..... నిన్ను గెలవడం సాధ్యం కాదని తెలిసే యుద్ధానికి పిలిచాడు. నీ చేతిలో చావు దెబ్బలు తిని పారిపోయాడు. అటువంటి వాడు మళ్ళీ యుద్ధానికి వచ్చాడంటే అనుమానించాలి. అతని కంఠ ధ్వనిలో ధైర్యం, గెలుస్తాననే నమ్మకం ఉన్నాయి. అతడు తన బలాన్ని నమ్ముకుని ఎదుర్కొనేందుకు రాలేదు. వేరొకరి సహాయాన్ని నమ్ముకుని ఇలా వచ్చాడు కుమారుడు అంగదుడు గూఢాచారుల వల్ల విన్న మాటలు నాకు చెప్పాడు. ఇక్ష్వాకు వంశీయులు ఈ అడవిలో నీ తమ్ముడిని వెదుక్కుంటూ వచ్చారని, వారిని జయించడం ఎవరివల్ల గాదని చెప్పాడు''.అని హితవు చెప్పింది. తన మాటను త్రోసిపుచ్చుతాడని తనవి ఊహకాదని గూఢాచారుల వల్ల తెలుసుకున్న విషయాన్ని వివరిస్తున్నానని తెలిపింది. రాజ్యపాలనలో ఎప్పటికప్పుడు రాజ్యం చుట్టు ప్రక్కలు ఏమి జరుగుతుందో తెలుసుకోవడం ఒక వీరుని భార్యకు ఉండాల్సిన ముఖ్య లక్షణం ఇక్కడ కన్పిస్తుంది.

అదే సమయంలో కుంటబ క్షేమాన్ని, దాని పట్ల గల ప్రేమను, బంధుజనుల మధ్య ఉండాల్సిన బాంధవ్యాల్ని వ్యక్తం చేస్తుంది.

సుగ్రీవో విపులగ్రీవో మహాబన్ధుర్మతస్తవ
భ్రాతృ సాహృదయాలమ్బనాన్యా గతిరిహస్తి తే.

(నీకు సుగ్రీవుడి కంటే గొప్ప బంధువుల వేరొకడు లేడు. అతడి పట్ల సోదరి ప్రేమ చూపించు అతణ్ణి సుఖపడనీ, నువ్వు క్షేమంగా ఉండు. ప్రస్తుతం అంతకు మించి నీకు వేరొక మార్గం లేదు)

యది తే మత్రియం కార్యం యది చావైషి మాం హితామ్
యాచ్యమాన: ప్రియత్వేన సాధు వాక్యం కురుష్యమే.

నువ్వునాకు ప్రాణాధికుడైన ప్రియుడివి నాకు నీక్షేమం కావాలి. అందుకే ప్రార్థిస్తున్నాను. నేను చెప్తున్న హిత వాక్యం విను. నా మాటలు విని కోపగించుకోకు. రామిడితో విరోధం రాకుడా జాగ్రత్తపడు.ఇలా తన దగ్గర గల అన్ని మార్గాల్లో భర్తకు హితువు చెప్పింది. గూఢాచారుల వల్ల తెలిసింది చెప్పింది. బంధువుల పట్ల ఉండాల్సిన అభి మానాన్ని వివరించింది. చివరకు ప్రియమైన భార్య మాటైనా వింటాడేమోనని ప్రేమతో తన మాటను వెలిబుచ్చింది.

కాని వాలి ఆమె మాటల్లోని లోతును పరిశీలించ కుండా స్త్రీ భావనతో ఒక చులకనను మనసు నందుంచు కుని "నీ హృదయం దర్శితా తావన్మయి భక్తి స్వయాకృతా" (నా పట్ల నీకున్న ప్రేమ వలన భక్తి వల మాట్లాడావు) ఇక చాలు మిగిలిన స్త్రీలతో వెనక్కు అంతఃపురంలోకి వెళ్ళమని శాసిస్తాడు.

సమర్థుల మాటను పాటించకపోతే కలిగే నష్టమే ఇక్కడ కల్గింది. వాలి మరణ వార్తవిని విలపిస్తుంది.

సుగ్రీవస్య త్వయాభార్యా హృతా సచ వివాసితః
యత్తత్తస్య త్వయా పుష్టిః ప్రాప్తేయం ప్లవగాధిప.

(వానర రాజ! సుగ్రీవుడిని రాజ్యం నుంచి వెళ్ళగొట్టావు. అతడి భార్యను అపహరించావు. దానికి ఫలితంగానే ఇంత ఆపద వచ్చింది. నీ క్షేమంకోరి చెప్పిన మాటలు తృణీకరించి వచ్చి యీ స్థితిలో పడ్డావు.

ధర్మాన్ని పాటించకపోతే, అహంకారం వదలకపోతే ఒక్కోసారి మరణాన్ని కూడా ఎదుర్కోవలసి వస్తుందని ఆమె ధర్మ విలాపమే గుర్తు చేస్తుంది.

విలపిస్తున్న తారతో హనుమంతుడు "సుగ్రీవుడు, అంగదుడూ దుఃఖంతో దిక్కుతోచకుండా వున్నారు. ఇప్పుడు అంగదుడికి యౌవనంగా జ్యాభిషేకం చేయాలి. సింహాసనం మీద కూర్చున్నా అంగదుడిని చూస్తే నీ దుఃఖం కొంత ఉపశమిస్తుంది. అనడంతో వానర రాజ్య క్షేమం కూడా ఆమె మీద ఆధారపడ్డట్టు చెప్తున్నాడు. ఆమె లేకపోతే, ఆమె కుటుంబ సారధ్యం వహించకపోతే సుగ్రీవుడు, అంగదుడు దిక్కుతోచని వారవుతారని చెప్పడంలో ఆమె ఉనికి ఆ కుటుంబానికి, రాజ్యానికి ఎంత క్షేమమే అర్థమవుతుంది. ఒక ఒక సమర్థవంతు రాలైన స్త్రీకి ప్రతీకగా ఇక్కడ హనుమంతుడు ఆమెను చిత్రీకరించాడు.

ఆమె సామర్థ్యాన్ని కూడా వాలి చనిపోతూ సుగ్రీవుడికి వివరిస్తాడు. ఆమె సలహా రాజ్యపాలనకు ఎంతో విలువై నదని వివరిస్తాడు. ఎప్పుడూ ఆమె మాటను తృణీకరించ వద్దని ఇలా సలహా ఇస్తాడు. "తార సుషేణుడి కూతురు. ఈమె అతి సుక్ష్మమైన విషయాలను గురించి చాలా చక్కగా ఆలోచించే శక్తి గలది. హఠాత్తుగా వచ్చిపడే పరిస్థితులను ఎలా ఎదుర్కోవాలో నిర్ణయించగల సమర్థురాలు. ఈ పని మంచిది అని యీమె నిర్ణయిస్తే మరో ఆలోచన లేకుండా ఆ పని చెయ్యవచ్చు. ఆమె అభిప్రాయం ఎప్పుడూ సరైనది. అది మారదు" అని తన అనుభవం ద్వారా ఆమె దక్షతను వివరించాడు.

"నాథా! నేను చెప్పిన మాట విని అంతఃపురంలో సుఖంగా ఉండవలిసిన వాడిని నా మాట వినకక ఇలా ఎగుడు దిగుడు నేలపై రాళ్లమీద పడి ఉన్నావా! ...." ఇలా స్త్రీకి సహజమైన శోకాన్ని ప్రదర్శిస్తూ రాముడితో తనను హత్య చేయమంటుంది. స్త్రీకి గల సహజ భావోద్వేగాలలోను తన మాట వినలేదని బాధ కన్పిస్తుంది. భర్త మొండితనానికి, అహంకారాటకి బలైన స్త్రీగా మిగులుతుంది.

రాముడికిచ్చిన మాటను మరచి కిష్కందలో సుగ్రీవుడు చాలాకాలానికి మళ్ళీ దొరికిన రాజభోగాలను తృప్తిగా అనుభవిస్తున్నాడు. తన భార్య రుమ, సౌందర్యవతి తార లభించడంతో రాజ్య భారమంతా మంత్రులకు వదిలేసి స్త్రీలతో ఏకాంతంగా గడుపుతువ్నడు. మంత్రులకు ధర్శనాన్ని కూడా నిరాకరిస్తున్నాడు. ఒకరోజు హను

మంతుడు రాముని గడువును గుర్తుచేసాడు. అన్ని దిక్కులలోని వానరసైన్యాలను వెంటనే కిష్కింధకు చేరమని ఆజ్ఞాపించు అని చెప్పి అంతఃపురంలోకి పోయాడు. ఇక ఆ విషయాన్ని వదిలేసిన సుగ్రీవుడి చర్యకు రాముడు వేదన చెంది కోపాన్ని ప్రదర్శించగా లక్ష్మణుడు కోపోద్రేకంతో కిష్కింధకు బయలు దేరాడు. రాజ్యంలో లక్ష్మణుడు ప్రవేశించిన విషయం తెలుసుకున్న సుగ్రీవుడు భయపడి అతనిని ఎదర్కోవడానికి తారనే పంపుతాడు.

ఇక్కడే అర్థమతుతుంది. మనకు రాజ్యంలో మంత్రులు, ఇతర సేనాధిపతులు, పరిపాలనాధిపతులు ఇంతమంది ఉండగా ఒక స్త్రీని లక్ష్మణుడిముందుకు పంపడంతో ఆమె వాక్చాతుర్య సామర్థ్యం, కార్యనిర్వహణ సమర్థత ఎంతటివో చెప్పకనే చెప్తాయి. అతని నమ్మకాన్ని ఒమ్ము చేయకుండా అంతే సమర్థతతో లక్ష్మణుడిని ఆహ్వానించి ఎదుర్కొని నిలబడి శాంతపరుస్తుంది. ఆమె మాటల్లోనే ఆమె ఎంత సూక్ష్మ పరిశీలనా శక్తి, లోకజ్ఞానం కలదో మనకు అర్థమవుతుంది.

సుగ్రీవుడి పొరబాటును అంగీకరిస్తూనే లక్ష్మణుడికి కోపం తగదనే హితువును, స్వాంతన వచనాన్ని పలుకు తుంది. రాకుమారా! నువ్వు గొప్పవీరుడివి. మీరు సాధించాలనుకుంటున్న మహాకార్యంలో స్వజనుల మీదనే కోపం తెచ్చుకుంటే ఎలా? సుగ్రీవుడు చేసింది పొరబాటే అయితే దానిని అర్థం చేసుకొని ఔదార్యంతో క్షమించాలి. మీ వంటి వారు కూడా కోపానికి వశమైతే ఎలా? అని సంభాషిస్తుంది. ఎంత భోగలాలసతలో ఉన్న మీ కార్య సాధనకు అవసమరైన ప్రయత్నాలను ఇంతకముందే ఆరంభించాడనీ వివరిస్తుంది. సుగ్రీవుని కామంపట్ల లక్ష్మణుడికి ఏహ్యం కల్గుతుందేమోననే భావంతో విశ్వామిత్రుడిని గుర్తు చేస్తుంది. మేనకతో పదేళ్ళు సంసార సుఖాన్ని అనుభవించి ఒక్క రోజుగానే భావిం చాడు. అంతటి మహాత్ముడికే ఆ స్థితి కల్గితే వానరుడైన సుగ్రీవుడి విషయం గురించి ఇక ఆలోచించక్కర లేదనే విషయాన్ని వివరించింది.

రామకార్యం పట్ల సుగ్రీవుడికున్న ఆసక్తిని తన వాక్చాతుర్యంతో ఇలా వివరించింది.

రుమాం మాం చాఙ్గదం రాజ్యం ధనధాన్యవసూనిచ
రామ ప్రియార్థం సుగ్రీవస్ప్రౌదిత మతిర్మయ

(రాముడికి మేలు చేయడానికి రుమనూ, నన్ను, అంగదుడిని, ధన ధాన్యాలను, రత్నాలనూ, రాజ్యాన్ని తృణ ప్రాయంగా త్యజించగలడు) ఏ సుఖాలతో ఐతే సుగ్రీవుడు మునిగి తేలుతున్నాడో వాటన్నింటిని రాముడికోసం విడవగలడనే సందేశాన్ని లక్ష్మణుడికి విన్న వించింది. దాని ద్వారా లక్ష్మణుడికి సుగ్రీవుడి పట్ల లక్ష్మణుడికి విశ్వాసాన్ని కల్గిస్తుంది.

"లంకలో అనేక కోట్ల మంది భయంకరమైన రాక్షసులు ఉన్నారట వారినందరినీ చంపనిదే రావణుడిని చంపలేరు. సీతను పొందలేరు. ఇదంతా రాముడు ఒక్కడూ చేయగలగినది కాదు. సుగ్రీవుడు చేయగలిగినది కాదు. అందుకే కోట్లమంది వానరవీరులను పిలుస్తన్నారు.

సుగ్రీవుడి తప్పును ఎత్తి చూపుతూనే వానర రాజుల అభిజాత్యం, ఆత్మ గౌరవాన్ని కాపాడుతుంది. సుగ్రీవుడి సాయం లేనిదే రాముడు సీతను చేరుకోలేడని రక్షేచలేడని హెచ్చరిస్తుంది. వానరసైన్య సహాయం అనివార్యమనే విషయాన్ని స్పష్టం చేస్తుంది. ఇంతలోనే స్త్రీత్వాన్ని ప్రదర్శిస్తూ 'అసలు అంత కోపంతో రక్తంలా ఎర్రగా ఉ న్న నీకళ్ళను చూచి మా వానర స్త్రీలంతా భయ పడు తున్నారు. వాలికి పట్టిన గతే సుగ్రీవుడికి పడుతుందని బెంబేలు పడుతున్నారని" అంతలోనే తాను భయాన్ని ప్రదర్శిస్తూ లక్ష్మణుడి పట్ల వినయాన్ని ప్రదర్శించడం తారకే చెల్లుతుంది. తారను దాటి సుగ్రీవుడిని చేరేటప్పటికి లక్ష్మణుడిని ఒక సౌమ్య మూర్తిగా తన మాటలతో మార్చేసిన విజ్ఞురాలు.

విజ్ఞత, సమయస్ఫూర్తి, ధర్మం, ఆత్మ గౌరవం కలది.

మాటను స్పష్టంగా ధైర్యంగా చెప్పగలిగే వివేకం కలగలది. నేటి పాలనా రంగ, సంస్థల అధికారులకు ఒక మంచి ప్రధాన కార్యనిర్వహణాధికారిగా తార మార్గదర్శకం వహించగలదు.

**ఆధార గ్రంథాలు :**

1. ఉషశ్రీ రామాయణం- తిరుమల తిరుపతి దేవస్థానంల ప్రచురణ
2. వాల్మీకి రామాయణం-తత్త్వ దర్శనం. - డా॥ఎమ్.జి.పి. శ్రీరామచంద్రమూర్తి.

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మార్చి 2022

అంతర్జాల జాతీయ సదస్సు
3-4 మార్చి 2022

భావిని ప్రత్యేక సంచిక

# తెలుగు సాహిత్యం - మహిళ






ప్రభుత్వ డిగ్రీ కళాశాల : చేబ్రోలు

(ఆచార్య నాగార్జున విశ్వవిద్యాలయ అనుబంధ కళాశాల)
చేబ్రోలు, గుంటూరు జిల్లా, ఆంధ్రప్రదేశ్, ఇండియా.



శ్రీ వైకెఆర్ & కె ప్రభుత్వ డిగ్రీ కళాశాల : కావూరు

(నిడుమోలు సుమంగళి విశ్వవిద్యాలయ అనుబంధ కళాశాల)
కావూరు, నెల్లూరు జిల్లా, ఆంధ్రప్రదేశ్, ఇండియా.

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# Impact Of Music On John Milton's Poetry Especially On Paradise Lost

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**Abstract**:

For centuries long many cliques of people of English Literature had appreciated Milton have still been thinking that Milton and his exceptional talent has to be confined only to his way and style of writing and very few knew his depth knowledge about music despite being the son of a musician since we could find a swell and sway to the verse, a delicacy of sound, the famous organ tone in his Paradise Lost. So, the present paper is to establish Milton's acquaintance with music and its very indelible impact upon his poetry.

**Keywords:** Milton, Poetry, Madrigal, Metrical, Music, Musician, Paradise Lost

## Introduction

The two extraordinary talented elements in arts music and poetry go hand in hand in respect to rhythm and sound. These, accordingly, are the musical qualities that can be detected in any poem. Hence, it can be exposed that Milton consciously borrowed from contemporary music for some of the rhythms of his Paradise Lost. And here it can be argued that the music by which he was consciously influenced by is the musical knowledge already hidden in him as bedrock which quality he hereditarily got from his father. Going beyond this somehow further, it can be stated that this theme and variation technique, his use of assonance, syncopation and all the rest is in some way Influenced by his musical background. And here in this aspect it may be noteworthy to mention that his poetry must have been influenced by his own music which quality has been kept aside unnoticed by many literature enthusiasts and here it may be assumed its only because many literature paramours do not have musical knowledge equally too. Despite all kinds of struggles and tribulations that clouded Milton's life with darkness, his tenacity, concentration and intrapersonal relationship that he maintained with poetry and music could not disturb and deviate him anymore of which Hilaire Belloc stated as "these two things in Milton, his love of music, his poetic art, must, then, be kept separate, the one does not explain the other, and Milton's love of music, his inheritance in music, his comprehension of music, belong to Milton the man not Milton the poet".

People used to think that the three arts of dancing, poetry and song in any way were inseparable. Even during the time of King David, who, on one occasion at least, danced as well as sang his psalms before the ark. Seventeenth century witnessed the tremendous and huge impact of music upon almost the total human kind of the planet irrespective of their place and position in the society. Indeed, no one was in a position to claim to be highly- educated one possessed substantial musical skill. Under such circumstances that existed then, it is not too astonishing to notice that Milton's father was a musician who is in fact was a composer of real merit of whom Aubrey opined that he was an

ingenious man: delighted in musique; composed many songs now in print, especially that of Oriana "who got a gold medal from a Polish prince for composing forty parts of an “In Nominee,”

As it is a well-known fact that Milton’s father was a musician and as rightly pointed out by Anthony Wood that “Milton himself had a delicate, tuneable voice, an excellent ear, could play on the organ, and bear a part in vocal and instrumental music," where it can be said with noteworthy probability that he was influenced by his musical background in the writing of his poetry especially Paradise Lost. Having been influenced by such a father and by paying his regular visits to the services in St. Paul’s hearing to the best sacred music the early Milton not only learned to sing a part in a madrigal or psalm at first sight but mastered keyboard instrument also where the organ music left an indelible impact on him as the following well-known lines of “Il Penseroso” testify:

“Then let the peeling organ blow
To the full- voiced choir below
In cervice high and anthem clear
As may with sweetness through mine ear
Dissolve me into ecstacies
And bring all Heaven before my eyes”
Il Penseroso

There can be found another edifying passage in “L’Allegro” in which Milton makes a mention of music married to immortal verse:

” In notes, with many a winding bout
Of linked sweetness long drawn out,
With wanton heed, and giddy cunning;
The melting voice through mazes running;
Untwisting all the chains that by
The hidden soul of harmony.”
L’Allegro

So, the intent of the present paper is to establish Milton's acquaintance with music and its very indelible impact upon his poetry.

John Milton is very brief and enigmatic on the theme of verse technique. His most striking sound on poetic rhythm is the few laconic words of the note proceeding Paradise Lost. “true musical delight…. consists only in apt Numbers, fit quantity of Syllables, and the sense variously drawn out from one Verse into another.”Related to Milton’s own practice this statement has a treasure of meaning. We can make ourselves concern here with the last phrase only, "the sense variously drawn out from one verse into another." Milton believed that the "sense" (meaning the line of thought) should not come to an extensive close, but should be "drawn out." He believed too, that this movement should be achieved "variously," Two important ideologies of poetic rhythm, then, can be inferred from this last phrase of the note to Paradise Lost. The first is incessant movement, and the second is variety. Here a significant resemblance can be found to the continuous flow and free-moving rhythms of the madrigal. The connection is predominantly striking when we consider some of Milton's own descriptions of rhythm and contemporary music. His poetic words on rhythm, for instance, of course, a redolent of the English madrigal:

“…. muses intricate
Eccentric, intervolved. Yet regular
Then most, when most irregular they seem:”
Paradise Lost, Book V, Lines 622-624

There were two important musical forms that were very famous and significant during Milton’s days. They are English Madrigal and English Metrical Psalter. Madrigal is a short lyrical poem in a strict poetic form that emerged during medieval period which was a complex music composition with polyphonic unaccompanied vocal piece. And the latter isa translation of one of the psalms into rhyming strict-metre verse usually sung as a hymn in worshipping the Lord in Churches. These two important musical forms can be found in the poetry of Milton especially in his great epic poem Paradise Lost being highly attributed by him few of which have been discussed hereunder.

To make a mention about of the madrigal as "drawn out" Milton seems to be referring to the method in which the correlation of voices is used to construct an effect of quiet, continuous, forward movement, with one voice taking up the

rhythmic weight before it has been dropped by another. It is this effect, so general in the madrigal and well understood by him, that Milton strove to reproduce in the rhythms of his heroic verse. In this regard what Mr. Symonds comments on Milton's verse mentioned below, seems very interesting which is pertinent to English Madrigal. “It not unfrequently happens that a portion at least of the sound belonging to a word at the commencement of a verse is owed to the cadence of preceding lines, so that the strain of the music which begins is wedded to that which dies by indescribable and almost imperceptible interpenetrations. The rhythmic dance may therefore be prolonged through sequences and systems of melody, each perfect in itself, each owing and lending something to that which follows and which went before through concords and affinities of modulatedsound.” Then coming to the point of incessant movement in the lines given hereunder from Paradise Lost may be the best exemplification for it where there is a continuous flow of rhythm with varied speed and strength of impulse, rising and falling and freely placed the break after any syllable in the line of course at times with two such breaks of which T. H Banks made a mention that “forty percent of full stops in Paradise Lost occur within the line.”

At once as far as Angels kenn he views
The dismal Situation waste and wilde,
A Dungeon horrible, on all sides round
As one great Furnace flam'd, yet from those flames
No light, but rather darkness visible
Serv'donely to discover sights of woe,
Regions of sorrow, doleful shades, where peace
And rest can never dwell, hope never comes
That comes to all; but torture without end
Still urges, and a fiery Deluge, fed
With ever-burning Sulphur unconsum'd:
Such place Eternal Justice had prepar'd
For those rebellious, here thir Prison ordain'd
In utter darkness, and thir portion set
As far remov'd from God and light of Heav'n
As from the Center thrice to th' utmost Pole.

Paradise Lost I, 59-74

Then, to make a mention of the music, of English metrical psalters, we can find certain common characteristics. Some tunes are printed not indicating any reference of bars and few notes are also with some unequal lengths. Both semibreves which are whole notes and minims which are also called as half notes are used which seems somehow in a disorganized system as they don’t represent the accents of the verse, and some could be divided into equal sections and some other not at all correspond any time-signature which may be out of the choice of tuning that the composer does may be in order to destruct the monotonous swing of the alternate eight and six with accents incessantly recurring in similar positions which to see may be confused but when played can be found that the long and short notes have been adjusted with great care. Sometimes an occasional whole note will intrude into such a sequence of halves and some regularly open and end with a whole note and few of the intervening notes are almost always halves.

So, it can be understood that lack of uniformity of correspondence between length of note and metrical accent established two important principles of which the first is that the speech accent does not influence the length of musical notes in the psalter where a syllable accented by the iambic prosody of the verse may be held by a whole note and the second is that the length of musical note does not repeatedly influence the verse. From this brief observation of the English metrical psalter then, three important factors can be discovered for the purpose of tracing the influence of music on poetry as on of Milton’s early biographer also says “David psalms were in esteem with him above all poetry”. Milton out of the jubilant and tenacious heart that he had sung many of the psalms of David which Milton’s father psalm harmonies like Psalm 114 and 136 and in 1648 Psalm 80 to 88 which his family also sang them at Bread Street, which psalm harmonies were composed by Young John Milton showing the influence of the note-for-syllable principle of the metrical Psalters. And then again with a gap of 25 years, Milton made his debut into psalms and put the first eight of them into verse. So, these

characteristics of English metrical had had an influence on Milton's poetry. In all this, we have an immediate parallel with the English metrical Psalter. For the long opening, note of each musical phrase encouraged reversal of the first foot in the verse and this is exactly what we find most common in Paradise Lost.

If we bring up now of Paradise Lost, we will be surprised to find the same characteristics in Paradise Lost. The effect of pitch on Paradise Lost is also an evident upon the reading of any long passage including the following the brief quotation and its important contribution should never go unnoticed.

……. Arms on Armour clashing bray'd
Horrible discord, and the madding Wheeles
Of brazen Chariots rag'd;
Paradise Lost VI, 209-211

In other passages various caesuras irregularly succeed one another. In these cases, they are not only conducive to metrical variety but serve to express the vehement feelings of the several speakers. A good example is Adam's indignant address to Eve after the Fall.

Out of my sight, /thou serpent, // that name best
Befits thee/with him leagu'd//thy self as false
And hateful://nothing wants, /but that thy shape
Paradise Lost X, 867-869

Apart from this, Milton, in his Paradise Lost, makes use of some other rhythmical tricks found in music. Few of the modern music examples like syncopation can be found throughout Paradise Lost as mentioned below Book XI

And over them triumphant Death hus Dart
Shook, delaid to strike.....
Paradise Lost XI, 491-492

And in Book XI too,

The multitude of Angels with a shout
Loud as from numbers without number
Paradise Lost III, 345-346

Putting the considerations of rhythm aside for a while and observe the poem, we can notice that Milton meticulously made use of onomatopoeia in almost all in his depictions, for instance to say of his mentioning of the Bacchants the following is the one.

….
the Race
Of that wilde Rout that tore the Thracian Bard.
Paradise Lost VII, 33-34

in which the violent deed is echoed in those very words.
Brusht with the hiss of russling wings
Paradise Lost I, 768

A kind of the technique in audibility with reverberation principle which is fairly common in music is concentrated by Milton in the lines mentioned below.

…….I fled and cry'd out Death;
Hell trembled at the hideous Name, and Sigh'd
From all her Caves, and back resounded Death.
Paradise Lost II, 787-789

Milton's exceptionally talented art is seen at its best in his use of alliteration which makes his lines high sounding and harmonious to understand for which the following opening lines of Paradise Lost are the best example.

Of Man's First Disobedience, and the Fruit
Of that Forbidden Tree
Paradise Lost I, 1-2

They hand ln hand with wandering steps and slow,
Through Eden took thir solitaire way.
Paradise Lost XII, 648-649

Milton is very clear and clever enough in distributing his alliterative words where the words used with one part of speech i.e., nouns the

same word when used again but with another part of speech i.e., adjectives as can be found in the following lines.

Dire was the tossing, deep the groans, despair
Tended the sick……
Paradise Lost XI, 489-490

…….. dire was the noise
Of conflict; over head the dismal hiss
Of fiery Darts in flaming volies flow
And flying volted either Host with fire
Paradise Lost VI, 211-214

Milton makes a combination of letters of his alliteration through the timings of "linked sweetness long drawn out" in such a way that the ear is able to trace the windings of the stream of harmony from the beginning of the sentence to its ends which may found and felt in almost all descriptions in Paradise Lost which mentioned hereunder in which we can notice that the alliteration lies not only in the initial letter, but in the use of liquids, labials at regular intervals.

….and what resounds
In Fable or Romance of Uthers Son
Begirt with British Armoroc Knights:
And all who since, Baptiz'd or Infidel
Jousted in Aspromont of Montalban,
Damasco, or MorocooTribisond
Or whom Biserta sent from Afric shore
When Charlemain with all his Peerage fell
By Fontarabbia.
Paradise Lost I, 579-587

It can be observed that Milton frequently made a combination of alliteration with resonance. As there is chance for a vowel sound to be pronounced for a longer time than a consonant, they seem to be more effective in producing similarity of sound than while parallelly they interfere themselves not as much of upon the observation either of the ear or eye. We may always not be able to recognize assonance unless we search for them as found in the lines from Paradise Lost mentioned below.

Dwelt from Eternitie, Dwelt then in thee,
Bright effluence of bright essence increate.
Paradise Lost III, 5-6

Of thir great potentate; for great indeed
His name, and great high was his degree in heaven;
Paradise Lost III, 706-707

We can come across another harmonious effect is secured by presenting like sounds near the beginning and also somewhere in the middle and finally at the end of a sentence. This is undistinguishable with an arrangement recognized to be satisfactory in music where the key-note of the melody is sounded at these places which can more clearly be understood by looking at the following example words.

The letters em followed by our, powers, how, en, most, offend, our and enemy:

And reassembling our afflicted Powers
Consult how we may henceforth most offend
Our Enemy…….
Paradise Lost I, 186-188.

The modulation in music can be found in the following passage when before one series of tone is ended another series is begun. It can now be observed here how the sounds like f, b, s, w and p as alliedto b, are introduced in overlapping series. The sounds of the whole passage as a result are intermingled together so as to produce ageneral effect of unity and progress.

….. the Aire
Floats, as the pass, fann'd with unnumbered plumes:
From Branch to Branch of the Smaller Birds with song
Solac'd the Woods and Spread their painted wings
Paradise Lost VII, 431-434.

The same method of transition is used in the following quotation.It has a subtle and artistic music all its own:

Followed with acclamation and the sound

Symphonious of ten thousand Harpes that tun'd
Angelic harmonies: the Earth, the Aire
Resounded, …
Paradise Lost VII, 558-561

Lastly, the outcome of pitch inParadise Lost is apparentupon the reading of any lengthy passage. Though the following is a brief quotation that is taken for example of that kind, its important contribution should never go unnoticed.

…. Arms on Armour clashing bray'd
Horrible discord, and the madding wheeles
Of brazen chariots rag'd; . . .
Paradise Lost VI, 209-211

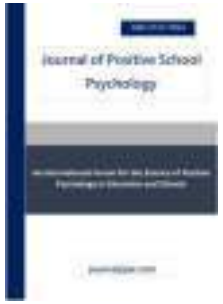
## Conclusion

After making a careful observation of Milton's poetry, it is conspicuously understood that a decent deal and a deep impact of music has been stirred up by Milton's to be used in his poetry. Despite being old, Milton's interest and tenacity was not found coming down as John Aubrey rightly said that "He had an organ in his house; He played on that most…. He would be cheerful even in his gowte-fitts, and sing." Dr. Samuel Johnson also says that after an hour's exercise from twelve to one O' clock Milton dined, "then played on the organ, and sang, or heard another sing; then studied till six."

So, this paper has made it clear that there are certain qualities in Paradise Lost that may be called musical. They are called musical because they are of the spirit of music, though they may be found secondarily in other arts. The present paper, however, has a deeper significance than this. It shows, as clearly as possible, that the influence of madrigal and metrical psalter are among the sources of Miltonic rhythm which means that music in some or the other way influenced Milton the poet. Purely based on this parameter, then, the other musical qualities noted in this paper are also, in an unsettled degree, credited to his knowledge and interest in music, the reason being that a man cannot control what he unconsciously derives. If Milton unconsciously derived certain elements from the madrigal and metrical psalter, it is judicious to say that he was undoubtedly influenced in some degree by other musical qualities.

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# PORTRAYAL OF WOMEN IN R. K. NARAYAN'S *THE DARK ROOM*

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## Abstract

The most prevalent Indian writer Rasipuram Krishna Swamy Narayan Iyer, popularly known as R.K. Narayan was born in a South Indian conservative Brahmin family in the Madras Presidency on 10th October1906. Narayan has covered the lean of human seasons from boyhood to the old age. He has depicted many varieties of characters with different ages and outlook. His characterization covers different levels of age from childhood, adolescent and age. Narayan tried to portray the real south Indian middle class society, their joys, sufferings, particularly of women. Narayan has shown his deep concern for women representing the middle class community. He has written novels in English, which is not the mother tongue of the characters. The approach is very realistic and genuine. Narayan has very light approach towards life which is resembled in many characters of his novels. With his native and fresh style of writing, Narayan has attracted the attentions of many writers like E.M. Foster, Graham Green and William Walsh. He presents his characters very natural with simple thought process which is easily understood by common readers. His characters speak in lucid English language which is easily understood by common readers. This made him easy to connect with south Indian middle class readers. They find themselves in the characters and own them. It's one of the reasons of Narayan's success.

**Keywords**: Domestic violence, tradition and culture, middle class and domination.

## Introduction

Many novels of Narayan are around middle class community, educated and semi-urban issues. Country side women are rarely depicted in his novels. Since all the novels of Narayan take place in the imaginary town "Malgudi" and it is a semi-urban locality, the people of Malgudi are also educated, cultured but innocent. As the time changes Malgudi was also updated with railway station, power facility and educational institutions. Though Narayan is very realistic writer, he did not touch the ugly side of reality. The situations are not very problematic unlike the other contemporary novelist, Mulk Raj Anand, Narayan seldom touched the social problems like domestic violence, caste system, untouchability, feudal domination, dowry system and other social inequalities. He quoted in an article that the mood of comedy, the sensitivity to atmosphere, the probing of psychological factors, are the necessary ingredients in fiction. Narayan strongly believed that life is illogical and man always tries to bring his fantasies into reality. Women of the society got adjusted to the patriarchal Hindu society and they are unaware that they are losing their rights and freedom. The family and society have tuned women that they have to accept and tolerate all their burdens, just because they are women. The male dominated society imposed them all for many years and they were not strange to them. Woman was always kept in a secondary place loosing individuality, stature and strength as shown in Hindu religious books. As the characters are

from middle class community, Narayan tries to craft middle class women out of the old fashioned, who are home makers but uneducated. Narayan also came from educated middle class family but he has broad thinking towards women. Many female characters find maximum space in many novels of Narayan.

**The Dark Room**:

The Dark Room is the third novel of Narayan. This is a special novel because it tries to up bring the domestic violence and women worries in Indian marital system. This novel was written in 1930. It deals with the contemporary social issues and challenges. The Dark Room was an inspiration by Isben's "A Dolls' House" in which the heroine comes out of the house for self-education. The concept of equality and education for women was a revolutionary concept. Savitri, the protagonist of the novel tries hard for identity and freedom. In 1930, the idea of questioning the family conditions and cultural practices was a big thing. The domination of male in the society and family was high in society. Savitri explains the situation,

"Men are impetuous. One moment they will be all in temper and the next all kindness. Men have to bear many worries and burdens, and you must overlook it if they are sometimes unreasonable."

The above lines tell us the mood and attitude of men of that age. The instability in the mind set of men how they respond due to their worries and burdens. Though men face outside problems, they enjoy certain domestic privileges. The society has given them many duties and rights also. These rights are mainly used to dominate women at home and in society. Ramani, husband of Savitri gets attracted to another woman at the office. Ramani works for the Englandia Insurance Company. Those were the days when men and woman started working out at offices. Obviously the attraction between the opposite genders takes place. According to Indian customs extra marital relationship is considered as sin. If a man and a woman want to have physical relation it must happen only after marriage. That relation was restricted only to wife and husband. The strong ethical and marital system of India taught the same to the society. When Savitri knows about the extra marital relationship of her husband with she cries,

"Do not touch me, you are dirty, you are impure.

Even if I burn my skin, I cannot cleanse myself of the impurity of your touch".

The physical relation between unmarried couple is considered to be very impure and sin. Savitri, who always bears all the pain in the silence breaks out with her husband and shouts. Savitri tries to control herself and tells him why she becomes like that. A family woman has to give birth to children and nurture them. She has to work for the house and family. She cannot follow trend and fashion. Just like a typical Indian woman, who believes that her whole life is her husband, Savitri jumps into a river. The timely arrival of Mari, a blacksmith and burglar who was crossing the river found Savitri floating on the water. Mari's wife Ponni tries to comfort her. The other choice to Savitri was to go to her parent's house and to live independently. But she doubts corning her bread and butter,

"If I take the train and go to my parents, I shall be living on my husband's earnings. What can I do myself? Unfit to earn a handful of rice except begging. If I had gone to college and studied, I might have become a teacher or something".

The above lines tell us the woman position of financial status. Due to the dependence over the husband, they are forced to survive on their husband's income. In the pre-independence India, women had no financial freedom, no right for education and marriage. RK Narayan shows the contemporary woman problems and tries to find out the traditional and modern thinking of woman. He ties to promote the status of women very consciously. It is a great achievement of RK Narayan's creative thinking that he tried to portray Indian women and then way of life without hurting or damaging the soul of Indian tradition and culture. The typical Indian woman is seen in the character Savitri, when her husband got attracted towards another woman, she tries to check herself and compares with Sanatabai in physical appearance

"What is she like?"

"I am not bad, am I"?

> "These strum pets with their power and paint!"
>
> "Has she as clear skin as mine without her paint"?

When a husband is diverted to another lady, an Indian woman feels envious because she could not manage to attract her husband as the other woman does.

Looking at the mirror Savitri says,

"Perhaps I'm not good enough for him".

"Let me admit my completion has become rather sooty, and these dark rings under the eyes".

"I am getting careless about my hair, and braid it any how".

Instead of finding fault from the husband side Savitri finds fault with herself. That's how the society has impact on the woman mind set and made her think that the problem and the root cause are taken and blamed herself. At the end of the novel, Savitri decides to give up her life to stop all these social and marital problems. But she gets a very brave idea, why can't I live and survive on my own. Instead loosing life I can live away from him and lead life. She also thinks off her children who would become orphans, if she dies. The women of 1930s, 1940s, their thinking and the women of 1980s and their thinking can be clearly observed in his novels. The first generation women were very loyal to the old social customs; they strictly followed them without any hesitation and questioning. The second generation women are educated and matured, unlike their parents and grandparents, they are assertive and modern. It was the time the western women started raising their voice for their rights too, but Narayan did not try to bring the transformation in the Indian women abruptly, it was slow and gradual within the limits. The beauty in Indian marriage system is family. When a male and female get married, they make a family. In any society, family is very important and backbone to society. For a strong society, we need strong family system which develops human and social values needed to survive in society. Family system develops relationships, affection and concern among family members. The complete responsibility shall be led by women in the family. The treatment to women characters is very assertive in his novels. We find almost all women characters as housewives and very few working with own self-image and desire for emancipation. The married women are found giving high respect to age-old traditions and practices. The typical Indian women are orthodox, submissive, docile, meek minded and follow age-old traditional, cultural and religious practices in the male dominated society.

## Conclusion:

The women characters are very realistic and very close to reality. The mindset and ideology is apt to the contemporary religious, cultural and social conditions. The impact of rich Indian culture, influence of epics, Indian philosophy and the Hindu Dharma play a vital role in the thinking behaviors and decision making. The Hindu philosophy has made lot of impact on the ideology of Indian woman and in their lifestyle. In every stage of their life the reference of Hindu religious characters are set as an example. The women are traditionally good, carried the reputation of the family and more responsible for good and bad in the society. Responsibility is the main characterization of Indian woman social outlook, following strong believes and having patience is generally made ornaments to woman. The characters of Narayan also have all the above mentioned qualities. The women of the era are found with very good tendencies . The supreme and divine qualities of love, sacrifice and courage are found in the woman characters. Women are not supposed to rise above man and lead them. The contemporary constrains of social and cultural practices are strictly followed by the women. Sufferings and struggles commonly appear in every woman's personal life and they are meant to bear with them.

Women are made responsible for all social and family circumstances. They never had the feeling that they were equivalent to men. Supremacy of man over woman is very natural and general thing. The trend got same change in the late 70s and 80s. Women have to accept life and society as it comes. R.K. Narayan's writing style and supports and represents the

same in his novels. Narayan has originally depicted the original tendencies and realistic nature of society, because the characters of Narayan are very original and natural, so they accept and respond to the situations so normally. Imagination is not permitted in his characters. Illusion and revolutionary ideology are not seen in the behaviors of the characters. In his long writing career, Narayan has presented the changes in the society and conditions of women accordingly. They behaved and responded to the contemporary conditions. Narayan never portrayed them responding contrast to the contemporary mindset. He never tried to be a reformer or improver but just presented the conditions of the women as natural as they are without addition or obliteration. Narayan's natural and genuine characterization stuns the readers and takes them to Malgudi. It would have been better if Narayan had brought some awareness or criticism on the contemporary evil practices like domestic violence, dowry system and equality through his characters. But, Narayan showcased the conditions to the readers and constrained himself as a presenter.

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# Deep reddish-orange emitting $Sr_3Gd(PO_4)_3$: $Sm^{3+}$ phosphors via modified citrate-gel combustion method

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ABSTRACT

The photoluminescence properties of different concentrations of $Sm^{3+}$ activated $Sr_3Gd(PO_4)_3$ phosphors synthesized by modified citrate gel-combustion method were investigated for white light emitting diode (w-LED) applications. The studied phosphors were characterized through powder x-ray diffraction (PXRD), Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), photoluminescence excitation, emission and lifetime studies. The PXRD profiles confirmed the body centred cubic structure of undoped and $Sm^{3+}$ -doped phosphors. The SEM studies showed the distribution and agglomeration of particles. The characteristic emission transitions such as $^4G_{5/2} \rightarrow {}^6H_{5/2}$ (~561 nm), $^4G_{5/2} \rightarrow {}^6H_{7/2}$ (~598 nm), $^4G_{5/2} \rightarrow {}^6H_{9/2}$ (~645 nm) and $^4G_{5/2} \rightarrow {}^6H_{11/2}$ (~705 nm) were noticed at their respective positions when excited at 403 nm wavelength. The highest luminescence intensity was found for 1.0 mol% of $Sm^{3+}$ doped phosphors at 403 nm excitation showing luminescence quenching and it was ascribed to dipole-dipole interaction type of energy transfer among the excited $Sm^{3+}$ ions at higher concentrations. The reddish-orange color of emitted luminescence was examined by evaluating the chromaticity coordinates. The experimental results confirm the potentiality of studied phosphors for w-LED applications.

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## 1. Introduction

In the past few years, rare earth (RE) ions activated phosphor materials play a key role in the design of light emitting diodes (LEDs) for various photonic applications due to their superior advantages compared to traditional light sources such as incandescent bulbs and fluorescent lamps. The incandescent bulbs consume more energy and the fluorescent lamps having coated with toxic materials cause harm to the mankind as well as environment [1,2]. The phosphor converted white LEDs have been the most suitable light sources in various fields owing to their reliability, long-life, low energy consumption, high fluorescence efficiency and environmental protection [3,4]. It is well known that there are two different approaches to design commercial white LEDs. In one approach, it has been fabricated combining blue emitting indium gallium nitride (InGaN) LED-chip with yellow emitting cerium activated yttrium aluminium garnet (YAG: $Ce^{3+}$). But it is not favorable for photonic applications due its low color-rendering index (CRI < 85) and high correlated color temperature (CCT ≥ 7615 K) [5,6]. Therefore, a w-LED source must have low CCT with good CRI and high color uniformity. In second approach, a near ultra violet light emitting diode (NUV-LED) chip has been combined with a tri-color (blue, green, red) phosphor [7]. Since the commercial red-emitting $Y_2O_2S$: $Eu^{3+}$ phosphor is not suggestable for photonic applications due to its fever efficiency at NUV excitation (370-410 nm) and harmful decomposition products [8], there is a need to search for new and novel red-emitting phosphors which can be effectively excited by NUV-LED chips producing intense and high efficient red-luminescence.

Among the available phosphates, the orthophosphate phosphors in the form $M_3N(PO_4)_3$, where M is di-valent cation, N is trivalent cation are more significant owing to its simple fabrication technique even at low temperatures with single phase, eco-friendly and non-toxic behavior, excellent thermal stability at high temperatures and good chemical durability [9–12]. It is well known

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that tri-valent samarium ($Sm^{3+}$) has been an essential activator to generate orange and/or reddish-orange luminescence through $^4G_{5/2} \rightarrow {}^6H_J$ ($J$ = 5/2, 7/2, 9/2, 11/2) transitions at NUV excitation [13–15]. Based on these advantageous characteristics, the $Sr_3Gd(PO_4)_3$ phosphor has been selected to investigate NUV excited luminescence properties of $Sm^{3+}$ ions for deep reddish-orange luminescence. In literature [14,15], $Sm^{3+}$ and $Sm^{3+}/Ce^{3+}$ doped $Sr_3Gd(PO_4)_3$ phosphor prepared by conventional solid state reaction method have been reported for reddish-orange emitting devices. This paper reports the modified citrate-gel combustion fabrication of $Sr_3Gd(PO_4)_3$: $Sm^{3+}$ phosphors, their structure, morphology and concentration dependent luminescence properties. The quenching in luminescence and lifetime $^4G_{5/2}$ emission state was investigated. The experimental results showed that the studied phosphors are the suitable candidates for deep reddish-orange emitting sources at NUV excitation.

## 2. Experimental techniques

### 2.1. Materials and method of synthesis

The $Sr_3Gd_{(1-x)}(PO_4)_3$:$xSm^{3+}$ phosphors, where $x$ = 0, 0.1, 0.5, 1.0 and 2.0 mol% were fabricated via modified citrate-gel combustion method using high-grade $Sr(NO_3)_2$ (99.0%), $Gd(NO_3)_3 \bullet 6H_2O$ (99.9%), $NH_4H_2PO_4$ (98%), $Sm(NO_3)_3.6H_2O$,(99.9%) and $C_6H_8O_7.H_2O$ (99.0%) as starting materials. 1.0 M solution of each were prepared by dissolving stoichiometric quantities in double-distilled water. All these solutions were mixed in drop-wise and stirred well for 30 min using a magnetic stirrer operating at 500 rpm. The metal nitrates and $C_6H_8O_7.H_2O$ (citric acid) in the ratio of 1:2wt% was taken to prepare the studied phosphors. The citric acid was used as a chelating agent to form transparent complex gel upon drying. The citric acid solution was prepared in 10 ml of double-distilled water and added in drop-wise to the compound solution with continuous stirring and then stirred further for 30 min. A light-brown colored powder was obtained after drying at 80 °C for 24 h and it was heat treated at 200 and 400 °C for 3 h in each step with intermediate grinding. Finally, the powders were sintered at 1250 °C for 5 h to produce milky-white $Sr_3Gd(PO_4)_3$:$xSm^{3+}$ ($0 \le x \le 2.0$ mol%) phosphors and they were referred as SGPSm$x$ phosphors where $x$ represents the concentration of $Sm^{3+}$ ions in mol%. A schematic diagram showing the various steps involved in modified citrate-gel combustion method is illustrated in Fig. 1.

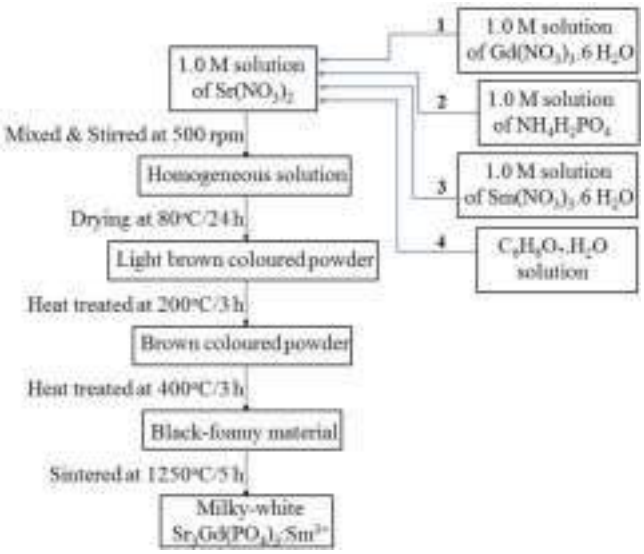



**Fig. 1.** Various steps involved in modified citrate gel-combustion method of fabrication of SGPSmx phosphors.

### 2.2. Characterization

The powder x-ray diffraction (PXRD) analysis of SGPSm$x$ ($0 \le x \le 2.0$ mol%) phosphors was carried out with a BRUCKER USA D8 advance diffractometer using 1.541 Å radiation from CuK$\alpha$ source. The KBr technique Fourier-transform infrared (FT-IR) spectral analysis was carried out with a PerkinElmer FT-IR spectrometer using a pellet made of KBr to sample ratio 300:1. The morphology was studied with FEI-Quanta FEG 200F high resolution-scanning electron microscope (HR-SEM). The photoluminescence excitation and emission studies were carried out with a FP-8300 JASCO fluorescence spectrometer provided with xenon flash lamp as a light source. The luminescence decay analysis was carried out with a FLS 1000 photoluminescence spectrometer using Xe-flash lamp in pulsed mode. All the measurements were carried out at room temperature only.

## 3. Results and discussion

### 3.1. Phase analysis

The powder X-ray diffraction (PXRD) patterns of SGPSm$x$ ($0 \le x \le 2.0$ mol%) phosphors shown in Fig. 2(a) are crystallized into body-centred cubic (BCC) crystal structure with a lattice constant of 10.11 Å ($a = b = c$; $\alpha = \beta = \gamma = 90°$) and they are good agreement with JCPDS No. 29–1301. A two-dimensional view of arrangement of $Sr_3Gd(PO_4)_3$ unit cells is shown in Fig. 3. The intensity of these PXRD patterns decreases with increase of $Sm^{3+}$ concentration with their positions remains undeviating. Taking into account the ionic radii of $Gd^{3+}$ (~0.0938 nm) and $Sm^{3+}$ (~0.0964 nm), one can suggest more probability for $Sm^{3+}$ ions to occupy the $Gd^{3+}$ sites without any modification in lattice phase. However, the variation in ionic radii introduces a negligible lattice distortion creating micro-strains that could affect the optical properties of $Sm^{3+}$ ions. The variation in intensity of a PXRD peak positioned at $2\theta$ = 27.88 ° corresponding to (310) crystal plane with increase of $Sm^{3+}$ ions concentration is illustrated in Fig. 2(b).

The average size of crystallites has been determined using Debye-Scherrer's equation, $D = 0.89\lambda/\beta.cos\theta$, where $\lambda$ denotes the wavelength of X-rays used (0.015,406 nm), $\beta$ denotes the full-width at half-maximum (in radians) and $\theta$ denotes the diffraction angle [16]. According to this equation, the value of D is found to be ~55 nm. The value of D is also calculated using Hall-Williamson's (H-W) equation, $(\frac{\beta.Cos\theta}{\lambda}) = (\frac{1}{D}) + (\frac{\varepsilon.Sin\theta}{\lambda})$, where $\varepsilon$ denotes the magnitude of micro-strains. The reciprocal of intercept of $(\beta Cos\theta/\lambda)$ vs. $(Sin\theta/\lambda)$, called H-W plot shown in Fig. 2(c) represents the average size of crystallites [17]. According to H-W, the magnitude of D is found to be ~58 nm which is in good agreement with that obtained from Debye-Scherrer method. The magnitude of microstrains ($\varepsilon$) due to lattice distortions is estimated to be ~0.00059 and it is relatively smaller than those reported for $SrEuMgAl_{10}O_{17}$ phosphor (~0.00,751 nm) [18].

### 3.2. FT-IR and SEM analysis

The FT-IR spectral profiles of undoped and 0.5 mol% $Sm^{3+}$ doped SGPSm phosphors are shown in Fig. 4. A group of IR absorption bands observed at about 1076, 1016, 999 and 949 $cm^{-1}$ have been ascribed to the asymmetric stretching vibrations of $(PO_4)^{3-}$ units [19,20]. The IR band noticed at ~685 $cm^{-1}$ corresponds to Sr–O symmetric stretching vibrations [21]. The bands positioned at about 592 and 520 $cm^{-1}$ have been related to O–P–O asymmetric bending vibrations and P–O asymmetric stretching vibrations,

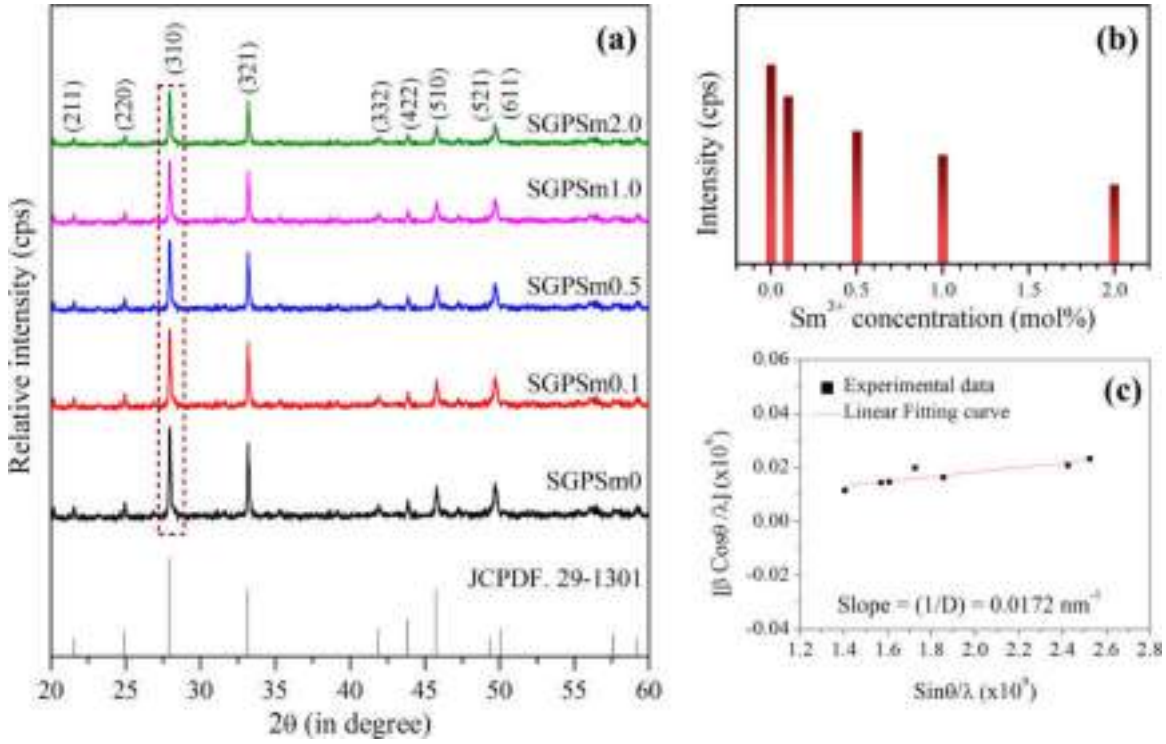



**Fig. 2.** PXRD patterns of SGPSmx phosphors (a), variation of intensity of PXRD peak ($2\theta = 27.88°$) as a function of $Sm^{3+}$ ions concentration (b) and the H-W plot of SGPSm1.0 phosphor (c).

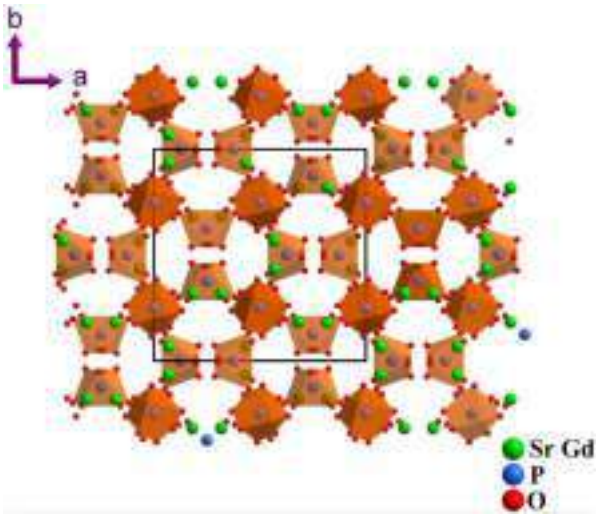



**Fig. 3.** Two-dimensional arrangement of BCC crystalline $Sr_3Gd(PO_4)_3$.

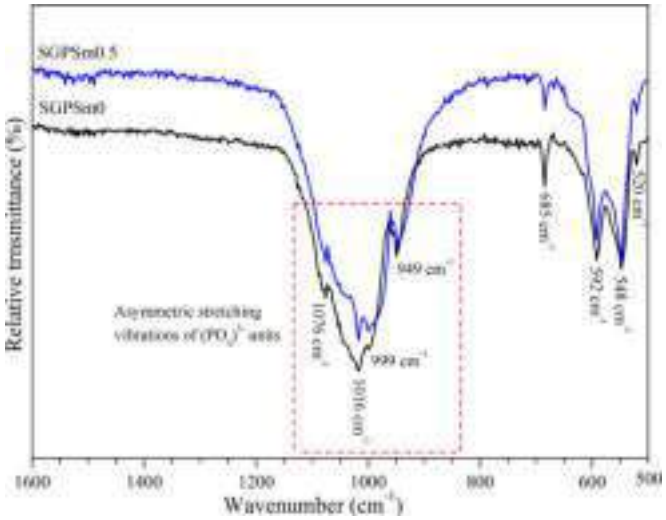



**Fig. 4.** FT-IR spectra of SGPSmx ($x = 0$ and 0.5 mol%) phosphors.

respectively [22,23]. The IR band located at ~548 $cm^{-1}$ has been assigned to Gd–O symmetric stretching vibrations [24].

The SEM analysis reveal about the surface morphology that includes the information about size, shape, orientation and distribution of particles. The HR-SEM micrograph of SGPSm1.0 phosphor is described in Fig. 5(a). This micrograph explores that the crystallized particles are agglomerated with different size and shape and oriented randomly with uneven distribution. The size of the particles has been estimated applying the ImageJ software and the corresponding histogram showing the particle size is shown in Fig. 5(b). The size of the agglomerated particles varies from 100 to 300 nm with average size of the order of 216 nm.

### 3.3. Photoluminescence analysis

The photoluminescence excitation (PLE) spectra of SGPSm*x* ($0 \leq x \leq 2.0$ mol%) phosphors in the spectral region 300-500 nm monitoring the emission at 598 nm corresponding to $^4G_{5/2} \rightarrow {}^6H_{7/2}$ transition are shown in Fig. 6. The observed transitions have been ascribed to $^6H_{5/2} \rightarrow {}^2F_{5/2}$ (302 nm), $^6H_{5/2} \rightarrow {}^4P_{5/2}$ (307 nm), $^6H_{5/2} \rightarrow {}^4P_{3/2}$ (312 nm), $^6H_{5/2} \rightarrow {}^2L_{15/2}$ (318 nm), $^6H_{5/2} \rightarrow {}^4G_{9/2}$ (333 nm), $^6H_{5/2} \rightarrow {}^4H_{9/2}$ (345 nm), $^6H_{5/2} \rightarrow {}^4D_{3/2}$ (361 nm), $^6H_{5/2} \rightarrow {}^6P_{7/2}$ (375 nm), $^6H_{5/2} \rightarrow {}^4L_{15/2}$ (391 nm), $^6H_{5/2} \rightarrow {}^4F_{7/2}$ (403 nm), $^6H_{5/2} \rightarrow {}^4L_{13/2}$ (416 nm), $^6H_{5/2} \rightarrow {}^4M_{19/2}$ (422 nm), $^6H_{5/2} \rightarrow {}^4G_{9/2}$ (438 nm), $^6H_{5/2} \rightarrow {}^4M_{17/2}$

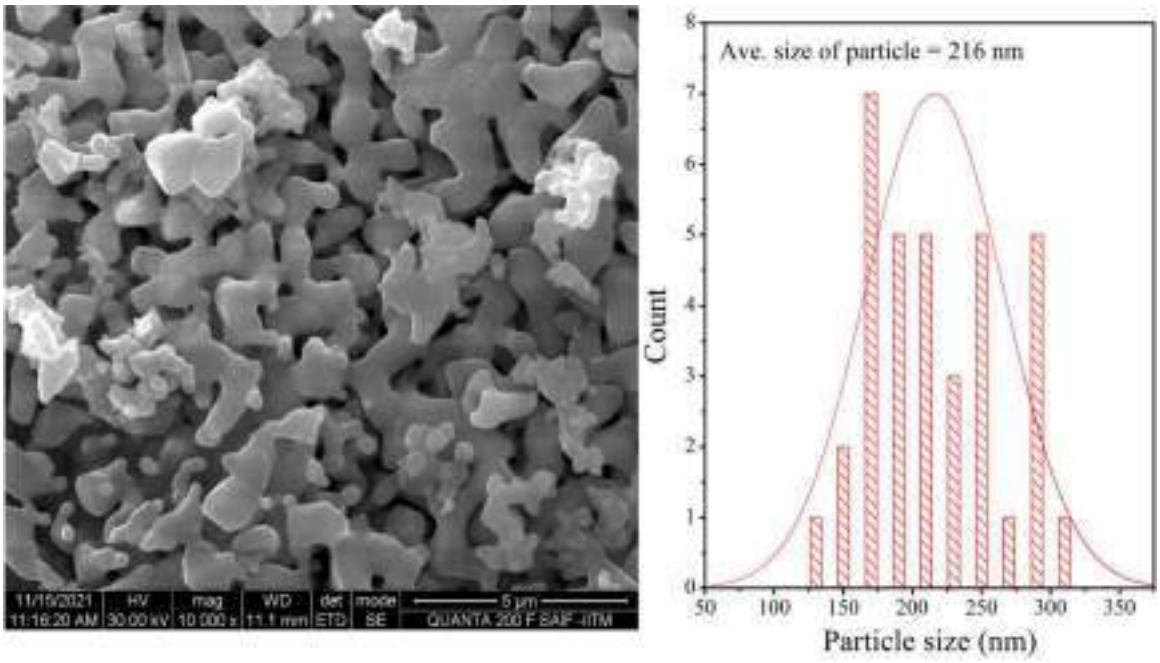



**Fig. 5.** HR-SEM micrograph of SGPSm1.0 phosphor (a) and the corresponding histogram showing the particle size distribution (b).

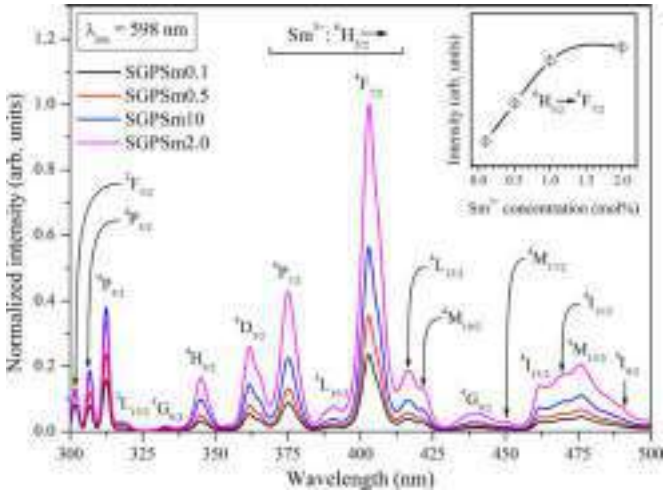



**Fig. 6.** PLE spectra of SGPSmx phosphors. Inset shows the variation of intensity of $^6H_{5/2} \rightarrow {}^4F_{7/2}$ transitions as a function of $Sm^{3+}$ concentration.

(450 nm), $^6H_{5/2} \rightarrow {}^4I_{13/2}$ (462 nm), $^6H_{5/2} \rightarrow {}^4M_{15/2}$ (476 nm) and $^6H_{5/2} \rightarrow {}^4I_{9/2}$ (490 nm) transitions [25].

Since the $Sm^{3+}$ ions exhibit intense and sharp PLE transitions in near UV region (370-410 nm), there is probability to replace the commercial red-emitting $Y_2O_2S$: $Eu^{3+}$ phosphor in designing white LEDs. As seen the PLE spectra, it is clear that the $^6H_{5/2} \rightarrow {}^4F_{7/2}$ (403 nm) transitions possess highest intensity compared to other transitions. Therefore, the SGPSm*x* phosphors can effectively excite at 403 nm wavelength to produce intense luminescence. Further, the intensity of these transitions increases with increase of concentration of $Sm^{3+}$ as illustrated in inset of Fig. 6 which indicates the intensity variation of $^6H_{5/2} \rightarrow {}^4F_{7/2}$ (403 nm) transition as a function of $Sm^{3+}$ ions concentration.

The emission spectra of SGPSm*x* ($0 \leq x \leq 2.0$ mol%) phosphors in the spectral region 500-725 nm at 403 nm excitation is shown in Fig. 7 and they are similar to those reported for $SrAl_2O_4$: $Sm^{3+}$ [13], $Sr_3Gd(PO_4)_3$: $Sm^{3+}/Ce^{3+}$ [14] and $Sr_3Gd(PO_4)_3$: $Sm^{3+}$

**Table 1**
Comparison of (ED/MD) intensity ratios in SGPSmx phosphors.

| Sample code | Intensity ratio, $I_R = (I_{ED}/I_{MD})$ | | | |
|---|---|---|---|---|
| | $(\frac{^4G_{5/2}\rightarrow{}^6H_{9/2}}{^4G_{5/2}\rightarrow{}^6H_{5/2}})$ | $(\frac{^4G_{5/2}\rightarrow{}^6H_{9/2}}{^4G_{5/2}\rightarrow{}^6H_{7/2}})$ | $(\frac{^4G_{5/2}\rightarrow{}^6H_{11/2}}{^4G_{5/2}\rightarrow{}^6H_{5/2}})$ | $(\frac{^4G_{5/2}\rightarrow{}^6H_{11/2}}{^4G_{5/2}\rightarrow{}^6H_{7/2}})$ |
| SGPSm0.1 | 0.316 | 0.82 | 0.075 | 0.029 |
| SGPSm0.5 | 0.313 | 0.998 | 0.098 | 0.031 |
| SGPSm1.0 | 0.329 | 0.972 | 0.098 | 0.03 |
| SGPSm2.0 | 0.321 | 0.974 | 0.095 | 0.092 |

[15]. These spectra reveal four characteristic emission transitions of $Sm^{3+}$ ions. The emission mechanism of $Sm^{3+}$ ions at 403 nm excitation is illustrated in a partial energy level diagram shown in Fig. 8. When excited at 403 nm wavelength, some of the $Sm^{3+}$ ions get excited to $^4L_{13/2}$ higher energy state which is more unstable according to uncertainty principle ($\Delta E.\Delta\tau \geq h/4\pi$). Immediately, these excited ions decays to $^4G_{5/2}$ metastable-energy state producing emission through $^4G_{5/2} \rightarrow {}^6H_{5/2}$ (561 nm), $^4G_{5/2} \rightarrow {}^6H_{7/2}$ (598 nm), $^4G_{5/2} \rightarrow {}^6H_{9/2}$ (645 nm) and $^4G_{5/2} \rightarrow {}^6H_{11/2}$ (705 nm) transitions.

It is well known that higher site symmetry around the RE active ions tend to enhance their emission intensity. The site symmetry of host environment around the active ions has been obtained by evaluating the intensity ratio of electric diploe (ED) to magnetic dipole (MD) transitions [$I_R = (I_{ED} + I_{MD})$]. For $I_R < 1$, the environment around the RE active ions becomes more symmetric and for $I_R > 1$, the environment becomes asymmetric [26]. According to the spectroscopic rules, the $Sm^{3+}$: $^4G_{5/2} \rightarrow {}^6H_{5/2}$, $^6H_{7/2}$ transitions belong to MD ($\Delta J = 0$ or $\Delta J = \pm 1$), while the $Sm^{3+}$: $^4G_{5/2} \rightarrow {}^6H_{9/2}$, $^6H_{11/2}$ transitions belong to ED ($\Delta J = \pm 2$ or $\Delta J \leq 6$) transitions [27]. The values of $I_R$ evaluated for various transitions found to be lesser than unity (see Table 1) showing more symmetric environment around the $Sm^{3+}$ ions in SGPSm*x* phosphors.

The Commission International de l'Eclairage (CIE-1931) coordinates evaluated from the emission spectra helps us to know the color perception of SGPSm*x* phosphors. They are found to be (0.527, 0.458), (0.576, 0.420), (0.585, 0.413) and (0.581, 0.416) for SGPSm*x* phosphors, respectively at 403 nm excitation and they are

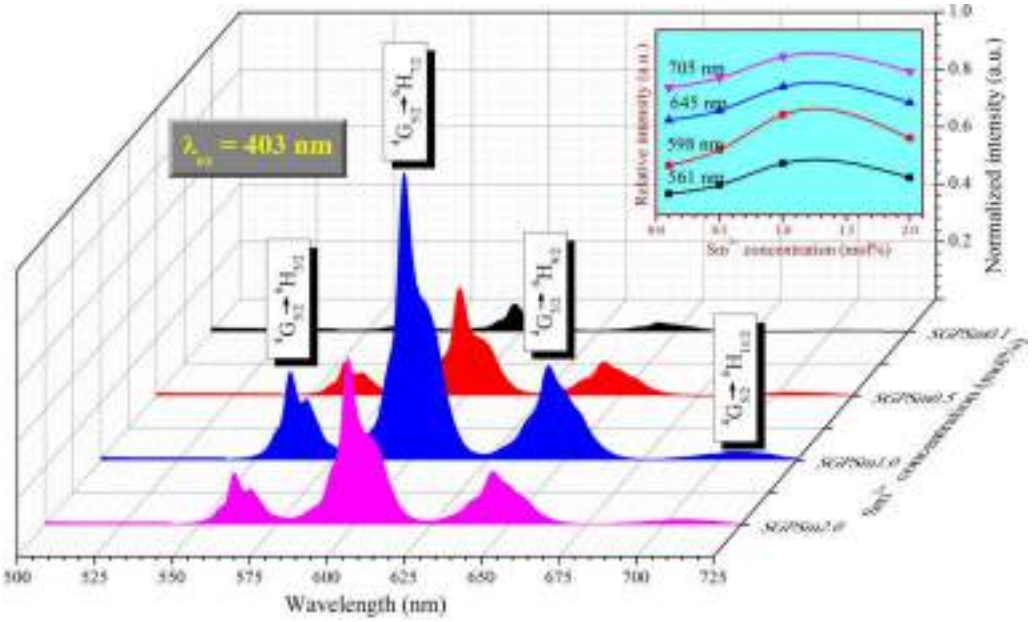



**Fig. 7.** Emission spectra of SGPSmx phosphors. Inset shows the variation of intensity of observed emission transitions as a function of $Sm^{3+}$ concentration.

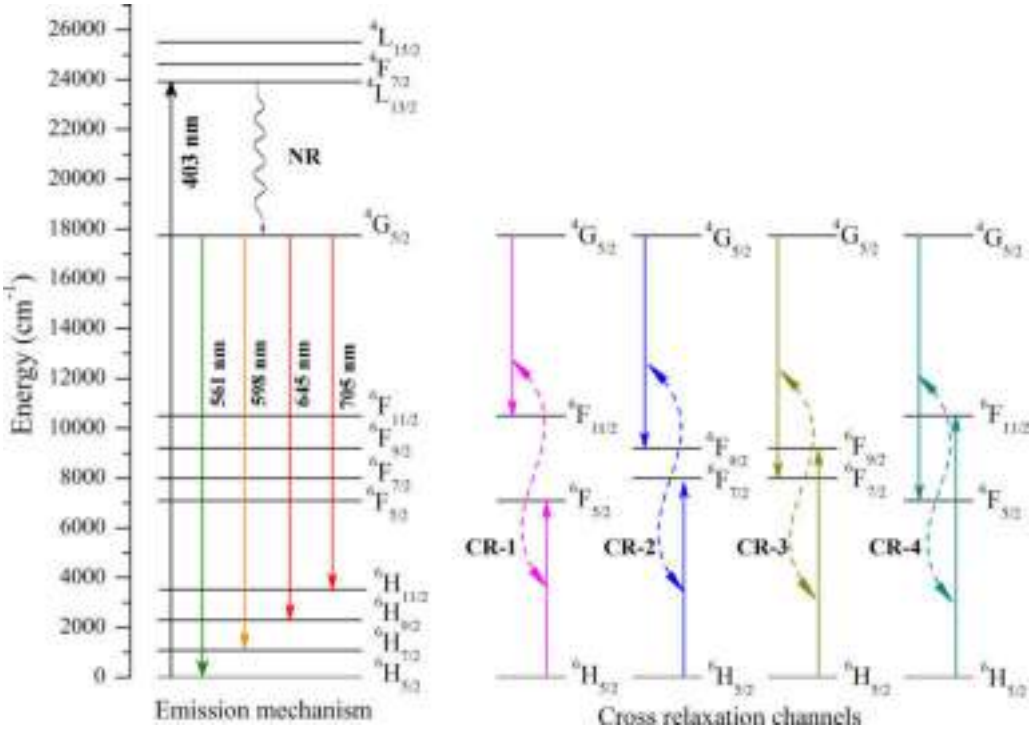



**Fig. 8.** Partial energy level diagram showing emission of SGPSmx phosphors at 403 nm and the corresponding cross-relaxation channels.

presented in a chromaticity diagram shown in Fig. 9. These results show that the color of emitted luminescence has been tuned from yellowish-orange for SGPSm0.1 to deep reddish-orange for SGPSm1.0. The CIE coordinates of SGPSm*x* ($x$ = 0.5, 1.0 and 2.0 mol%) phosphors are found very close to those reported for Amber LED NSPAR70BS commercial reddish-orange phosphor. The CIE coordinates of SGPSm*x* phosphors are also close to other phosphor materials available in literature [15,28–38]. A comparison of CIE coordinates of different phosphors activated with certain RE ions exhibiting orange and/or reddish-orange luminescence is shown in Table 2.

### 3.4. Luminescence decay

The luminescence decay curves of $Sm^{3+}$: $^4G_{5/2}$ emission state has been studied by exciting at 403 nm by monitoring the emission at 598 nm and they are presented in Fig. 10(a). For all $Sm^{3+}$ ions concentration, the behavior of these decay curves is fitted to single exponential function, $I = I_0.e^{-t/\tau}$, where $I_0$ indicates the initial intensity and $\tau$ indicates the lifetime which can be determined by taking the first e-folding times the initial intensity at $t$ = 0 s. For SGPSm*x* phosphors the lifetime is estimated to be 1.42, 1.39, 1.31 and 1.28 ms for $x$ = 0.1, 0.5, 1.0 and 2.0 mol%, respectively.

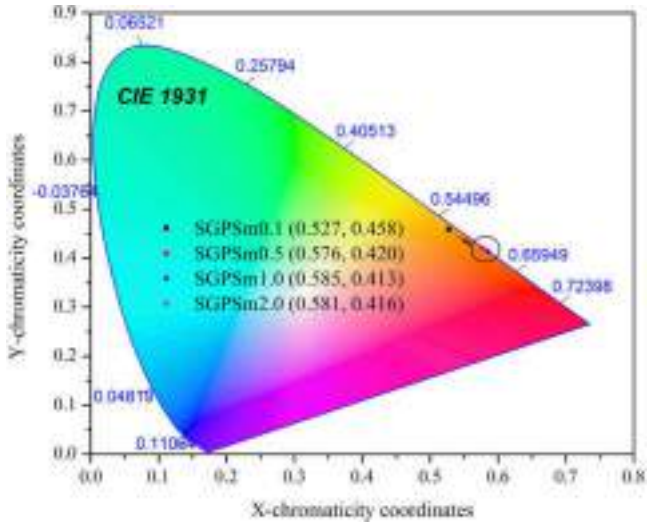



**Fig. 9.** CIE chromaticity diagram of SGPSmx phosphors excited at 403 nm radiation.

### 3.5. Quenching mechanism

As seen the emission spectra shown in Fig. 7, it is clear that the intensity of emitted luminescence increase with increase of $Sm^{3+}$ concentration reach to maximum at $x$ = 1.0 mol% and then decrease showing concentration luminescence. The inset of Fig. 7 shows the variation of intensity of different transitions with peak maximum at ~561 nm ($^4G_{5/2} \rightarrow {}^6H_{5/2}$), 598 nm ($^4G_{5/2} \rightarrow {}^6H_{7/2}$), 645 nm ($^4G_{5/2} \rightarrow {}^6H_{9/2}$) and 705 nm ($^4G_{5/2} \rightarrow {}^6H_{11/2}$) as a function of $Sm^{3+}$ concentration. Therefore, $x$ = 1.0 mol% is known as optimum or critical concentration of $Sm^{3+}$ ions showing efficient emission in SGPSm$x$ phosphors. Similarly, from the observed values of lifetime it is clear that they decrease with increase of $Sm^{3+}$ ions concentration leading to energy transfer (ET) among the excited $Sm^{3+}$ ions at higher concentrations. Fig. 10(b) represents the variation of lifetime of $Sm^{3+}$: $^4G_{5/2}$ emission state as a function of $Sm^{3+}$ ions concentration in SGPSm$x$ phosphors. The process of ET at higher concentrations has been ascribed to non-radiative transitions that occur through exchange type of interaction or multi-pole interaction or radiation reabsorption process. The exchange interaction is active for critical transfer distance between the dopant ions of the order 3-4 Å only. Beyond this, the multi-pole interaction such as dipole-dipole (d-d), dipole-quadrupole (d-q) and quadrupole-quadrupole (q-q) become active [39]. The type of interaction responsible for non-radiative energy transfer has been identified by evaluating the critical transfer distance ($R_c$) [40].

$$R_c \approx 2\left(\frac{3V}{4\pi x_c N}\right)^{1/3} \quad (1)$$

where $V$ is the volume of unit cell, $N$ is the number of available sites for the occupation of dopant ions in the unit cell and $x_c$ is the critical concentration of dopant ions. In case of SGPSm$x$ phosphors, $V$= 1034.59 Å, $x_c$= 1.0 mol% and $N$= 4 [41]. The value of $R_c$ is found to be 7.91 Å indicating multi-pole interaction is the major reason for non-radiative transfer of energy among the excited dopant ions leading to concentration quenching. According to the theory of sensitized luminescence in solids by Dexter [39], the emission intensity (I) per activator concentration ($x$) is given as

$$\left(\frac{I}{x}\right) = \frac{K}{\beta . x^{Q/3}} \; (For \beta \gg 1) \quad (2)$$

where K and $\beta$ are constants for a particular interaction mechanism under the same excitation condition in a given host matrix and Q corresponds to exchange, d-d, d-q and q-q interactions for 3, 6, 8 and 10, respectively. According to the above equation, the plot of log(I/$x$) versus log($x$) is a straight line with a slope equal to (-Q/3). For SGPSm$x$ phosphors, the slope of log(I/$x$) versus log($x$) plot shown in Fig. 10(c) is equal to 1.844 and the corresponding

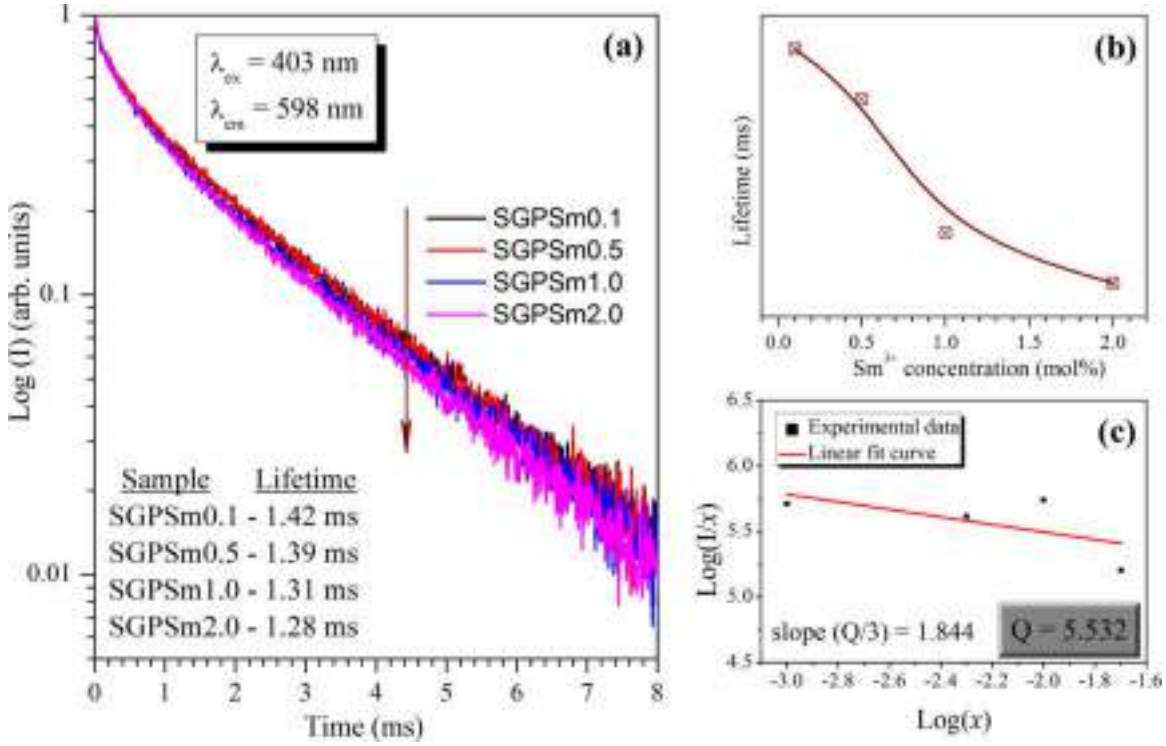



**Fig. 10.** Luminescence decay curves of $Sm^{3+}$: $^4G_{5/2}$ emission state in SGPSmx phosphors (a), variation of lifetime as a function of $Sm^{3+}$ concentration (b) and logarithmic plot of (I/$x$) vs. $x$ in SGPSmx phosphors (c).

**Table 2**
Comparison of CIE chromaticity coordinates and quantum yields ($\eta_{QE}$) in different phosphors.

| Host | $\lambda_{ex}$ (nm) | CIE coordinates | Emitted color | Reference |
|---|---|---|---|---|
| SGPSm0.1 | 403 | (0.527, 0.458) | Yellowish-orange | [This work] |
| SGPSm0.5 | 403 | (0.576, 0.420) | Reddish-orange | [This work] |
| SGPSm1.0 | 403 | (0.585, 0.413) | Deep reddish-orange | [This work] |
| SGPSm2.0 | 403 | (0.581, 0.416) | Reddish-orange | [This work] |
| Aber LED NSPAR70BS | – | (0.575, 0.425) | Reddish-orange | Nichia corporation |
| $Sr_3Gd(PO_4)_3$: $Sm^{3+}$ | 365 | (5463, 0.4481) | Reddish-orange | Yang et al. [15] |
| $NaBi(WO_4)_2$: $Sm^{3+}$ | 404 | (0.5903, 0.4023) | Reddish-orange | Krishnapriya et al. [28] |
| $BaLa_2ZnO_5$: $Sm^{3+}$ | 413 | (0.5794, 0.4198) | Reddish-orange | Sehrawat et al. [29] |
| $BaZnO_2$: $Eu^{3+}$ | 395 | (0.53, 0.40) | Yellowish-orange | Lohia et al. [30] |
| $CaAl_4O_7$: $Sm^{3+}$ | 403 | (0.5386, 0.4531) | Orange | Singh et al. [31] |
| $NaGd(MoO_4)(WO_4)$: $Sm^{3+}$ | 406 | (0.553, 0.404) | Reddish-orange | Fan et al. [32] |
| MgO: $Sm^{3+}$ | 404 | (0.583, 0.405) | Reddish-orange | Kiran et al. [33] |
| $BaNb_2O_6$: $Sm^{3+}$ | 405 | (0.557, 0.440) | Orange | Vishwakarma and Jayasimhadri [34] |
| $NaGd(WO_4)_2$: $Sm^{3+}$ | 406 | (0.554, 0.414) | Orange | Durairajan et al. [35] |
| SGSO: $Sm^{3+}$ | 404 | (0.597, 0.402) | Reddish-orange | Hussain et al. [36] |
| $Ba_3Y(PO_4)$: $Sm^{3+}$ | 403 | (0.5558, 0.4380) | Orange | Xu et al. [37] |
| $Y_2O_3$: $Eu^{3+}$/$Tb^{3+}$ | 254 | (0.54, 0.40) | Orange | Som and Sharma [38] |

value of $Q \approx 6$ which leads to d-d interaction ET among the excited $Sm^{3+}$ ions and it is possible through the cross-relaxation channels illustrated below [42] and they are illustrated in Fig. 8.

$$CR-1: \left[{}^4G_{5/2}, {}^6H_{5/2}\right] \rightarrow \left[{}^6F_{11/2}, {}^6F_{5/2}\right]$$
$$CR-2: \left[{}^4G_{5/2}, {}^6H_{5/2}\right] \rightarrow \left[{}^6F_{9/2}, {}^6F_{7/2}\right]$$
$$CR-3: \left[{}^4G_{5/2}, {}^6H_{5/2}\right] \rightarrow \left[{}^6F_{7/2}, {}^6F_{9/2}\right]$$
$$CR-4: \left[{}^4G_{5/2}, {}^6H_{5/2}\right] \rightarrow \left[{}^6F_{5/2}, {}^6F_{11/2}\right]$$

## 4. Conclusions

The SGPSm$x$ ($0 \leq x \leq 2.0$ mol%) phosphors of composition $Sr_3Gd_{(1-x)}(PO_4)_3$:$xSm^{3+}$ with BCC structure have been successfully synthesized via modified citrate-gel combustion method and it is confirmed by the PXRD studied. The studied phosphors are crystallized into 55-58 nm in size with a lattice distortion of the order ~0.00059. The FT-IR spectral analysis confirms the presence of $(PO_4)^{3-}$ units, Sr–O, Gd–O, O–P–O and P–O bonds with different vibrational modes. The HR-SEM micrograph shows the agglomerated and randomly distributed particles of different size and shape. The 403 nm wavelength corresponding to ${}^6H_{5/2} \rightarrow {}^4F_{7/2}$ transition has highest potentiality to excite the studied phosphors generating deep reddish-orange luminescence. The luminescence quenching noticed beyond $x = 1.0$ mol% has been ascribed to exchange interaction type of energy transfer among the excited $Sm^{3+}$ ions at higher concentrations. The decay profiles of ${}^4G_{5/2}$ emission state are well fitted to single exponential function supporting the d-d interaction mechanism. The reddish-orange color perception has been studied by evaluating the chromaticity coordinates. The experimental results confirm the SGPSm1.0 phosphor has highest potentiality to replace commercial red emitting phosphors in the design of phosphor-converted white LED devices.

## Data availability statement

Data will be made available on reasonable request.

## Declaration of Competing Interest

The authors declare that they have no conflict of interest.

## CRediT authorship contribution statement

**P. Shahab Khan:** Methodology, Writing – original draft. **B.C. Jamalaiah:** Conceptualization, Software, Investigation, Writing – review & editing, Supervision, Project administration. **M. Jayasimhadri:** Software, Writing – review & editing. **Harpreet Kaur:** Methodology, Investigation. **N. Madhu:** Validation, Resources. **P. Raghupathi:** Methodology, Investigation. **K. Pavani:** Data curation, Validation, Writing – review & editing.

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# Optical properties of $Sr_3Gd(PO_4)_3$: $Eu^{3+}$ phosphors for white LED sources

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ABSTRACT

The SGPEu*x* phosphors of composition $Sr_3Gd_{(1-x)}(PO_4)_3$:$xEu^{3+}$ were synthesized by modified citrate-gel combustion method for white LED sources. The optimum conditions of synthesis were obtained from thermogravimetric and differential scanning calorimetry. The synthesized phosphors were crystallized into BCC structure with JCPDS No. 29–1301. The presence of various bonds due to stretching and bending vibrations of different functional groups were studied through Fourier transform infrared spectroscopy. The morphology was examined using high-resolution scanning electron microscopy. The luminescence analysis was carried out through photoluminescence excitation and emission studies. The charge transfer band and f-f transitions of $Gd^{3+}$ and $Eu^{3+}$ ions cause a transfer of energy from $Gd^{3+}$ to $Eu^{3+}$. A suitable excitation wavelength for efficient luminescence was selected as 273 nm by studying the emission properties at different excitations. The quenching in luminescence noticed beyond 2.0 mol% was assigned to non-radiative transitions at higher $Eu^{3+}$ concentrations. The analysis of colour perception and colour temperature of emitted luminescence was studied using chromaticity coordinates evaluated from the emission spectra. The observed results suggest that the 2.0 mol% of $Eu^{3+}$ doped SGPEu phosphor has more proficiency to design new class of w-LED sources.

## 1. Introduction

Since few decades, research on light emitting diodes has become more significant owing to their fabulous properties such as high brightness, high luminescence efficiency, non-toxic nature, low-energy consumption, relatively long lifetime, stable luminous output, energy-saving and eco-friendly behaviour [1–3]. Compared to conventional incandescent and fluorescent lighting devices, the white light emitting diodes (w-LEDs) are more favourable. Commercial w-LEDs have been designed combining InGaN-LED blue-chip with YAG: $Ce^{3+}$ yellow-phosphor and it was unfavourable due to its low colour-rendering index (CRI) of the order 85 and relatively high correlated colour temperature (CCT) of the order 7615 K [4,5]. In order to fabricate a w-LED with more superior properties such as low

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CCT and high colour uniformity with good CRI, ultra violet light emitting diode (UV-LED) chip can be combined with a tri-colour (blue, green, red) phosphor [6]. Therefore, the LED-based lighting technology requires variety of novel phosphor materials with good thermal and chemical stability, strong absorption in UV or near-UV region with high conversion efficiency. Many researchers across the globe focused a light to fabricate new, novel and low energy consumption phosphor materials to meet the requirement of present technology [7–9].

Among all the available host matrices investigated, orthophosphate host with general formula $A_3M(PO_4)_3$, where A represents di-valent cation, M represents tri-valent cation, has been considered as a prominent one due to its ease of fabrication, low synthesis temperature, non-toxicity, good thermal and chemical stability and good rare earth (RE) ion solubility for solid-state lighting (SSL) applications. Depending on different A and M, many compounds such as $Ca_3Y(PO_4)_3$: $Eu^{2+}$, $Mn^{2+}$ [10], $Ba_3Lu(PO_4)_3$:$Sm^{3+}$ [11], $Sr_3La(PO_4)_3$: $Eu^{2+}$, $Mn^{2+}$ [12], $Sr_3Y(PO_4)_3$:$Eu^{3+}$ [13] and so on have been fabricated through different techniques such as conventional sloid-state method, combustion technique, sol-gel method, coprecipitation, etc. Among these orthophosphate, $Sr_3Gd(PO_4)_3$ is more promising host as it crystallizes into single-phase at relatively low temperatures and favourable to enhances the luminescence efficiency of RE ions.

Among trivalent RE ions, $Eu^{3+}$ is more significant due to its characteristics such as non-degenerate ground ($^7F_0$) and excited ($^5D_0$) energy states and simple energy-level system. It has been used as a spectroscopic probe to investigate site symmetry around it and fluorescence probe to study the surface morphology and homogeneity of any kind of host matrix [14–16]. The $Eu^{3+}$ ions are capable of producing intense luminescence through $^5D_0 \rightarrow {}^7F_{0,1,2,.6}$ transitions in many hosts however, the emission due to $^5D_{1,2} \rightarrow {}^7F_1$ transitions become insignificant [17,18]. A tunable warm-white-light emitting single component $Sr_3Gd(PO_4)_3$:$Eu^{2+}$,$Mn^{2+}$ phosphor was synthesized via conventional solid state reaction method for w-LEDs [19]. The $Ba_3La(PO_4)_3$:$Eu^{3+}$/$Tb^{3+}$ phosphors were prepared and characterized for plasma display panels and Hg-free lamps [20]. $Eu^{3+}$ -doped $BaNb_2O_6$ [21], $Na_3Gd(PO_4)_2$ [22] and $SrAl_2O_4$ [23] phosphors were reported as potential candidates to use in w-LEDs.

The present work focused a light on modified citrate-gel combustion method of synthesis of $Sr_3Gd(PO_4)_3$:$Eu^{3+}$ (SGPEu) phosphors for w-LED sources. The thermal, structural, morphological and luminescence properties were discussed. Optical analysis was carried out by exciting at various near UV wavelengths. The colour perception and CCT analysis was carried out using chromaticity co-ordinates evaluated from the emission spectra. The applicability of studied phosphors for w-LED sources was also discussed.

## 2. Experimental techniques

### 2.1. Materials and method of synthesis

The SGPEu*x* phosphors of composition $Sr_3Gd_{(1-x)}(PO_4)_3$:$xEu^{3+}$, where $x = 0$, 0.1, 0.5, 1.0, 2.0 and 5.0 mol% were synthesized following modified citrate-gel combustion method. High purity $Sr(NO_3)_2$ (99.0%, Honeywell), $Gd(NO_3)_3.6\ H_2O$ (99.9%, Sigma Aldrich), $NH_4H_2PO_4$ (98%, Alfa Aesar), $Eu(NO_3)_3{\cdot}H_2O$,( 99.9%, Sigma Aldrich) and $C_6H_8O_7{\cdot}H_2O$ (99.0%, Sigma Aldrich) were used without further purification. The stoichiometric amounts of starting materials were dissolved in double-distilled water and stirred for 30 min using a magnetic stirrer at 500 rpm to get 1.0 M homogeneous solution of each. The starting materials and citric acid ($C_6H_8O_7{\cdot}H_2O$) were taken in the ratio 1:2 wt%. The citric acid solution was prepared by dissolving stoichiometric amounts in 10 ml double-distilled water and it can act as a chelating agent to form transparent complex gel upon drying. The citric acid solution was added in drop-wise to the mixed solution and stirred for 30 min. The resultant homogeneous solution was dried at 80 °C for 24 h producing light-brown coloured powder. This powder was heat treated at 200 and 400 °C for 3 h in each step with intermediate grinding using pestle and agate motor producing black-foamy material and it was sintered at different temperatures to obtain final

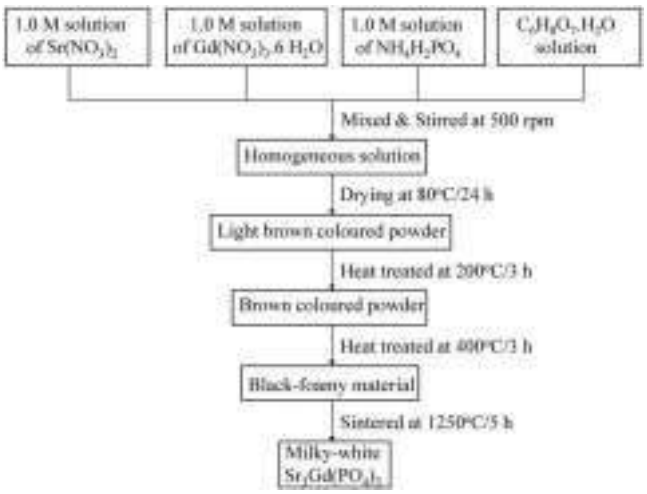



**Fig. 1.** Various steps involved in modified citrate gel-combustion method of synthesis of SGPEu*x* phosphors.

product.

The powder X-ray diffraction (PXRD) patterns of precursor sample sintered at 1250 °C for 3 h are close to the joint committee on powder diffraction standards (JCPDS) number 29–1301 with slight deviation in their positions. To optimize the duration of sintering process, the precursor powders were further sintered at 1250 °C for 5 and 7 h. The PXRD profiles obtained for a precursor powder sintered at 1250 °C for 5 h were well matched with the JCPDS No. 29–1301. The fabrication conditions for SGPEu*x* ($0 \leq x \leq 5.0$ mol%) phosphors through modified citrate-gel combustion method were optimized to be 1250 °C for 5 h. Fig. 1 represents the various steps involved in the modified citrate-gel combustion method of synthesis of SGPEu*x* phosphors. For convenience, the synthesized phosphor materials were referred as SGPEu0, SGPEu0.1, SGPEu0.5, SGPEu1.0, SGPEu2.0 and SGPEu5.0 according to $x = 0$, 0.1, 0.5, 1.0, 2.0 and 5.0 mol%, respectively.

### 2.2. Characterization

Thermal analysis of the SGPEu phosphors were carried out through thermo-gravimetry and differential scanning calorimetry (TG-DSC) using NETZSCH STA 449 F3 Thermal Analyzer in the presence of air-atmosphere at 5.0 K/min. in the temperature range 50–1400 °C using as-prepared precursor powders. The crystalline phase analysis was carried out with BRUCKER USA D8 advance diffractometer with $\lambda_{CuK\alpha} = 1.541$ Å. The Fourier-transform infrared (FT-IR) study was done with a PerkinElmer FT-IR spectrometer following KBr technique using a pellet made of KBr to sample ratio 300:1. The surface morphology was studied using FEI-Quanta FEG 200 F high resolution-scanning electron microscope (HR-SEM). The room temperature photoluminescence excitation and emission studies were carried out with FP-8300 JASCO fluorescence spectrometer and the decay studies were carried out with a Jobin YVON Fluorolog-3 spectrofluorimeter. All the measurements were carried out at room temperature only.

## 3. Results and discussions

### 3.1. Thermal analysis

To know the various reaction processes such as endothermic and exothermic reactions and respective weight loss mechanism in the process of formation of SGPEu phosphors have been investigated through TG-DSC study of precursor powder. The TG-DSC curve in the temperature ranges from 25 to 1400 °C are presented in Fig. 2. The endothermic peak noticed at ~180 °C belongs to evaporation of $NH_3$ and $H_2O$ and the corresponding weight loss is of the order of ~5.38%. An endothermic peak at ~324 °C corresponds to a weight loss of ~3.68% and it could be due to the removal of acetone and moisture. A major weight loss takes place from 324 to 900 °C with a peak maximum at ~750 °C corresponds to a weight loss of ~19.08% and it is mainly due to the release of $CO_2$ gas. The weak exothermic peak identified at ~1250 °C shows the formation of SGP phase [21,24] leading to a total weight loss of ~28.14% during the process of formation of SGP phase indicating a good amount of yield through modified citrate-gel combustion method.

### 3.2. Powder X-ray diffraction analysis

In order to confirm the phase of SGPEu phosphors, the precursor powders are heat treated for 3 h at different temperatures such as 625 °C, 750 °C, 915 °C, 1015 °C, 1115 °C, 1225 °C, 1250 °C and 1275 °C and the corresponding powder x-ray diffraction (PXRD) profiles are shown in Fig. 3**(a)**. The PXRD profiles heat treated at 1225 °C, 1250 °C and 1275 °C are found identical but deviate in intensity. From Fig. 3**(a)** one can notice that the PXRD profiles of the precursor powders heat treated at 1250 °C are found more intense than that of 1225 °C and 1275 °C. To optimize the sintering time required to get SGP phase without impurities, the precursor is heat

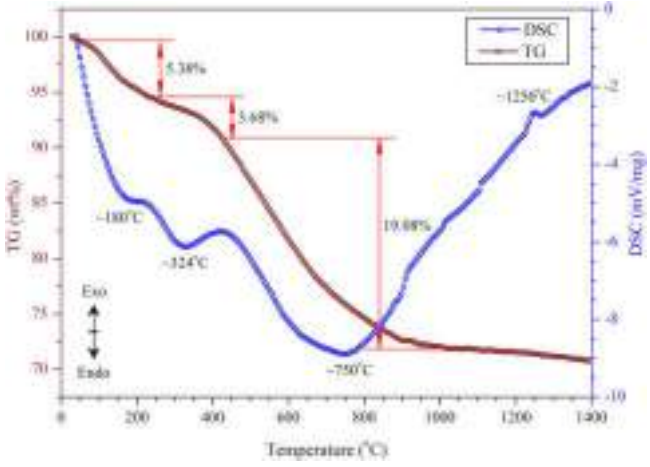



**Fig. 2.** TG-DSC curves for SGPEu0 precursor powder.

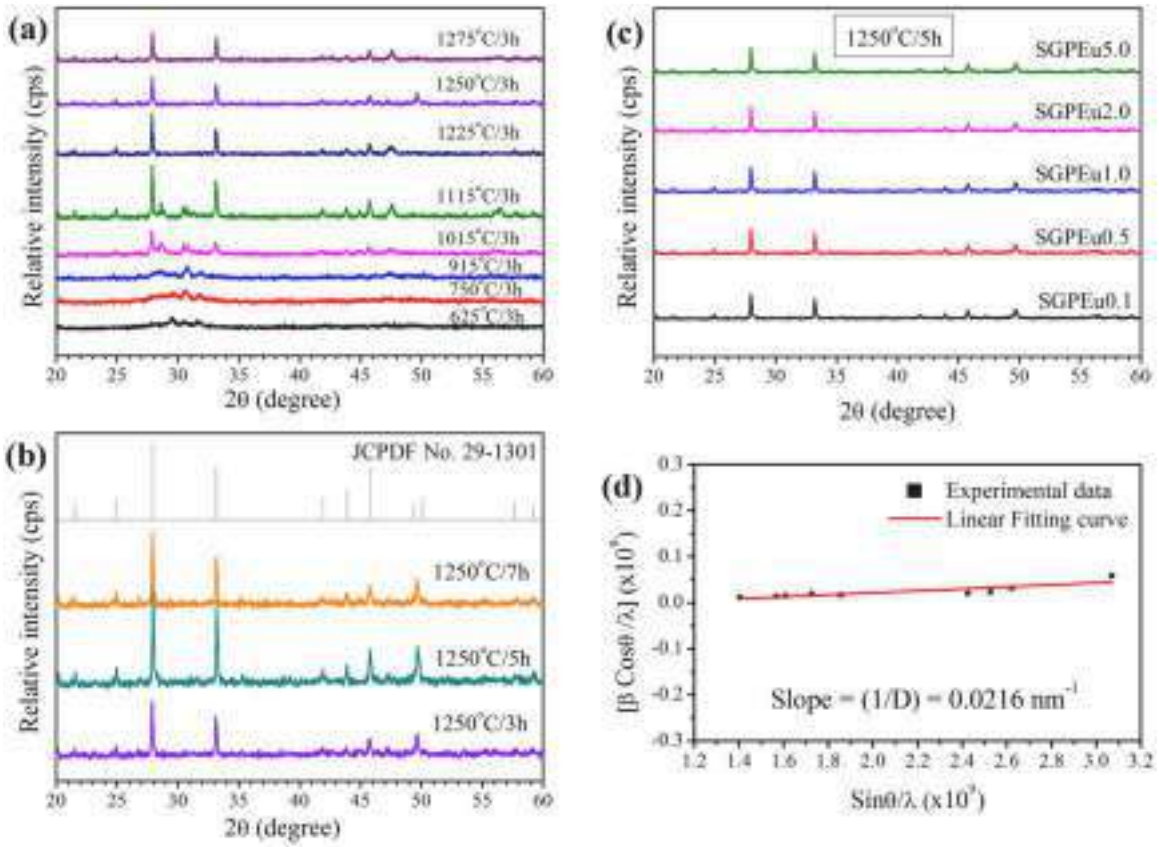



**Fig. 3.** PXRD profiles of SGPEu0 precursor heat treated at different temperatures for 3 h (a), sintered at 1250 °C for different time (b), SGPEu*x* phosphors sintered at 1250 °C/5 h (c) and the Hall-Williamson plot for SGPEu0 precursor sintered at 1250 °C/5 h (d).

treated at 1250 °C for 3, 5 and 7 h and the corresponding PXRD profiles are shown in Fig. 3**(b)**. From these results it is clear that the PXRD profiles obtained at 1250 °C for 5 h are found more intense than those obtained for 3 and 7 h. The synthesized phosphors are crystallized into a body centered cubic (BCC) structure with lattice parameters a = b = c = 10.11 Å, α = β = γ = 90° and they are well matched with JCPDS No. 29–1301. The PXRD profiles of SGPEu*x* ($0 \leq x \leq 5.0$ mol%) phosphors sintered at 1250 °C for 5 h are described in Fig. 3**(c)**.

The PXRD profiles reveal a monotonic decrease in intensity with increase of concentration of $Eu^{3+}$ indicating uniform distribution of $Eu^{3+}$ ions among the SGP crystal lattice. Taken into account the ionic radii of $Eu^{3+}$ (~0.095 nm) and $Gd^{3+}$ (~0.0938 nm) and the absence of deviation in PXRD peak position, it can be concluded that the $Eu^{3+}$ ions suitably replace the $Gd^{3+}$ sites in SGPEu phosphors. The average size of crystallites (D) has been obtained following a well-known Debye-Scherrer's equation.

$$D = \frac{0.89 \times \lambda}{\beta \times Cos\theta} \tag{1}$$

where λ indicates the wavelength of incident X-rays from CuKα source (1.5406 Å), β indicates the full-width at half-maximum (in radians) and θ indicates the angle of diffraction. The average size of crystallites is determined to be ~47 nm and it can be confirmed from the Hall-Williamson's (H-W) equation [25] shown below.

$$\left(\frac{\beta \,.\, Cos\theta}{\lambda}\right) = \left(\frac{1}{D}\right) + \left(\frac{\varepsilon \,.\, Sin\theta}{\lambda}\right) \tag{2}$$

here ε is a constant representing the magnitude of micro-strains present in the given phosphor materials. A graph drawn taking ($\beta\, Cos\theta/\lambda$) on Y-axis and ($Sin\,\theta/\lambda$) on X-axis is known as H-W curve. The reciprocal of intercept of H-W curve gives the average size of crystallites. For SGPEu phosphors, the average size of crystallites is found to be ~46 nm from the H-W curve shown in Fig. 3**(d)**. These results show that the average size of SGPEu crystallites obtained from the Debye-Scherrer method is in good agreement with that of H-W method.

The presence of defects or stress or crystal plane distortion results micro-strain ($\varepsilon$) which can affect the optical properties of doped RE active ions. According to Cullity and Stock [26], the angle of diffraction and the micro-strain are related as, $\varepsilon = (\beta . Cos\theta)/4$. Further, smaller the size of nanoparticles more will be the micro-strain. According to this equation, the micro-strain present in SGPEu

phosphors is estimated to be 0.00059 for crystallites of average size 46–47 nm. Verma et al. [27] reported the micro-strain presented in $Sr_{1-x}Eu_xMgAl_{10}O_{17}$ phosphor as ~0.00751 nm for crystallites of average size 14–20 nm. The value of micro-strain increases from 0.00059 to 0.00072 when the concentration of $Eu^{3+}$ changes from 0 to 5.0 mol%.

### 3.3. FT-IR and SEM analysis

To know the presence of various functional groups in SGPEu phosphors, the FT-IR spectrum of SGPEu0 phosphor is recorded and shown in Fig. 4. A strong IR absorption band with sub-peaks at about 1076, 1016, 999 and 949 $cm^{-1}$ has been associated with asymmetric stretching vibrations of $(PO_4)^{3-}$ units [28,29]. A narrow band centered at about 592 $cm^{-1}$ is related to the O–P–O asymmetric bending vibrations [30]. Another narrow band located at about 520 $cm^{-1}$ is assigned to the P–O asymmetric stretching vibrations [31]. The IR absorption bands noticed at about 685 and 548 $cm^{-1}$ have been related to the Sr–O and the Gd–O vibrations, respectively [32,33].

The morphology which plays a key role in optimizing the luminescence properties of a phosphor material has been studied using HR-SEM and its micrograph for SGPEu0 phosphor is shown in Fig. 5**(a)**. This micrograph explores that the crystallized particles are appear to be agglomerated with irregular morphology with an average particle size of the order of 250 nm obtained using ImageJ software. The histogram showing the particle distribution is illustrated in Fig. 5**(b)**. The PXRD investigations show that the average size of crystallites is of the order of 46–47 nm only, while the average particle size is calculated to be 250 nm from the HR-SEM micrograph confirming the agglomeration of crystallites. The agglomeration of particles leads non-radiative losses due to the multiple-scattering effect.

### 3.4. Photoluminescence excitation spectra

The optical analysis of SGPEu$x$ ($0 \leq x \leq 5.0$ mol%) phosphors has been carried out by studying the photoluminescence excitation (PLE), emission and the luminescence decay dynamics. The PLE spectra in the spectral region from 220 nm to 500 nm monitoring the emission at 612 nm corresponding to $Eu^{3+}$: $^5D_0 \rightarrow {}^7F_2$ transition is shown in Fig. 6. As seen these spectra, one can notice a broad charge transfer band (CTB) in the spectral range 220–270 nm with sub-peaks along with sharp and intense excitation bands due to $Gd^{3+}$ and $Eu^{3+}$ ions indicating the efficient energy transfer (ET) from the host to $Eu^{3+}$ ions. The CTB has been ascribed to $O^{2-} \rightarrow Eu^{3+}$ [34] and a similar kind of broad band was observed for $SrAl_2O_4$: $Eu^{3+}$ phosphors [23].

The $Gd^{3+}$ ions display $^8S_{7/2} \rightarrow {}^6D_{7/2}$ (246 nm), $^8S_{7/2} \rightarrow {}^6D_{9/2}$ (253 nm), $^8S_{7/2} \rightarrow {}^6I_{13/2}$ (273 nm), $^8S_{7/2} \rightarrow {}^6I_{17/2}$ (276 nm) and $^8S_{7/2} \rightarrow {}^6I_{7/2}$ (279 nm) transitions [35] while the $Eu^{3+}$ ions demonstrate excitation transitions originated from $^7F_0$ ground and $^7F_1$ first excited energy states. They have been assigned to $^7F_1 \rightarrow {}^5G_5$ (246 nm), $^7F_1 \rightarrow {}^5K_9$ (253 nm), $^7F_1 \rightarrow {}^5K_6$ (273 nm), $^7F_0 \rightarrow {}^5K_5$ (276 nm), $^7F_1 \rightarrow {}^5K_5$ (279 nm), $^7F_0 \rightarrow {}^5F_5$ (294 nm), $^7F_0 \rightarrow {}^5F_1$ (299 nm), $^7F_1 \rightarrow {}^5F_2$ (305 nm), $^7F_1 \rightarrow {}^3P_0$ (312 nm), $^7F_0 \rightarrow {}^5H_5$ (319 nm), $^7F_1 \rightarrow {}^5H_3$ (328 nm), $^7F_0 \rightarrow {}^5D_4$ (362 nm), $^7F_1 \rightarrow {}^5D_4$ (366 nm), $^7F_0 \rightarrow {}^5G_3$ (376 nm), $^7F_1 \rightarrow {}^5G_3$ (382 nm), $^7F_0 \rightarrow {}^5L_5$ (394 nm), $^7F_1 \rightarrow {}^5L_5$ (400 nm), $^7F_1 \rightarrow {}^5D_3$ (415 nm), $^7F_0 \rightarrow {}^5D_2$ (465 nm) and $^7F_1 \rightarrow {}^5D_2$ (470 nm) transitions [36]. Increase of $Eu^{3+}$ concentration has no impact on the intensity of $Gd^{3+}$ transitions while it considerably enhances the intensity of $Eu^{3+}$ excitation bands. The variation of intensity of $Eu^{3+}$: $^7F_0 \rightarrow {}^5L_5$ (394 nm) transitions as a function of $Eu^{3+}$ ions concentration is shown as inset of Fig. 6. Among the observed excitation bands, the $Gd^{3+}$: $^8S_{7/2} \rightarrow {}^6I_{13/2}$ (273 nm), $Eu^{3+}$: $^7F_1 \rightarrow {}^5F_2$ (305 nm), $Eu^{3+}$: $^7F_1 \rightarrow {}^3P_0$ (312 nm) and $Eu^{3+}$: $^7F_0 \rightarrow {}^5L_5$ (394 nm) transitions found significant intense and sharper.

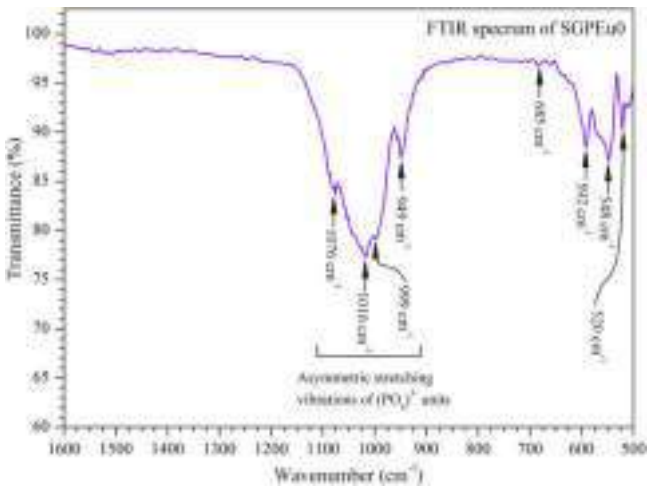



**Fig. 4.** FT-IR transmission spectrum of SGPEu0 phosphor.

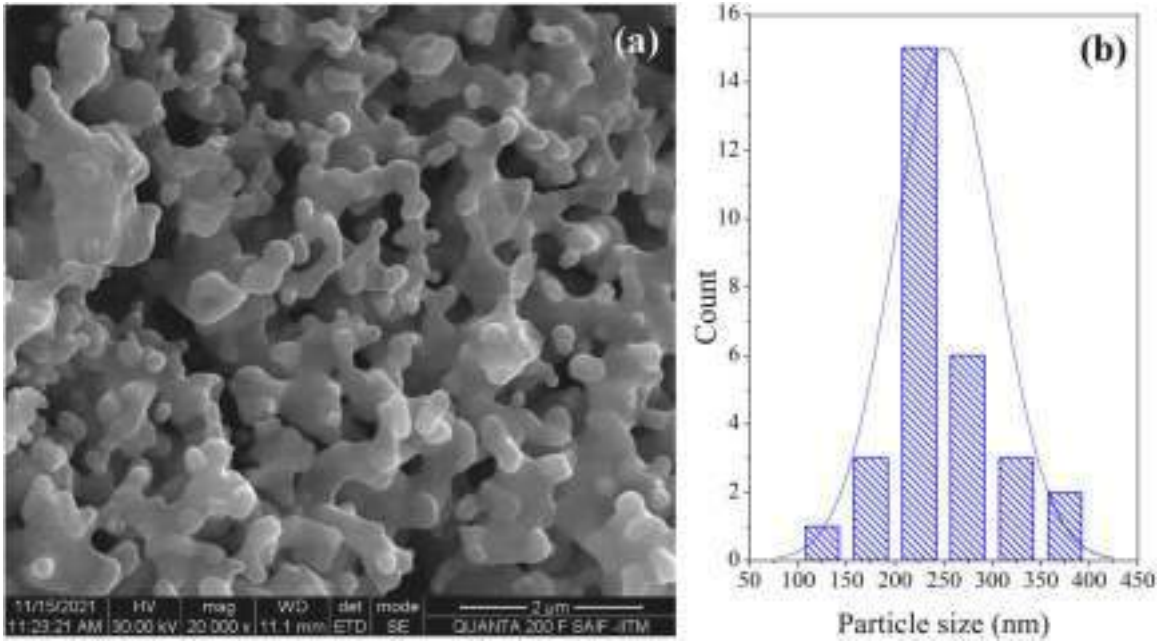



**Fig. 5.** HR-SEM micrograph of SGPEu0 phosphor (a) and particle size distribution histogram (b).

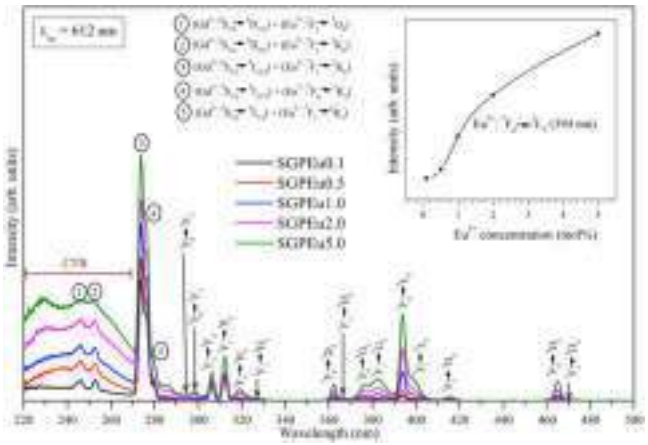



**Fig. 6.** PLE spectra of SGPEu phosphors ($\lambda_{em}$ = 612 nm).

### 3.5. Emission spectra

In order to optimize the excitation wavelength, the emission spectra of SGPEu1.0 phosphor in the spectral region from 525 to 725 nm are recorded at different excitations such as 273, 305, 312 and 394 nm. The emission spectra along with the assignment of observed emission transitions are shown in Fig. 7. These spectra reveal two groups of emission bands due to $^5D_1 \rightarrow {}^7F_J$ and $^5D_0 \rightarrow {}^7F_J$ transitions. As can see these spectra, it is clear that the intensity of emission transition obtained at 273 nm are found more potential compared to other excitations. The inset figure shows the variation of intensity of $^5D_0 \rightarrow {}^7F_2$ transition as a function of $Eu^{3+}$ ions concentration. Therefore, the excitation wavelength has been optimized to be 273 nm for efficient luminescence from SGPEu*x* phosphors.

The emission spectra of SGPEu*x* ($0 \leq x \leq 5.0$ mol%) phosphors in the spectral region from 400 to 725 nm at 273 nm excitation are described in Fig. 8. These spectra are normalized w.r.t the intensity of $^5D_0 \rightarrow {}^7F_1$ transition of SGPEu2.0 phosphor. These spectra exhibit three groups of emission bands in blue, green and yellow-to-red regions corresponding to $^5D_2 \rightarrow {}^7F_J$, $^5D_1 \rightarrow {}^7F_J$ and $^5D_0 \rightarrow {}^7F_J$ transitions. The observed emission bands have been ascribed to $^5D_2 \rightarrow {}^7F_0$ (450 nm), $^5D_2 \rightarrow {}^7F_1$ (468 nm), $^5D_2 \rightarrow {}^7F_2$ (483 nm), $^5D_1 \rightarrow {}^7F_0$ (536 nm), $^5D_1 \rightarrow {}^7F_1$ (545 nm), $^5D_0 \rightarrow {}^7F_0$ (580 nm), $^5D_0 \rightarrow {}^7F_1$ (594 nm), $^5D_0 \rightarrow {}^7F_2$ (612 nm), $^5D_0 \rightarrow {}^7F_3$ (653 nm) and $^5D_0 \rightarrow {}^7F_4$ (685 nm) transitions [35]. It is well known that the emission due to $^5D_0 \rightarrow {}^7F_{5,6}$ transitions cannot be observed as they belong to IR

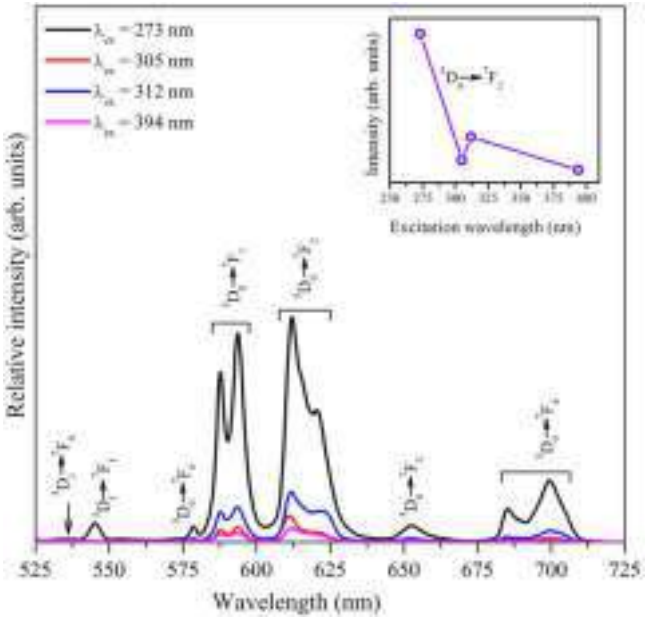



**Fig. 7.** Emission spectra of SGPEu1.0 phosphor at different excitations.

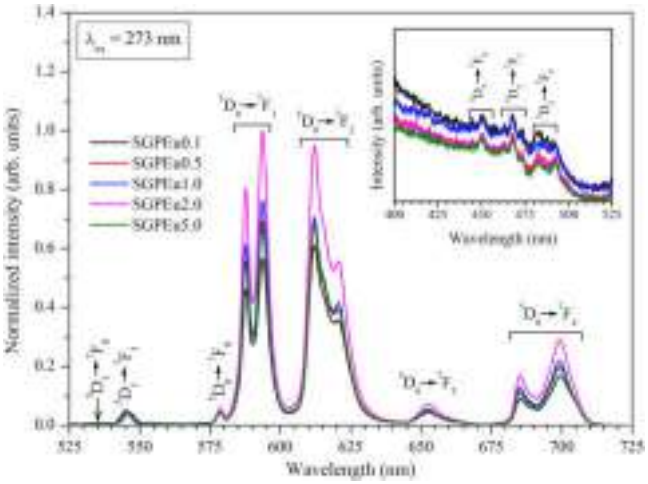



**Fig. 8.** Emission spectra of SGPEu*x* phosphors at 273 nm excitation.

region.

The emission mechanism of $Eu^{3+}$ ions in SGPEu*x* phosphors is illustrated in a partial energy level diagram shown in Fig. 9. Upon 273 nm excitation, the ground state $Gd^{3+}$ ions get excited to $^6I_J$ energy states. Since, the $Eu^{3+}$: $^5K_5$, $^5K_6$, $^5K_9$, $^5G_5$ energy states are equally positioned to that of $Gd^{3+}$: $^6I_J$, $^6D_J$ energy states, the excited $Gd^{3+}$ ions interact with ground state $Eu^{3+}$ ions and excite them to higher energy states through energy transfer (ET) process. The light photons of incident radiation corresponding to 273 nm wavelength also interact directly with some of the ground state $Eu^{3+}$ ions and get excite them to $Eu^{3+}$: $^5K_6$ higher energy state. As the $Eu^{3+}$: $^5K_6$ state is more uncertain according to the uncertainty principle ($\Delta E \,.\, \Delta\tau \geq h/4\pi$), a fast non-radiative (NR) decay happens resulting to enhance the population of $Eu^{3+}$: $^5D_{2,1,0}$ energy states leading to produce emission in blue, green and yellow-red regions.

As can see the emission spectra obtained at 273 nm excitation (see Fig. 8), it is clear that the intensity of observed emission transitions increases with increase of concentration of $Eu^{3+}$ ions reaches to maximum at $x = 2.0$ mol% and then decrease for further higher concentrations showing the concentration quenching phenomenon. The variation of intensity of $Eu^{3+}$: $^5D_0 \rightarrow {}^7F_J$ ($J = 0,1,2,3,4$) transitions as a function of $Eu^{3+}$ ions concentration is illustrated in Fig. 10**(a)**. The observed luminescence quenching has been ascribed to self-absorption and/or non-radiative (NR) energy transfer among the excited $Eu^{3+}$ ions at higher concentrations. The non-radiative energy transfer includes cross-relaxation (CR) channels and the resonant energy transfer (RET) mechanism. Some of the possible CR and RET channels are shown below and they are illustrated in Fig. 9.

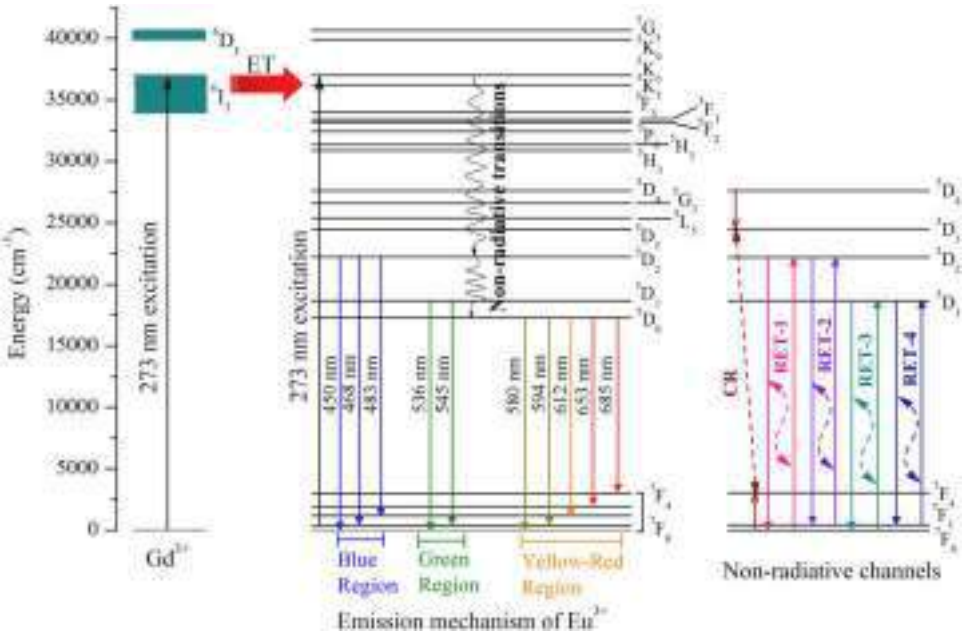



**Fig. 9.** Partial energy level diagram showing the emission mechanism of SGPEux phosphors at 273 nm excitation along with possible non-radiative channels.

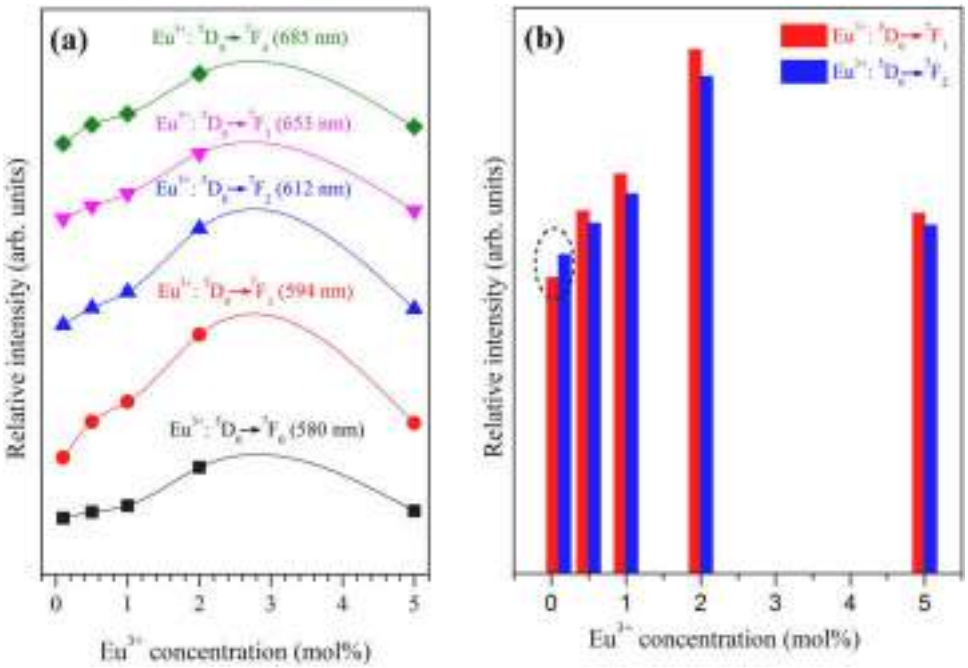



**Fig. 10.** Variation of intensity of $Eu^{3+}$: $^5D_0 \rightarrow {}^7F_{0-6}$ transitions (a) and comparison of intensity of $Eu^{3+}$: $^5D_0 \rightarrow {}^7F_1$ and $Eu^{3+}$: $^5D_0 \rightarrow {}^7F_2$ transitions (b) as a function of $Eu^{3+}$ ions concentration.

CR:[$^5D_4$, $^7F_0$] → [$^5D_3$, $^7F_4$].
RET-1:[$^5D_2$, $^7F_0$] → [$^7F_0$, $^5D_2$].
RET-2:[$^5D_2$, $^7F_1$] → [$^7F_1$, $^5D_2$].
RET-3:[$^5D_1$, $^7F_0$] → [$^7F_0$, $^5D_1$].
RET-4:[$^5D_1$, $^7F_1$] → [$^7F_1$, $^5D_1$].
The $Eu^{3+}$: $^5D_0 \rightarrow {}^7F_1$ and $Eu^{3+}$: $^5D_0 \rightarrow {}^7F_2$ transitions exhibit magnetic and electric dipole behaviour according to the spectroscopic

selection rules $\Delta J = 1$ and $\Delta J = 2$, respectively [37]. These transitions have been used as a spectroscopic probe to study the local site-symmetry of any host matrix around the $Eu^{3+}$ ions. The intensity ratio of observed electric and magnetic dipole transitions ($I_R$) provides the information regarding the local site-symmetry and it can be obtained using the integrated intensities of $Eu^{3+}$: $^5D_0 \rightarrow {}^7F_2$ and $Eu^{3+}$: $^5D_0 \rightarrow {}^7F_1$ transitions. When the site symmetry around $Eu^{3+}$ ions is asymmetric, then the intensity of $Eu^{3+}$: $^5D_0 \rightarrow {}^7F_2$ transition predominates the intensity of $Eu^{3+}$: $^5D_0 \rightarrow {}^7F_1$ transition and the corresponding intensity ratio become higher than unity and vice-versa. The values of $I_R$ for SGPEu1.0 phosphor under different excitations and for different doping levels at 273 nm excitation are summarized in Table 1.

When the SGPEu1.0 phosphor is excited at different wavelengths, the intensity ratio is found to be less than unity showing higher symmetric environment around the $Eu^{3+}$ ions in SGPEu1.0 phosphor. In order to confirm the site-symmetry of SGPEu*x* host environment at different doping levels, they are excited at 273 nm. The value of $I_R$ is found to be 1.08 for SGPEu0.1 phosphor showing asymmetric environment and the intensity of $Eu^{3+}$: $^5D_0 \rightarrow {}^7F_2$ transition is found higher than the intensity of $Eu^{3+}$: $^5D_0 \rightarrow {}^7F_1$ transition. Fig. 10**(b)** illustrates the comparison of intensity of $Eu^{3+}$: $^5D_0 \rightarrow {}^7F_1$ and $Eu^{3+}$: $^5D_0 \rightarrow {}^7F_2$ transitions as a function of $Eu^{3+}$ ions concentration. For other doping concentrations ($x = 0.5$, 1.0, 2.0 and 5.0 mol%), the value of $I_R$ is found to be less than unity and the intensity of $Eu^{3+}$: $^5D_0 \rightarrow {}^7F_1$ transition predominates the intensity of $Eu^{3+}$: $^5D_0 \rightarrow {}^7F_2$ transition. These results confirm that at higher concentrations ($x \geq 0.5$ mol%) there is symmetric environment around the $Eu^{3+}$ ions owing to increased micro-strain which tend to distribute $Eu^{3+}$ ions uniformly in SGPEu lattice.

### 3.6. Colour perception and colour temperature

The colour perception of emitted luminescence has been investigated by evaluating the Commission International de I'Eclairage (CIE-1931) chromaticity coordinates (x, y). The human-eye can recognize the visible light through three different cone cells like short, middle and long spectral regions corresponding to blue (420–440 nm), green (530–540 nm) and red (560–580 nm) regions, respectively. The tri-stimulus parameters X, Y and Z related to these cone cells illustrate the colour perception. Wright [38] and Guild [39] proposed a simple way to evaluate X, Y and Z tri-stimulus parameters using the following equations.

$$X = \int_0^\infty I_{(\lambda)} \,.\, T_{(\lambda)} \,.\, \bar{x}_{(\lambda)} \,.\, d\lambda \tag{3}$$

$$Y = \int_0^\infty I_{(\lambda)} \,.\, T_{(\lambda)} \,.\, \bar{y}_{(\lambda)} \,.\, d\lambda \tag{4}$$

$$Z = \int_0^\infty I_{(\lambda)} \,.\, T_{(\lambda)} \,.\, \bar{z}_{(\lambda)} \,.\, d\lambda \tag{5}$$

where $I_{(\lambda)}$ and $T_{(\lambda)}$ indicates the intensity of illuminant spectrum and the transmission spectrum of the filter ($0 \leq T \leq 1$), respectively. The functions $\bar{x}(\lambda)$, $\bar{y}(\lambda)$ and $\bar{z}(\lambda)$are known as the CIE colour matching functions. The colour of emitted luminescence can be specified in a chromaticity diagram using two colour coordinates (x, y) which can be obtained from the following equations.

$$x = \frac{X}{X + Y + Z} \tag{6}$$

$$y = \frac{Y}{X + Y + Z} \tag{7}$$

The CIE colour coordinates of SGPEu*x* phosphors excited at 273 nm have been evaluated following the above said procedure and they are summarized in Table 2. All these coordinates are close to the standard CIE white illuminant coordinates (0.333, 0.333) and they are well located in the white region of CIE diagram shown in Fig. 11. These coordinates are found close to the standard daylight illuminant-D50, cool white fluorescent illuminant-F2, broad fluorescent illuminant-F8 and daylight simulator-B [40,41]. They are also close to those reported for $SrAl_2O_4$:1.0 $Eu^{3+}$ [23], $BaMg_2V_2O_8$:0.01 $Eu^{3+}$ [42], $Ca_2Gd_8(SiO_4)_6O_2$: $Dy^{3+}$ [43] and $YAl_3(BO_3)_4$: 2.0% $Eu^{3+}$/ 0.5%$Tb^{3+}$ [44] phosphors.

The correlated colour temperature (CCT) expressed in the Kelvin units is a measure of appearance of colour of light emitted from a

**Table 1**
Comparison of intensity ratios of SGPEu1.0 phosphor at different excitations and the SGPEu*x* ($0 \leq x \leq 5.0$ mol%) phosphors at 273 nm excitation.

| SGPEu1.0 different excitations | | At 273 nm excitation | |
|---|---|---|---|
| $\lambda_{ex}$ (nm) | $I_R$ | Doping (mol%) | $I_R$ |
| 273 | 0.95 | $x = 0.1$ | 1.08 |
| 305 | 0.97 | $x = 0.5$ | 0.97 |
| 312 | 0.92 | $x = 1.0$ | 0.95 |
| 394 | 0.94 | $x = 2.0$ | 0.94 |
| | | $x = 5.0$ | 0.92 |

**Table 2**
Comparison of chromaticity coordinates (x, y) of different phosphors.

| Sample code | CIE coordinates | CCT (K) | Reference |
|---|---|---|---|
| SGPEu0.1 | (0.349, 0.335) | 4785 | [This work] |
| SGPEu0.5 | (0.351, 0.335) | 4713 | [This work] |
| SGPEu1.0 | (0.352, 0.335) | 4677 | [This work] |
| SGPEu2.0 | (0.358, 0.336) | 4435 | [This work] |
| SGPEu5.0 | (0.351, 0.335) | 4701 | [This work] |
| Illuminant-D50 (Daylight) | (0.345, 0.358) | 5003 | [40] |
| Illuminant-F2 (Cool white fluorescent) | (0.372, 0.375) | 4230 | [40] |
| Illuminant-F8 (Broadband fluorescent) | (0.345, 0.358) | 5000 | [41] |
| Daylight simulator-B | (0.348, 0.351) | 4874 | [41] |
| $SrAl_2O_4$:1.0 $Eu^{3+}$ | (0.343, 0.238) | – | [23] |
| $BaMg_2V_2O_8$:0.01 $Eu^{3+}$ | (0.363, 0.386) | – | [42] |
| $Ca_2Gd_8(SiO_4)_6O_2$: $Dy^{3+}$ | (0.353, 0.382) | – | [43] |
| $YAl_3(BO_3)_4$: 2.0%$Eu^{3+}$/ 0.5%$Tb^{3+}$ | (0.365, 0.336) | – | [44] |

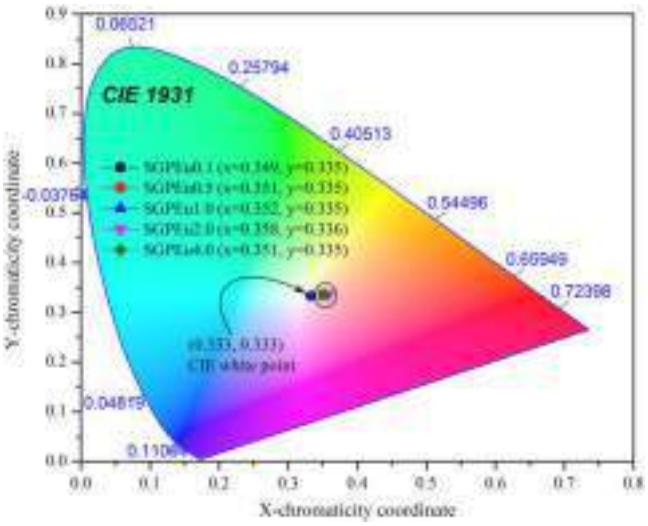



**Fig. 11.** CIE chromaticity diagram of SGPEu*x* phosphors at 273 nm excitation.

source of light. Commonly, the CCT of a light source found between 2700 K and 6500 K and it is independent of its temperature. Light source with CCT rating 2700–3000 K appear as warm-white, 3000–4000 K appear as neutral-white and 4000–6500 K appear as cool-white. So higher the Kelvin rating, the cooler the light source will appear. Generally, warm-white light is more significant for the relaxation of eyes and softening the skin-tone by reducing imperfections. Therefore, warm-white light sources have been used in bedrooms, dining rooms and gardens. The cool-white light has been used for better brightness and it has been used in lounges and living rooms. The neutral-white light sources reproduce all colours equally and they have been used to illuminate the objects in art gallery and photography [45].

McCamy [46] evaluated the CCT values of light sources using the equation, $CCT = -449\,z^3 + 3525\,z^2 - 6823.3\,z + 5520.33$. The constant $z = (x - x_e)/(y - y_e)$, where ($x_e = 0.3320$, $y_e = 0.1858$) represents the coordinates of epicenter point and ($x$, $y$) represents the CIE coordinates of light source. Upon 273 nm excitation, the CCT values of SGPEu*x* phosphors are found close to the standard daylight illuminant-D50, cool white fluorescent illuminant-F2, broad fluorescent illuminant-F8 and daylight simulator-B [40, 41]. The evaluated CCT values confirm that the studied phosphors could be the best choice to replace the cool-white light sources. A comparison of CCT values of various light sources is also given in Table 2. It is well known that the phosphor coatings on lighting devices enhances their working efficiency by reducing their surface temperature [47–50]. Based on the experimental results it can be suggested that the SGPEu2.0 phosphor can have more proficiency to be used to design a novel and new class of w-LED sources with relatively good working efficiency.

### 3.7. $Eu^{3+}$: $^5D_0$ decay dynamics

To confirm the presence of NR transitions at higher $Eu^{3+}$ ions concentration, the luminescence decay dynamics of the $Eu^{3+}$: $^5D_0$ emission state has been studied monitoring the emission and excitation wavelengths at 612 and 273 nm, respectively and they are presented in Fig. 12**(a)**. The decay curves of SGPEu*x* ($x = 0.1$, 0.5, 1.0 and 2.0 mol%) phosphors have been well fitted to a single

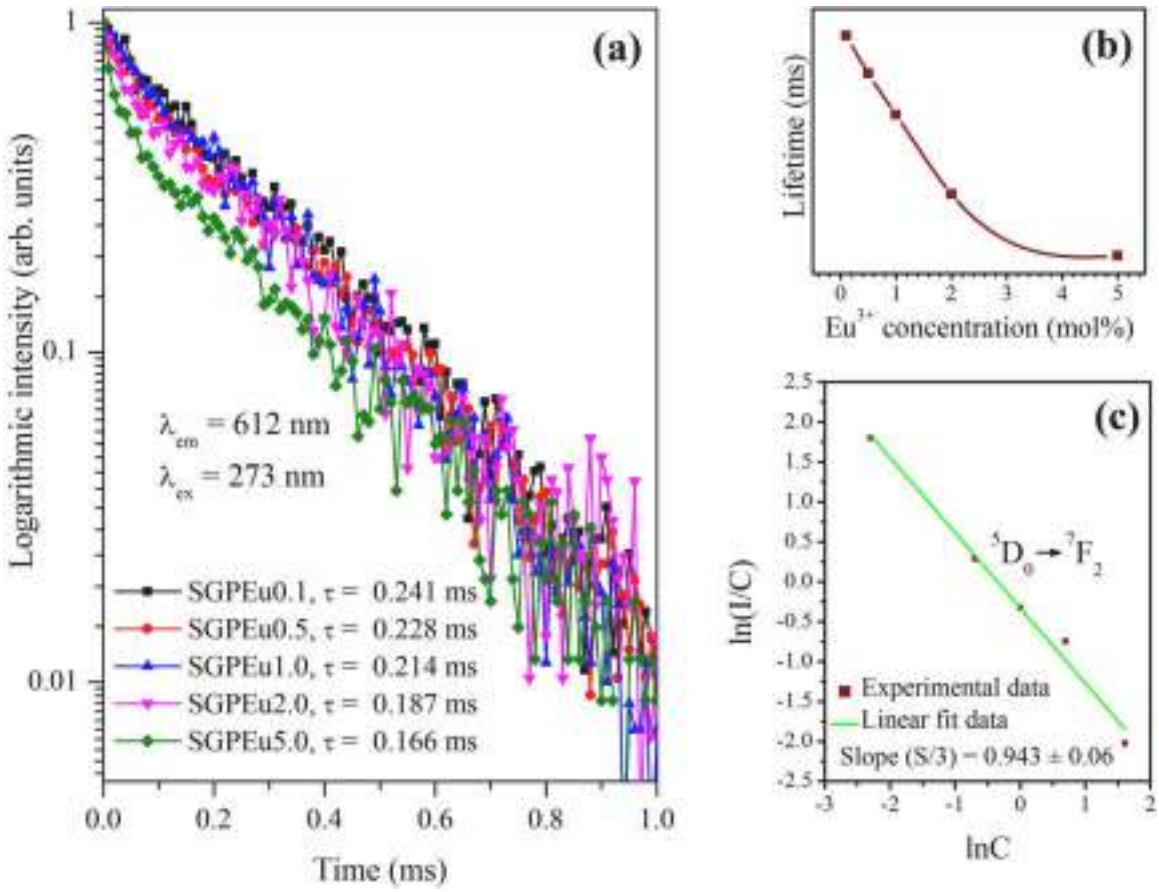



**Fig. 12.** Logarithmic plot of decay profile of $Eu^{3+}$: $^5D_0$ emission state (a) and the variation of lifetime as a function of $Eu^{3+}$ concentration (b). The ln (I/C) vs. ln C plots for $^5D_0 \rightarrow {}^7F_2$ (612 nm) transition in SGPEu*x* phosphors.

exponential function, $I = I_0.e^{-t/\tau}$, where $I_0$ is the initial luminescence intensity at t = 0 s and τ is the lifetime of the emission state. The lifetime values have been obtained taking the first e-folding time the initial intensity at t = o seconds and they are found to be 0.241, 0.228, 0.214 and 0.187 ms for *x* = 0.1, 0.5, 1.0 and 2.0 mol% doped SGPEu*x* phosphors, respectively. The decay curve of SGPEu5.0 phosphor is fitted to $I = [A_1.\exp(-t/\tau_1) + A_1.\exp(-t/\tau_1)]$, where $\tau_1$ and $\tau_2$ represents the lifetimes of slow and fast decay, respectively. The average lifetime has been calculated as 0.166 ms using the relation, $\langle\tau\rangle = \frac{A_1\tau_1^2 + A_2\tau_2^2}{A_1\tau_1 + A_2\tau_2}$. The observed values of lifetime decrease with increase of $Eu^{3+}$ ions concentration indicating the energy transfer among the excited $Eu^{3+}$ ions at higher concentrations. The variation of lifetime of $Eu^{3+}$: $^5D_0$ emission state as a function of $Eu^{3+}$ concentration is shown in Fig. 12**(b)**.

To know the reasons behind the quenching of luminescence and the gradual decrease of lifetime with the addition of $Eu^{3+}$ ions has been assigned to ET process among the excited ions. According to Blasse [51], the exchange and/or multi-polar interaction mechanisms like dipole-dipole (d-d), dipole-quadrupole (d-q) and quadrupole-quadrupole (q-q) are responsible for ET process among the excited active ions. According to Dexter [52], the exchange interaction mechanism plays a key role in the critical transfer distance ($R_c$) range 3–4 Å only. Beyond this limit, the multi-polar interaction mechanisms predominate. The value of $R_c$ has been evaluated using the following equation.

$$R_c = 2\left(\frac{3\,V}{4\,\pi\,x_c\,N}\right)^{1/3} \tag{8}$$

where *V*, $x_c$ and *N* indicates the unit cell volume, critical concentration and number of crystallographic-sites available to replace the active ions. In case of SGPEu*x* phosphors, the *V*, $x_c$ and *N* values are 1034.59 Å, 2.0 mol% and 4, respectively [53]. The evaluated value of $R_c$ is estimated to be ~29 Å for SGPEu*x* phosphors indicates that the multi-polar interaction mechanisms play a key role in ET process. The type (i.e., d-d, d-q, q-q) of interaction mechanism has been identified following Van Uitert [54] equation.

$$\ln\left(\frac{I}{C}\right) = K - \left(\frac{S}{3}\right).\ln(C) \tag{9}$$

where I stand for intensity of emission transition and C stands for concentration of active ions. Here K is a constant related to a particular excitation and (S/3) indicates the slope of $\ln\left(\frac{I}{C}\right)$ versus $\ln(C)$ plot and it is shown in Fig. 12**(c)**. The parameter S can have values 3, 6, 8 and 10 corresponding to exchange, d-d, d-q and q-q interactions, respectively. From the evaluated value of slope 0.943 $\pm$ 0.06, the parameter S is nearly equal to 3 indicating exchange interaction type of ET among the excited $Eu^{3+}$ ions at higher concentrations.

## 4. Conclusions

A series of different concentrations of $Eu^{3+}$ ions doped SGPEu*x* ($0 \leq x \leq 5.0$ mol%) phosphors have been synthesized by modified citrate-gel combustion method for w-LED sources. The PXRD studies show that the SGPEu phosphors are crystallized into BCC structure with JCPDS No. 29–1301 and the average size of crystallites has been estimated to be 46–47 nm. The HR-SEM micrograph illustrates the agglomeration of crystallites with irregular morphology with an average particle size of ~250 nm. A suitable excitation wavelength for efficient luminescence has been selected as 273 nm corresponding to $Gd^{3+}$: $^8S_{7/2} \rightarrow {}^6I_{13/2}$ + $Eu^{3+}$: $^7F_1 \rightarrow {}^5K_6$ transitions by studying the emission at different excitations. The quenching in luminescence is observed beyond 2.0 mol% and it can be assigned to non-radiative losses among the excited $Eu^{3+}$ ions. Upon 273 nm excitation, the SGPEu*x* phosphors emit cool-white light with CCT rating 4785–4758 K. Based on the experimental results, it is suggested that the SGPEu2.0 phosphor is the best choice to be used to design new w-LED sources.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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# Optical analysis of $Pr^{3+}$-doped $Li_6AlGd(BO_3)_4$ phosphors for white LEDs

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## ABSTRACT

A series of LAGBPr phosphors of composition $Li_6AlGd_{(1-x)}(BO_3)_4$: $x$ $Pr^{3+}$ ($0 \leq x \leq 2.0$ mol%) were prepared by solid-state reaction method and characterized through thermal, structural, morphological and photoluminescence studies. Thermal investigation shows that the LAGBPr phosphors crystallize at 640 °C. The powder X-ray diffraction studies show that the size of crystallites is of the order of 77 nm. The excitation spectra reveal a charge transfer band due to $O^{2-} \rightarrow Pr^{3+}$ (230–250 nm), host-related ($Gd^{3+}$) bands from 205 to 315 nm and some f-f transitions of $Pr^{3+}$ ions from 420 to 500 nm. The fluorescence properties were investigated by exciting within the host and within dopant ($Pr^{3+}$) ions. A tunable fluorescence from orange-red to white to bluish-white was observed when excited at 274 nm and a bluish-white fluorescence at 449 nm excitation. Upon 449 nm excitation, a blue-shift is observed with increase of concentration of $Pr^{3+}$ ions. The optimal concentration of $Pr^{3+}$ ions for efficient fluorescence is confirmed to be 1.0 mol%, and a quenching in fluorescence was noticed and it was ascribed to the non-radiative transfer of energy through $[^3P_0, {}^3H_4] \rightarrow [^1D_2, {}^3H_6]$, $[^3P_0, {}^3H_4] \rightarrow [^3H_6, {}^1D_2]$ and $[^1D_2, {}^3H_4] \rightarrow [^3H_4, {}^1D_2]$ channels. The LAGBPr1.0 phosphor has more proficiency to be used in LED applications.

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## 1 Introduction

Currently, the fast-growing phosphor technology focussed a light on new and novel phosphor materials with enhanced physical, thermal, chemical and optical properties to fulfil the needs in solid-state lighting technology (SSLT) which can reduce the utilization of energy to generate light compared to conventional incandescent lamps [1–3]. Using light emitting diodes (LEDs), the white light generation is possible in two different approaches, combining blue LED with commercial red and green phosphors or with yellow phosphor. The operating temperature imposes limitations for fluorescence efficiency and colour rendering index of these commercial phosphors. The white light generation is possible by rectifying these limitations combining tri-colour phosphor with UV-LED-chip [4–6]. Thus, LEDs play a crucial role in SSLT due to their long life, thermal stability, low energy-consumption and echo-friendly nature [7–11]. The phosphor-converted light emitting diodes (PCLEDs) with relatively high quantum yield are necessary in designing advanced SSL devices. However, the working efficiency of PCLEDs has been affected by the emitted fluorescence properties of phosphor materials used to fabricate them and there must be a special interest for the design and development of new and highly efficient phosphor materials.

From the literature [12–15], it is known that the compounds with aluminate group and borate group have potential applications as non-linear optical materials owing to their excellent absorption in vacuum ultra violet (VUV) region, chemical durability, bright emission in visible region and tunability in fluorescence properties of rare earth (RE) ions. Further, borate-based phosphors have good thermal stability and require low temperatures for their fabrication. The incorporation of gadolinium and lithium to aluminate-based phosphors favours in enhancing the fluorescence properties of REs by reducing non-radiative centres [16–18]. The merits of borate group, aluminate, gadolinium and lithium in improving the strength of optical transitions of RE active ions and to design a new and novel host matrix for phosphor-converted white LEDs, the $Li_6AlGd(BO_3)_4$ phosphor host has been selected. The thermal, structural and morphological studies impose for better luminescence properties of RE active ions. M.M. Yawalkar et al. [19] investigated the photoluminescence and thermoluminescence properties of $Eu^{3+}$ -doped $Li_6Gd(BO_3)_3$ phosphor prepared by solid-state reaction method and assigned its phase to JCPDS No. # 80–0843. The addition of $Al^{3+}$ ions promotes the fluorescence intensity due to the local site distortion under near ultra violet (nUV) excitation [20, 21]. Based on these merits, it is assumed to be noteworthy to investigate the $Li_6AlGd(BO_3)_4$ phosphor as an outstanding host matrix for SSL applications.

Among the available RE ions, $Pr^{3+}$ has been the most promising ion due to its simultaneous emission in blue, green and red regions. The intense fluorescence in 600–700 nm spectral region makes them appropriate for red emission centres for PC-WLEDs. The presence of multiple metastable emission states such as $^3P_0$, $^3P_1$ and $^1D_2$ makes $Pr^{3+}$ ions to exhibit a tunable emission from greenish-blue to intense red. The presence of numerous energy states of $Pr^{3+}$ ions facilitates us to understand the different relaxation processes like multi-phonon relaxation (MPR) process, cross-relaxation (CR) process and the resonant energy transfer (RET) processes in different host matrices. The $Pr^{3+}$ -doped different phosphor materials have been synthesized and investigated for various scientific, industrial and household applications. For example, $SrMoO_4$: $Pr^{3+}$ phosphors for optical thermometric application [22], $LiPbB_5O_9$: $Pr^{3+}$ phosphors to convert blue light into red light for WLEDs [23], $YVO_4$: $Pr^{3+}$ [24] and $BaNb_2O_6$: $Pr^{3+}$ [25] phosphors for thermal sensing applications and $BaMoO_4$: $Pr^{3+}$ [26] phosphors for cathode luminescence and solid-state lighting applications. These virtues imposed a keen interest in investigating the fluorescence properties of $Pr^{3+}$ ions in $Li_6AlGd(BO_3)_4$ phosphor.

In the present research work, $Li_6AlGd(BO_3)_4$ phosphors activated with different concentrations of $Pr^{3+}$ ions were prepared through solid-state reaction method and characterized. The concentration-dependent fluorescence properties were studied at near UV excitation. Reasons for the tunable emission for different concentrations and the quenching in fluorescence intensity were discussed in detail. The suitability of these phosphors for SSL devices is also discussed.

## 2 Experimental techniques

### 2.1 Materials and method of synthesis

High purity grade $Li_2CO_3$ (98.0%, TCS, JAPAN), $Al_2O_3$ (90.0%, Molychem, INDIA), $Gd_2O_3$ (99.9%, Molychem, INDIA), $H_3BO_3$ (99.5%, Merk, INDIA) and $Pr_2O_3$ (99.9%, Alfa Aesar, US) in stoichiometric quantity were used to prepare LAGBPr$x$ phosphors of composition $Li_6AlGd_{(1-x)}(BO_3)_4$: $x$ $Pr^{3+}$ ($x$ = 0, 0.05, 0.1, 0.5, 1.0 and 2.0 mol%) through conventional solid-state reaction method. The following solid-state reaction shows the formation of $Li_6AlGd(BO_3)_4$: $Pr^{3+}$ phase.

$$3\,Li_2CO_3 + \frac{1}{2}Al_2O_3 + \left(\frac{1-x}{2}\right)Gd_2O_3 + 4\,H_3BO_3 + \left(\frac{x}{2}\right)Pr_2O_3 \rightarrow Li_6AlGd_{(1-x)}(BO_3)_4{:}\,xPr + 3\,CO_2\uparrow + 6\,H_2O\uparrow + 1.5\,O_2\uparrow \quad (1)$$

A batch composition of 3.0 g homogeneous powders in stoichiometric ratio with an additional amount of 2.0 wt% of $H_3BO_3$ (to compensate the evaporation of $H_3BO_3$ at higher temperatures) was prepared in the presence of acetone using agate mortar and pestle. The as-prepared samples were heat treated at 200 °C for 2 h and then sintered at different temperatures for different timings. These samples were referred as LAGBPr0, LAGBPr0.05, LAGBPr0.1, LAGBPr0.5, LAGBPr1.0 and LAGBPr2.0 according to $x$ = 0, 0.05, 0.1, 0.5, 1.0 and 2.0%, respectively.

### 2.2 Characterizations

The thermogravimetry and differential scanning calorimetry (TG-DSC) study was carried out with a NETZSCH STA 449 F3 Thermal Analyzer in the presence of air-atmosphere at 5.0 K/min. using the as-prepared un-doped homogeneous powder. The crystalline phases of prepared samples were examined with BRUCKER USA D8 advance diffractometer with $\lambda_{CuK\alpha}$ = 1.541 Å. The Fourier-transform infrared (FTIR) spectrum was recorded with PerkinElmer FT-IR spectrometer following KBr technique using KBr to sample ratio 300:1. The morphology of LAGBPr0 phosphor was studied on FEI-Quanta FEG 200F high-resolution-scanning electron microscope (HR-SEM). The room temperature photoluminescence excitation and emission studies were carried out with FP-8300 JASCO Fluorescence Spectrometer. The decay studies were carried out on FLS 1000 photoluminescence spectrometer provided with Xe-flash lamp in pulsed mode.

## 3 Results and discussions

### 3.1 Thermal analysis

In order to know the various reaction processes, the thermal analysis of the as-prepared homogeneous LAGBPr0 powder has been done using TG-DSC. The TG data coupled with DSC in the temperature range 50 °C–1000 °C shown in Fig. 1 reveal a major weight loss step accompanied by a broad and intense endothermic peak positioned at around 515.0 °C with two considerably weak overlapping endothermic peaks positioned at around 389.5 and 727.2 °C and an exothermic peak at around 640.0 °C. The positions of these two overlapping peaks have been identified applying the Gaussian deconvolution procedure (see inset of Fig. 1). The endothermic peak noticed at 389.5 °C is attributed to the vapourization of acetone and $H_2O$ and the endothermic peak at 727.2 °C is assigned to the release of $CO_2$ [27]. The strong and broad endothermic peak at 515.0 °C corresponds to the phase transition of LAGBPr0. The exothermic peak observed at 640.0 °C is ascribed to the formation of final phase of LAGBPr0 phosphor.

### 3.2 Crystalline phase analysis

The powder X-ray diffraction (PXRD) patterns of LAGBPr0 sample heat treated at 200, 400, 600, 620, 640, 670 and 700 °C for 1 h are shown in Fig. 2a.

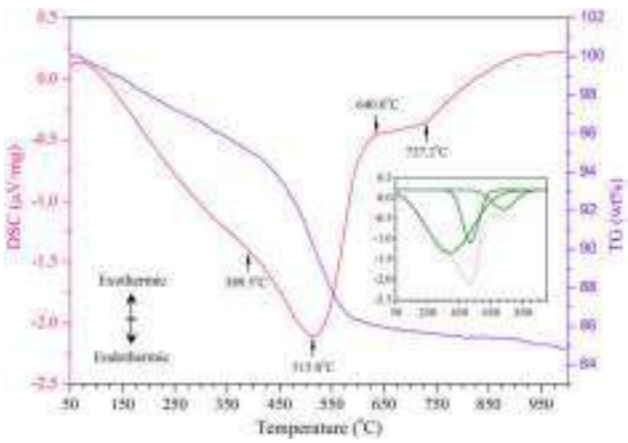



**Fig. 1** TG-DSC profiles of LAGBPr0 sample

These PXRD patterns show that no considerable change in phase is noticed beyond 640 °C, and thus, the sintering temperature is optimized to be 640 °C. In order to optimize the time of sintering, the samples are heat treated at 640 °C for 1 h, 2 h and 3 h and their PXRD profiles are illustrated in Fig. 2b. As seen in these profiles, the PXRD patterns obtained at 640 °C/2 h appear to be sharp and intense. So, the LAGBPr$x$ phosphors show a steady phase when sintered at 640 °C/2 h.

From the literature, no reports are found on the crystalline phase of $Li_6AlGd(BO_3)_4$ phosphor; however, it is close to $Li_6Al_2(BO_3)_4$ phase (JCPDF No. 70–2044), which has been crystallized into primitive anorthic structure with lattice parameters, a = 6.13 Å, b = 4.82 Å, c = 8.23 Å, α = 90.0°, β = 118.0°, γ = 90.0° and space group $P\bar{1}$ (2) [28]. The PXRD profiles of LAGBPr0 along with standard XRD data of $Li_6Al_2(BO_3)_4$ are presented in Fig. 3. This figure reveals that the positions of PXRD peaks of LAGBPr0 phosphor are almost the same as that of $Li_6Al_2(BO_3)_4$ structure except a slightly variation in their intensity. This figure also reveals the presence of impure phase that belongs to $Gd_2O_3$ phase (JCPDF No. 86–2477). The assignment of some of the intense PXRD peaks of $Gd_2O_3$ phase is displayed in Fig. 3. The large ionic radius of $Gd^{3+}$ (1.08 Å) compared to $Al^{3+}$ (0.68 Å) could be one of the reasons for intensity variation of observed PXRD peaks of LAGBPr0 sample. The difference in ionic radii of $Gd^{3+}$ and $Al^{3+}$ ions might be responsible for the $Gd_2O_3$ phase.

The PXRD profiles of different concentrations of $Pr^{3+}$ -doped LAGBPr$x$ ($0 \le x \le 2.0$ mol%) phosphors sintered at 640 °C/2 h show an identical pattern with a little variation in intensity which decrease with the increase of concentration of $Pr^{3+}$ ions (see Fig. 2c). The decrease in intensity of PXRD peaks indicates that the $Pr^{3+}$ ions suitably replace the $Gd^{3+}$ sites without any modification in phase of $Li_6AlGd(BO_3)_4$ phosphor. The average size of crystallites (D) has been calculated using the Debye–Scherrer's equation.

$$D = \frac{0.89 \times \lambda}{\beta \times \mathrm{Cos}\theta} \tag{2}$$

where λ is the wavelength of incident X-rays ($\lambda_{CuK\alpha}$ = 1.5406 Å), β is the full-width at half-maximum (in radians), and θ is the diffraction angle. According to Debye–Scherrer's equation, the average

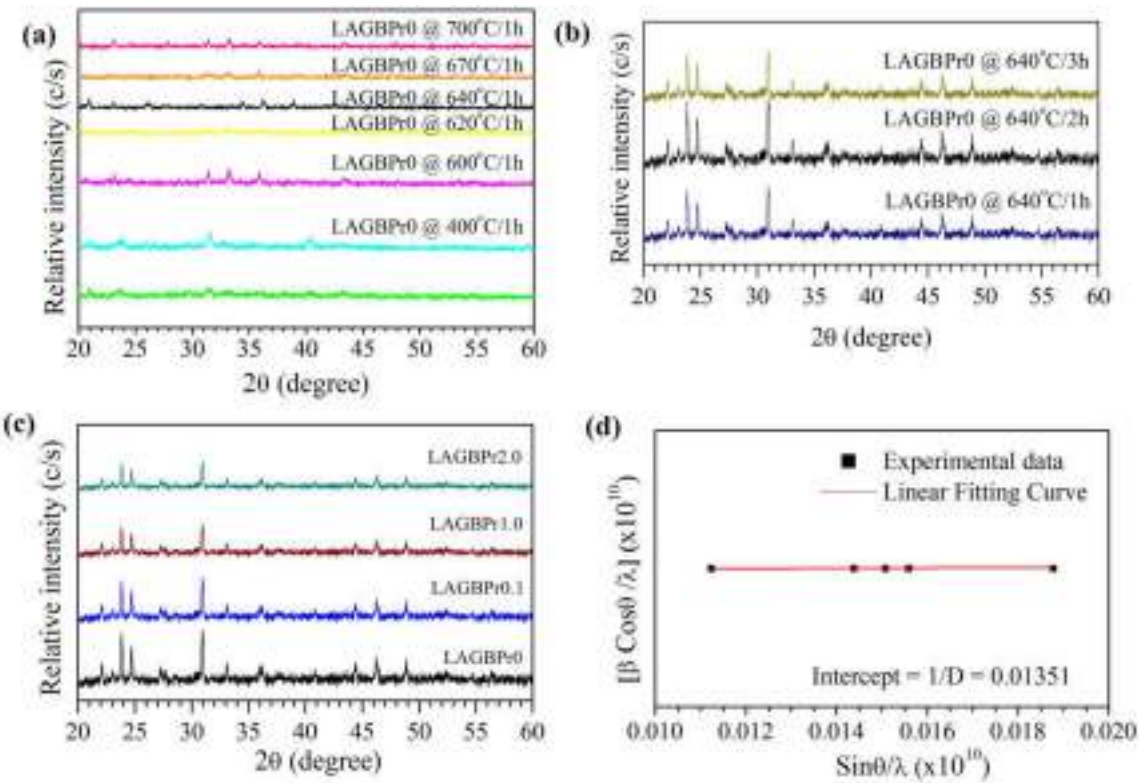



**Fig. 2** PXRD profiles of LAGBPr0 sample at different temperatures (**a**), sintered at 640 °C for different times (**b**), LAGBPr$x$ samples sintered at 640 °C/2 h (**c**) and the Hall–Williamson plot for LAGBPr0 sample (**d**)

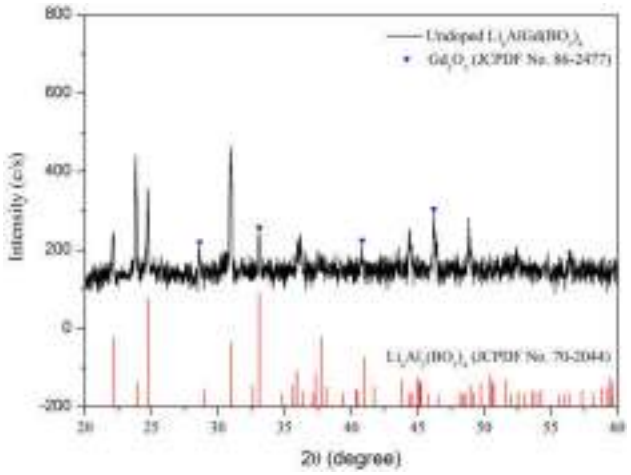



**Fig. 3** PXRD profile of LAGBPr0 along with standard XRD data of JCPDS No. 70–2044

size of crystallites is obtained as ~ 77 nm. The crystallite size can also be obtained from the Hall-Williamson's (H-W) method [29].

$$\left(\frac{\beta \times \mathrm{Cos}\theta}{\lambda}\right) = \left(\frac{1}{D}\right) + \left(\frac{\varepsilon \times \mathrm{Sin}\theta}{\lambda}\right) \quad (3)$$

Here ε is a constant and it is the measure of micro-strains present in the prepared phosphors. The reciprocal of the intercept of H-W curve shown in Fig. 2d represents the average size of crystallites. According to H-W method, the average size of crystallites is found to be ~ 74 nm which is very close to that obtained from the Debye–Scherrer's method. The micro-strain has been calculated using the following equation [30]:

$$\varepsilon = \frac{\beta \times \mathrm{Cos}\theta}{4} \quad (4)$$

In case of LAGBPr*x* phosphors, the value of ε is estimated to be $0.44 \times 10^{-3}$ which is smaller than the strain reported for CdS nanoparticle (ε ~ 0.0494) synthesized by chemical precipitation method [31].

### 3.3 FTIR and SEM analysis

To investigate the presence of various structural bonds, the LAGBPr*x* phosphors are examined through FTIR investigation. Usually, borate vibrational modes have been identified in three different regions: (i) B-O asymmetric stretching vibrations in $BO_3$ units from 1200 to 1500 $cm^{-1}$, (ii) B-O symmetric stretching vibrations in $BO_4$ units from 800 to 1500 $cm^{-1}$ and (iii) B-O-B bending vibrations between $BO_3$ and $BO_4$ units from 600 to 800 $cm^{-1}$ [32, 33]. The FTIR spectrum of LAGBPr0 sample in the region from 1600 to 400 $cm^{-1}$ presented in Fig. 4 reveals nearly nineteen IR absorption bands. The IR bonds noticed at around 1496, 1440, 1334, 1258 and 1214 $cm^{-1}$ correspond to B-O asymmetric stretching vibrations in $BO_3$ units [34]. The IR bond located at around 1102 $cm^{-1}$ refers to the Al-O stretching vibration mode [35]. The IR bonds noticed at around 985, 948, 933 and 905 $cm^{-1}$ belong to the B-O symmetric stretching vibrations in $BO_4$ units [32, 36]. The IR bond located at around 867 $cm^{-1}$ refers to the Li–O vibrational mode [37]. The IR bond located at around 762 $cm^{-1}$ refers to the $AlO_4$ tetrahedral aluminate units [38]. The IR bonds identified at around 721, 709 and 600 $cm^{-1}$ have been assigned to B-O-B bending vibrations between $BO_3$ and $BO_4$ units [39, 40]. The IR bond peaked at around 553 and 494 $cm^{-1}$ has been ascribed to the Gd-O vibrations [41]. The IR bond located at around 443 $cm^{-1}$ refers to $AlO_4$-$LiO_4$ lattice vibrations [42], while the bond positioned at around 419 $cm^{-1}$ attributed to Al-O vibrations [43].

The morphological investigation of phosphor materials gives the information regarding the size, shape, orientation and distribution of particles. As a reference, the HR-SEM image of LAGBPr0 sample is shown in Fig. 5. As seen in this image, one can notice a leaf-like morphology for the LAGBPr particles which are distributed uniformly with random orientation. The average size of the particles over the surface of leaf has been measured to be 1100 nm using image-J software.

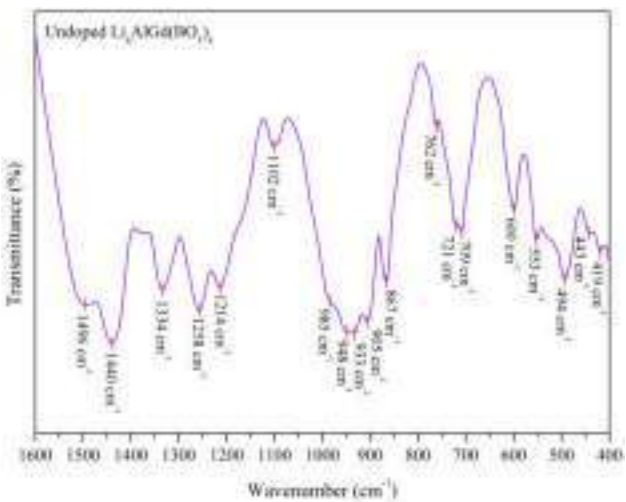



**Fig. 4** FTIR profile of LAGBPr0 sample

### 3.4 Fluorescence properties

The visible fluorescence properties of LAGBPr$x$ ($0 \leq x \leq 2.0$ mol%) phosphors have been investigated through photoluminescence excitation, emission and decay studies. The excitation spectra have been recorded in the spectral region from 220 to 500 nm monitoring the emission at 613 nm corresponding to $Pr^{3+}$: $^3P_0 \rightarrow {}^3H_6$ transition. The spectra normalized with respect to the intensity of $Gd^{3+}$: $^8S_{7/2} \rightarrow {}^6I_{11/2}$ (274 nm) transition are shown in Fig. 6. They reveal broad band ranges from 230 to 250 nm and it can be attributed to the charge transfer band (CTB) of $O^{2-} \rightarrow Pr^{3+}$ ions [44]. The presence of CTB indicates the possibility of energy transfer (ET) from the host (donor) to the $Pr^{3+}$ luminescent centres (acceptor). The sharp excitation bands located from 250 to 315 nm (see Fig. 6a) can be ascribed to $Gd^{3+}$ ions and the considerably weak bands are due to f-f transitions of $Pr^{3+}$ ions that ranges from 420 to 500 nm (see Fig. 6b).

The transitions due to $Gd^{3+}$ ions have been ascribed to $^8S_{7/2} \rightarrow {}^6D_{9/2}$ (253 nm), $^8S_{7/2} \rightarrow {}^6I_{11/2}$ (274 nm), $^8S_{7/2} \rightarrow {}^6I_{9/2}$ (277 nm), $^8S_{7/2} \rightarrow {}^6I_{7/2}$ (284 nm), $^8S_{7/2} \rightarrow {}^6P_{8/2}$ (302 nm), $^8S_{7/2} \rightarrow {}^6P_{5/2}$ (307 nm) and $^8S_{7/2} \rightarrow {}^6P_{1/2}$ (313 nm) transitions, while the transitions due to $Pr^{3+}$ ions have been assigned to $^3H_4 \rightarrow {}^3P_2$ (449 nm), $^3H_4 \rightarrow {}^3P_1$ (473 nm) and $^3H_4 \rightarrow {}^3P_0$ (485 nm) transitions [25, 45–49]. The presence of $Gd^{3+}$ and $Pr^{3+}$ transitions is an indication for the uniform distribution of $Pr^{3+}$ ions in LAGBPr$x$ phosphors. As seen in the excitation spectra, it is clear that the intensity of excitation bands due to $Gd^{3+}$ ions decreases, while the intensity of $Pr^{3+}$ ions increases with the increase of concentration of $Pr^{3+}$ ions. The variation of intensity of $Gd^{3+}$: $^8S_{7/2} \rightarrow {}^6I_{11/2}$ (274 nm) and $Pr^{3+}$: $^3H_4 \rightarrow {}^3P_2$ (449 nm) transitions is illustrated in Fig. 6c. The CTB with peak maximum at around 243 nm and the sharp and intense excitation band located at around 274 nm ($Gd^{3+}$: $^8S_{7/2} \rightarrow {}^6I_{11/2}$) indicate efficient transfer of energy from the host to $Pr^{3+}$ ions. Therefore, the fluorescence properties of LAGBPr$x$ ($0 \leq x \leq 2.0$ mol%) phosphors have been investigated by exciting at near UV and visible radiations corresponding to 274 nm (within the host, $Gd^{3+}$: $^8S_{7/2} \rightarrow {}^6I_{11/2}$) and 449 nm (within dopant ions, $Pr^{3+}$: $^3H_4 \rightarrow {}^3P_2$) wavelengths, respectively.

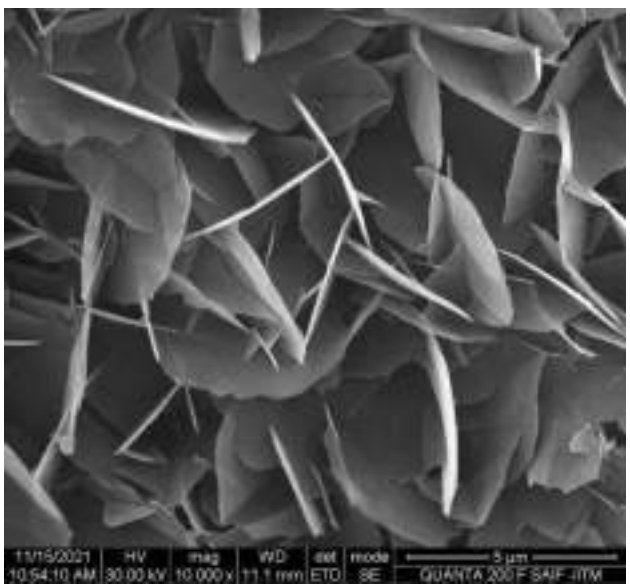



**Fig. 5** HR-SEM image of LAGBPr0 sample

#### 3.4.1 *Within the host excitation*

When the LAGBPr$x$ ($0 \leq x \leq 2.0$ mol%) phosphors are excited at 274 nm (i.e. within host excitation) corresponding to $Gd^{3+}$: $^8S_{7/2} \rightarrow {}^6I_{11/2}$ transition, the emission spectra reveal nine emission transitions due to $^3P_1 \rightarrow {}^3H_5$ (547 nm), $^3P_1 \rightarrow {}^3H_6$ (580 nm), $^1D_2 \rightarrow {}^3H_4$ (594 nm), $^3P_0 \rightarrow {}^3H_6$ (613 nm), $^3P_1 \rightarrow {}^3F_2$ (625 nm), $^3P_0 \rightarrow {}^3F_2$ (647 nm), $^3P_1 \rightarrow {}^3F_3$ (662 nm), $^3P_0 \rightarrow {}^3F_3$ (694 nm) and $^1D_2 \rightarrow {}^3H_5$ (706 nm) transitions. The spectral profiles along with their assignment are presented in Fig. 7. Among the observed emission transitions, the $^3P_0 \rightarrow {}^3H_6$ (613 nm) transition possess highest intensity compared to other transitions. Additionally, the intensity of these transitions decreases monotonically with the increase of $Pr^{3+}$ ions concentration. The variation of intensity of $^3P_0 \rightarrow {}^3H_6$ (613 nm) transition as function of $Pr^{3+}$ ions concentration is illustrated as inset of Fig. 7. The emission mechanism of LAGBPr$x$ phosphors is illustrated in partial energy level diagram shown in Fig. 8.

When excited at 274 nm wavelength, the ground state $Gd^{3+}$ ions interact with the incident light photons and get excited into $Gd^{3+}$:$^6I_J$ energy states. Immediately they transit non-radiatively to $Gd^{3+}$:$^6P_J$ energy states. In the present phosphors it can be predicted that the $Pr^{3+}$:$4f^15d^1$ configuration is located below the $Pr^{3+}$:$^1S_0$ energy state resulting to produce $4f^15d^1 \rightarrow 4f^2$ inter-configurational transitions [50]. The $Gd^{3+}$ ions sensitize $Pr^{3+}$ ions efficiently by

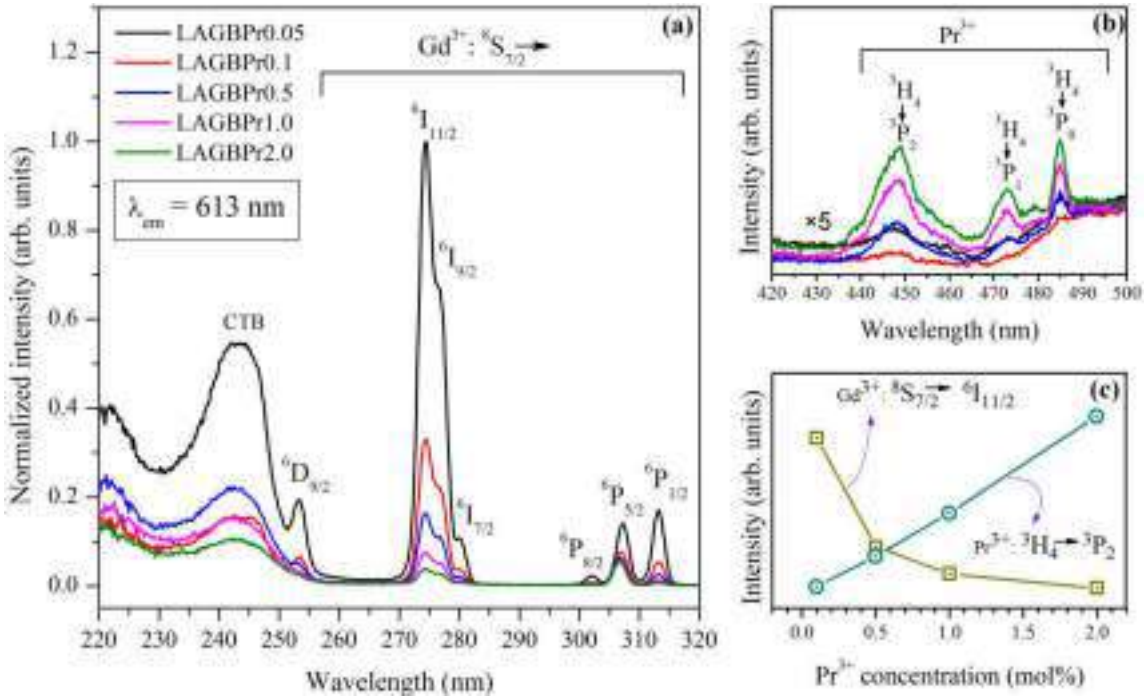



**Fig. 6** Excitation spectra of LAGBPr*x* phosphors from 220–320 nm (**a**), 420–500 nm (**b**) and the variation of intensity of excitation bands as a function of $Pr^{3+}$ ions concentration (**c**)

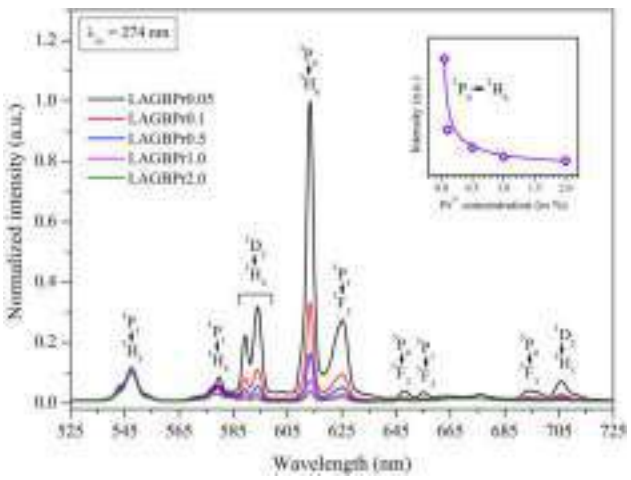



**Fig. 7** Emission spectra of LAGBPr*x* phosphors ($\lambda_{ex}$ = 274 nm). Inset shows the variation of intensity of $Pr^{3+}$: $^3P_0 \rightarrow {}^3H_6$ transition as a function of $Pr^{3+}$ ions concentration

transferring energy from $Gd^{3+}$:$^6P_J$ energy states to $Pr^{3+}$:$4f^15d^1$ configuration. From there a fast non-radiative (NR) decay materializes to $Pr^{3+}$:$^3P_J$ energy states producing different radiative transitions illustrated in Fig. 8.

The colour perception of emitted fluorescence has been studied by finding the Commission International de I'Eclairage (CIE-1931) colour coordinates (x, y) using the emission spectral profiles. It is well known that human eye can identify the light through three different cone cells in the spectral regions 420–440 nm (short), 530–540 nm (middle) and 560–580 nm (long). The parameters related to tri-stimulus values X, Y and Z of three types of cone cells describe the colour sensation and they are given below [48, 51]:

$$X = \int_0^\infty I_{(\lambda)} \,.\, T_{(\lambda)} \,.\, \overline{x}_{(\lambda)} \,.\, d\lambda \tag{5}$$

$$Y = \int_0^\infty I_{(\lambda)} \,.\, T_{(\lambda)} \,.\, \overline{y}_{(\lambda)} \,.\, d\lambda \tag{6}$$

$$Z = \int_0^\infty I_{(\lambda)} \,.\, T_{(\lambda)} \,.\, \overline{z}_{(\lambda)} \,.\, d\lambda, \tag{7}$$

where $I_{(\lambda)}$ represents intensity of illuminant spectrum and $T_{(\lambda)}$ represents the transmission spectrum of the filter ($0 \le T \le 1$). $\overline{x}(\lambda)$, $\overline{y}(\lambda)$ and $\overline{z}(\lambda)$ represent the CIE colour matching functions. The colour of emitted light obtained from the tri-stimulus values (X, Y and Z) has been represented graphically, called the chromaticity diagram using colour coordinates (x, y).

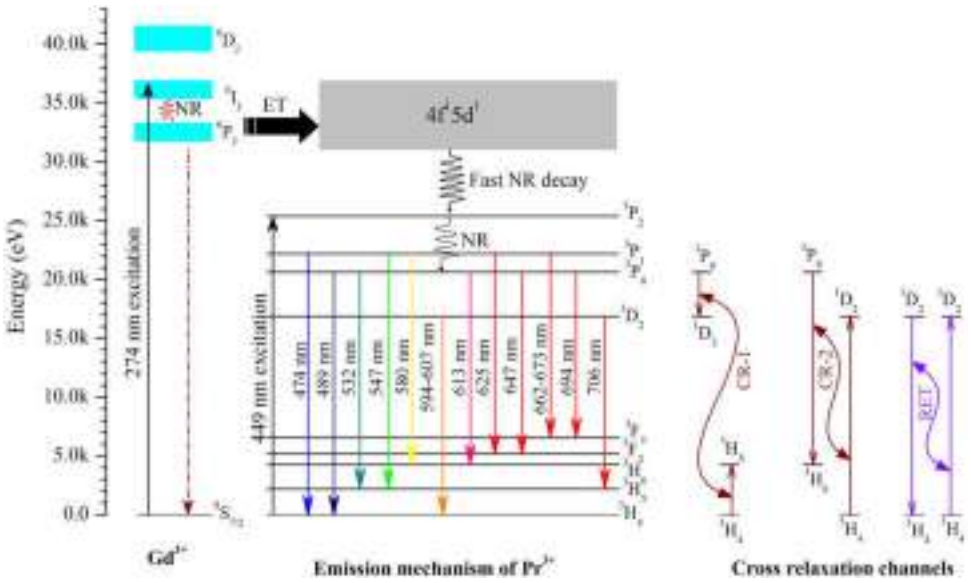



**Fig. 8** Partial energy level diagram showing the emission mechanism of $Pr^{3+}$ ions at 274 nm and 449 nm excitations and the cross-relaxation channels responsible for energy transfer

$$x = \frac{X}{X+Y+Z} \tag{8}$$

$$y = \frac{Y}{X+Y+Z} \tag{9}$$

The evaluated colour coordinates of LAGBPr*x* phosphors at 274 nm excitation are summarized in Table 1 and they are located in CIE chromaticity diagram shown in Fig. 9. The colour purity (CP) of emitted luminescence has been determined using a well-known equation shown below:

$$Colour\,purity = \frac{\sqrt{(x-x_e)^2+(y-y_e)^2}}{\sqrt{(x_d-x_e)^2+(y_d-y_e)^2}} \times 100, \tag{10}$$

where $(x, y)$, $(x_e, y_e)$ and $(x_d, y_d)$ are the coordinates corresponding to CIE, equal energy point and dominant wavelength point, respectively. The value of CP varies from 5 to 41% for different concentrations of $Pr^{3+}$ in LAGBPr*x* phosphors when excited at 274 nm and they are summarized in Table 1. The value of CP of the order ~ 5% obtained for $x$ = 1.0 mol% clears that the LAGBPr1.0 phosphor exhibits intense white light at 274 nm excitation. The correlated colour temperature (CCT) has been used to know the colour appearance of emitted luminescence. A light source with CCT ranges from 2700–3000 K emits warm-white light, from 3000–4000 K emits neutral-white light and from 4000–6500 K emits cool-white light. The value of CCT has been found following McCamy [52].

$$CCT = -449\,z^3 + 3525\,z^2 - 6823.3\,z + 5520.33, \tag{11}$$

where $z = (x - x_e)/(y - y_e)$ is a constant and the coordinates of epicentre point are ($x_e$ = 0.3320, $y_e$ = 0.1858). The CIE coordinates of LAGBPr1.0 phosphor (0.316, 0.312) with CCT ~ 6446 K are almost close to standard daylight illuminant-D65 (0.3127, 0.3290) of CCT ~ 6500 K and daylight fluorescent source F5 (0.3137, 0.3453) of CCT ~ 6350 K.

**Table 1** Comparison of CIE coordinates and colour purities of LAGBPr*x* phosphors

| Sample code | CIE coordinates | | Colour purity (%) | CIE coordinates | | Colour purity (%) |
|---|---|---|---|---|---|---|
| | $\lambda_{ex}$ = 274 nm | | | $\lambda_{ex}$ = 449 nm | | |
| | x- | y- | | x- | y- | |
| LAGBPr0.05 | 0.492 | 0.330 | ~ 41 | 0.222 | 0.250 | ~ 55 |
| LAGBPr0.1 | 0.403 | 0.320 | ~ 15 | 0.223 | 0.236 | ~ 55 |
| LAGBPr0.5 | 0.362 | 0.329 | ~ 7 | 0.232 | 0.269 | ~ 55 |
| LAGBPr1.0 | 0.316 | 0.312 | ~ 5 | 0.221 | 0.248 | ~ 55 |
| LAGBPr2.0 | 0.261 | 0.259 | ~ 32 | 0.218 | 0.249 | ~ 55 |

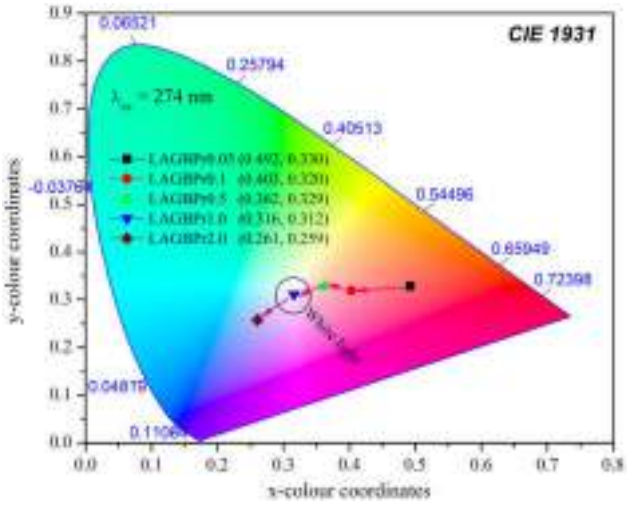



**Fig. 9** CIE chromaticity diagram showing the colour coordinates of LAGBPr*x* phosphors at 274 nm excitation

As seen in the chromaticity diagram shown in Fig. 9, one can observe that the colour of emitted fluorescence has been tuned from orange-red to white and then to bluish-white with the increase of concentration of $Pr^{3+}$ ions from $x = 0.05$ mol% to $x = 2.0$ mol%. The colour coordinates obtained for LAGBPr*x*1.0 phosphor ($x = 0.316$, $y = 0.312$) are very close to the standard white colour ($x = 0.333$, $y = 0.333$). Therefore, LAGBPr*x* phosphors can be used as excitation source to generate white light from the PCLEDs and/or as a white light source at 274 nm excitation. The CIE coordinates of LAGBPr1.0 phosphor are close to those reported for $Lu_{0.94}Pr_{0.06}MoO_6$ (0.315, 0.312), $Lu_{1.92}Pr_{0.08}MoO_6$ (0.352, 0.316) [53] and $Pr^{3+}$: $Ba_2CaWO_6$ (0.29, 0.35) [54] phosphors.

### 3.4.2 *Within the active ($Pr^{3+}$) ion excitation*

When the LAGBPr*x* ($0 \le x \le 2.0$ mol%) phosphors are excited at 449 nm (i.e. within the $Pr^{3+}$ ions) corresponding to $Pr^{3+}$: $^3H_4 \rightarrow {}^3P_2$ transition, a broad emission band is noticed in the spectral region from 450 to 590 nm with sub-peaks and some emission bands originated from the f-f transitions of $Pr^{3+}$ ions. The presence of broad emission band can be ascribed to the host emission. In literature, a host emission band has also been reported for $Pr^{3+}$-activated $SiO_2$ matrix [46]. In this case, the emission spectra reveal six emission transitions due to $^3P_1 \rightarrow {}^3H_4$ (474 nm), $^3P_0 \rightarrow {}^3H_4$ (489 nm), $^3P_0 \rightarrow {}^3H_5$ (532 nm), $^1D_2 \rightarrow {}^3H_4$ (607 nm), $^3P_0 \rightarrow {}^3F_2$ (646 nm) and $^3P_1 \rightarrow {}^3F_3$ (673 nm) transitions. The partial energy level diagram shown in Fig. 8 also describes the emission mechanism of LAGBPr*x* phosphors at 449 nm excitation. As a reference, the emission spectrum of LAGBPr1.0 phosphor along with the assignment of observed transitions are described in Fig. 10a. Interestingly, a fluorescence quenching has been noticed beyond $x = 1.0$ mol% and it can be attributed to the ET among the excited $Pr^{3+}$ ions. The variation in intensity of $Pr^{3+}$: $^3P_1 \rightarrow {}^3H_4$ transition as a function of $Pr^{3+}$ ions concentration is shown as inset of Fig. 10a.

The spectra normalized w.r.t the intensity of $Pr^{3+}$: $^3P_1 \rightarrow {}^3H_4$ transition are shown in Fig. 10b. As seen in these emission profiles, one can perceive a blue-shift with increase of concentration of $Pr^{3+}$ ions. This shift has been ascribed to the slight variation in ionic radii of $Pr^{3+}$ ions (1.13 Å) and $Gd^{3+}$ ions (1.08 Å) leading to site distribution of $Pr^{3+}$ ions in the vicinity of $Gd^{3+}$ ions in LAGBPr*x* phosphors [55]. The inset of Fig. 10b presents the blue-shift noticed for $Pr^{3+}$: $^3P_1 \rightarrow {}^3H_4$ transition. The CIE colour coordinates of LAGBPr*x* phosphors at 449 nm excitation are also listed in Table 1 and they are located in CIE chromaticity diagram shown in Fig. 11. Further, the value of CP is found to be ~ 55% for LAGBPr*x* phosphors when excited at 449 nm. As seen in this CIE diagram, it is clear that all the colour coordinates are well fitted in the bluish-white region causing the absence of tunability for emitted fluorescence. The $YNbO_4$: $Pr^{3+}$-$Yb^{3+}$ [56], $YInGe_2O_7$: $Pr^{3+}$ [57] and $Sr_5Ta_4O_{15}$: $Pr^{3+}$ [58] phosphors exhibit bluish or bluish-white fluorescence under suitable excitations.

## 3.5 Decay time analysis

The fluorescence decay time of $Pr^{3+}$: $^3P_0$ emission state has been determined by exciting the phosphor samples at 274 nm wavelength and monitoring the emission at 613 nm corresponding to $^3P_0 \rightarrow {}^3H_6$ transition and they are shown in Fig. 12. The decay time has been measured taking 1/e times the initial intensity and they are found to be 88.2, 74.3, 57.8, 53.2 and 46.0 µs for $x = 0.05$, 0.1, 0.5, 1.0 and 2.0 mol%, respectively. The measured decay time values decrease with the increase of $Pr^{3+}$ concentration as shown in inset of Fig. 12. The decrease in fluorescence decay time could be due to ET among the excited $Pr^{3+}$ ions at higher concentrations.

The observed quenching in fluorescence of various emission transitions of $Pr^{3+}$ ions at 449 nm excitation could be due to self-absorption and/or non-radiative

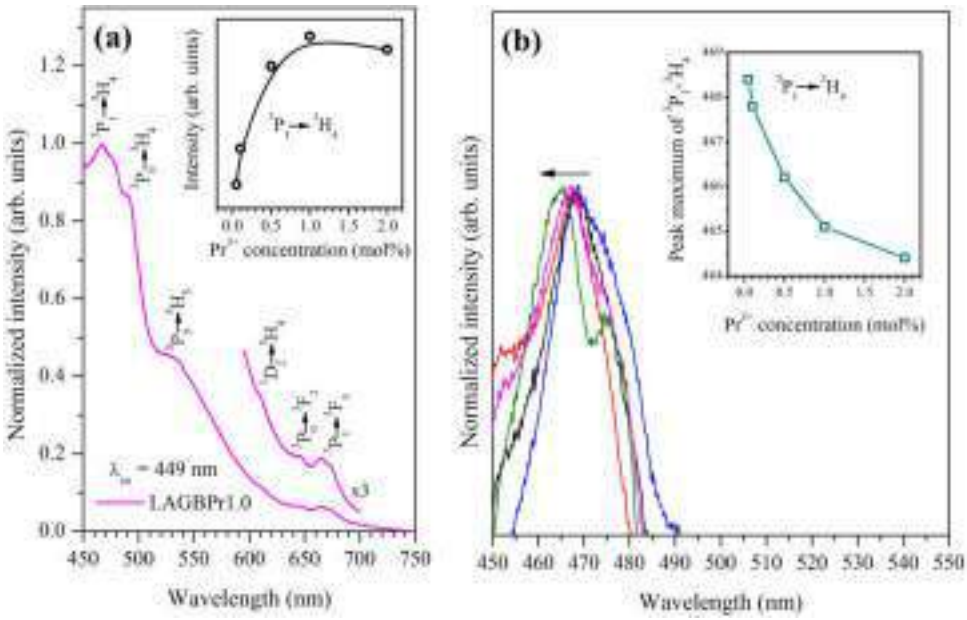



**Fig. 10** **a** Emission spectrum of LAGBPr1.0 phosphors ($\lambda_{ex}$ = 449 nm) and the variation of intensity of $Pr^{3+}$: $^3P_1 \rightarrow {}^3H_4$ transition as a function of $Pr^{3+}$ ions concentration. **b** Normalized emission spectra of LAGBPr*x* phosphors and the variation of peak maximum of $Pr^{3+}$: $^3P_1 \rightarrow {}^3H_4$ transition as a function of $Pr^{3+}$ ions concentration

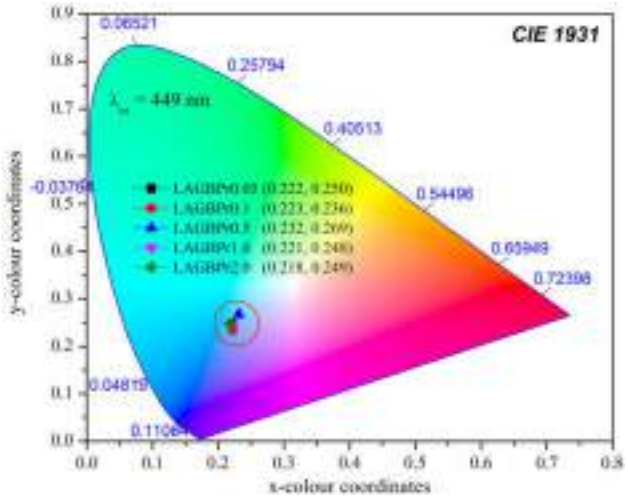



**Fig. 11** CIE chromaticity diagram showing the colour coordinates of LAGBPr*x* phosphors at 449 nm excitation

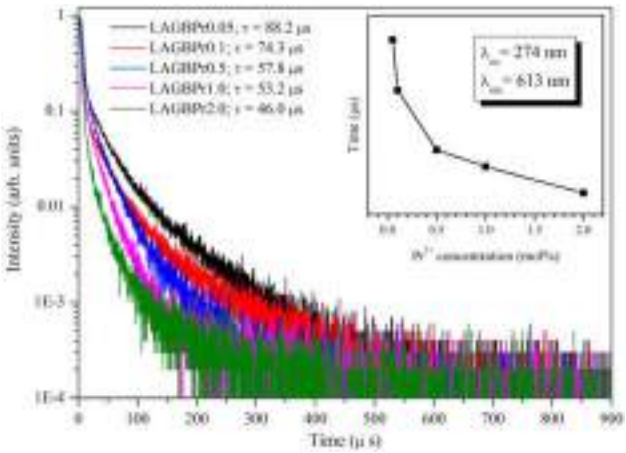



**Fig. 12** Fluorescence decay profiles of $Pr^{3+}$: $^3P_0$ emission state in LAGBPr*x* phosphors. Inset shows the variation of lifetime as a function of $Pr^{3+}$ concentration

transfer of energy among the excited $Pr^{3+}$ ions. The non-radiative (NR) transfer of energy has been assigned to the cross-relaxation (CR) channels and the resonant energy transfer (RET) mechanism is described below and is illustrated clearly in Fig. 8.

$$CR-1: \left[{}^3P_0, {}^3H_4\right] \rightarrow \left[{}^1D_2, {}^3H_6\right]$$

$$CR-2: \left[{}^3P_0, {}^3H_4\right] \rightarrow \left[{}^3H_6, {}^1D_2\right]$$

$$RET: \left[{}^1D_2, {}^3H_4\right] \rightarrow \left[{}^3H_4, {}^1D_2\right]$$

In general, white light can be generated by two different ways, by combining GaN blue LED-chip with YAG: $Ce^{3+}$ yellow phosphor or using a tri-colour phosphor excited at near UV radiation. The efficiency of white light source designed by the first method is not favourable due to low colour rendering index and poor illumination compared to near UV excited tri-colour phosphors. Furthermore, a phosphor coating on LED improves its efficiency and helps in quenching its surface temperature [59–62]. The observed experimental results suggest that the LAGBPr1.0 phosphor is suitable for lighting applications.

## 4 Conclusions

The LAGBPr$x$ ($0 \leq x \leq 2.0$ mol%) phosphors were synthesized by solid-state method and characterized for white LED applications. Thermal analysis through TG-DSC study explores an endothermic peak at 515.0 °C corresponding to the phase transition and an exothermic peak at 640.0 °C confirming the final phase of LAGBPr$x$ phosphors. A monatomic decrease in intensity of XRD peaks with the increase of concentration of $Pr^{3+}$ ions indicates the suitable replacement of $Pr^{3+}$ ions in $Gd^{3+}$ ion sites and uniform distribution of $Pr^{3+}$ ions in LAGBPr$x$ phosphors. The average size of crystallites is found to be ~ 77 nm and ~ 74 nm from the Debye–Scherrer and the Hall-Williamson methods, respectively. The magnitude of micro-strain presents is of the order of $0.44 \times 10^{-3}$. The FTIR investigations reveal the presence of B-O asymmetric and symmetric stretching vibrations, B-O-B bending vibrations, Al-O stretching vibrational modes, $AlO_4$ tetrahedral aluminate units, $AlO_4$-$LiO_4$ lattice vibrations and Gd-O vibrations. The HR-SEM image of LAGBPr0 phosphor shows a leaf-like morphology with random orientation of particles. The excitation spectra reveal a charge transfer band due to $O^{2-} \rightarrow Pr^{3+}$ ions (230–250 nm), host-related ($Gd^{3+}$) bands along with some f-f transitions of $Pr^{3+}$ ions. Upon 274 nm excitation, a tunable fluorescence from orange-red to white to bluish-white is observed, while at 449 nm excitation bluish-white fluorescence only observed. Upon 449 nm excitation, a blue-shift is noticed with the increase of concentration of $Pr^{3+}$ ions. The optimal concentration of $Pr^{3+}$ ions for efficient optical properties is confirmed to be 1.0 mol%. At 449 nm excitation, a quenching in luminescence is identified beyond 1.0 mol% and it has been assigned to the non-radiative transfer of energy through [$^3P_0$, $^3H_4$] → [$^1D_2$, $^3H_6$] and [$^3P_0$, $^3H_4$] → [$^3H_6$, $^1D_2$] cross-relaxation channels and [$^1D_2$, $^3H_4$] → [$^3H_4$, $^1D_2$] resonant energy transfer mechanism. From the experimental results, it can be concluded that the LAGBPr1.0 phosphor has more proficiency for lighting applications.

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## Author Contributions

Conceptualization BCJ, MJ; Methodology: BCJ, PR; Formal analysis and investigation: PR, PSK, HK, NM, KP; Writing—original draft preparation: PR; Writing—review and editing: BCJ, PR; Funding acquisition: VN, KP; Resources: BCJ, VN, MJ; Supervision: BCJ.

## Data Availability

Data will be made available on reasonable request.

## Declarations

**Conflict of interest** The authors declare that they have no conflict of interest.

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# Spectroscopic and luminescent properties of $Ce^{3+}$ -doped $TeO_2$-$WO_3$-$GeO_2$ glasses

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ABSTRACT

Different concentrations of $Ce^{3+}$-doped $TeO_2$-$WO_3$-$GeO_2$-$Ce_2O_3$ (TWGCe) glasses were prepared by melt-quenching method and characterized. Different spectroscopic and luminescence properties were evaluated using room temperature absorption and emission spectra. The absence of sharp X-ray diffraction peaks and the presence of broad band from 18° to 35° shows the amorphous phase of studied glasses. The Fourier transform infrared absorption spectra show the presence of various vibrational bonds. The optical properties of TWGCe glasses were studied by exciting the glass samples at 323 nm ultraviolet wavelength. The quenching in luminescence is noticed at × = 0.5 mol% along with a red-shift at higher $Ce^{3+}$ concentrations. The decay time was found decrease with increase of concentration of $Ce^{3+}$ ions. These glasses emit intense blue luminescence with CIE coordinates (0.161, 0.018) when excited at 323 nm radiation. These glasses are favourable as blue light sources in the design of phosphor-based white LEDs.

## 1. Introduction

The multi-component glasses are of most significant compared to single crystals. They are of interest due to their low fabrication cost, flexibility in manufacturing different sizes and shapes. The glassy materials have been used to produce various optical components with excellent transparency. They exhibit intense emission in near ultraviolet and visible regions, possesses relatively high density and more rare earth (RE) ion solubility [1–4]. They have tremendous applications as host materials for variety of RE ions doped laser sources, fiber amplifiers in communication, dispersion-control devices, sensors in industry, scintillators in radio-physics, etc…[5,6]. The trivalent cerium ($Ce^{3+}$) ions are the most commonly used REs for intense luminescence in the spectral range of 300–600 nm. These are most significant in designing oxide-based scintillators owing to their high fluorescence yield strength and short lifetime of the order of $10^{-8}$ – $10^{-9}$ s. The $Ce^{3+}$ -doped scintillators find wide range of applications in the fields of bio-imaging, defense, communication and high-energy physics [7,8]. The emission of strong blue light from $Ce^{3+}$ activated multi-component glass or glass-ceramics have been used to generate white light in phosphor based white light emitting diodes (w-LEDs) [9,10].

The tellurite-based glasses are of noteworthy due to their excellent non-linear optical properties with low phonon energy, relatively good thermal stability with chemical durability, low manufacturing temperature. These glasses are more advantages in enhancing the fluorescence efficiency by reducing multi-phonon relaxations rates [11,12]. The presence of $TeO_4$, $TeO_{3+1}/TeO_3$, $WO_6$, $WO_4$ and $GeO_6$ structural units which help in strengthening glass network, glass forming ability and hence thermal stability. The structural, physical and thermal properties [13] and the shielding properties [14] of $TeO_2$-$WO_3$-$GeO_2$ glasses have been studied. Certain $RE^{3+}$ ions activated $TeO_2$-$WO_3$-$GeO_2$ glasses were fabricated and characterized for various visible and fiber laser sources [15–17]. This work reports on the structural and photoluminescence properties of $TeO_2$-$WO_3$-$GeO_2$-$CeO_2$ (TWGCe) glasses. The optimization of $Ce^{3+}$ concentration and photometric properties were also discussed.

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## 2. Materials, method of preparation and instrumentation

The TWGCe*x* glasses of composition (85-*x*) $TeO_2$-5 $WO_3$-10 $GeO_2$-*x* $Ce_2O_3$ (*x* = 0, 0.1, 0.5 and 1.0 mol%) were prepared by melt-quenching method using $TeO_2$ (≥99.5 %), $WO_3$(≥99 %), $GeO_2$(99.999 %) and $Ce_2O_3$(99.9 %) as precursor materials. The stoichiometric amounts of precursor materials of 20 g batch each were thoroughly mixed in the presence of acetone and melted at 875 °C for 40 min using alumina crucible. The melt was air-quenched by pouring onto a preheated brass mould and annealed at 300 °C for 10 h and then cooled to room temperature producing bubble-free and transparent glasses (see Fig. 1**a**). All these glass samples were polished for optical quality with 0.18 cm thick and then used for other characterizations. The prepared glass samples were referred as TWGCe*x* glasses, where × stands for the concentration of $Ce^{3+}$ ions in mol%.

The Archimedes principle was applied to obtain density measurements using double-distilled water as an immersion-fluid. The Abbes' refractometer illuminated with sodium vapour lamp (λ = 5893 Å) was used to find the refractive indices. The room temperature optical absorption spectra were recorded on Agilent Cary 60 UV–Visible spectrometer. The transmittance mode infrared absorption spectra were recorded with PerkinElmer FT-IR spectrometer following KBr technique. The scanning electron microscopy-energy dispersive X-ray spectrum (SEM-EDS) was recorded on VEGA3 TESCAN provided with BrukerEasy EDS equipment. The excitation and emission spectra were carried out with Jobin Yvon Fluorolog-3 spectrofluorimeter and the lifetime measurements were done using FLS 1000 photoluminescence spectrometer with light source in pulsed mode. All the optical measurements were performed at room temperature.

## 3. Results and discussion

### 3.1. Basic characteristic parameters

The phase of TWGCe*x* glasses has been examined by powder X-ray diffraction (XRD) studies. The XRD profiles shown in Fig. 1**b** reveal a broad-bump range from 18° to 35° and it has been assigned to the combined effect of multiple-scatterings at non-uniformly distributed atoms leading to exhibit amorphous phase of studied glasses. Some of the significant basic parameters of TWGCe*x* glasses are summarized in Table 1. The values of refractive index (n) and density (d) increase with increase of $Ce^{3+}$ concentration and their variation are illustrated in Fig. 2. The decrease in molar volume ($V_m$) with $Ce^{3+}$ concentration leads compactness of elements. The reflection loss is found to be ~ 18 % for all the samples indicating negligible loss of incident light intensity or the studied glasses allow most of the incident light to absorb or transmit through them. The ratio of molar refraction ($R_m$) to molar volume ($V_m$) has been used to predict metallic or non-metallic behaviour of glass samples. ($R_m/V_m$) > 1 for metallic nature of solids while ($R_m/V_m$) < 1 for non-metallic nature of solids [18]. In the present investigation, the value of ($R_m/V_m$) is found to be ~ 0.63 for all TWGCe*x* glasses indicating their non-metallic nature. The increased concentration of $Ce^{3+}$ ions (C) cause a decrease in inter-ionic distance ($r_i$) resulting to energy transfer among the excited $Ce^{3+}$ ions at higher concentrations.

In order to evaluate the optical band gap energy of prepared TWGCe*x* glass samples, the room temperature optical absorption spectra were measured and presented in Fig. 1**c**. The optical band gap energy is one of

**Table 1**
Comparison of basic parameters of TWGCe*x* glasses.

| Parameter | TWGCe0 | TWGCe0.1 | TWGCe0.5 | TWGCe1.0 |
|---|---|---|---|---|
| Optical path length, *l* ± 0.01 cm | 0.18 | 0.18 | 0.18 | 0.18 |
| Density, d ± 0.001 g/cm$^3$ | 4.454 | 5.067 | 5.086 | 5.102 |
| Refractive index, n ± 0.001 | 2.448 | 2.453 | 2.458 | 2.462 |
| Reflection losses, $R_L$ ± 0.02 % | ~18 | ~18 | ~18 | ~18 |
| Molar refraction, $R_m$ ± 0.01 cm$^3$ | 22.12 | 19.48 | 19.45 | 19.42 |
| Molar volume, $V_m$ ± 0.01 cm$^3$ | 35.41 | 31.13 | 31.02 | 30.94 |
| ($R_m$ / $V_m$) ± 0.02 | ~0.63 | ~0.63 | ~0.63 | ~0.63 |
| Concentration, C ± 0.02 × $10^{20}$ ions/cm$^3$ | – | 1.10 | 5.53 | 11.03 |
| Inter-ionic distance, $r_i$ ± 0.01 Å | – | 20.84 | 12.18 | 9.68 |
| Indirect band gap energy, $E_g$ ± 0.02 eV | 2.56 | 2.40 | 2.24 | 2.16 |
| Direct band gap energy, $E_g$ ± 0.02 eV | 2.84 | 2.74 | 2.54 | 2.42 |

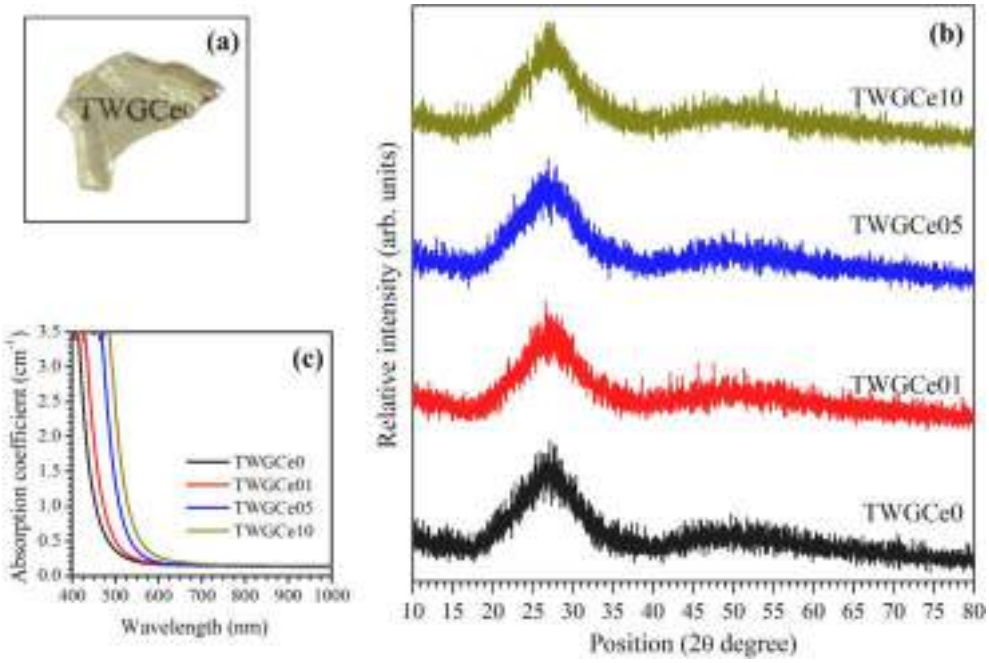



**Fig. 1.** Image of TWGCe05 glass (a), XRD profiles(b) and absorption spectra (c) of TWGCe*x* glasses.

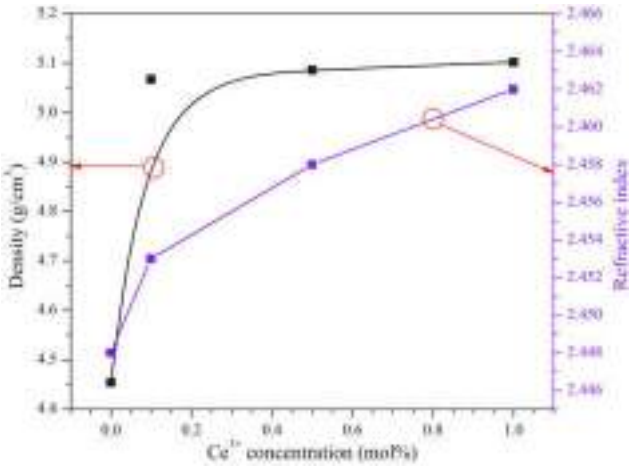



**Fig. 2.** Variation of density and refractive index of TWGCe*x* glasses as a function of $Ce^{3+}$ concentration.

the significant properties to analyze the optical transitions of active ions doped in a glassy matrix and it can be determined using UV–VISabsorption spectra (see Fig. 1**c**). The absorption coefficient (α = Absorbance /optical path length) near the absorption edge and the photon energy (hν)of incident radiation are related as shown below [19].

$$\alpha\,.\,(h\nu) \;=\; B\,(h\nu - E_{opt})^{q} \tag{1}$$

where B is a constant and it is independent of photon energy. The integer q represents the type of transition (direct/indirect) and it has 1/2, 1/3, 2 and 3 for direct allowed, direct forbidden, indirect allowed and indirect forbidden transitions, respectively. This condition is applicable under negligible reflectance. In case of glassy material, the reflectance can be minimized by polishing them to optically high quality [20–24]. The value of indirect and direct band gap energies has been obtained by extrapolating the linear region of Tauc's plots to meet the hν axis as shown in Fig. 3. In the present investigation, both indirect and direct band gap energies found decrease with increase of $Ce^{3+}$ concentration (see Table 1). The addition of low concentrations of dopant ions decreases the energy band gap and it could be due to small separation distance between dopant ions [25].

### 3.2. FTIR and SEM analysis

The FTIR spectra help us to know various structural vibrations present in the glass host. The FTIR spectra of TWGCe0 and TWGCe05 glasses shown in Fig. 4 are similar and they are identical to other tellurite glass [26]. The IR bands at ~ 3437, ~2361 and ~ 1713 $cm^{-1}$ belongs to the symmetric stretching vibrations of $HO^{-}$ group [5,27], the IR band noticed at ~ 871 $cm^{-1}$ is related to asymmetric stretching vibrations of Ge-O-Ge and W-O-W units [26]. The bands at ~ 721 and 642 $cm^{-1}$ have been ascribed to Te-O stretching vibrations in $TeO_4$ and $TeO_3$ units respectively [28]. The presence of $OH^{-}$ content influence the luminescence properties of RE active ions in a glassy matrix [29] and it can be evaluated using the equation,$\alpha_{OH} = \ln(T_0/T_D)/l$, where $T_o$ is the maximum transmittance, $T_D$ is transmittance corresponding to 3000 $cm^{-1}$by assuming the reflectance as zero and *l* is the optical path length.

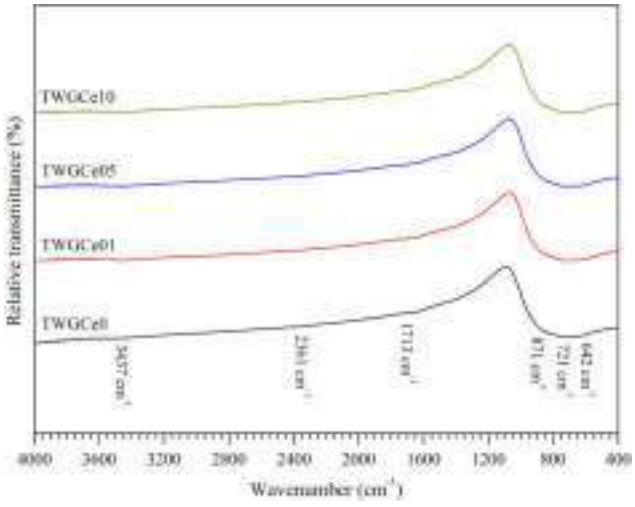



**Fig. 4.** FTIR spectra of TWGCe*x* glasses.

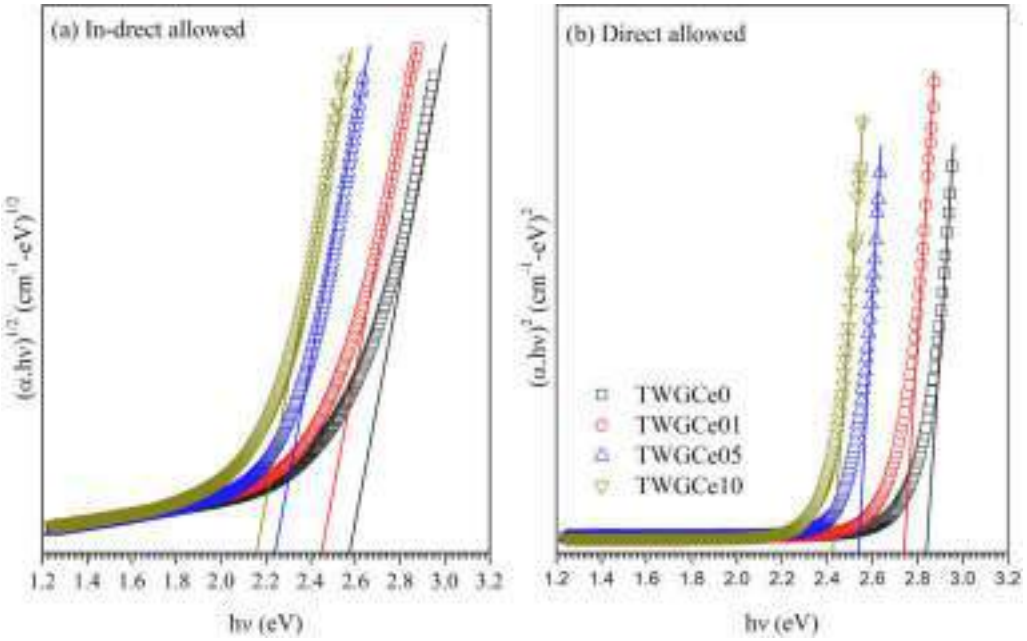



**Fig. 3.** Tauc's plots for indirect (a) and direct (b) allowed transition in TWGCe*x* glasses.

Lower the $OH^-$ content lesser will be the non-radiative losses. The value of $\alpha_{OH}$ is found to be 0.51 and 0.48 ± 0.02 $cm^{-1}$ for TWGCe0 and TWGCe05 glasses, respectively. The addition of $Ce_2O_3$ content reduces the $\alpha_{OH}$ value resulting to enhance the luminescence properties.

The SEM micrograph with EDS spectrum of TWGCe05 glass is shown in Fig. 5. As can see the SEM micrograph, one can notice that the prepared glass samples have good amorphous phase and they are free from air-bubbles, clusters and defects. The EDS spectrum shows the presence of all elements distributed uniformly indicating the proposed chemical composition. The atomic weight percentages of different elements present in the TWGCe05 glass are 61.77 at%, 4.52 at%, 31.53 at%, 1.69 at% and 0.49 at% for oxygen (O), germanium (Ge), tellurium (Te), tungsten (W) and cerium (Ce) and the corresponding mole percentages are 23.98 mol%, 23.60 mol%, 30.81 mol%, 16.87 mol% and 4.74 mol%.

### 3.3. Luminescence properties

The excitation and emission spectra of TWGCe*x* glasses are shown in Fig. 6. The excitation spectra monitoring the emission at 408 nm consists of a broad band extended from 243 nm to 360 nm and has been assigned to $Ce^{3+}$: $4f \rightarrow 5d$ transition [see Fig. 6**(a)**]. This broad band appears having three sub-peaks with maximum at ~ 255, ~274 and ~ 323 nm. The emission spectra recorded at 323 nm excitation consists of a broad and intense band due to $Ce^{3+}$: $5d \rightarrow 4f$ (408 nm) transitions. The intensity of excitation band increases with increase of $Ce^{3+}$ concentration, while the intensity of emission bands increases with increase of $Ce^{3+}$ concentration reach to maximum at × = 0.5 mol% and then decrease for further rise of concentration showing luminescencequenching phenomenon beyond × = 0.5 mol% due to energy transfer (ET) among the excited $Ce^{3+}$ ions at higher concentrations. The emission profiles of TWGCe glasses are similar to those reported for gadolinium oxyfluoroborate [5] and $P_2O_5$-$Li_2CO_3$-$GdBr_3$-$Al_2O_3$ [30] glasses.

As can see the normalized emission spectra shown as inset of Fig. 6 **(b)**, one can notice a red-shift in emitted luminescence with increase of $Ce^{3+}$ concentration. The peak maximum of $Ce^{3+}$: $5d \rightarrow 4f$ transition shifts from 403 nm for × = 0.1 mol% to 408 nm for × = 0.5 mol% and finally to 410 nm for × = 1.0 mol%. The observed red-shift has been ascribed to the site distribution of $Ce^{3+}$ ions in the ligand fields [31]. It is well known that when the energy of incident light photons is equal or greater than band gap energy of the material then the photons are absorbed by the material and excites the active ions to higher energy levels. When excited at 323 nm wavelength, the ground state $Ce^{3+}$: $4f$ ions get excited to $Ce^{3+}$: $5d$ emission state resulting to exhibit intense luminescence through $Ce^{3+}$: $5d \rightarrow 4f$ transition. The emission mechanism of $Ce^{3+}$ ions in TWGCe*x* glasses at 323 nm excitation is illustrated in Fig. 7**(a)**.

The Commission International de I'Eclairage (CIE-1931) chromaticity coordinates evaluated from the emission spectral profiles have been used to know the colour purity (CP) and correlated colour temperature (CCT) of emitted luminescence. For TWGCe*x* glasses excited at 323 nm, the CIE chromaticity coordinates are obtained as (x = 0.161, y = 0.018).The CP and CCT values have been determined using the equations shown below.

$$CP = \frac{\sqrt{(x - x_e)^2 + (y - y_e^2)}}{\sqrt{(x_d - x_e)^2 + (y_d - y_e^2)}} \times 100 \quad (2)$$

$$CCT = -449\,z^3 + 3525\,z^2 - 6823.3\,z + 5520.33 \quad (3)$$

where $(x_e, y_e)$ represents the coordinates of epicenter point and $(x_d, y_d)$ represents the coordinates for dominant-wavelength-point. Generally, the typical coordinates for equal-energy point are (0.333, 0.333). The constant z can be obtained using the formula, $z = (x - x_e)/(y - y_e)$. The evaluated CIE coordinates are located in the intense blue region of CIE diagram shown in Fig. 7**(b)**. The colour purity is estimated to be 98 % and the corresponding CCT rating is 1802 K. It is well known that the light sources with CCT < 3000 K emit warm light useful for living room illumination. It is known that the generation of white light from phosphor-based LEDs requires blue light excitation. The observed results show that the studied glasses emits intense and warm blue light suitable for decorative lighting sources as well as replacement for blue light source in phosphor-based w-LEDs.

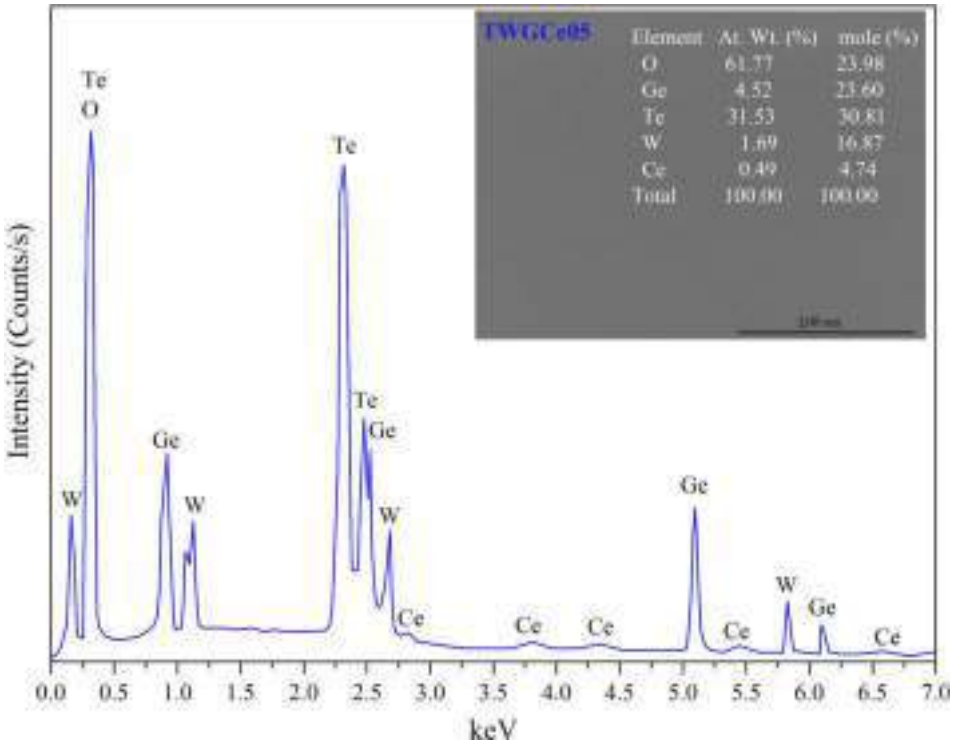



**Fig. 5.** EDS profile of TWGCe05 glass. Insets show the SEM micrograph and elemental analysis.

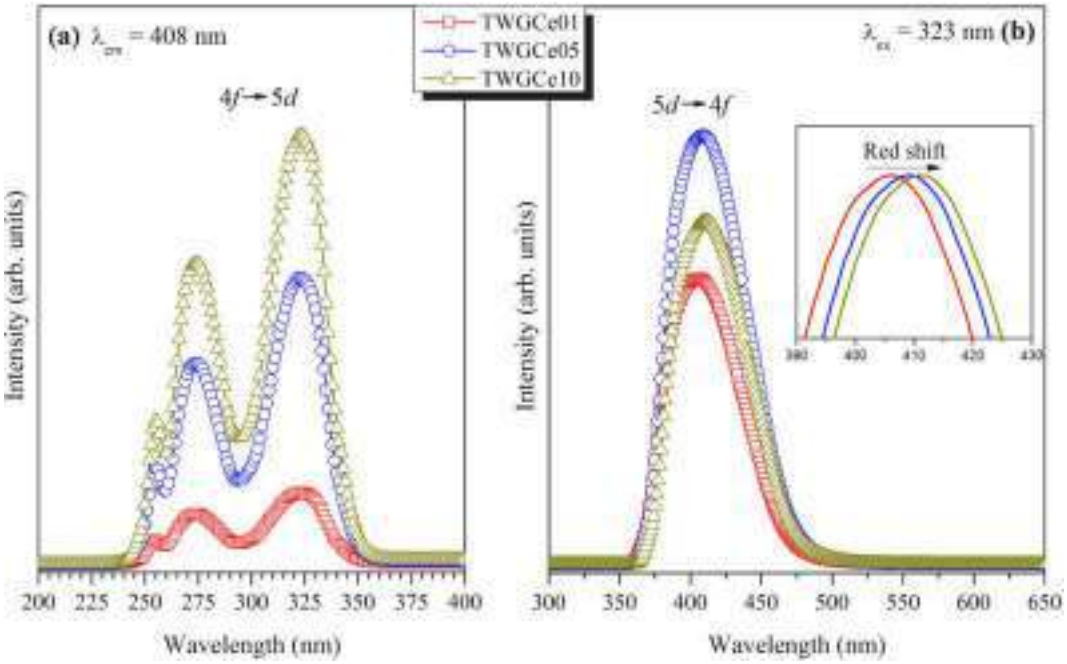



**Fig. 6.** Excitation (a) and emission (b) spectra of TWGCe*x* glasses. Inset shows a red-shift in emission spectra at 323 nm excitation.

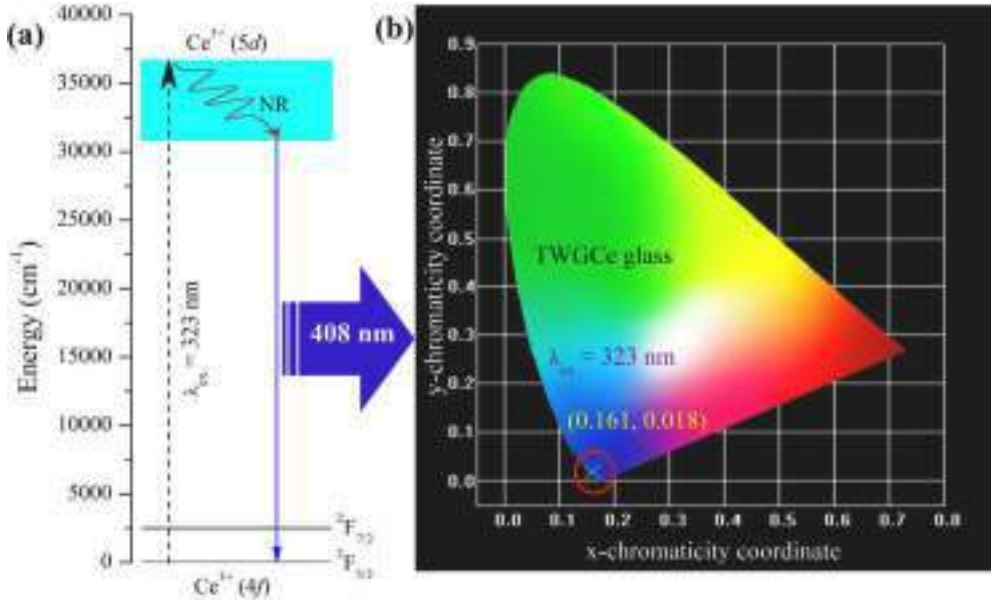



**Fig. 7.** Emission mechanism of $Ce^{3+}$ ions at 323 nm excitations (a) and the chromaticity diagram of TWGCe*x* glasses.

The process of ET among the excited active ions occurs either due to exchange interaction or multi-polar interaction process depending upon the critical transfer distance but not on inter-ionic distance. According to Dexter's theory of sensitized luminescence in solids [32], the exchange interaction type of ET is possible for $R_c \leq 5$ Å and beyond this limit ($R_c >$ 5 Å) the multi-polar interaction come into play for the transfer of energy among the excited ions. The inter-ionic distance ($r_i$) is the average distance among the sites of $Ce^{3+}$ ions in TWGCe glass host matrix, while the critical transfer distance ($R_c$) represents the mean distance among the $Ce^{3+}$ ions for which threshold transfer of energy occurs at suitable excitation. The value of $R_c$ responsible for ET mechanism has been estimated using the following formula [33].

$$R_c = \left(\frac{M}{N_A . d . C}\right)^{1/3} \quad (4)$$

where M is the molar mass, $N_A$ is the Avagadro's number, d is the density and C is the concentration of active ions (in g/mol). The value of $R_c$ is found to be 5.56, 3.82 and 3.03 Å for × = 0.1, 0.5 and 1.0 mol%, respectively. These values suggest that the exchange interaction mechanism play a key role in ET for TWGCe*x* glasses.

### 3.4. Luminescence decay

The luminescence decay curves of $Ce^{3+}$ in TWGCe*x* glasses monitoring the emission and excitation wavelengths at 408 nm and 323 nm

respectively are illustrated in Fig. 8. These decay curves are well fitted to a double exponential function, $I(t) = A_1 . e^{-t/\tau_1} + A_2 . e^{-t/\tau_2}$, where I(t) represent the emission intensity as a function of time t, $A_1$ & $A_2$ are constants and $\tau_1$ & $\tau_2$ are the short and long decay times, respectively. The average decay time $\langle\tau\rangle$ has been estimated using well known equation, $\langle\tau\rangle = \frac{A_1 . \tau_1^2 + A_2 . \tau_2^2}{A_1 . \tau_1 + A_2 . \tau_2}$. In the present case, the values of $\langle\tau\rangle$ are determined as 23.92, 22.15 and 19.32 ns for TWGCe0.1, TWGCe0.5 and TWGCe1.0 glasses, respectively. The gradual decrease in decay time with the addition of $Ce^{3+}$ ions in TWG glass host is an indication of energy transfer among the excited $Ce^{3+}$ ions at higher concentrations.

## 4. Conclusions

The TWGCe*x* glasses have been prepared with perfect amorphous phase by conventional melt-quench method are free from bubbles and impurities. The ratio of molar refraction to molar volume is found lesser than unity [$(R_m/V_m) > 1$] showing non-metallic nature of TWGCe*x* glasses. The $OH^-$ content of the order 0.51 – 0.48 $cm^{-1}$ is favourable to improve the luminescence properties. The SEM micrograph confirms the absence of impurities and bubbles and the EDS results show the presence of all the elements distributed uniformly. These glasses exhibit deep-blue luminescence through $Ce^{3+}$: $5d \rightarrow 4f$ transition when excited at 323 nm wavelength. The observed concentration quenching has been ascribed to the exchange interaction among the excited $Ce^{3+}$ ions at higher concentrations. For all TWGCe*x* glasses, the lifetime is found to be 1.02 ns. The colour perception and CCT rating values are found to be 99 % and 1802 K, respectively are more favourable for decorative lighting sources. The intense and fast luminescence signal is more suitable to be used as a scintillator material. The observed results suggest that the TWGCe05 glass is more favourable to design decorative blue light sources for living rooms and a suitable blue light source to design w-LEDs.

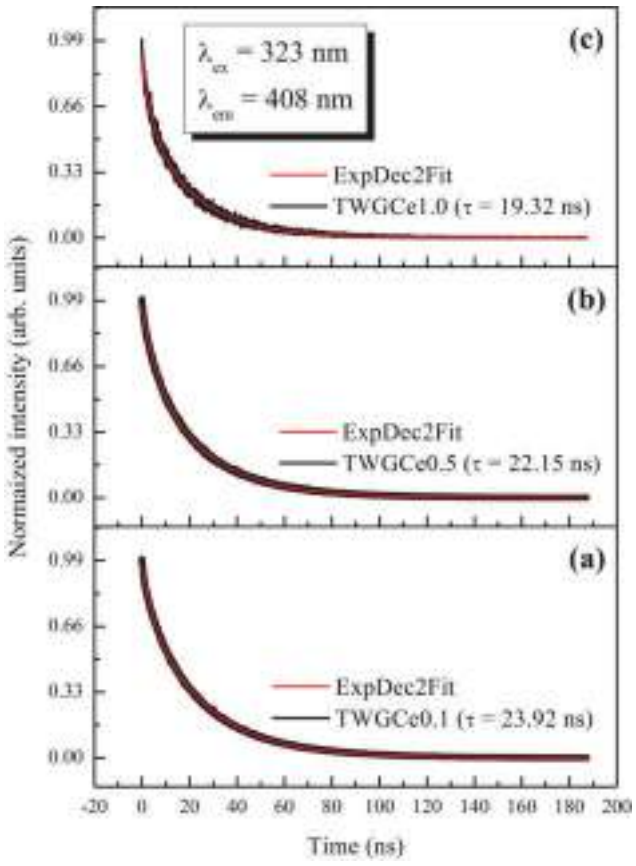



**Fig. 8.** Luminescence decay profiles of TWGCe*x* glasses.

## CRediT authorship contribution statement

**G. Pullaiah:** Methodology, Writing – original draft. **K. Venkata Rao:** Software, Investigation, Writing – review & editing, Supervision. **B.C. Jamalaiah:** Conceptualization, Software, Investigation, Writing – review & editing. **N. Madhu:** Software, Validation, Writing – review & editing. **Venkatramaiah Nutalapati:** Validation, Writing – review & editing.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data Availability Statement

Data will be made available on reasonable request.

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# Structural and optical analysis of $YAl_3(BO_3)_4$: $Pr^{3+}$ phosphors for lighting applications

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ABSTRACT

A series of $Pr^{3+}$ activated $YAl_3(BO_3)_4$ phosphors were fabricated by solid-state reaction technique and they were characterized via phase, morphology and photoluminescence studies. Powder X-ray diffraction peaks were suitably matched to JCPDS No. 72–1978. The presence of various vibrational bonds was identified using Fourier transform infrared spectroscopy. High resolution scanning electron microscopic investigations show that the phosphor particles were distributed uniformly and presented a rod-like shape. The photoluminescence results show that the studied phosphors were easily excited by visible wavelength to produce intense-yellow to pale-yellow tunable emission. The decrease in luminescence intensity and lifetime was assigned to dipole-dipole interaction energy-transfer among excited $Pr^{3+}$ ions. Observed results show that the 0.05 mol% of $Pr^{3+}$ activated phosphor produce intense-yellow luminescence at 480 nm excitation.

## 1. Introduction

Currently, there is a need for new, novel, low power consumption, low pollution and high efficiency materials in the fields of science & engineering, agriculture, medicine, defense, industry and communication [1–3]. Compared to other lighting sources, the light-emitting-diode (LED) based devices are more favorable owing to their high brightness, long lifetime, less energy consumption, low heat production [4]. The phosphor converted LEDs have been the most suitable light sources in various fields owing to their reliability, long-life, low energy consumption, high fluorescence efficiency and environmental friendly behavior as they are free from toxic elements like Cd, S and Cl [5]. The superior qualities of pc-LEDs initiate many researchers to design and develop new red or yellow emitting materials for white-LEDs. Recently, the oxide-based phosphors have been the subject for many applications such as white light generation for screens in PDPs and FEDs, for green emission in horticulture due to their great resistance to moisture, excellent thermal and chemical stability compared to other phosphors like silicates, nitrides and so on[6–9].

Trivalent rare-earth (RE) ions doped $YAl_3(BO_3)_4$ phosphors have been the potential candidates for spectacular optoelectronic applications owing to their extensive iso-morphous substitutions, UV transparency, thermal constancy, chemical strength and non-

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linear optical properties [10,11]. In $YAl_3(BO_3)_4$ structure, the $O^{2-}$ ions forms trigonal prisms with $Y^{3+}$ ions at the center and they are separated from each other by $(BO_3)^{3-}$ groups [12]. Thus, the structure of $YAl_3(BO_3)_4$ lattice facilitates to activate relatively huge concentrations of $RE^{3+}$ active ions without considerable agglomeration as they do not require any charge compensation. It is well known that the $Pr^{3+}$ ions show complex emission spectral profiles compared to other RE ions. Since the emission transitions of $Pr^{3+}$ ions are sensitive to the host environment around it, they exhibit blue (~480 nm), green (~540 nm), yellow (~580 nm), red (~600–650 nm), near UV (~800–1500 nm) luminescence through $^1D_2$, $^3P_1$,$^3P_0$ and $^1G_4$ excited energy states to their lower lying energy states [13,14]. The presence of prominent emission levels responsible for outstanding emission transitions in near-UV, visible and near-IR regions facilitate the trivalent praseodymium ($Pr^{3+}$) ions to used in the design of various optoelectronic devices. Based on the diverse applications, the $Dy^{3+}$, $Tm^{3+}$, $Dy^{3+}/Tm^{3+}$, $Dy^{3+}/Ce^{3+}$, $Sm^{3+}/Tb^{3+}$, $Eu^{3+}/Tb^{3+}$ and $Ho^{3+}/Tm^{3+}$ ions activated $YAl_3(BO_3)_4$ phosphors have been prepared and analyzed for various photonic applications [15–21]. The characteristic features of $YAl_3(BO_3)_4$ phosphor matrix initiated to design and investigate the optical properties of $Pr^{3+}$ ions to meet the current technological applications.

The $Ca_9Y(PO_4)_7$:$Ln^{3+}$ (Ln = Ce, Gd, Pr) phosphors for high luminescence efficiency and thermal-stability [22], the $O^{2-}$-$Pr^{2+}$ charge transfer and luminescence properties of $Pr^{3+}$ ions in $YF_3$–$Y_2O_3$ system [23], the YOF:Pr nanoparticles for temperature sensing applications [24] and the $Y_2MoO_6$: $xPr^{3+}$ phosphors for white LED applications [25] were reported. Further, the influence of $Pr^{3+}$ concentration on the luminescence of $BaY_{1.94}Al_4SiO_{12}$:$0.06Ce^{3+}$ phosphor prepared by solid state method has been reported for white LEDs [26]. The present research work explores the fabrication, structural, and optical characterization, optimization of $Pr^{3+}$ concentration for efficient luminescence, color purity of emitted luminescence and the decay analysis of $Pr^{3+}$:$^1D_2$ emission state. The energy transfer (ET) phenomenon among excited $Pr^{3+}$ ions also discussed.

## 2. Experimental procedure

### 2.1. Materials, method of preparation

High purity and analytical grade $Y_2O_3$ (99.99 % purity), $Al_2O_3$ (99.9 % purity), $H_3BO_3$ (≥99.5 % purity), and $Pr_2O_3$ (99.9 % purity) were used directly for the synthesis of YABPr*x* phosphors of composition $Y_{(1-x)}Al_3(BO_3)_4$: $xPr^{3+}$, where $x$ = 0,0.01, 0.02, 0.05,0.1,0.5,1.0 and 2.0 mol% via solid-state reaction technique. A batch composition of about 5.0 g homogeneous-powders (in stoichiometric-amounts) with an additional-amount of 3.0 wt% of $H_3BO_3$ (to avoid its evaporation at higher temperatures) were prepared and heat treated at 200 °C and 600 °C temperatures for 3 h following intermediate grinding. These grinded powders were sintered at 1200 °C for 3 h and cooled to room temperature to produce YABPr*x* phosphors.

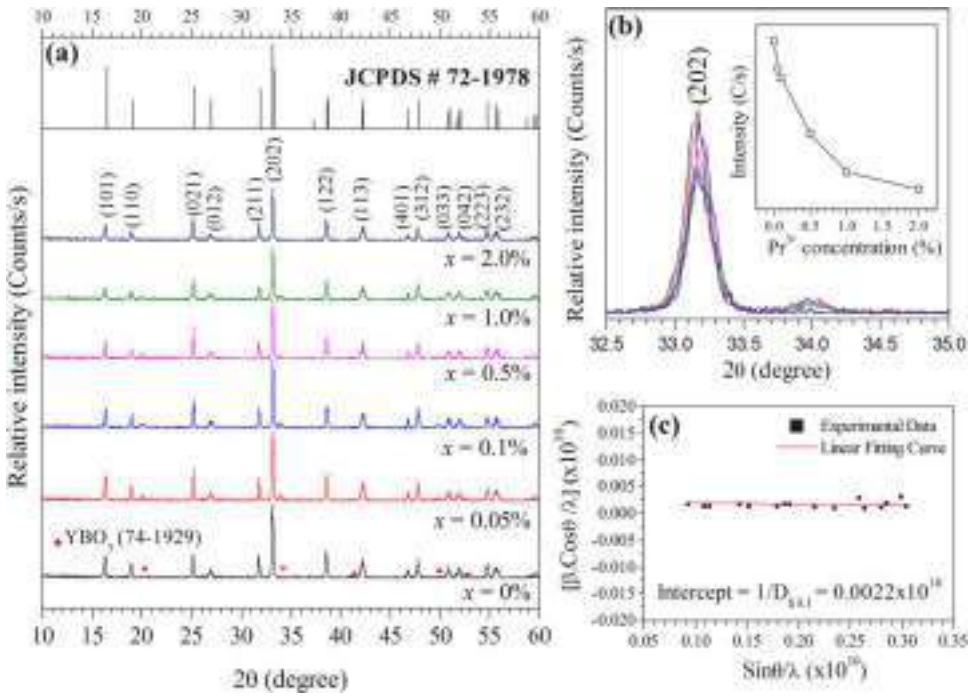



**Fig. 1.** PXRD patterns of YABPr*x* phosphors (a), magnified image of PXRD peak corresponding (202) Miller plane along with intensity vs. $Pr^{3+}$ concentration (b) and the H-W plot for YABPr1.0 phosphor.

### 2.2. Recording of various characteristics

Powder X-ray diffraction (PXRD) measurements were carried out with X′ Pert Pro Materials Research Diffractometer provided with Cu-Kα radiation of wavelength 1.5406 Å. The Fourier transform infrared spectral analysis was carried out by KBr technique with a PerkinElmer FT-IR spectrometer. The morphology of studied samples was examined with FEI-Quanta-FEG-200 F high-resolution scanning electron microscope (HR-SEM). The photoluminescence excitation, emission and decay analysis were carried out with FLS-1000 photoluminescence spectrometer containing xenon flash lamp in pulsed mode as a light source.

## 3. Results and discussion

### 3.1. Structure and morphology

The PXRD profiles of YABPr*x* ($0 \leq x \leq 2.0$ mol%) phosphors are illustrated in Fig. 1(a). These patterns are suitably fitted to JCPDS card No. 72–1978 belonging to $CaMg_3(CO_3)_4$ mineral huntite structure [27]. A two-dimensional crystal structure of $YAl_3(BO_3)_4$ lattice is shown in Fig. 2. As can see the PXRD profiles, one can notice a negligible $YBO_3$ phase and it has fever effect on the optical properties of RE ions and it has been ascribed to loss of boron at higher temperatures and slow reaction of $Al_2O_3$ with $Y_2O_3$ and $H_3BO_3$ [28]. A monotonous decrease in intensity of PXRD patterns with the addition of concentration of $Pr^{3+}$ ions is observed. The magnified image of a PXRD peak corresponding to (202) Miller plane in the 2θ ranges from 32.5 to 35°and the variation of its intensity versus $Pr^{3+}$ ions concentration is described as inset of Fig. 1(b). The close ionic radii of $Y^{3+}$ (0.090 nm) and $Pr^{3+}$ (0.1013 nm) may lead suitable replacement of $Pr^{3+}$ ions in place of $Y^{3+}$ sites. The mean size of crystallite has been determined as ~46 nm using to Debye-Scherrer method [29] and it is very close to the Hall-Williamson's (H-W) method (~45 nm) [30]. The H-W plot (β.cosθ/λ vs. sinθ/λ) for YABPr1.0 phosphor is presented in Fig. 1(c). The small deviation in ionic radii of $Y^{3+}$ and $Pr^{3+}$ may cause negligible lattice distortions resulting micro strains of the order 0.0074 which is found smaller than that of $SrEuMgAl_{10}O_{17}$ (~0.00751 nm) phosphor [31].

The FT-IR spectral profiles of YABPr*x* ($x = 0$ and 0.5 mol%) phosphors shown in Fig. 3 exhibit fourteen IR absorption bands showing the presence of various vibrations responsible for optical properties of RE active ions. A broad-band with a peak utmost at ~3030 $cm^{-1}$ and a group of bands at ~2354, ~2322 and ~2247 $cm^{-1}$ belongs to O–H stretching vibration and moisture in the sample, while the band at ~1355 $cm^{-1}$ is related to phonon frequency of YAB phosphor [32,33]. The IR bands observed at ~1414, ~1252 and ~500 $cm^{-1}$ belongs to B-O asymmetric stretching and asymmetric bending vibrations in orthoborate group, O-B-O bending vibrations, respectively, while the band at ~707 $cm^{-1}$ belongs to both B-O-B bending and Al-O bending vibrations [34,35]. The IR bands positioned at ~1064, 918 and 869 $cm^{-1}$have been related to the $YBO_3$ phase [28,36] and the IR band at ~776 $cm^{-1}$ has been ascribed to Al-O stretching vibrations [37]. The IR bands noticed at ~613, 542 and 461 $cm^{-1}$ have attributed to Y-O stretching vibrations [38].

The shape, size, orientation and distribution of particles have been known by studying the morphology. The HR-SEM micrograph of YABPr0 phosphor shown in Fig. 4 presented a rod-like shape with uniformly distributed particles. From this image one can notice that all the particles are oriented distinctly in a particular direction. This type of morphology helps in improving the optical properties of RE active ions [39]. The mean size of particles is calculated as ~105 nm with length varies from 500 to 1000 nm supporting the nano-crystalline phase of YABPr*x* phosphors.

### 3.2. Photoluminescence analysis

In order to gain access to higher energy states and hence to select appropriate excitation wavelength producing efficient emission, the photoluminescence excitation (PLE) spectrum of YABPr*x* phosphors have been recorded controlling the emission at about 598 nm corresponding to $Pr^{3+}: {}^1D_2 \rightarrow {}^3H_4$ transition. These spectra reveal three excitation bands at around 448, 470 and 480 nm

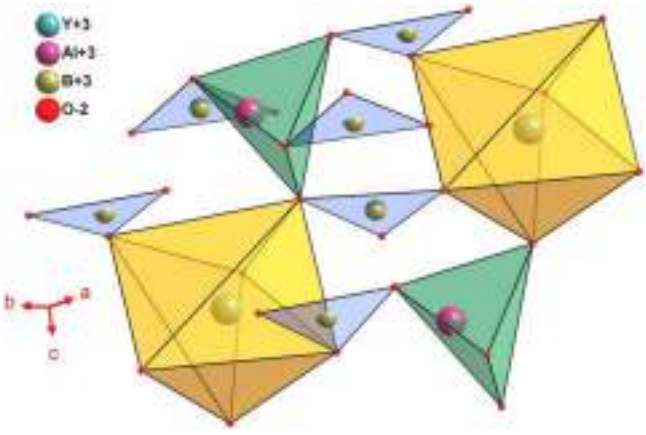



**Fig. 2.** Representation of two-dimensional YAB lattice.

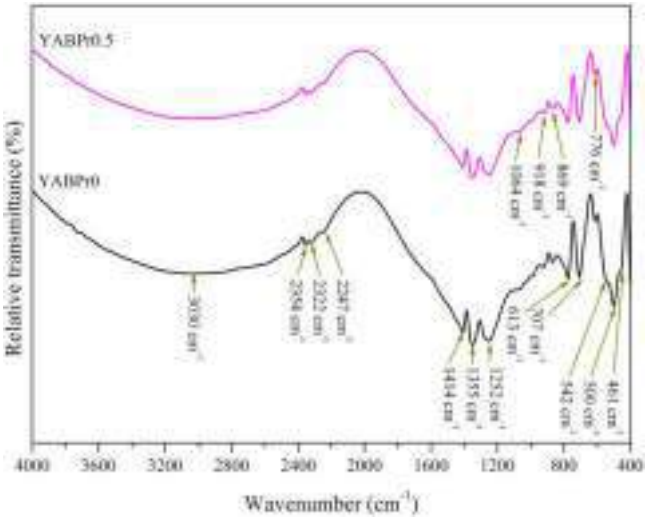



**Fig. 3.** FT-IR spectra of YABPr*x* ($x = 0$ and 0.5 mol%) phosphors.

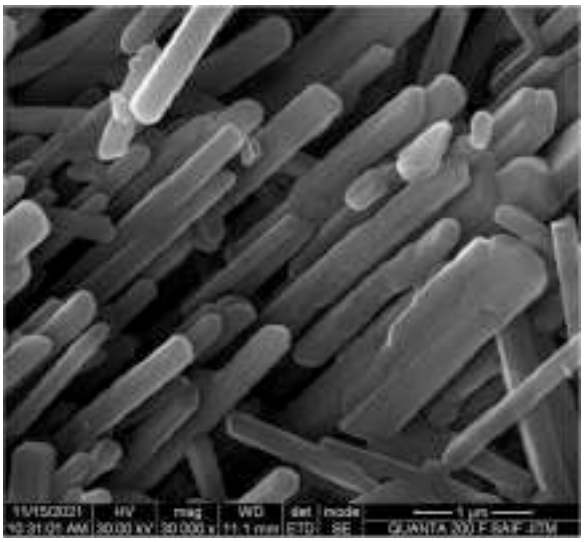


**Fig. 4.** HR-SEM micrograph of YABPr0 phosphor.

corresponding to $Pr^{3+}: {}^3H_4 \rightarrow {}^3P_{2,1,0}$transitions, respectively. The observed spectral profiles are identical to those reported for $Li_2SrSiO_4$: $Ce^{3+}$, $Pr^{3+}$ Phosphors [40]. The excitation spectra of YABPr*x* phosphors with the assignment of PLE bands noticed are depicted in Fig. 5. The intensity of $Pr^{3+}: {}^3H_4 \rightarrow {}^3P_J$ ($J = 0,1,2$) transitions increased with enhancement of concentration of $Pr^{3+}$ ions. The inset of Fig. 5 shows the variation of strength of $Pr^{3+}: {}^3H_4 \rightarrow {}^3P_J$ transitions as a function of $Pr^{3+}$ concentration. Since the PLE band with peak maximum at ~480 nm ($Pr^{3+}: {}^3H_4 \rightarrow {}^3P_0$) is broad and intense, this wavelength can be used to excite YABPr*x* phosphors more efficiently compared to other two wavelengths.

Upon 480 nm excitation, the emission spectra of YABPr*x* phosphors in the spectral region from 500 to 725 nm illustrated in Fig. 6 show different transitions originated from $^3P_0$ and $^1D_2$ emission states. The first group of emission bands (523, 528, 534, 538 and 542 nm) with peak maximum at 528 nm has been attributed to $^3P_0 \rightarrow {}^3H_4$transition, the second group of bands (554, 558 and 563 nm) with maximum at 563 nm has been attributed to $^3P_0 \rightarrow {}^3H_5$ transition, the third group of bands (594, 598, 603 and 611 nm) with maximum at 598 nm has been assigned to $^1D_2 \rightarrow {}^3H_4$ transition, the fourth group of bands (625, 630 and 633 nm) with maximum at 625 nm has been allocated to $^3P_0 \rightarrow {}^3H_6$ transition, the fifth group of bands (637, 647 and 656 nm) with maximum at 637 nm has been allotted to $^3P_0 \rightarrow {}^3F_2$ transition, the sixth group of bands (663, 670, 676 and 684 nm) with maximum at 670 nm has been ascribed to $^1D_2 \rightarrow {}^3H_5$ transition, and the seventh group of bands (696 and 706 nm) with maximum at 696 nm has been assigned to $^3P_0 \rightarrow {}^3F_3$ transition [41].

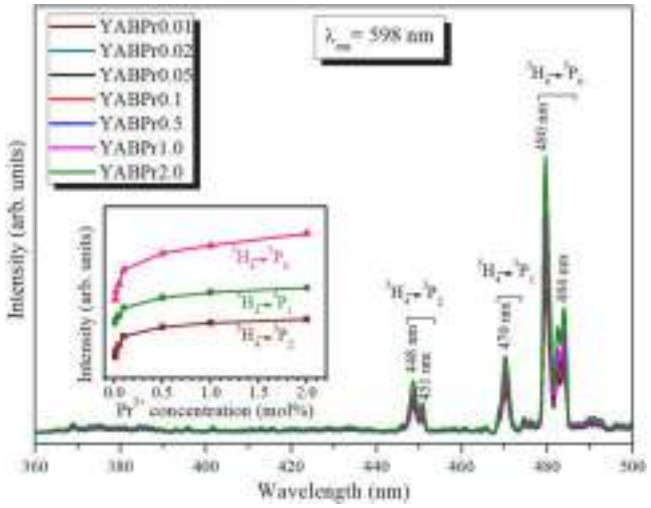



**Fig. 5.** PLE spectra of YABPr*x* phosphors ($\lambda_{em} = 598$ nm). Inset shows the variation of intensity of $Pr^{3+}$ : $^3H_4 \rightarrow {}^3P_{2,1,0}$transitions as a function of $Pr^{3+}$ concentration.

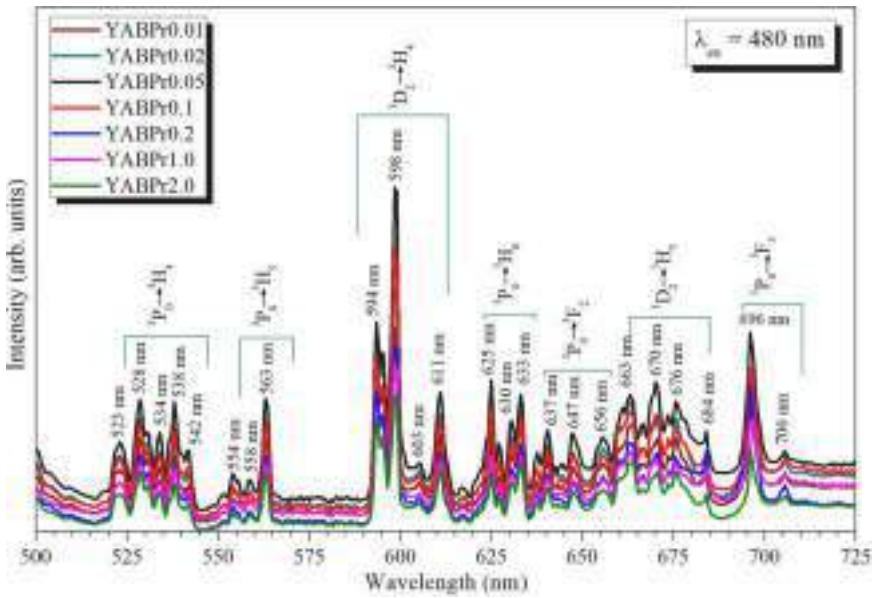



**Fig. 6.** Emission spectra of YABPr*x* phosphors at 480 nm excitation.

From the emission spectra, it is found that the strength of observed transitions increases reaches to maximum at $x = 0.05$ mol% and then decrease monotonically with the enhancement of $Pr^{3+}$ concentration signifying efficient energy transfer (ET) among the exited $Pr^{3+}$ ions at 480 nm excitation. It is due to the reason that at lowest concentrations the absence of energy transfer among the $Pr^{3+}$ active ions initiates feeble interactions resulting to enhance the intensity of emitted luminescence. This process continues up to a limiting concentration called the optimum concentration ($x = 0.05$ mol%). As the concentration increases beyond the optimum, the energy transfer among the $Pr^{3+}$ ions increase slowly due to increased interactions among $Pr^{3+}$ ions enhancing non-radiative transitions resulting a decrease in luminescence intensity with increase of $Pr^{3+}$ concentration. This process of variation in intensity with the concentration of active ions is known as luminescence quenching. To understand the luminescence quenching process, the magnified emission spectra in the spectral region from 590 nm to 604 nm and the variation of intensity of $Pr^{3+}$ : $^1D_2 \rightarrow {}^3H_4$ transition versus $Pr^{3+}$ concentration are described in Fig. 7(a) and Fig. 7(b), respectively.

Upon 480 nm excitation, the incident light photons interact with the ground state $Pr^{3+}$ ions and excite them to $Pr^{3+}$: $^3P_0$ emission state resulting to produce radiative transitions through $^3P_0 \rightarrow {}^3H_{4,5,6}$ and $^3P_0 \rightarrow {}^3F_{2,3}$transitions along with non-radiative (NR) transitions through $^3P_0 \rightarrow {}^1D_2$transition. The population of $^1D_2$ emission state increases enormously due to its long lifetime compared to

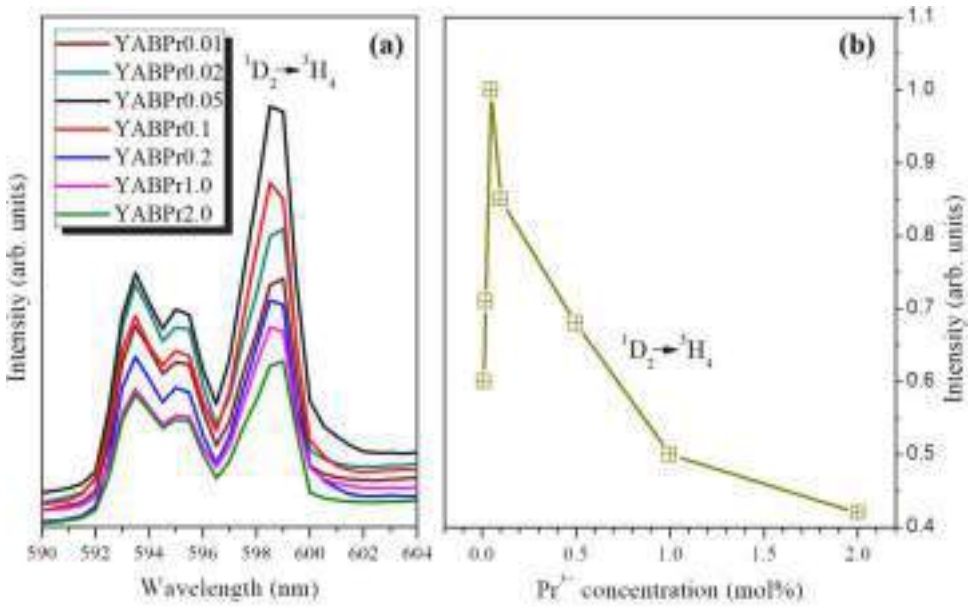



**Fig. 7.** Magnified image of $^1D_2 \rightarrow {}^3H_4$transition of YABPr*x* phosphors at $\lambda_{ex} = 480$ nm (a) and its intensity variation as a function of $Pr^{3+}$ concentration (b).

$^3P_0$ state. It is well known that the intensity of emitted luminescence due to $\Psi J \rightarrow \Psi^{|}J^{|}$ transition varies proportionally to the population density of higher energy state ($\Psi J$). The higher population of $^1D_2$ energy state results a maximum intensity for 598 nm ($^1D_2 \rightarrow {}^3H_4$) luminescence. The emission mechanism of $Pr^{3+}$ ions in YABPr*x* phosphors at 480 nm excitation has been described in a partial energy level diagram shown in Fig. 8.

### 3.3. Color-purity and color-temperature

The analysis of *colour purity*(CP) and *correlated colour temperature* (CCT) of emitted-light has been done by evaluating *Commision International de l'Eclairage* $(CIE - 1931)$color coordinates$(x, y)$. The $Pr^{3+}$ ions exhibit either red or yellow or green luminescence depending upon the host environment in which they are located. The $YVO_4$: $Pr^{3+}$ [42] and $CaLaB_7O_{13}$: $Pr^{3+}$ [43] emit red luminescence, the $LaMgAl_{11}O_{19}$: $Pr^{3+}$ [44] emit yellow luminescence and the $Pr^{3+}$: NGW [8] emits green luminescence. The evaluated CIE coordinates show a tunable luminescence from intense-yellow to pale yellow as illustrated in CIE diagram shown in Fig. 9. The YABPr0.05 phosphor with coordinates (x = 0.492, y = 0.485) exhibits an intense yellow luminescence similar to that of $LaMgAl_{11}O_{19}$: $Pr^{3+}$(0.4497, 0.5306) [44] and $Ba_2GdNbO_6$: $Sm^{3+}$ (0.496, 485) [45]. According to McCamy [46], the appearance of color of emitted luminescence has been expressed by CCT and the color sensitivity by CP. The values of CIE coordinates, CCT rating and CP for YABPr*x* phosphors are abridged in Table 1. The *CCT*rating of YABPr*x* phosphors is in the vicinity of warm-white light indicating safer for environmental and human activities.

### 3.4. Luminescence-decay dynamics

Generally, the lifetime ($\tau$) of an emission state will remain constant in the presence of radiative transitions and it decreases due to non-radiative (NR) transitions which cause ET among excited active ions or active and sensitizer ions. The decay curves of $Pr^{3+}$: $^1D_2$ emission state of YABPr*x* phosphors at $\lambda_{em} = 598$ nm and $\lambda_{ex} = 480$ nm are shown in Fig. 10(a). All-these decay-profiles are fitted to one-exponential function, $I = I_0.e^{-t/\tau}$, where $I_0$ represents the intensity at $t = 0$ *s*. Since the deviation in lifetimes of YABPr0.01 (74.8 $\pm$ 0.2 μs) and YABPr0.02 (74.7 $\pm$ 0.2 μs) phosphors are negligible and found almost the same as that of YABPr0.05, the decay profiles of YABPr0.01 and YABPr0.02 phosphors are not depicted in Fig. 10(a). The lifetime values are estimated to be 74.6, 68.7, 47.1, 40.4 and 38.6( $\pm$ 0.2 μs) for different values of *x*, respectively and they shrink with enhance of $Pr^{3+}$ ions concentration. The decrease in strength of luminescence intensity and the value of $\tau$ is mainly due to ET amongst the excited $Pr^{3+}$ ions at higher concentrations. Fig. 10 (b) demonstrates the variation of lifetime as a function of $Pr^{3+}$ ions concentration.

The working performance of an optical material has been estimated by evaluating its quantum efficiency, $\eta = \int I(t).\, dt/\tau$, where I (t) is the integrated emission intensity and τ is the lifetime [47]. For optimized concentration (YABPr0.05), the value of quantum efficiency is estimated to be 38 %. Blasse [48] reported that either exchange or multi-polar interaction mechanisms such as dipole-dipole (d-d), dipole-quadrupole (d-q) and quadrupole-quadrupole (q-q) play a key role for ET among the activators and also activator and sensitizer ions. The exchange interaction mechanism type of ET is possible up to a critical transfer distance ($R_c$) of up to

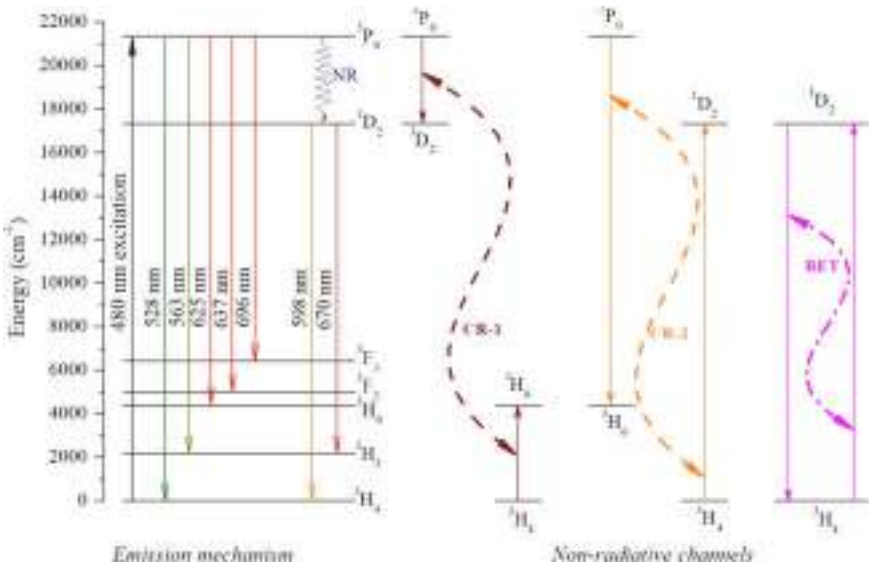



**Fig. 8.** Partial energy level diagram showing the emission mechanism of YABPr*x* phosphors at 480 nm excitation and the possible non-radiative channels responsible for energy transfer among the excited $Pr^{3+}$ ions.

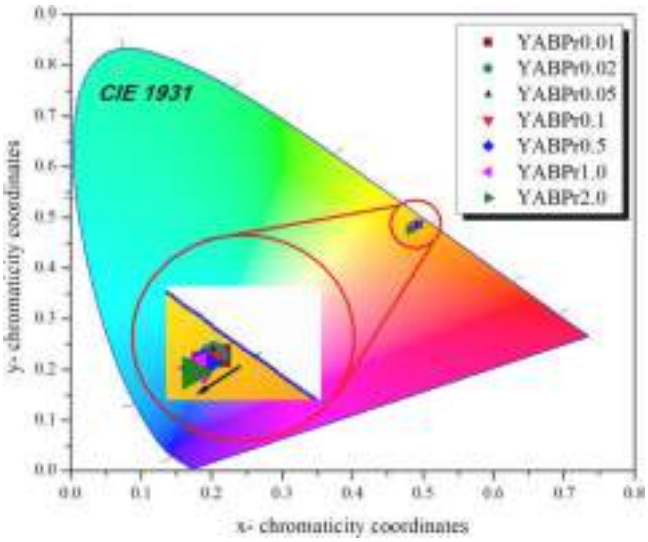



**Fig. 9.** CIE chromaticity diagram of YABPr*x* phosphors at 480 nm excitation.

**Table 1**
Comparison of CIE coordinates, CCT rating and CP values of YABPr*x* phosphors.

| Doping, *x* (mol%) | CIE coordinates (x, y) | CCT rating (K) | CP (%) |
|---|---|---|---|
| $x = 0.01$ | (0.495, 0.486) | 2783 | ~93 |
| $x = 0.02$ | (0.493, 0.484) | 2794 | ~93 |
| $x = 0.05$ | (0.492, 0.485) | 2811 | ~93 |
| $x = 0.1$ | (0.489, 0.483) | 2893 | ~93 |
| $x = 0.5$ | (0.487, 0.481) | 2844 | ~92 |
| $x = 1.0$ | (0.484, 0.478) | 2861 | ~91 |
| $x = 2.0$ | (0.482, 0.475) | 2866 | ~90 |

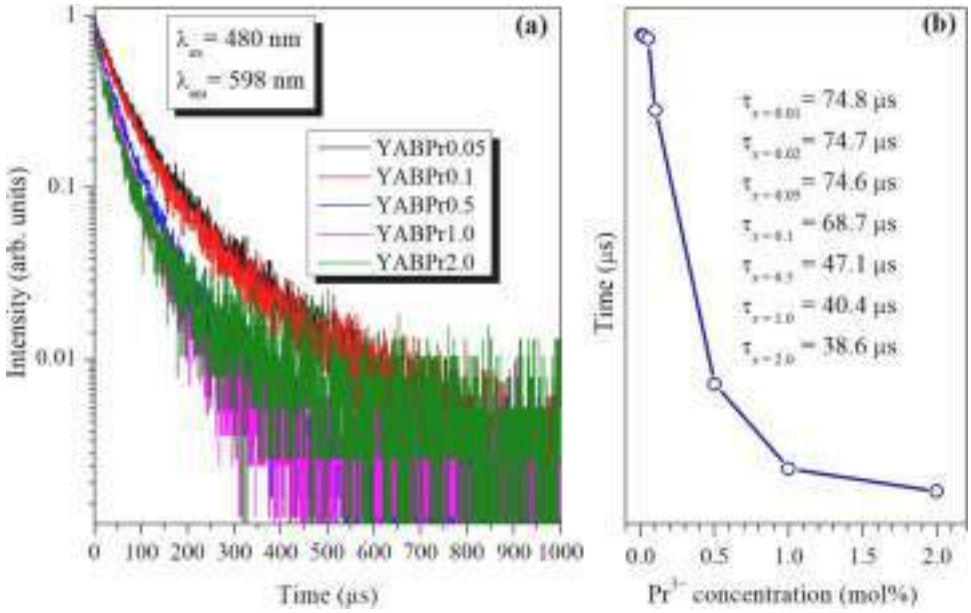



**Fig. 10.** Decay curves of $Pr^{3+}$: $^1D_2$ emission state in YABPr*x* phosphors (a) and the variation of lifetime as a function of $Pr^{3+}$ concentration (b).

5 Å only [49]. In case of YABPr*x* phosphors, the number of available crystallographic sites per unit cell for the active ions is 3, the volume of unit cell is 541.94 Å and the critical concentration is 0.05 mol% and the corresponding value of $R_c$is ~19.0 Å leading to multi-polar interaction mechanism. According to Dexter's theory of sensitized-luminescence in solids [49], the slope of logarithmic plot of emission intensity per activator versus activator concentration [Log(I/C) vs. Log(C)] is equal to Q/3 which helps us to identify the type of interaction mechanism accountable for ET. The ET parameter, Q = 3, 6, 8, 10 for exchange, d-d, d-q, q-q interactions, respectively. From Log(I/C) vs. Log(C) plot presented in Fig. 11, the value of Q is found to be nearly 6 indicating $d-d$ interaction ET among the excited $Pr^{3+}$ ions at 480 nm excitation. This transfer of energy is possible through non-radiative channels like cross-relaxation (CR) and resonant energy transfer (RET) channels. The probable CR and RET channels responsible for ET are shown below and they are illustrated in Fig. 8.

$$CR-1: \left[^3P_0,\ ^3H_4\right] \rightarrow \left[^1D_2,\ ^3H_6\right]$$

$$CR-2: \left[^3P_0,\ ^3H_4\right] \rightarrow \left[^3H_6,\ ^1D_2\right]$$

$$RET: \left[^1D_2,\ ^3H_4\right] \rightarrow \left[^3H_4,\ ^1D_2\right]$$

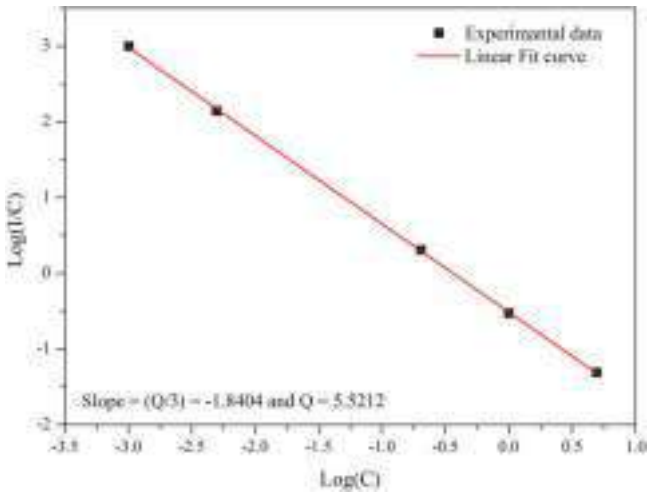



**Fig. 11.** Logarithmic plot of emission intensity per activator versus activator concentration in YABPr*x* phosphors.

## 4. Conclusions

The optical analysis of different concentrations of $Pr^{3+}$ ions activated YABPr$x$ ($0 \leq x \leq 2.0$ mol%) phosphors fabricated by solid-state reaction technique have been investigated. The PXRD analysis state that the studied phosphors are crystallized with an average size of 45–46 nm and suitably matched to JCPDS No. 72–1978. The HR-SEM micrograph presented a rod-like shape with uniform distribution of particles. The PLE spectra obtained by controlling the emission at 598 nm show $^3H_4 \rightarrow {}^3P_{2,1,0}$ transitions positioned at 448, 470 and 480 nm, respectively. Upon 480 nm excitation, the emission spectra exhibit different transitions originated from $^3P_0$ and $^1D_2$ emission states to their lower lying energy states leading to produce tunable luminescence from intense yellow to pale yellow. The decay curves of $Pr^{3+}$: $^1D_2$ emission state are suitably fitted to one exponential function. The addition of $Pr^{3+}$ concentration results a decrease in luminescence intensity and the lifetime of $^1D_2$ emission state due to ET through $d-d$ interaction among the excited $Pr^{3+}$ ions. Based on the observed results it can be concluded that the YABPr0.05 phosphor generates intense and pure yellow luminescence at 480 nm excitation and it is useful for solid state lighting.

## Declaration of Competing Interest

The authors declare that they have no conflict of interest.

## Data availability

Data will be made available on reasonable request.

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ORIGINAL RESEARCH ARTICLE

# Photoluminescence Properties of $SrAl_2O_4$: $Pr^{3+}$ Phosphors for Red Light Sources

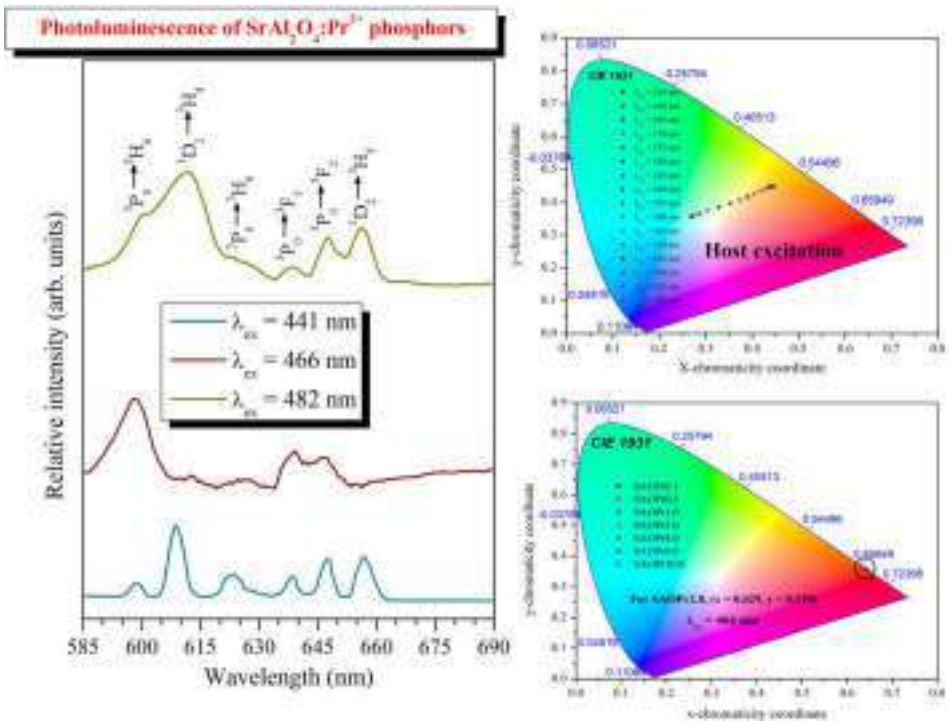
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## Abstract

A series of trivalent praseodymium ($Pr^{3+}$) ion-activated $SrAl_2O_4$ phosphors were prepared by solid-state reaction and characterized. The morphology of prepared phosphors was examined through SEM and TEM studies. The adjacent spacing of lattice fringes was estimated to be ~0.28 nm for the (310) crystal plane of the $SrAl_2O_4$ structure. The luminescence properties were studied by exciting the prepared phosphors within the host as well as $Pr^{3+}$ ions. For efficient luminescence, the concentration of $Pr^{3+}$ ions was optimized to be 2.0 mol.%. The colour perception of emitted luminescence was examined by evaluating the chromaticity coordinates. The observed quenching in luminescence and the gradual decrease in lifetime with increase of $Pr^{3+}$ concentration was assigned to the multi-polar interaction mechanism among the excited $Pr^{3+}$ ions at higher concentrations. The studied phosphors show more proficiency for solid-state red light sources.

## Graphical Abstract




**Keywords** $SrAl_2O_4$ phosphor · praseodymium ions · photoluminescence · solid-state lighting device · red light sources

Extended author information available on the last page of the article

## Introduction

Among the various energy saving materials, the trivalent rare earth (RE) ion-activated phosphors are more useful due to their excellent absorption from vacuum ultraviolet to near infrared (near-IR), good thermal and chemical stability, sharp emission lines, good colour rendering index and eco-friendly properties.[1–4] They are more favourable in designing various photonic devices owing to their low energy consumption, compact size, long lifetime and good quantum efficiency.[5,6] They effectively enhance the working efficiency of different kinds of photonic devices such as solid-state lasers, flat panel displays, optical sensors, surface coatings, energy-storage devices and light emitting devices.[7–10] The selection of $SrAl_2O_4$ host, its importance and applications in solid state lighting (SSL) technology was described in detail in our previous work.[11,12] Different RE ion-activated $SrAl_2O_4$ phosphors have been synthesized and characterized for various technological applications for the benefit of mankind and the environment. $SrAl_2O_4$:$Ce^{3+}$-$Li^{3+}$ co-doped phosphors were investigated to enhance white light emission.[13] The luminescence enhancement of $SrAl_2O_4$: $Eu^{3+}$ phosphors in the presence of $B^+$, $Li^+$, $Na^+$, and $K^+$ was reported for white LED applications.[14,15] $SrAl_2O_4$:$Eu^{3+}$ phosphors[16] prepared by combustion were investigated for the applications of mechanoluminescence dosimetry. Long-lasting and the afterglow photoluminescence properties of $SrAl_2O_4$:$Eu^{3+}$, $Dy^{3+}$ phosphors were studied for the fabrication of various photonic devices.[17,18] $Sm^{3+}$, $Tb^{3+}$ and $Tb^{3+}$/$Bi^{3+}$ -doped $SrAl_2O_4$ phosphors[19–21] were developed and characterized for various lighting applications.

Among the RE ions, the $Pr^{3+}$ ion is a user-friendly luminescent center due to its closely packed energy level structure and prominent emission transitions in ultraviolet (UV), visible and near-IR spectral regions. The emission spectra of $Pr^{3+}$ ions are more sensitive to the host environment and hence significantly differ in different hosts resulting to produce red, yellow, green and blue emissions as well as NIR emission. The emission transitions from $^1D_2$, $^3P_1$ and $^3P_0$ energy states to their lower lying energy states are responsible for red, yellow and green luminescence, the transitions from $^1S_0$ energy state results a blue luminescence while the transitions corresponding to 4f-5d energy state are responsible for UV emission.[22–25] These features have attracted the researchers to investigate $Pr^{3+}$ activated different phosphor materials as colour centers. Different concentrations of $Pr^{3+}$ ions activated $PbGdB_7O_{13}$ phosphors[22] were prepared and characterized for potential red luminescence. Under blue light irradiation, green to yellow tunability with an increase of $Pr^{3+}$ concentration in $BaY_2ZnO_5$:$Pr^{3+}$ phosphors has been reported.[23] $NaGd(WO_4)_2$:$Pr^{3+}$ phosphors[24] synthesized by sol-gel method were investigated for intense green luminescence. Guan et al.[25] studied the concentration-dependent luminescence and energy transfer among the $Pr^{3+}$ ions in $BaGd_2(MoO_4)_4$ crystals.

The broad yellow-orange emitting $SrAl_2O_4$:$Pr^{3+}$ phosphors[26] containing 2.0 to 4.0 mol.% of $Pr^{3+}$ ions mixed with 1.0 wt.% of carbon powder were sintered at 1200°C and investigated through powder X-ray diffraction (PXRD), scanning electron microscopy (SEM), photoluminescence excitation (PLE), emission and time-resoled decay studies for SSL applications. Broad emission through $Pr^{3+}$:($^3P_0$, $^1D_2$) → $^3H_J$ transition has been assigned to the crystal field effect of $SrAl_2O_4$. In the present work, the $SrAl_2O_4$:$Pr^{3+}$ phosphors have been prepared varying the concentration of $Pr^{3+}$ ions from 0.1 to 10.0 mol.% without mixing the carbon powder and sintered at a relatively low temperature on the order of 1050°C for 3 h.

The current research work focused a light on the synthesis and characterization of $SrAl_2O_4$:$Pr^{3+}$ phosphors through PXRD, SEM, transmission electron microscopy (TEM), Fourier transform infrared (FTIR) spectroscopy, FT-Raman spectroscopy, excitation, emission and luminescence decay studies. The concentration dependent luminescence was investigated by exciting the samples within the host matrix as well as dopant ($Pr^{3+}$) ions. The optimization of concentration of $Pr^{3+}$ ions for efficient luminescence was reported. The possible reasons for quenching in luminescence and decay time were also reported. The colour perception studies illustrate that the $SrAl_2O_4$:$Pr^{3+}$ phosphor samples show an efficient red luminescence upon different excitations. The obtained results show that the studied phosphors exhibit quite interesting luminescence properties under different excitations compared to earlier work.[26–28]

## Experimental

### Materials Used and Preparation Technique

Different concentrations of $Pr^{3+}$ ion-activated $Sr_{(1-x)}Al_2O_4$:$x$ $Pr^{3+}$ ($x$ = 0 mol.%, 0.1 mol.%, 0.5 mol.%, 1.0 mol.%, 2.0 mol.%, 4.0 mol.%, 6.0 mol.% and 10.0 mol.%) phosphors were prepared by solid-state reaction using high-grade $SrCO_3$ (99%), $Al_2O_3$ (99.9%) and $Pr_2O_3$ (99.9%). The batch compositions of about 2.0 g of homogeneous powders were prepared with stoichiometric ratios. Additionally, 2.0 wt.% of $H_3BO_3$ (99.5%) was added as a flux material for easy decomposition of $SrCO_3$. These powder samples were heat-treated at 200°C for 3 h and sintered at 1050°C for 3 h following intermediate grinding producing milky-white $Sr_{(1-x)}Al_2O_4$:$x$ $Pr^{3+}$ phosphors. The obtained phosphor

materials were labeled as SAOPr*x*, where *x* stands for the concentration of $Pr^{3+}$ ions (in mol.%).

### Characterizations

The crystalline phase of SAOPr*x* ($0 \le x \le 10.0$ mol.%) phosphors was studied with an X' Pert Pro Materials Research Diffractometer ($\lambda_{CuK\alpha}$ = 1.5406 Å). A KBr pellet was employed to study the Fourier transform infrared (FTIR) absorption spectrum with a Perkin Elmer Spectrum One FTIR spectrometer. A Bruker RFS27 FT-Raman spectrometer using a Nd-YAG laser ($\lambda$ = 1064 nm) was used to record Raman spectra. Morphological study was carried out with a Hitachi SU-70 scanning electron microscope (SEM) and an FEI-TECNAI G2 F20 high-resolution transmission electron microscope (HR-TEM). The photoluminescence excitation and emission studies were carried out witha Jobin Yvon Fluorolog-3 spectrofluorimeter with a xenon lamp of 450 W in continuous mode, while the decay dynamics were carried out on the same instrument with a xenon lamp in pulsed mode. All the characterizations were recorded at room temperature only.

## Results and Discussion

### Structure, Composition and Morphology Studies

The PXRD profiles of SAOPr*x* phosphors for a 2θ range from 15 to 50° are shown in Fig. 1a. These profiles are well fitted to the monoclinic $SrAl_2O_4$ structure (JCPDS No. 34-0379). All the PXRD profiles are found to be identical except in their intensity showing the same crystalline phase. The intensity of PXRD profiles decreases with the increase in concentration of $Pr^{3+}$ ions showing the uniform distribution of $Pr^{3+}$ ions in SAOPr*x* lattice. The variation of intensity of the PXRD peak corresponding to the (310) crystal plane was seen at $2\theta = 35.28°$ as a function of $Pr^{3+}$ ion concentration is shown in Fig. 1b.

The monoclinic crystalline phase of $SrAl_2O_4$ phosphor has been confirmed from the Rietveld refinement following Fullprof software[19] and the corresponding lattice parameters were noted as $a$ = 8.4419 Å, $b$ = 8.8217 Å and $c$ = 5.1592 Å. The mean crystallite size (D) of SAOPr*x* phosphors is estimated to be 36 nm using Debye-Scherrer's

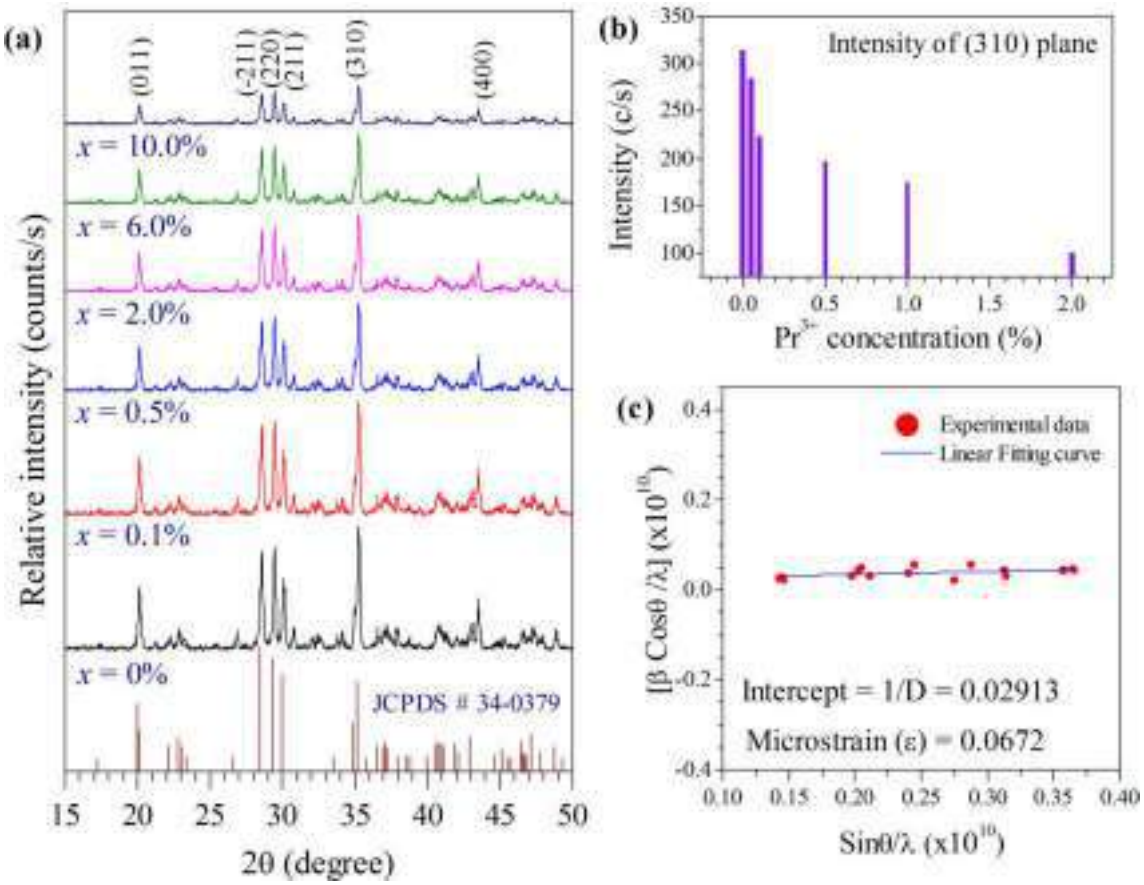



**Fig. 1** PXRD profiles of SAOPrx phosphors (a), variation of intensity of (310) crystal plane as a function of $Pr^{3+}$ concentration (b) and the Williamson–Hall curve of SAOPr1.0 phosphor (c).

formula, $D = \frac{0.89\,\lambda}{\beta\,.\,\cos\theta}$, where λ is the wavelength of x-rays (1.5406 Å), $\beta$ is the full-width at half maximum (in radians) and $\theta$ is the diffraction angle. The size of crystallites has also been obtained using the Williamson–Hall (W–H) equation.[29] According to W–H, the crystallite size (D) and the angle of diffraction ($\theta$) are related as

$$\frac{\beta\cos\theta}{\lambda} = \frac{1}{D} + \frac{\varepsilon\sin\theta}{\lambda} \quad (1)$$

The mean crystallite size and the magnitude of microstrain ($\varepsilon$) present in the material can be found from the $\left(\frac{\beta\cos\theta}{\lambda}\right)$ *versus* $\left(\frac{\sin\theta}{\lambda}\right)$ plot, known as the W–H curve and it is shown in Fig. 1c. The slope and reciprocal of the intercept of the W–H curve represent the microstrain and the mean crystallite size (D), respectively. The magnitude of microstrain and the mean crystallite size are found to be 0.0672 and 34 nm, respectively. The value of D obtained from the W–H curve is close to that obtained from Debye-Scherrer's formula.

The FTIR profile of SAOPr1.0 phosphor in the spectral range from 950 to 400 $cm^{-1}$ shown in Fig. 2a reveals a number of significant vibrational modes associated with Al–O and Sr–O. The IR bands located from 892 to 838 $cm^{-1}$ belong to the formation of $SrAl_2O_4$.[30] The IR peaks identified at 802, 772 and 712 $cm^{-1}$ have been assigned to the $AlO_6$ and $AlO_4$ groups, respectively.[31] The IR peaks noticed at around 668 $cm^{-1}$ and 642 $cm^{-1}$ have been ascribed to the Sr-O vibration.[32] The peaks at around 614, 594 and 556 $cm^{-1}$ have been attributed to the mixed stretching and bending mode of Al-O-Al.[33] The IR bands located at 532, 518 and 502 $cm^{-1}$ have been attributed to the Al–O vibration.[32] The IR peaks observed at 446, 444 and 414 $cm^{-1}$ have been assigned to O–Al–O symmetric vibration.[34] The FT-Raman spectrum of SAOPr1.0 phosphor shown in Fig. 2b reveals the presence of various molecular units as well as the confirmation of monoclinic phase. This spectrum consists of nearly 15 weak Raman modes possible for monoclinic $SrAl_2O_4$. These weak Raman modes have been ascribed to the overlap of certain symmetry vibrations. An intense and sharp peak at around 467 $cm^{-1}$ has also been noticed along with weak modes confirming the monoclinic phase of SAOPr1.0 phosphor and it can be attributed to the O-Al-O bending vibrations.[35,36]

The SEM/TEM analysis provides not only the surface morphology but also the details regarding the distribution of particles and their orientation. The TEM analysis has also been used to confirm the crystallite size, i.e., whether they crystallized into nanoscale or not. The elemental analysis is also possible from both SEM and TEM

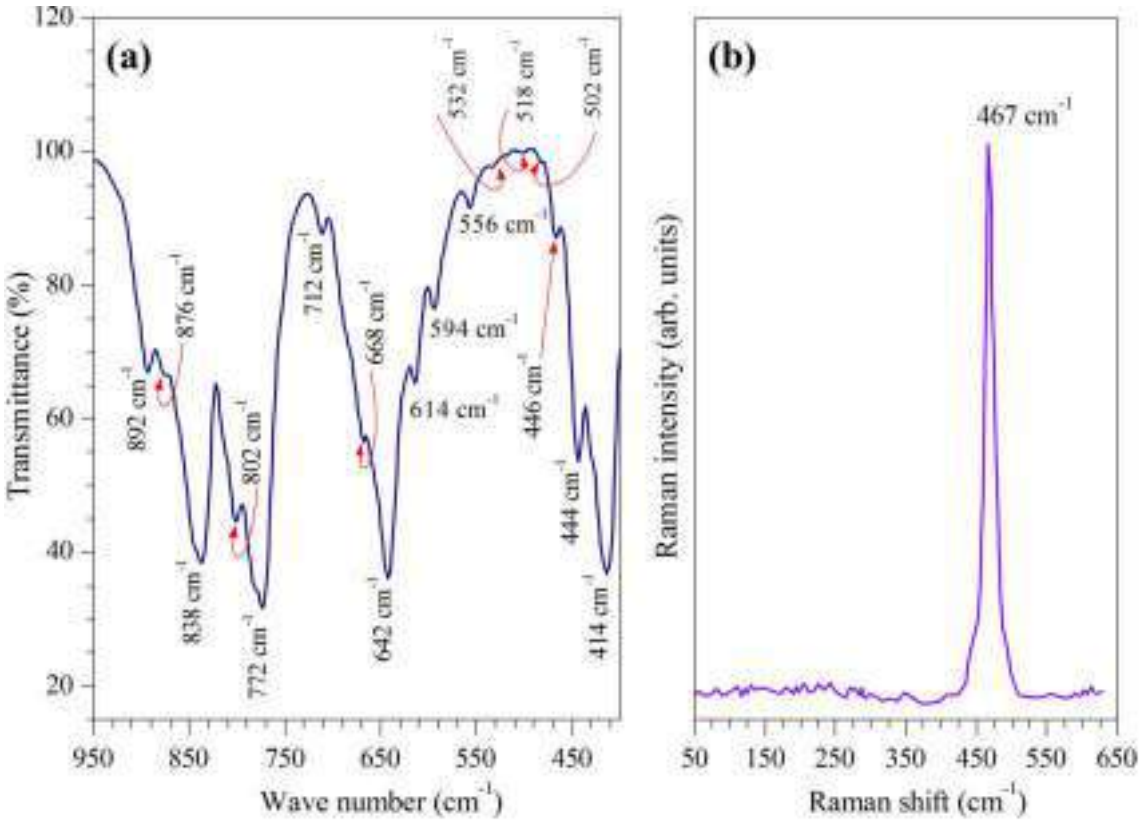



**Fig. 2** FTIR (a) and FT-Raman (b) spectra of SAOPr1.0 phosphor.

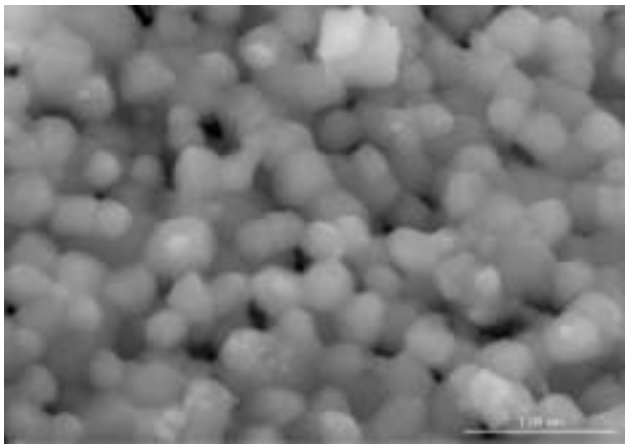


**Fig. 3** SEM micrograph of SAOPr1.0 phosphor.

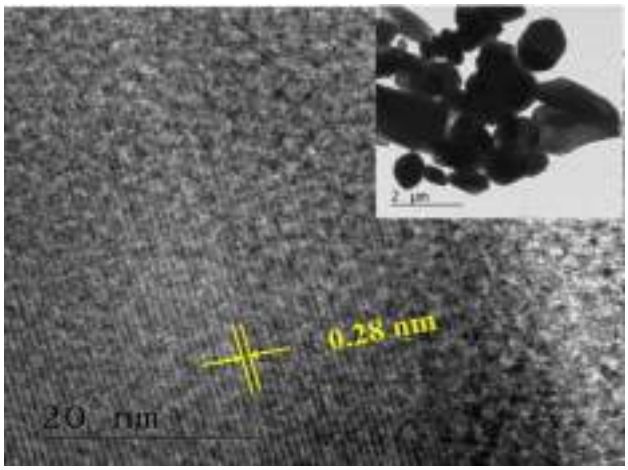



**Fig. 4** HR-TEM image of SAOPr1.0 phosphor. Inset shows its TEM micrograph.

micrographs. The present research work is not focused on the elemental analysis. The SEM image of SAOPr1.0 phosphor shown in Fig. 3 represents homogeneous distribution of particles crystallized into spherical shape with different size. The TEM image of SAOPr1.0 phosphor (see inset of Fig. 4) reveals the uniform distribution of $SrAl_2O_4$ particles that are crystallized into nanoscale. The adjacent spacing of the lattice fringes corresponding to (310) crystal plane is estimated to be 0.28 nm from the HR-TEM image illustrated in Fig. 4. The interplanar spacing was also evaluated using the following equation.[37]

$$\frac{1}{d_{hkl}^2} = \frac{1}{\sin^2\beta}\cdot\left[\frac{h^2}{a^2} + \frac{k^2\sin^2\beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl\cos\beta}{a.c}\right] \quad (2)$$

For the monoclinic SAOPr1.0 phosphor, the lattice parameters have been obtained as $a = 8.4419$ Å, $b = 8.8217$ Å and $c = 5.1592$ Å from the Rietveld refinement (not shown) and $\beta$ is on the order of 93.415º. For the (310) crystal plane, the value of $d_{hkl}$ is found to be 0.267 nm which is very close to that obtained from the HR-TEM analysis.

## Photoluminescence Excitation

The photoluminescence (PL) analysis has been carried out through excitation, emission and lifetime studies. The excitation spectra of SAOPr2.0 phosphor has been recorded controlling the emission at 488 nm, 548 nm, 609 nm, 648 nm and 658 nm and presented in Fig. 5a. These spectra are comparable to other reports[28] and they contain a broad excitation band in the spectral region from 240 to 300 nm which can be assigned to the $SrAl_2O_4$ host excitation band.[11] These spectra reveal five excitation bands due to $Pr^{3+}$: $^3H_4 \rightarrow {}^3P_2$ (~441 nm), $Pr^{3+}$: $^3H_4 \rightarrow {}^1I_6$ (~448 nm), $Pr^{3+}$: $^3H_4 \rightarrow {}^3P_1$ (~466 nm), $Pr^{3+}$: $^3H_4 \rightarrow {}^3P_0$ (~482 nm) and $Pr^{3+}$: $^3H_4 \rightarrow {}^1D_2$ (~583 nm) transitions.[22,37–40] To study the effect of $Pr^{3+}$ concentration, the excitation spectra of SAOPr*x* phosphors have been recorded monitoring the emission at 648 nm ($Pr^{3+}$: $^3P_0 \rightarrow {}^3F_2$) wavelength (not shown). The intensity of observed excitation bands increases with increase of $Pr^{3+}$ concentration showing uniform distribution of $Pr^{3+}$ ions in SAOPr lattice. The variation of intensity of $^3H_4 \rightarrow {}^3P_1$ (466 nm) transition as a function of $Pr^{3+}$ ions concentration is shown in Fig. 5b. Since, the wavelengths corresponding to $Pr^{3+}$: $^3H_4 \rightarrow ({}^3P_J, {}^1D_2)$ transitions are covered by the emission of commercial InGaN LED chip (440 nm – 490 nm), the SAOPr*x* phosphors can be suitably excited by it. From the excitation spectra, it is also clear that the SAOPr phosphors can be suitably excited within the host and the dopant ($Pr^{3+}$) ions at 441 nm ($Pr^{3+}$:$^3H_4 \rightarrow {}^3P_2$), 466 nm ($Pr^{3+}$:$^3H_4 \rightarrow {}^3P_1$) and 482 nm ($Pr^{3+}$:$^3H_4 \rightarrow {}^3P_0$) wavelengths.

## Host Excited Luminescence Properties

Upon different excitations within the host matrix (250 nm ≤ $\lambda_{ex}$ ≤ 330 nm), the emission spectra of SAOPr2.0 phosphor in the spectral region from 460 to 740 nm are presented in Fig. 6a. These spectra reveal a broad and strong emission band corresponding to the host emission[11] with sub-peaks at about 468 nm , 488 nm, 548 nm, 609 nm, 648 nm and 658 nm corresponding to $^3P_1 \rightarrow {}^3H_4$, $^3P_0 \rightarrow {}^3H_4$, $^3P_2 \rightarrow {}^3F_2$, $^1D_2 \rightarrow {}^3H_4$, $^3P_0 \rightarrow {}^3F_2$ and $^1D_2 \rightarrow {}^3H_5$ transitions, respectively. The intensity of observed emission transitions increases with the increase of excitation wavelength reaching a maximum at $\lambda_{ex}$ = 270 nm and then decreases for higher excitation wavelengths. This could be due to variation in population of $Pr^{3+}$ ions at various emission states. The variation of intensity of $^3P_0 \rightarrow {}^3F_2$ (648 nm) transition as a function of

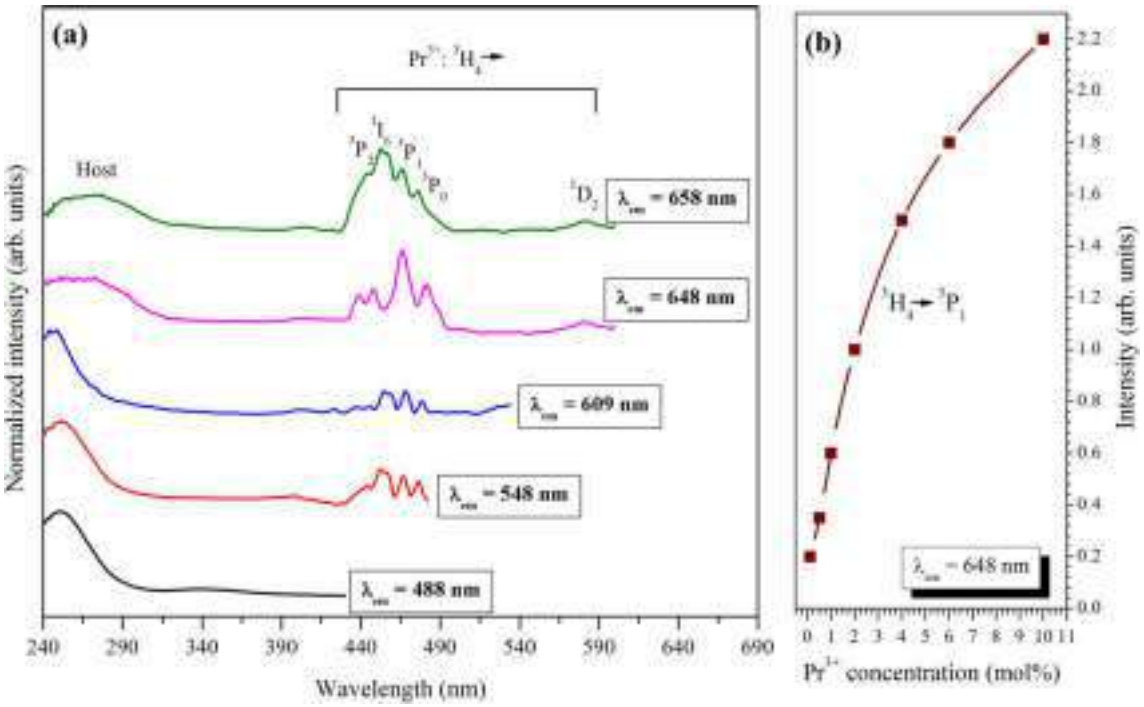



**Fig. 5** Excitation spectra of SAOPr2.0 phosphor at different emission wavelengths (a) and the variation of intensity of $^3H_4 \rightarrow {}^3P_1$ (466 nm) transition as a function of $Pr^{3+}$ concentration at $\lambda_{em} = 648$ nm.

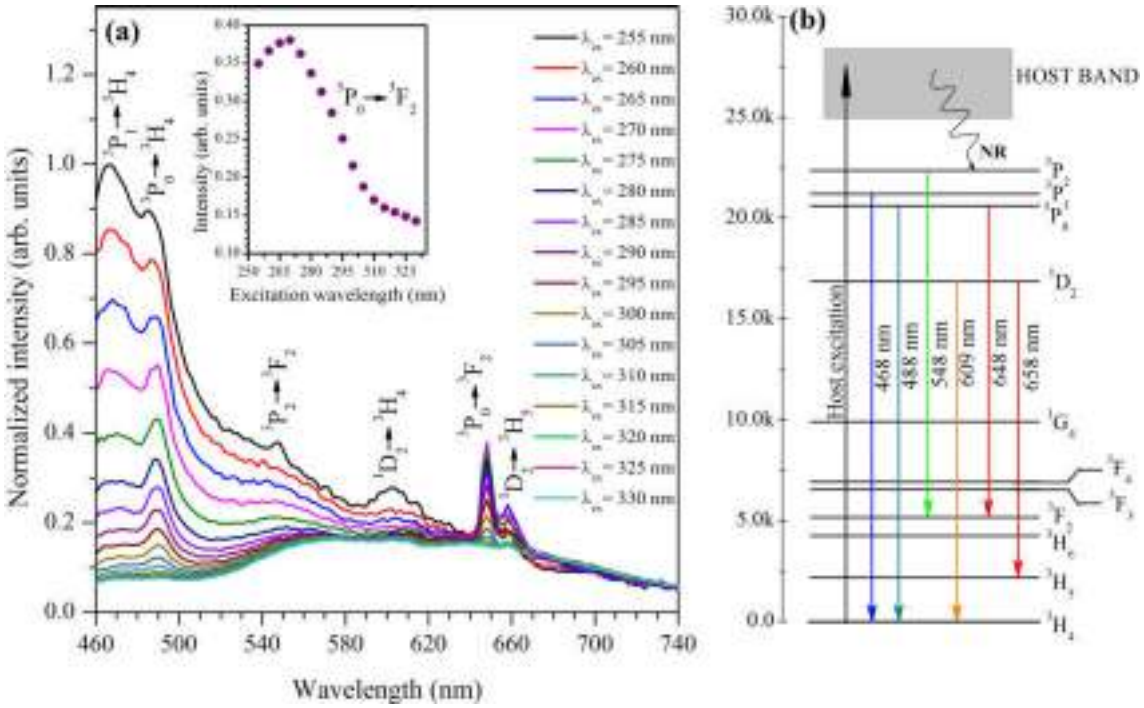



**Fig. 6** Emission spectra of SAOPr2.0 phosphor under different host excitations (a) Inset shows the variation of intensity of $^3P_0 \rightarrow {}^3F_2$ (648 nm) transition as a function of $Pr^{3+}$ concentration. The partial energy level diagram showing the emission mechanism of $Pr^{3+}$ ions under host excitation (b).

$Pr^{3+}$ ions concentration is described as inset of Fig. 6a. The emission mechanism of SAOPr2.0 phosphor under different host excitation wavelengths is illustrated in a partial energy level diagram shown in Fig. 6b.

The colour perception of emitted luminescence has been studied by evaluating the Commission International de I'Eclairage (CIE) 1931 chromaticity coordinates ($x$, $y$), which are summarized in Table I, and they are represented in the CIE diagram shown in Fig. 7. From this figure one can notice that the colour of emitted luminescence varies from bluish-green to yellow when the excitation wavelength changes from 255 to 330 nm. The variation in population density at different emission energy states results the tunability in emitted luminescence.

## Dopant ($Pr^{3+}$) Ion Excited Luminescence Properties

### Luminescence Properties at 466 nm Excitation

When excited at 466 nm ($Pr^{3+}$: $^3H_4 \rightarrow {}^3P_1$), the SAOPr$x$ phosphors show emission profiles as shown in Fig. 8a. These spectra reveal six emission bands at about 598, 609, 622, 638, 648 and 656 nm corresponding to $^3P_1 \rightarrow {}^3H_6$, $^1D_2 \rightarrow {}^3H_4$, $^3P_1 \rightarrow {}^3F_2$, $^3P_1 \rightarrow {}^3F_3$, $^3P_0 \rightarrow {}^3F_2$ and $^1D_2 \rightarrow {}^3H_5$ transitions, respectively. The intensity of emitted transitions originating from $Pr^{3+}$: $^3P_J$ emission states show a luminescence quenching beyond $x = 2.0$ mol.%, while the transitions originating from the $Pr^{3+}$: $^1D_2$ emission state shows luminescence quenching beyond $x = 4.0$ mol.%. The variation in intensity of $^3P_1 \rightarrow {}^3H_6$ and $^1D_2 \rightarrow {}^3H_4$ transitions as a function of $Pr^{3+}$ ion concentration is presented in Fig. 8b. From the literature, it is well known that the emission from the $Pr^{3+}$: $^1I_6$ energy state is not significant in many hosts.[22–28]

When excited at 466 nm, the interacting photons stimulate the ground state $Pr^{3+}$ ions and excite to $^3P_1$ state (~21460 $cm^{-1}$). These excited $Pr^{3+}$ ions transit to lower lying $^3P_0$ and $^1D_2$ emission states through a fast non-radiative (NR) process producing $^3P_0 \rightarrow {}^3F_2$ (648 nm), $^1D_2 \rightarrow {}^3H_4$ (609 nm) and $^1D_2 \rightarrow {}^3H_5$ (656 nm) transitions. However, some of the $Pr^{3+}$ ions decay radiatively resulting $^3P_1 \rightarrow {}^3H_6$ (598 nm), $^3P_1 \rightarrow {}^3F_2$ (622 nm) and $^3P_1 \rightarrow {}^3F_3$ (638 nm) transitions. These emission spectral profiles are similar to $CaTa_2O_6$:$Pr^{3+}$[39] phosphors. The emission mechanism of SAOPr$x$ phosphors at 466 nm excitation is described in the partial energy level diagram shown in Fig. 9a.

To study the colour perception, the CIE chromaticity coordinates have been calculated using the emission spectra shown in Fig. 8a and they are summarized in Table II. These chromaticity coordinates are close to those reported for National Television Standard Committee (NTSC) ($x = 0.67$, $y = 0.33$), $Y_2O_3$:$Eu^{3+}$ commercial red emitting phosphor ($x = 0.655$, $y = 0.345$), $Ca_{2.96}Sm_{0.02}Na_{0.02}B_2O_6$ ($x = 0.608$, $y = 0.365$),[41] $NaSrPO_4$:$Sm^{3+}$ ($x = 0.60$, $y = 0.39$),[42] SAOSm10 (x = 0.605, y = 0.362)[21] phosphors. The location of these chromaticity coordinates is presented in Fig. 10. From this figure it is clear that all the samples show an intense red luminescence when excited at 466 nm wavelength.

**Table I** CIE chromaticity coordinates of SAOPr2.0 phosphor at different excitation wavelengths

| S. No. | Excitation wavelength (nm) | CIE chromaticity coordinates | |
|---|---|---|---|
| | | $x$ | $y$ |
| 1 | 255 | 0.269 | 0.357 |
| 2 | 260 | 0.274 | 0.360 |
| 3 | 265 | 0.87 | 0.366 |
| 4 | 270 | 0.304 | 0.375 |
| 5 | 275 | 0.329 | 0.386 |
| 6 | 280 | 0.353 | 0.397 |
| 7 | 285 | 0.373 | 0.407 |
| 8 | 290 | 0.391 | 0.417 |
| 9 | 295 | 0.405 | 0.426 |
| 10 | 300 | 0.418 | 0.435 |
| 11 | 305 | 0.428 | 0.442 |
| 12 | 310 | 0.436 | 0.446 |
| 13 | 315 | 0.441 | 0.448 |
| 14 | 320 | 0.444 | 0.447 |
| 15 | 325 | 0.446 | 0.448 |
| 16 | 330 | 0.447 | 0.449 |

### Luminescence Properties at 482 nm Excitation

In the case of 482 nm ($Pr^{3+}$: $^3H_4 \rightarrow {}^3P_0$) excitation, the SAOPr$x$ phosphors show a different emission profile. These emission spectra show six emission bands at about 600, 612, 623, 638, 647 and 656 nm corresponding to $^3P_1 \rightarrow {}^3H_6$, $^1D_2 \rightarrow {}^3H_4$, $^3P_0 \rightarrow {}^3H_6$, $^3P_0 \rightarrow {}^3F_3$, $^3P_0 \rightarrow {}^3F_2$ and $^1D_2 \rightarrow {}^3H_5$ transitions, respectively. For reference, the emission spectrum of the SAOPr2.0 phosphor is shown in Fig. 11a. Among the observed emission transitions, the $^1D_2 \rightarrow {}^3H_4$ (612 nm) transition is found to be more intense and broader compared to other transitions. The variation of intensity of the $^1D_2 \rightarrow {}^3H_4$ transition as a function of $Pr^{3+}$ ion concentration is presented as the inset of Fig. 11a.

The colour perception of SAOPr$x$ phosphors has been investigated by evaluating the CIE chromaticity coordinates using the emission spectra obtained by exciting the samples at 482 nm wavelength and they are also summarized in Table II. These chromaticity coordinates are close to those obtained at 466 nm excitation and they are well located in the red region of the CIE diagram shown in Fig. 12.

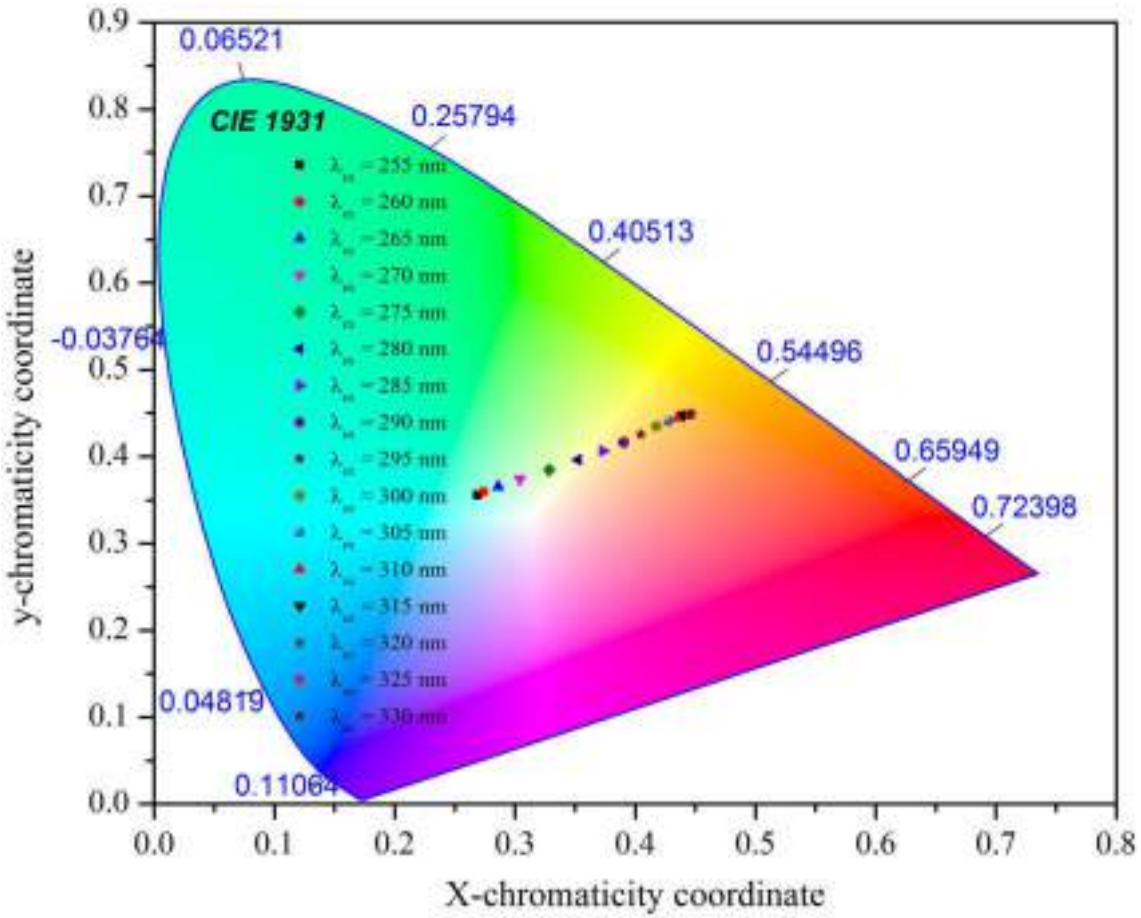



**Fig. 7** CIE chromaticity diagram of SAOPr2.0 phosphor under different host excitations.

### Luminescence Properties at 441-nm Excitation

Upon 441 nm ($Pr^{3+}$: $^3H_4 \rightarrow {}^3P_2$) excitation, the SAOPr*x* phosphors show interesting emission properties. These emission spectra reveal six transition peaks at around 598, 609, 623, 638, 647 and 657 nm corresponding to $^3P_1 \rightarrow {}^3H_6$, $^1D_2 \rightarrow {}^3H_4$, $^3P_0 \rightarrow {}^3H_6$, $^3P_0 \rightarrow {}^3F_3$, $^3P_0 \rightarrow {}^3F_2$ and $^1D_2 \rightarrow {}^3H_5$ transitions, respectively. For reference, the emission spectrum of SAOPr2.0 phosphor in the region from 580 to 680 nm is shown in Fig. 13a. Among the observed emission transitions, the $^1D_2 \rightarrow {}^3H_4$ (609 nm) transition is found to be more intense compared to other transitions. The variation of intensity of $^1D_2 \rightarrow {}^3H_4$ transition as a function of $Pr^{3+}$ ion concentration is presented in Fig. 13b. Upon 441-nm excitation, the SAOPr*x* phosphors emit red luminescence and the corresponding chromaticity diagram is shown in Fig. 14. The CIE chromaticity coordinates of SAOPr*x* phosphor under 441-nm excitation are also close to those obtained at 466-nm excitation and they are summarized in Table II.

The comparative emission spectra of SAOPr2.0 phosphor under 441-, 466- and 482-nm excitations is shown in Fig. 15. These spectra show that the studied phosphors have different emission profiles with slight deviation in emission peak maxima. Additionally, the $Pr^{3+}$ concentration hardly influences the emission color upon excitation at 441, 466 and 482 nm. The PXRD studies reveal that the crystalline peak positions do not vary with the increase of $Pr^{3+}$ ions concentration indicating suitable occupancy of $Pr^{3+}$ ions in $Sr^{2+}$ ion sites. A slight variation in ionic radii and electronic configuration leads to a slight deviation in emission peak maxima at different excitation wavelengths.[43]

### Luminescence Quenching

As seen the Figs. 8b, 11a and 13b, one can notice a quenching in luminescence at higher $Pr^{3+}$ ion concentration. Upon 441- and 482-nm excitations, luminescence quenching has been observed beyond 2.0 mol.% of $Pr^{3+}$ ion concentration for all the emitted energy states. When excited at 466 nm, the luminescence quenching is noticed beyond 4.0 mol.% of $Pr^{3+}$ ion concentration for $^1D_2$ emission state and beyond 2.0 mol.% for other excited energy states. This quenching

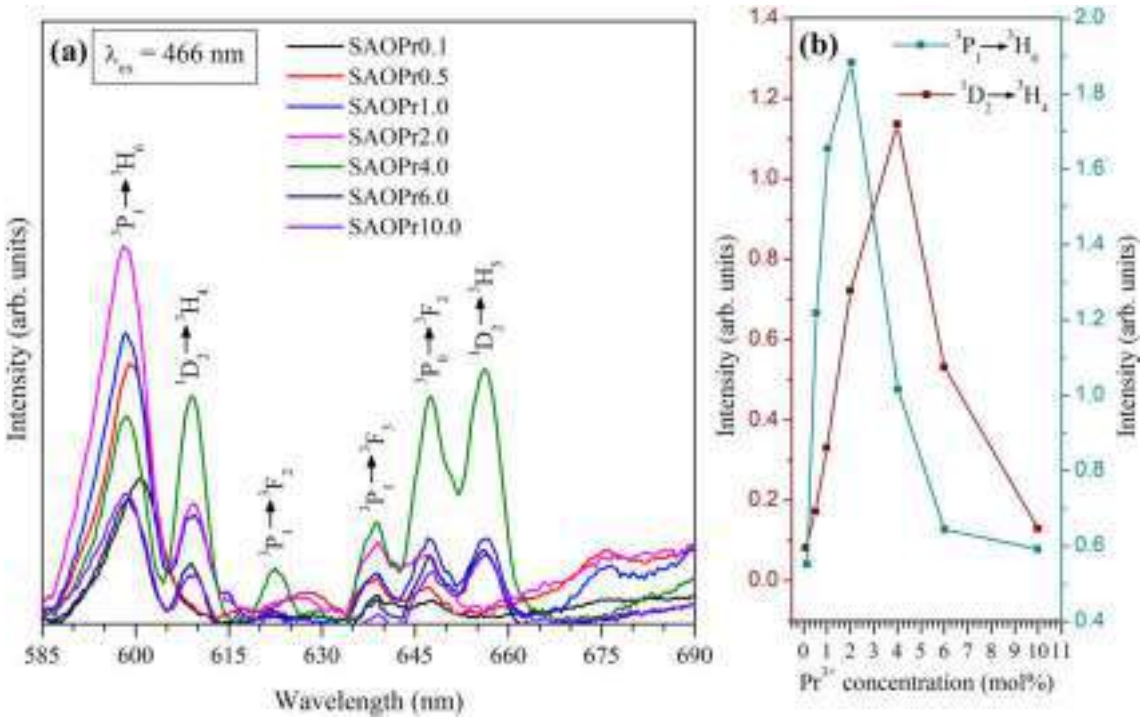



**Fig. 8** Emission spectra of SAOPrx phosphors at $\lambda_{ex}$ = 466 nm (a) and the variation of intensity of $^3P_1 \rightarrow {}^3H_6$ and $^1D_2 \rightarrow {}^3H_4$ transitions as a function of $Pr^{3+}$ concentration (b).

in luminescence is mainly due to the efficient energy transfer (ET) among the excited $Pr^{3+}$ ions at higher concentrations. It is well known that the transfer of energy among the exited RE ions at higher concentration is mainly due to the exchange and/or multi-polar interaction mechanism such as dipole-dipole (d-d), dipole-quadrupole (d-q) and quadrupole-quadrupole (q-q) mechanisms. Based on the critical transfer distance ($R_c$), the exchange or multi-polar interaction mechanism play a key role in ET.[44] The magnitude of $R_c$ can be obtained using the formula shown below.

$$R_c = 2\left(\frac{3V}{4\pi x_c N}\right)^{1/3} \tag{3}$$

where $V$, $x_c$ and $N$ represents the volume of unit cell, critical concentration of active ions and number of crystallographic-sites available for the occupation of active ions. The exchange interaction mechanism has been responsible when the value of $R_c$ is less than 5 Å only.[45] In case of SAOPr phosphors, the volume of unit cell is found to be 383.68 $Å^3$, the critical concentration of $Pr^{3+}$ ions is around 2.0 mol.% and the number of crystallographic-sites occupied by $Pr^{3+}$ ions is 6. The value of $R_c$ is found to be 18.28 Å which indicates that the multi-polar interaction mechanism is responsible for the transfer of energy among the excited $Pr^{3+}$ ions.

When the migration of energy among the excited RE active ions becomes prominent than the direct energy transfer, then the luminescence quenching is a function of the concentration of active ions.[46] The type interaction mechanism responsible for ET among the excited RE active ions has been known using the following equation considering the relationship between the emission intensity and the concentration of active ions.

$$\ln\left(\frac{I}{C}\right) = K - \left(\frac{S}{3}\right).\ln(C) \tag{4}$$

where I is the emission peak intensity, C is the concentration of RE active ions and the constant K belongs to a particular excitation of the material. The parameter S = 3 for exchange interaction, S = 6 for d-d interaction, S = 8 for d-q interaction and S = 10 for q-q interaction. The value of S has been found from the slope (S/3) of $\ln\left(\frac{I}{C}\right)$vs. $\ln(C)$ plot. Upon 466-nm excitation, the $\ln\left(\frac{I}{C}\right)$ vs. $\ln(C)$ plots are drawn for $^3P_1 \rightarrow {}^3H_6$ (598 nm) and $^1D_2 \rightarrow {}^3H_4$ (609 nm) transitions and they are illustrated in Fig. 16a and Fig. 16b, respectively. From these plots the value of the slope is found to be 1.76 ± 0.13 and 3.38 ± 0.25 for $^3P_1 \rightarrow {}^3H_6$ (598 nm) and $^1D_2 \rightarrow {}^3H_4$ (609 nm) transitions and the corresponding S values are 5.28 and 10.14, respectively. These results confirm that both d-d and q-q interaction mechanisms are responsible for ET among the excited $Pr^{3+}$ ions when excited at 466-nm radiation.

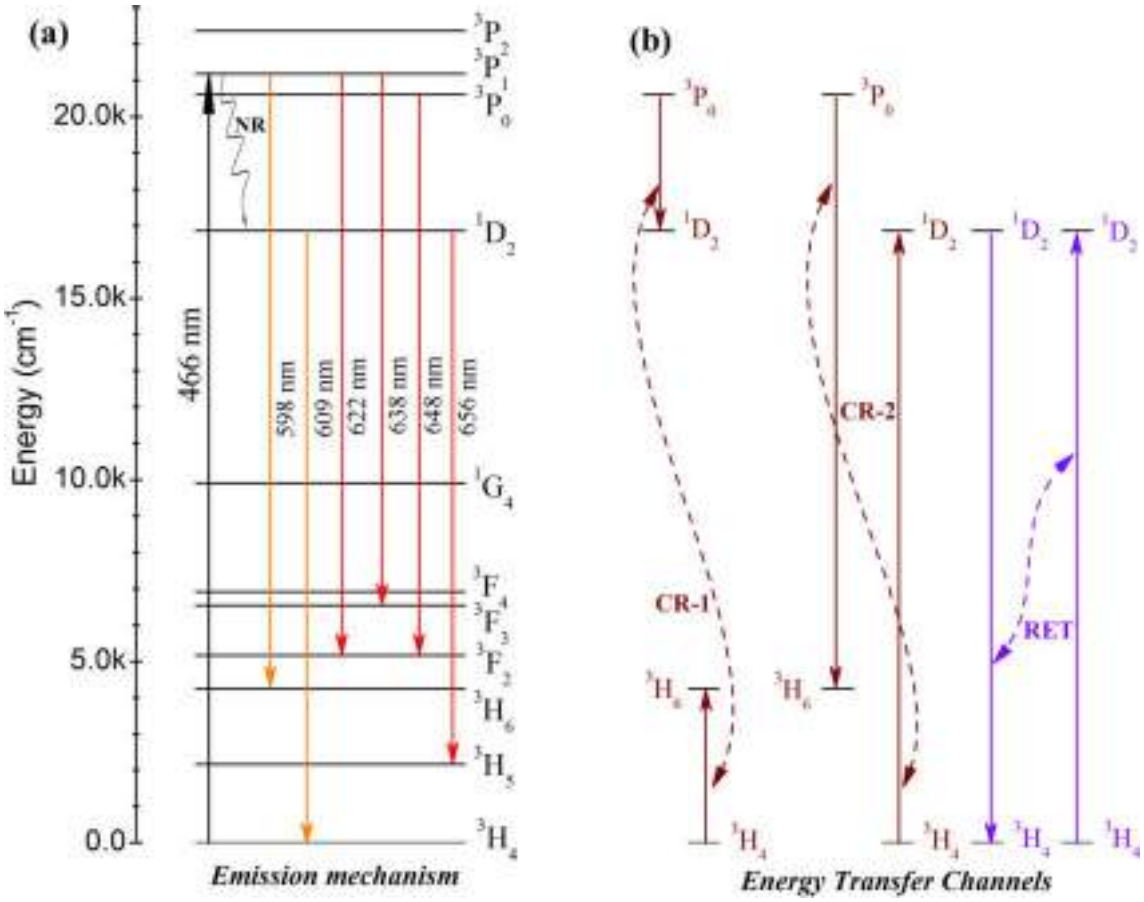



**Fig. 9** Partial energy level diagram showing the emission mechanism of $Pr^{3+}$ ions at 466 nm excitation (a) and the possible energy transfer channels (b).

**Table II** CIE chromaticity coordinates of SAOPrx phosphors

| Doping *x* (mol%) | CIE chromaticity coordinates | | | | | |
|---|---|---|---|---|---|---|
| | $\lambda_{ex}$ = 441 nm | | $\lambda_{ex}$ = 466 nm | | $\lambda_{ex}$ = 482 nm | |
| | *x* | *y*- | *x* | *y*- | *x* | *y*- |
| 0.1 | 0.633 | 0.367 | 0.637 | 0.363 | 0.641 | 0.359 |
| 0.5 | 0.632 | 0.368 | 0.645 | 0.354 | 0.632 | 0.368 |
| 1.0 | 0.633 | 0.366 | 0.631 | 0.368 | 0.637 | 0.362 |
| 2.0 | 0.633 | 0.366 | 0.629 | 0.370 | 0.631 | 0.368 |
| 4.0 | 0.634 | 0.365 | 0.637 | 0.363 | 0.642 | 0.358 |
| 6.0 | 0.633 | 0.367 | 0.642 | 0.357 | 0.646 | 0.354 |
| 10.0 | 0.632 | 0.367 | 0.642 | 0.358 | 0.646 | 0.353 |

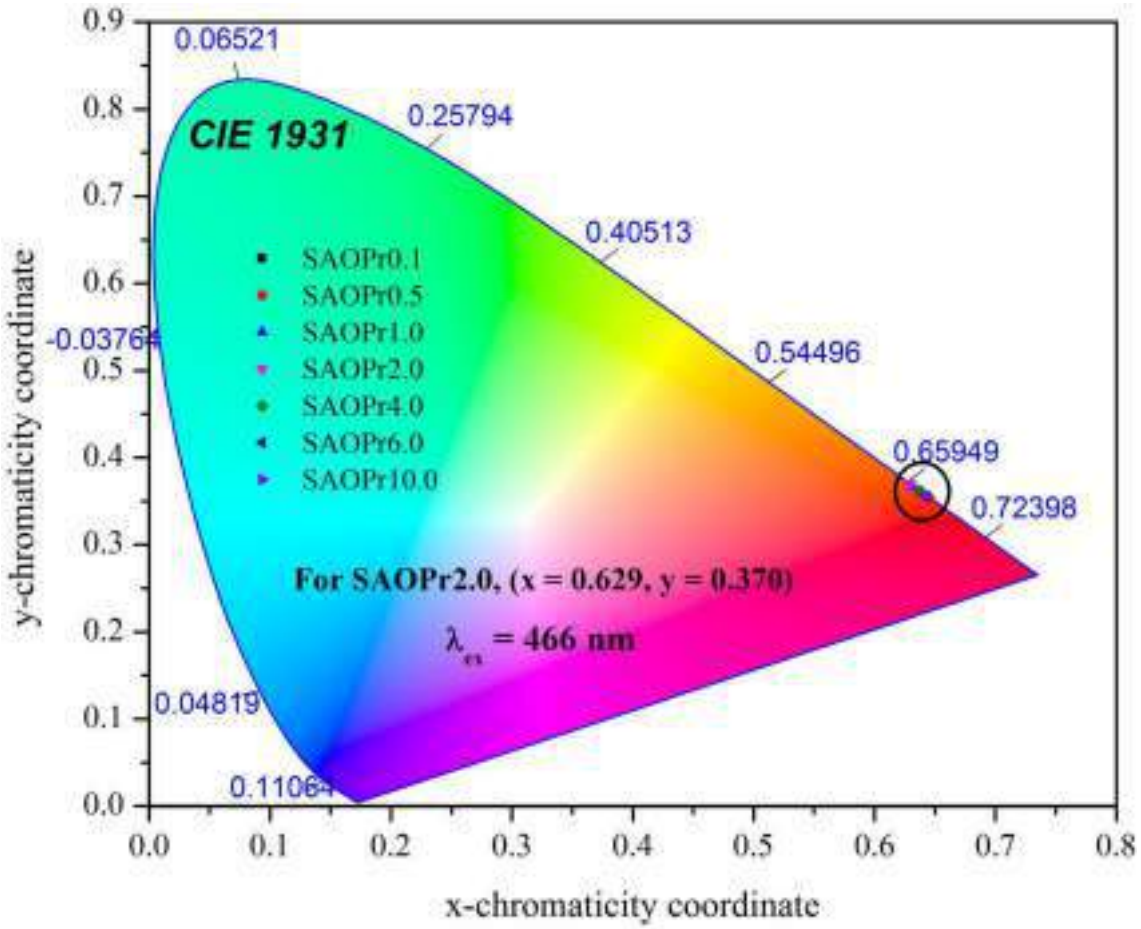



**Fig. 10** CIE chromaticity diagram of SAOPrx phosphors at 466 nm excitation.

When excited at 482 nm, the slope of $\ln\left(\frac{I}{C}\right)$ vs. $\ln(C)$ plot for $^1D_2 \rightarrow {}^3H_4$ (612 nm) transition (see Fig. 11b) is noted as 1.82 ± 0.13 and the corresponding value of S is on the order of 5.37 confirming the d-d interaction mechanism type of ET among the excited $Pr^{3+}$ ions. Similarly, when excited at 441-nm radiation, the slope of $\ln\left(\frac{I}{C}\right)$ vs. $\ln(C)$ plot for $^1D_2 \rightarrow {}^3H_4$ (609 nm) transition (see Fig. 13c) is noted as 1.68 ± 0.10 and the corresponding S value is of the order of 5.04 confirming the d-d interaction mechanism type of ET among the excited $Pr^{3+}$ ions. From this discussion it can be concluded that the d-d interaction mechanism plays a significant role for ET among the excited $Pr^{3+}$ ions.

## Lifetime Analysis

The luminescence decay profiles of $Pr^{3+}$: $^1D_2$, $^3P_0$ and $^3P_1$ emission states in SAOPrx phosphors have been studied by exciting the phosphors at 466-nm wavelength monitoring the emission at 609 nm, 648 nm and 598 nm, respectively, and they are shown in Fig. 17. The decay times of SAOPr0.1, SAOPr0.5 and SAOPr1.0 are found to be almost the same. Therefore, the decay profiles of SAOPr0.1 and SAOPr0.5 are

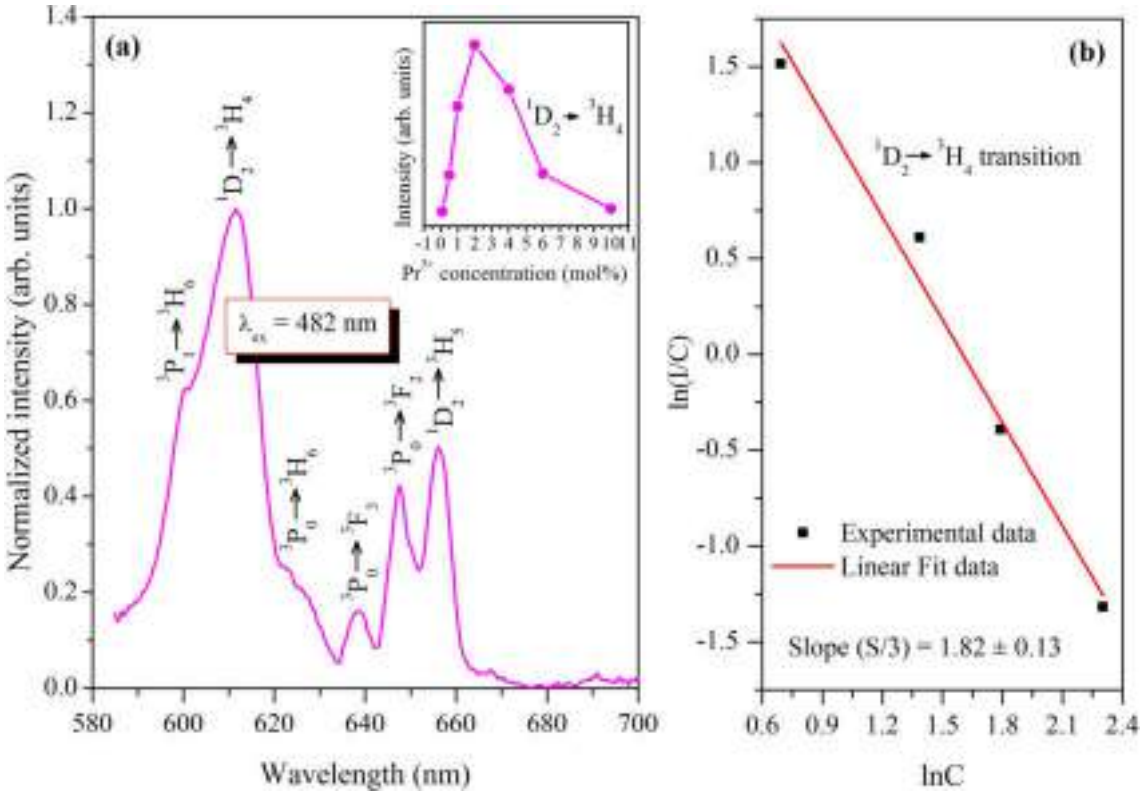



**Fig. 11** Emission spectrum of SAOPr2.0 phosphor at $\lambda_{ex} = 482$ nm (a). Inset shows the variation of intensity of $^1D_2 \rightarrow {}^3H_4$ transition as a function of $Pr^{3+}$ concentration. The ln (I/C) vs. ln(C) plot for $^1D_2 \rightarrow {}^3H_4$ transition (b).

not shown. All the decay profiles of $Pr^{3+}$: $^1D_2$, $^3P_0$ and $^3P_1$ emission states are well fitted to a two-exponential function, $I = I_0 + A_1.\exp(-t/\tau_1) + A_2.\exp(-t/\tau_2)$, where $I$ describes the intensity as function of time $t$ and $I_0$ is the intensity at $t = 0$ s. $\tau_1$ and designates the long and short decay time components. The average decay time has been evaluated using the equation, $\langle\tau\rangle = \frac{A_1\tau_1^2 + A_2\tau_2^2}{A_1\tau_1 + A_2\tau_2}$ where $A_1$ and $A_2$ are constants corresponding to $\tau_1$and, respectively.[47,48] The lifetime of a particular emission state at different concentrations is summarized in Table III. As seen Table III, one can notice that the lifetime of $Pr^{3+}$: $^1D_2$, $^3P_0$ and $^3P_1$ emission states decrease with increase of concentration of $Pr^{3+}$ ions as illustrated in Fig. 18. The values of decay time are comparable to those reported for $Pr:SrAl_2O_4$ crystals.[27]

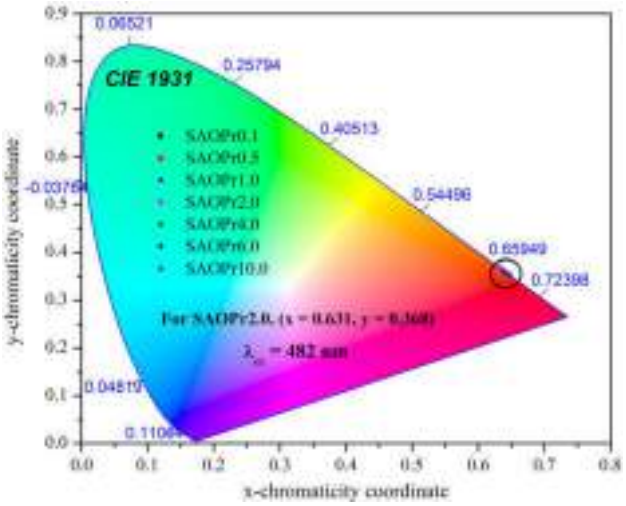



**Fig. 12** CIE chromaticity diagram of SAOPrx phosphors at 482 nm excitation.

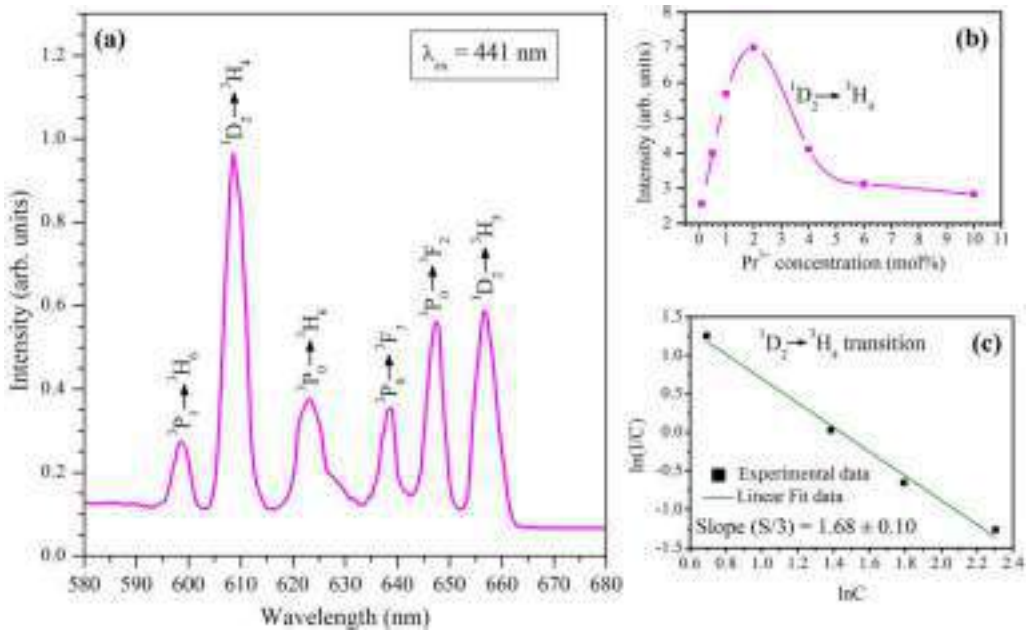



**Fig. 13** Emission spectrum of SAOPr2.0 phosphor at $\lambda_{ex}$ = 441 nm (a) the variation of intensity of $^1D_2 \rightarrow {}^3H_4$ transition as a function of $Pr^{3+}$ concentration (b) the ln (I/C) vs. ln C plot for $^1D_2 \rightarrow {}^3H_4$ transition (c).

The self-absorption and the non-radiative ET among the excited $Pr^{3+}$ ions cause a monotonic decrease in lifetime and hence luminescence quenching. The self-absorption and non-radiative ET can be ascribed to the following possible cross-relaxation (CR) and resonant energy transfer (RET) channels which are clearly illustrated in Fig. 9b.

$$\mathrm{CR}-1:\ \left({}^3P_0, {}^3H_4\right) \rightarrow \left({}^1D_2, {}^3H_6\right)$$

$$\mathrm{CR}-2:\ \left({}^3P_0, {}^3H_4\right) \rightarrow \left({}^3H_6, {}^1D_2\right)$$

$$\mathrm{RET}:\ \left({}^1D_2, {}^3H_4\right) \rightarrow \left({}^3H_4, {}^1D_2\right)$$

The photoluminescence emission studies at visible excitation (441, 466 nm and 482 nm) show that the $Pr^{3+}$ ions emit efficient red luminescence when $x = 2.0$ mol.%. It can be concluded that the optimum concentration for intense and efficient luminescence is 2.0 mol.%. The studied phosphors can suitably excite either at 441 nm or 466 nm or 482 nm to generate red luminescence while they produce feeble bluish-white luminescence at 255 nm excitation. From the literature, it is clear that LEDs coated with phosphor enhances their working efficiency and hence lowers the surface temperature.[49,50] Therefore, the SAOPr*x* phosphors would be the best choice to fabricate red light emitting solid-state light sources.

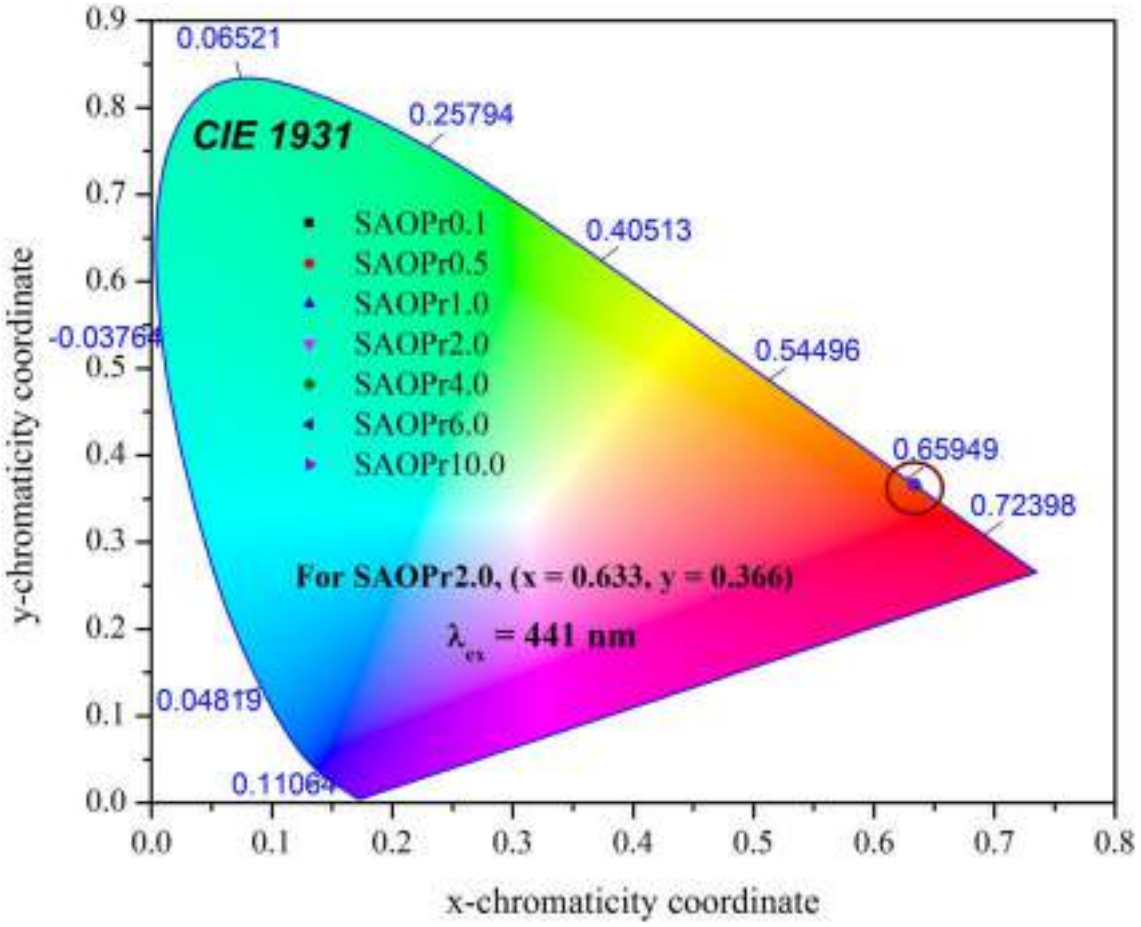



**Fig. 14** CIE chromaticity diagram of SAOPrx phosphors at 441-nm excitation.

## Conclusions

The $SrAl_2O_4$:$x$$Pr^{3+}$ phosphors have been prepared by conventional solid-state technique sintering at 1050°C for 3 h with average crystallite size of 34–36 nm. The SEM image establishes homogeneous distribution of particles of spherical shape with different sizes. The adjacent spacing of the lattice fringes corresponding to (310) crystal plane is estimated as 0.28 nm from the HRTEM image. The concentration of $Pr^{3+}$ ions has been optimized to be 2.0 mol.% for efficient luminescence. The quenching in luminescence and lifetime has been ascribed to the ET among the excited $Pr^{3+}$ ions through d-d and q-q multipolar interaction mechanism. The colour perception of emitted luminescence has been investigated by evaluating chromaticity coordinates. The studied phosphors generate strong red luminescence at 441, 466 and 482 nm excitations, while they produce feeble bluish-white luminescence at 255 nm excitation. Based on the observed results it can be concluded that the SAOPr2.0 phosphor could be the best choice for solid state red light emitting sources.

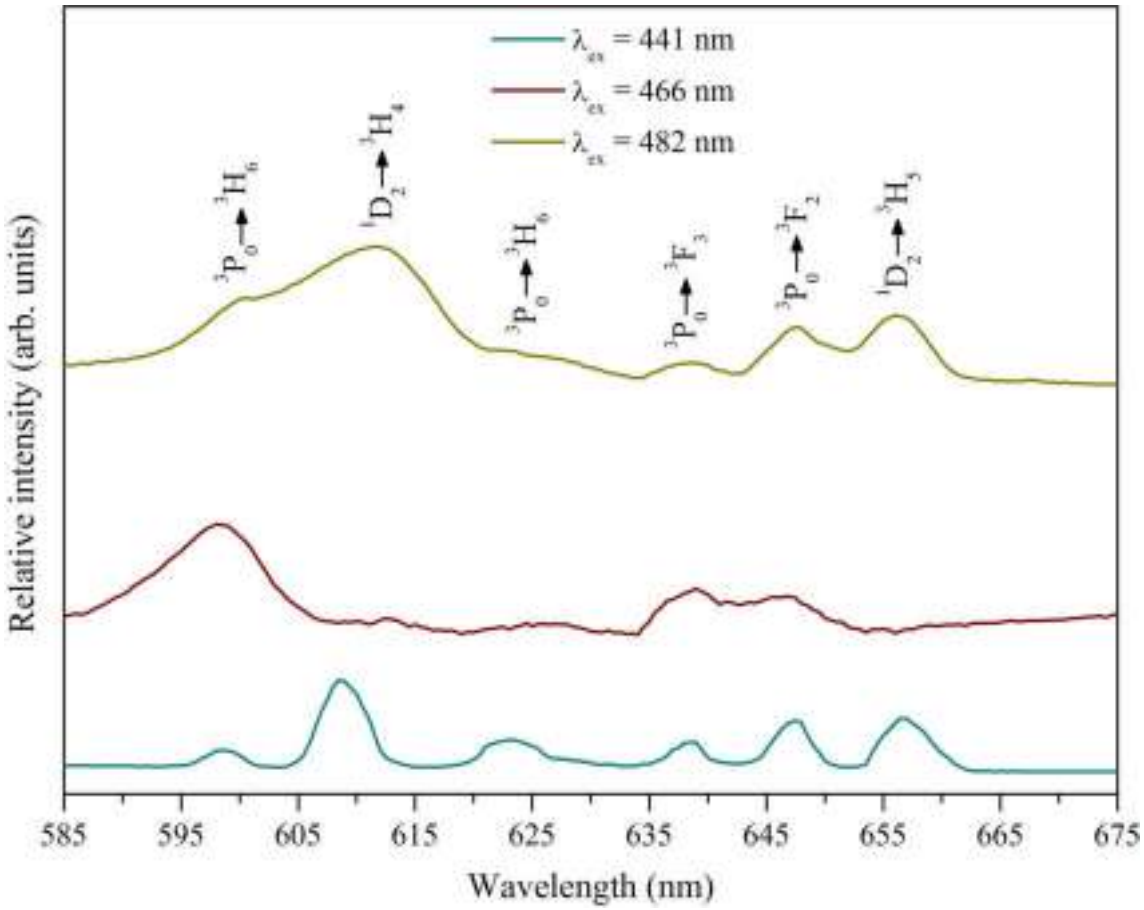



**Fig. 15** Comparative emission spectra of SAOPr2.0 phosphor at different excitations.

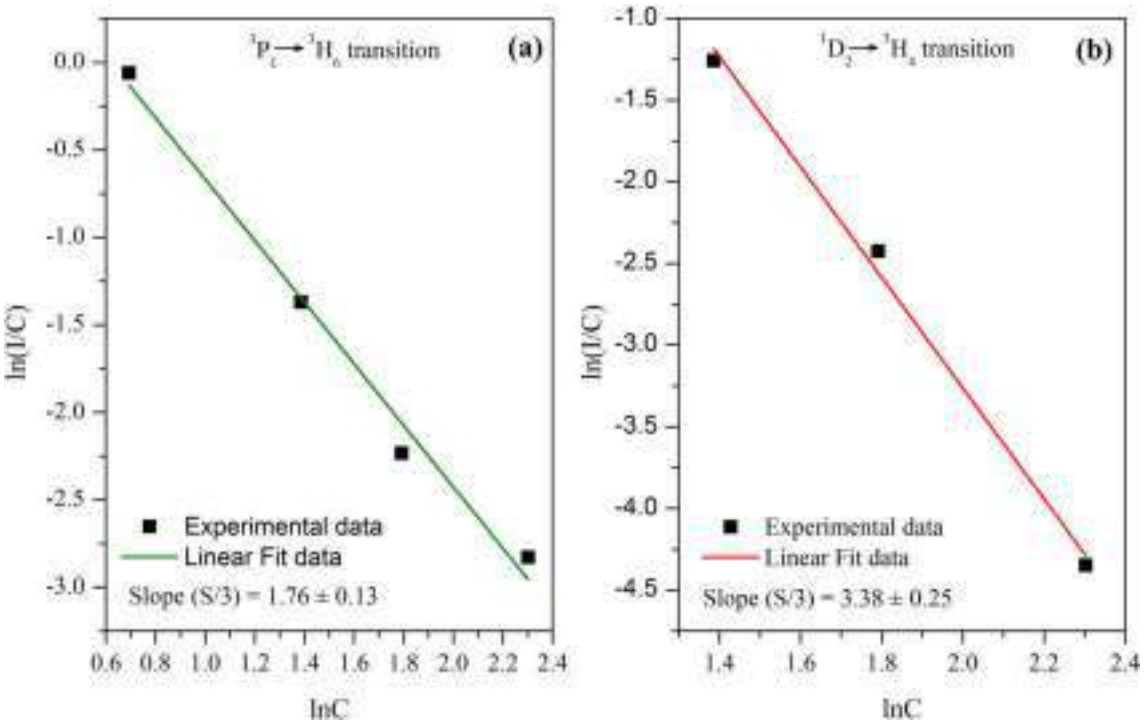



**Fig. 16** The ln (I/C) vs. ln C plots for $^3P_1 \rightarrow {}^3H_6$ (598 nm) transition (a) and $^1D_2 \rightarrow {}^3H_4$ (609 nm) transition (b).

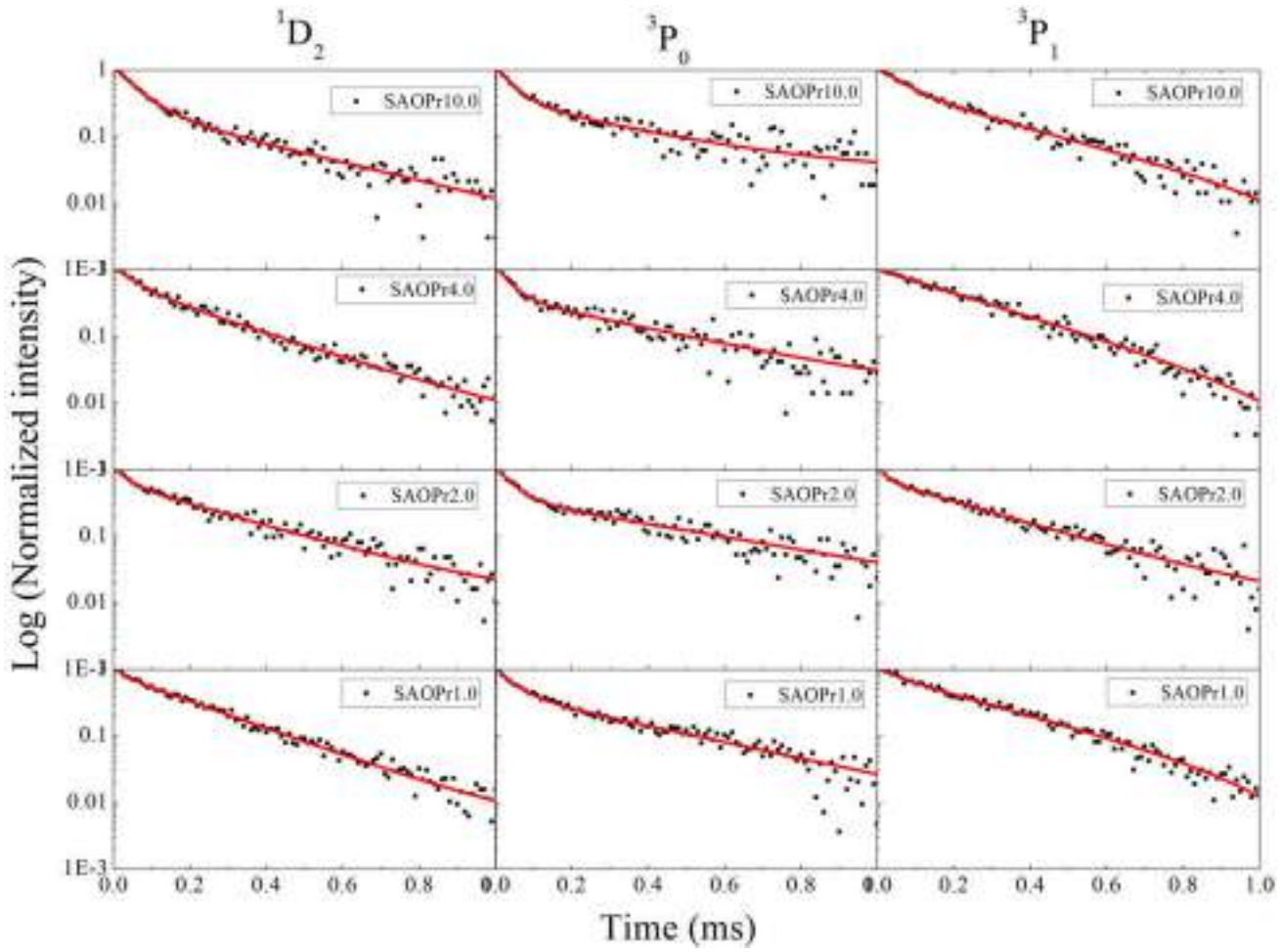



**Fig. 17** Decay curves of the $Pr^{3+}$: $^1D_2$ [$\lambda_{ex}$ = 466 nm; $\lambda_{em}$ = 609 nm] (a), $Pr^{3+}$: $^3P_0$ [$\lambda_{ex}$ = 466 nm; $\lambda_{em}$ = 648 nm] (b) and $Pr^{3+}$: $^3P_1$ [$\lambda_{ex}$ = 466 nm; $\lambda_{em}$ = 598 nm] (c) emission states.

**Table III** Comparison of lifetime of $Pr^{3+}$: $^1D_2$, $^3P_0$ and $^3P_1$ emission states in SAOPrx phosphors

| Sample | Lifetime (τ, ms) | | |
|---|---|---|---|
| | $Pr^{3+}$:$^1D_2$ | $Pr^{3+}$:$^3P_0$ | $Pr^{3+}$:$^3P_1$ |
| SAOPr1.0 | 0.219 ± 0.004 | 0.154 ± 0.006 | 0.252 ± 0.005 |
| SAOPr2.0 | 0.188 ± 0.004 | 0.120 ± 0.006 | 0.228 ± 0.005 |
| SAOPr4.0 | 0.139 ± 0.004 | 0.098 ± 0.006 | 0.203 ± 0.005 |
| SAOPr10.0 | 0.108 ± 0.004 | 0.074 ± 0.006 | 0.158 ± 0.005 |

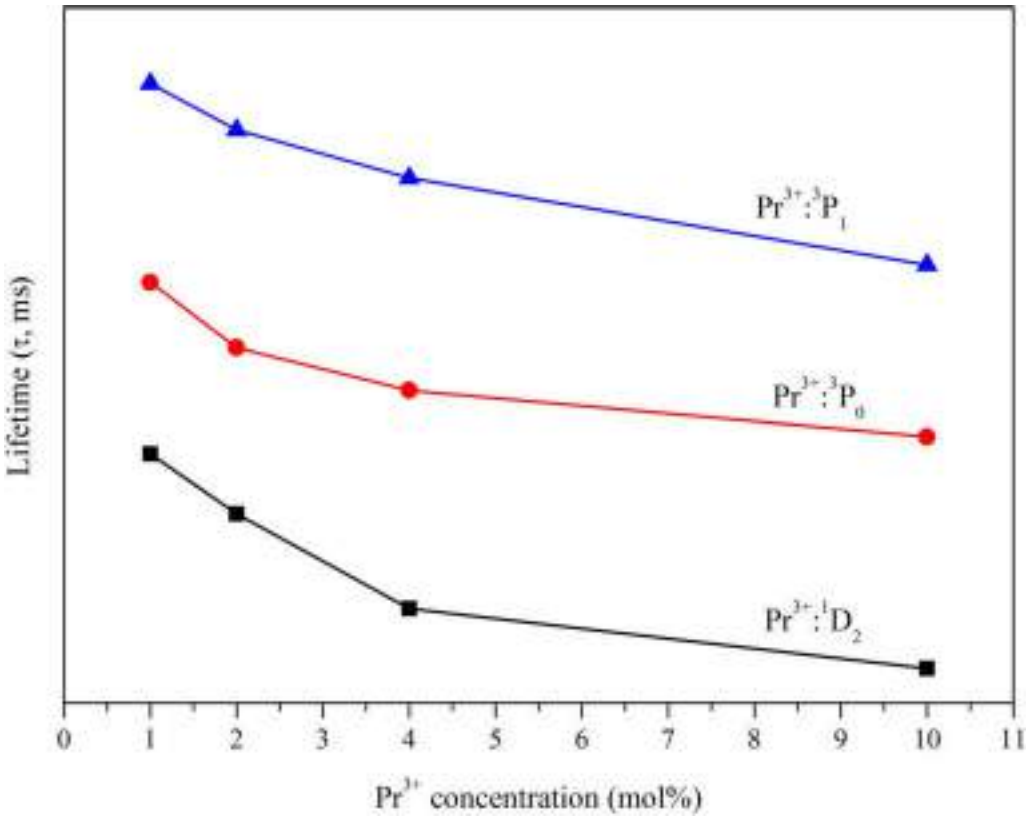



**Fig. 18** Variation of lifetime as a function of $Pr^{3+}$ concentration in SAOPrx phosphors.

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**Author contributions** B.C. Jamalaiah: Conceptualization, Software, Investigation, Writing-Original draft preparation, Writing-Reviewing and Editing, N. Madhu: Investigation, Writing-Reviewing and Editing, K. Pavani: Conceptualization, Data curation, Writing-Reviewing and Editing, A.J. Neves: Conceptualization, Validation, Writing-Reviewing and Editing

**Data availability** Data will be made available on reasonable request.

**Conflict of interest** On behalf of all authors, the corresponding author states that there is no conflict of interest.

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# Green luminescent $Sr_3Gd(PO_4)_3$: $Tb^{3+}$ phosphors for lighting applications

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ABSTRACT

The inorganic phosphors doped with different rare earth ions are of more significant to develop new class of lighting devices to fulfill the present technological desires owing to their compact size, high colour rendering index with high luminescence efficiency, eco-friendly behaviour. The present research work reports the synthesis, structural, morphological and optical analysis of $Sr_3Gd(PO_4)_3$: $Tb^{3+}$ phosphors for lighting applications. These phosphors were synthesized *via* modified citrate gel-combustion technique with varied concentrations of $Tb^{3+}$ and they were crystallized into BCC phase. The morphological investigations reveal an agglomeration of particles distributed non-uniformly in the crystal lattice. Upon excited at near UV radiation, the phosphors emit intense green luminescence through $^5D_4 \rightarrow {}^7F_J$ transitions. The colour perception studies were carried out by evaluating the chromaticity coordinates (x, y). The experimental investigations explore that the studied phosphors are more suitable for lighting applications.

## 1. Introduction

Now-a-days, trivalent rare earth (RE) ions activated phosphors play a key role in solid state lighting (SSL) technology due to their high brightness with significant luminescence efficiency, low-energy consumption with eco-friendly and non-toxic nature and stable luminous output with relatively long-life [1–3]. The light emitting diode (LED) based light show tremendous advantages compared to conventional incandescent blubs and fluorescent lamps. However, the use of LEDs has become difficult due to their low colour rendering index (CRI) of the order 85 and high colour temperature (CCT) of the order 7615 K. The phosphor-converting LEDs can meet the requirement of LED-based lighting due to their relatively low CCT rating with good CRI [4,5]. Therefore, the researchers have focused a light to design and develop better, efficient and novel phosphor materials for LED sources.

The $A_3M(PO_4)_3$ (A–divalent cation and M–trivalent RE cation) orthophosphate phosphor has been the most noteworthy as it can be synthesized easily at low temperature with good chemical and thermal stability and its non-toxic nature. Among the available orthophosphate phosphors [6–8], the $Sr_3Gd(PO_4)_3$ phosphor has single-phase with good RE ion solubility. The modified citrate-gel combustion method of synthesis of $Sr_3Gd(PO_4)_3$ phosphor is possible at very low temperatures leading to environmental friendly by consuming low electric power. This method of synthesis yields good yields of final products with single phase that enables the optical properties of $RE^{3+}$ activators which suitably replace the $Gd^{3+}$ sites without disturbing the BCC structure of $Sr_3Gd(PO_4)_3$ lattice. The $Sr_3Gd(PO_4)_3$ phosphors doped with different RE ions and co-doped with transition metal-ions were reported for white light generation and solar cell applications [9–11]. The $Tb^{3+}$ ions exhibit their characteristic emission bands corresponding to ($^5D_3$, $^5D_4$) $\rightarrow {}^7F_J$ transitions under suitable excitation. These ions are capable of exhibiting luminescence quenching and concentration ($x$) dependent optical properties in different host environments. In general, they emit blue light through $^5D_3 \rightarrow {}^7F_J$ transitions for $x < 0.5\%$ and green light through $^5D_4 \rightarrow {}^7F_J$ transitions for $x \geq 0.5\%$. Therefore, $Tb^{3+}$ ions have been used for green to blue tunable emission resulting to generate white light [12,13]. They can also be used as effective sensitizers to improve the luminescence efficiency of certain RE ions [11,14,15].

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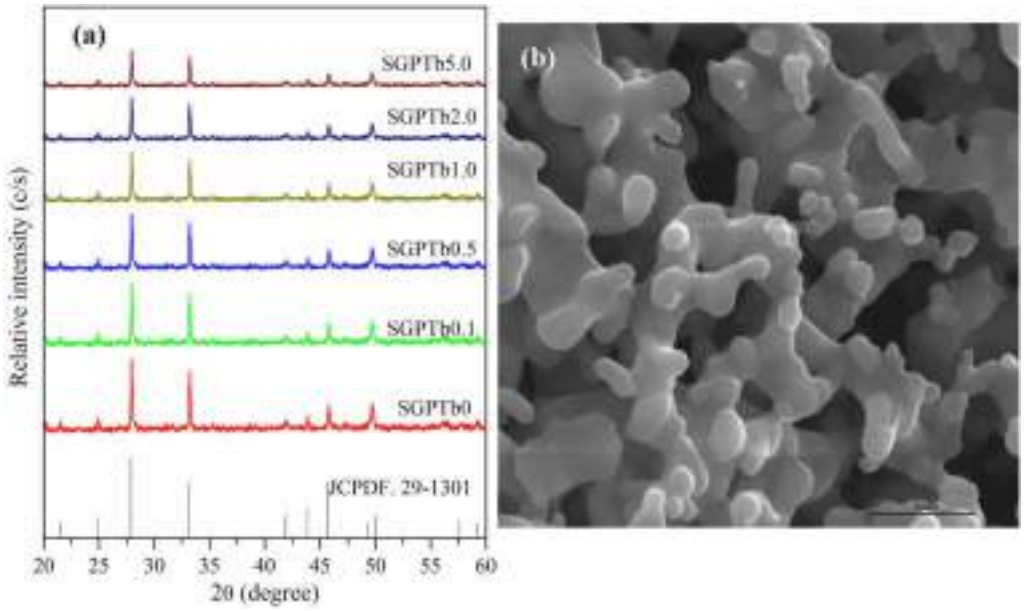



**Fig. 1.** The PXRD profiles of SGPTb*x* phosphors (a) and the HR-SEM micrograph of SGPTb2.0 phosphor (b).

The luminescence and energy transfer properties of $Ce^{3+}$ and $Tb^{3+}$ co-doped $Sr_3Gd(PO_4)_3$ phosphors synthesized through solid-state reaction method were examined for white LEDs by J. Sun et al. [16]. The study describes that the spectral overlap of $Ce^{3+}$ emission band and $Tb^{3+}$ excitation band results an effective sensitization of $Tb^{3+}$ by $Ce^{3+}$ producing improved luminescence. The present research work reports on the synthesis, concentration dependent luminescence and energy transfer properties of a series of different concentrations of $Tb^{3+}$ doped $Sr_3Gd(PO_4)_3$ phosphors for various lighting applications. The crystalline phase, surface morphology, presence of various functional groups that help to enhance the optical properties were discussed. The photoluminescence excitation, emission, decay and energy transfer properties were explored. The enhanced luminescence of $Tb^{3+}$ ions in $Sr_3Gd(PO_4)_3$ phosphors due to the effect of sensitization of $Tb^{3+}$ active ions by host lattice was discussed in detail.

## 2. Experimental techniques

### 2.1. Materials and method of synthesis

Different concentrations of $Tb^{3+}$ activated SGPTb*x* phosphors of composition $Sr_3Gd_{(1-x)}(PO_4)_3$:$xTb^{3+}$, where $x = 0$, 0.1, 0.5, 1.0, 2.0, 3.0 and 5.0 mol% were synthesized by modified citrate-gel combustion method using high pure nitrates such as $Sr(NO_3)_2$, $Gd(NO_3)_3.6H_2O$ and $Tb(NO_3)_3.5H_2O$, ammonium dihydrogen phosphate ($NH_4H_2PO_4$) and citric acid ($C_6H_8O_7.H_2O$) without further purification. 1.0 M solution of each was prepared by dissolving stoichiometric amounts of starting materials in double-distilled water and stirred well for 30 min using magnetic stirrer operating at 500 rpm. The citric acid solution was prepared in 10 mL of double-distilled water taking into account the starting materials and citric acid in the ratio 1:2. All these compound solutions were mixed in drop-wise and stirred well for 30 min resulting to produce homogeneous solution which turned into light-brown coloured powder upon dried at 80 °C for 24 h and it was heat treated at 200 and 400 °C for 3 h with intermediate grinding producing black-foamy material. The fine powder of black-foamy material was sintered at 1250 °C for 5 h producing milky-white SGPTb*x* phosphors.

### 2.2. Characterization

The crystalline phase of SGPTb*x* phosphors were carried out with BRUCKER USA D8 advance diffractometer using CuKα radiation of wavelength 1.541 Å. Fourier-transform infrared (FT-IR) analysis (KBr technique) was carried out with PerkinElmer FT-IR spectrometer using a pellet consisting of KBr:Sample = 300:1. The morphological investigation was carried out on **FEI-Quanta FEG 200F** high resolution-scanning electron microscope (HR-SEM). The photoluminescence excitation and emission studies were carried out with FP-8300 JASCO Fluorescence Spectrometer. The decay analysis was done using FLS 1000 photoluminescence spectrometer provided with Xe-flash lamp in pulsed mode. All the measurements were carried out at room temperature only.

## 3. Results and discussions

### 3.1. Structure and morphology

The crystalline phase of SGPTb*x* ($0 \leq x \leq 5.0$ mol%) phosphors has been analyzed using the powder X-ray diffraction (PXRD) studies shown in Fig. 1(a). These PXRD profiles are suitably matched to the JCPDS No. 29–1301 showing body-centered cubic (BCC) crystal structure with lattice parameters $a = b = c = 10.11$ Å, $\alpha = \beta = \gamma = 90°$. The intensity of PXRD peaks found to be decreased with the addition of $Tb^{3+}$ ions concentration with out any deviation in their positions. Earlier reports reveal that the $Tb^{3+}$ ions occupy the $Gd^{3+}/La^{3+}$ sites in $Ba_3Ln(PO_4)_3$:$Tb^{3+}$ (Ln = La, Gd) phosphor [17] and $Y^{3+}/Gd^{3+}/Lu^{3+}$ sites in $K_2Ln(PO_4)(WO_4)$:$Tb^{3+}$, $Eu^{3+}$ (Ln = Y, Gd and Lu) phosphor [18]. In the present research work also there is more probability for $Tb^{3+}$ ions to replace $Gd^{3+}$ sites as the ionic radius of $Tb^{3+}$ (~0.0923 nm) is very close to that of $Gd^{3+}$ (~0.0938 nm). According to Debye-Scherrer's equation, the average crystallite size (D) has been estimated to be 52 nm and it is very close to that obtained from the Hall-Williamson's method (55 nm) [19,20]. Considerably small variation in ionic radii of $Tb^{3+}$ and $Gd^{3+}$ results a lattice distortion leading to micro-strains of the order ~0.00064 which is found smaller than that of $SrEuMgAl_{10}O_{17}$ phosphor (~0.00751 nm) [21].

The HR-SEM is a powerful tool for materials characterization and it provides the information regarding the presence of various microstructures and a qualitative chemical analysis. The HR-SEM micrograph of SGPTb2.0 phosphor shown in Fig. 1(b) reveals that the particles are appeared to be agglomerated and interconnected together making a continuous structure of irregular shape. The FT-IR spectra of SGPTb*x* ($x = 0$ and 1.0 mol%) phosphors in the spectral region from 500 to 1600

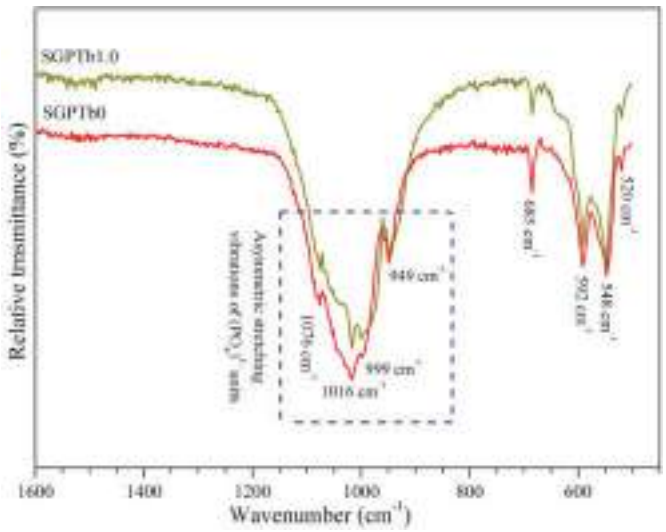



**Fig. 2.** FT-IR spectra of SGPTb$x$ ($x$ = 0 and 1.0 mol%) phosphors.

**Table 1**
Assignment of FT-IR bands in SGPTb$x$ phosphors.

| S. No. | FT-IR band position (cm$^{-1}$) | Assignment | Reference |
|---|---|---|---|
| 1 | 1076<br>1016<br>999<br>949 | Asymmetric stretching vibrations of $(PO_4)^{3-}$ units | [22,23] |
| 2 | 685 | Sr–O symmetric stretching vibrations | [24] |
| 3 | 592 | O–P–O asymmetric bending vibrations | [25] |
| 4 | 548 | Gd–O symmetric stretching vibrations | [26] |
| 5 | 520 | P–O asymmetric stretching vibrations | [27] |

cm$^{-1}$ shown in Fig. 2 reveals eight IR absorption bands at about 1076, 1016, 999, 949, 685, 592, 548 and 520 cm$^{-1}$ corresponding to various functional groups [22–27] and their assignment has been summarized in Table 1.

### 3.2. Photoluminescence analysis

The photoluminescence excitation (PLE) spectra help us to obtain suitable excitation wavelength and hence to have access to higher energy states of RE ions leading to get efficient emission from a luminescent material. The PLE spectra monitoring the emission at 543 nm ($Tb^{3+}$: $^5D_4 \rightarrow {}^7F_5$) in the spectral range 220–500 nm shown in Fig. 3 reveal three groups of transitions corresponding to $PO_4^{3-}$, $Gd^{3+}$ and $Tb^{3+}$. A broad and intense host excitation band (HEB) with a peak maximum at about 224 nm has been assigned to $PO_4^{3-}$ [14]. The PLE bands positioned from 246 to 312 nm have been related to both $Gd^{3+}$ and $Tb^{3+}$, while the bands from 318 to 486 nm to $Tb^{3+}$ ions only [28,29] and their assignments are summarized in Table 2. The $PO_4^{3-}$, $Gd^{3+}$: $^8S_{7/2} \rightarrow {}^6I_{11/2}$ and $Tb^{3+}$: $^7F_6 \rightarrow {}^5D_3$ transitions are found to be more prominent and the wavelengths

**Table 2**
Assignment of PLE band positions in SGPTb$x$ phosphors.

| PLE band position (nm) | Assignment | |
|---|---|---|
| | $Tb^{3+}$ ions | $Gd^{3+}$ ions |
| 246 | $^7F_6 \rightarrow {}^5K_8$ | $^8S_{7/2} \rightarrow {}^6D_{7/2}$ |
| 253 | $^7F_6 \rightarrow ({}^3P, {}^5D)_2$ | $^8S_{7/2} \rightarrow {}^6D_{9/2}$ |
| 273 | $^7F_6 \rightarrow {}^5F_3$ | $^8S_{7/2} \rightarrow {}^6I_{11/2}$ |
| 276 | – | $^8S_{7/2} \rightarrow {}^6I_{9/2}$ |
| 280 | $^7F_6 \rightarrow {}^5F_4$ | $^8S_{7/2} \rightarrow {}^6I_{7/2}$ |
| 302 | $^7F_6 \rightarrow {}^5H_6$ | $^8S_{7/2} \rightarrow {}^6P_{3/2}$ |
| 307 | – | $^8S_{7/2} \rightarrow {}^6P_{5/2}$ |
| 312 | – | $^8S_{7/2} \rightarrow {}^6P_{1/2}$ |
| 326 | $^7F_6 \rightarrow {}^5D_1$ | – |
| 342 | $^7F_6 \rightarrow {}^5L_8$ | – |
| 352 | $^7F_6 \rightarrow {}^5D_2$ | – |
| 359 | $^7F_6 \rightarrow {}^5G_5$ | – |
| 369 | $^7F_6 \rightarrow {}^5L_{10}$ | – |
| 379 | $^7F_6 \rightarrow {}^5D_3$ | – |
| 486 | $^7F_6 \rightarrow {}^5D_4$ | – |

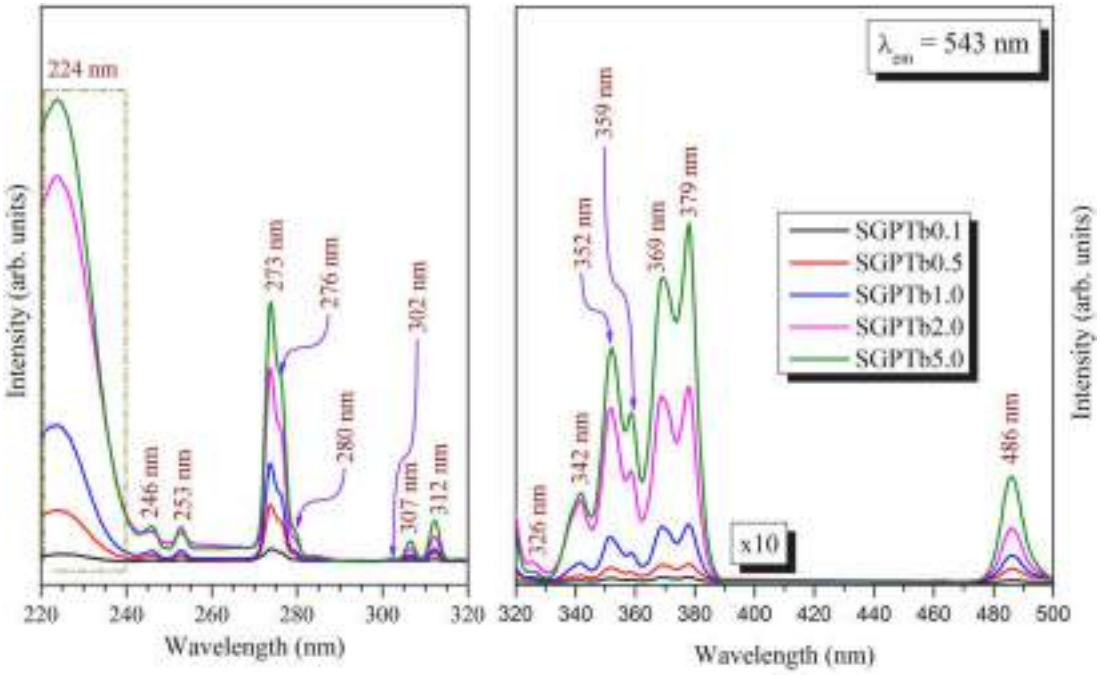



**Fig. 3.** PLE spectra of SGPTb$x$ phosphors monitoring the emission at $\lambda_{em}$ = 543 nm.

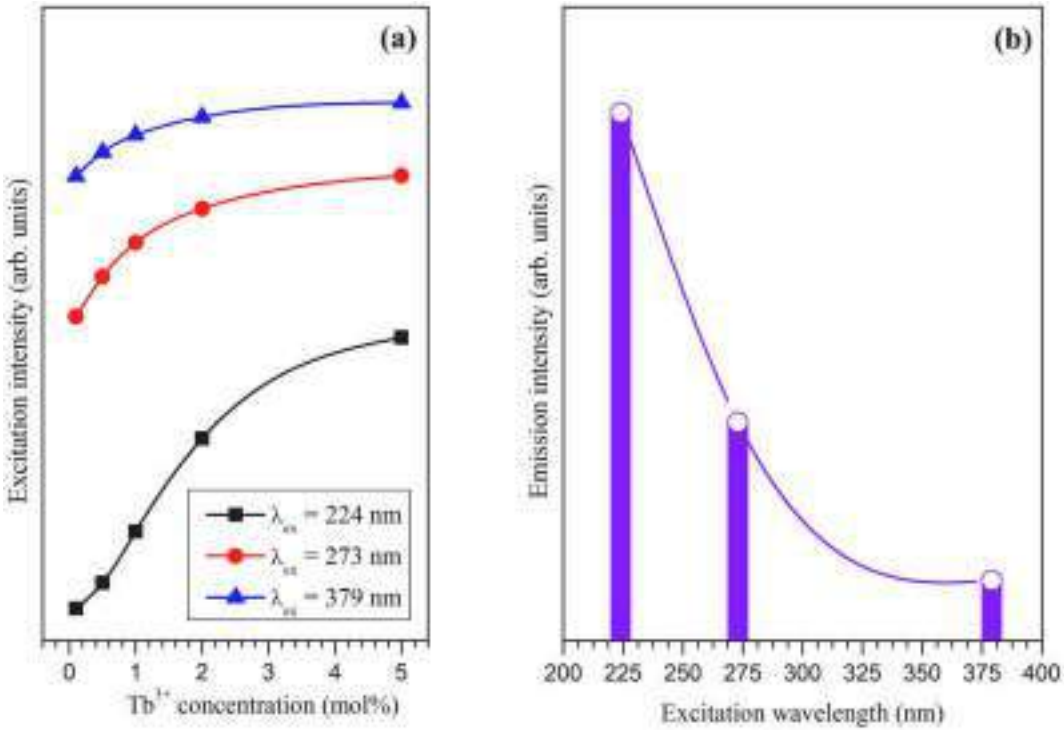



**Fig. 4.** The variation of excitation intensity of different PLE bands (a) and the emission intensity of $Tb^{3+}$: $^5D_4 \rightarrow {}^7F_5$ transition (b) as a function of $Tb^{3+}$ ions concentration in SGPTb*x* phosphors.

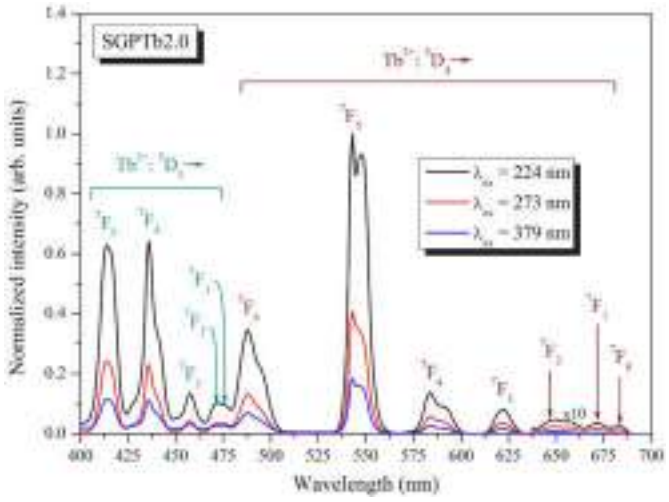



**Fig. 5.** Emission spectra of SGPTb2.0 phosphors at different excitation wavelengths.

corresponding to these probably produce intense luminescence from SGPTb*x* phosphors. From the PLE spectra it is clear that the intensity of observed transitions increases with increase of $Tb^{3+}$ ions concentration. The variation of intensity of 224 nm ($PO_4^{3-}$), 273 nm ($Gd^{3+}$: $^8S_{7/2} \rightarrow {}^6I_{11/2}$) and 379 nm ($Tb^{3+}$: $^7F_6 \rightarrow {}^5D_3$) bands as a function of $Tb^{3+}$ ions concentration is shown in Fig. 4(a).

To optimize the suitable excitation wavelength for efficient emission of $Tb^{3+}$ ions, the emission spectra of SGPTb2.0 phosphor have been recorded at 224, 273 and 379 nm excitations and they are shown in Fig. 5. These spectra reveal two groups of emission transitions originated from $Tb^{3+}$: $^5D_3 \rightarrow {}^7F_J$ (blue region) and $Tb^{3+}$: $^5D_4 \rightarrow {}^7F_J$ (green-red region) transitions. The positions of these transitions remain unchanged except in their intensity which decrease with increase of excitation wavelength as illustrated in Fig. 4(b). The SGPTb*x* phosphors show strong and intense luminescence when excited at 224 nm ($PO_4^{3-}$) compared to 273 nm ($Gd^{3+}$: $^8S_{7/2} \rightarrow {}^6I_{11/2}$) and 379 nm ($Tb^{3+}$: $^7F_6 \rightarrow {}^5D_3$). The observed emission transitions have been ascribed to $^5D_3 \rightarrow {}^7F_5$ (414 nm), $^5D_3 \rightarrow {}^7F_4$ (436 nm), $^5D_3 \rightarrow {}^7F_3$ (458 nm), $^5D_3 \rightarrow {}^7F_2$ (472 nm), $^5D_3 \rightarrow {}^7F_1$ (476 nm), $^5D_4 \rightarrow {}^7F_6$ (488 nm), $^5D_4 \rightarrow {}^7F_5$ (543 nm), $^5D_4 \rightarrow {}^7F_4$ (583 nm), $^5D_4 \rightarrow {}^7F_3$ (622 nm), $^5D_4 \rightarrow {}^7F_2$ (648 nm), $^5D_4 \rightarrow {}^7F_1$ (673 nm) and $^5D_4 \rightarrow {}^7F_0$ (683 nm) transitions [29].

The emission spectra of SGPTb*x* ($0 \leq x \leq 5.0$ mol%) phosphors at 224 nm excitation shown in Fig. 6(a) exhibit interesting emission results i.e., the $Tb^{3+}$: $^5D_3 \rightarrow {}^7F_J$ transitions show luminescence quenching beyond $x = 2.0$ mol%, while the intensity of $Tb^{3+}$: $^5D_4 \rightarrow {}^7F_J$ transitions increase with increase of $Tb^{3+}$ concentration. The variation of intensity of $^5D_3 \rightarrow {}^7F_5$ (414 nm) and $^5D_4 \rightarrow {}^7F_5$ (543 nm) transitions as a function of $Tb^{3+}$ concentration is illustrated in Fig. 6(b). It is well known that the quenching of luminescence depends on the concentration of active ions and the host environment. For example, the $Tb^{3+}$: $^5D_4 \rightarrow {}^7F_J$ transitions exhibit luminescence quenching at higher concentrations in $SrAl_2O_4$: $Tb^{3+}$ nanophosphors [30]. The process of luminescence quenching is mainly due to the energy transfer (ET) among the excited $Tb^{3+}$ ions at higher concentrations through non-radiative (NR) transitions. The green-to-blue luminescence ($I_G/I_B$) intensity ratio represents the clustering and/or homogeneous distribution of $Tb^{3+}$ ions in a unit cell in any host matrix i.e., $(I_G/I_B) > 1$ indicates uniform distribution and $(I_G/I_B) < 1$ shows clustering of $Tb^{3+}$ ions [31]. In the present research work, the value of $(I_G/I_B)$ is found to be higher than unity and it increases with increase of $Tb^{3+}$ concentration showing the uniform distribution of $Tb^{3+}$ ions in SGPTb*x* lattice.

Upon 224 nm excitation, some of the incident light photons has been absorbed by $PO_4^{3-}$ and get excited to higher energy states. These excited $PO_4^{3-}$ transfer their energy to $Gd^{3+}$ *via* Stoke's shift resulting to excite them to $Gd^{3+}$: $^6D_J$ and $^6I_J$ states. These excited $Gd^{3+}$ ions decays to $Gd^{3+}$:$^6P_J$ energy states through a quick non-radiative process and excite $Tb^{3+}$ ions to higher energy state above the $Tb^{3+}$: $^5D_3$ energy state by transferring their energy. Due to host sensitization, efficient energy

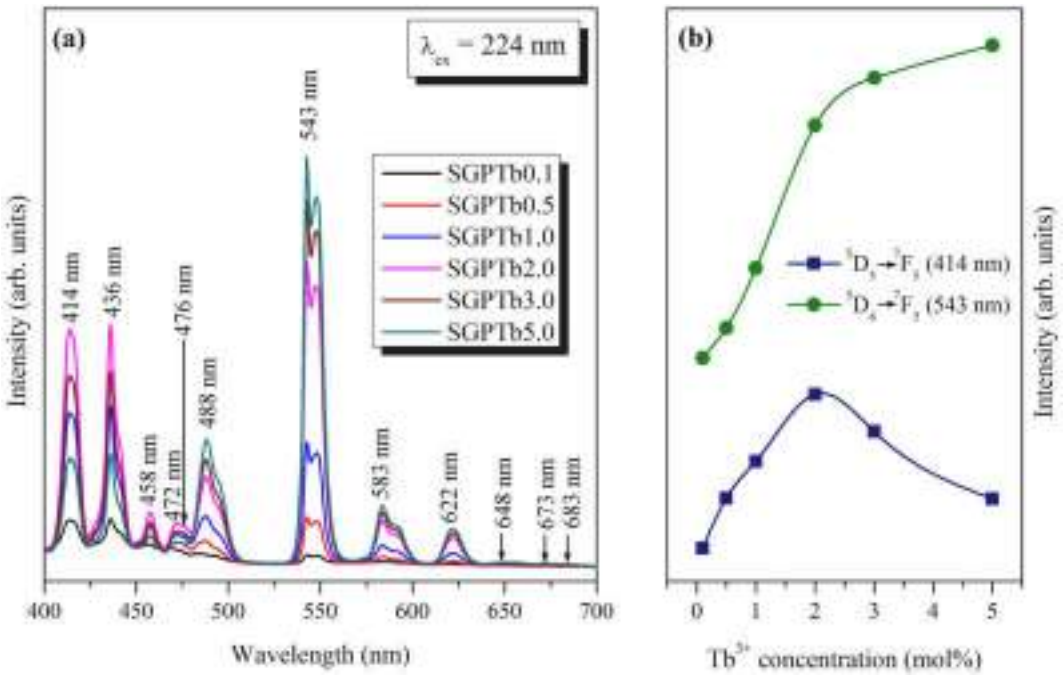



**Fig. 6.** Emission spectra of SGPTb*x* phosphors at 224 nm excitation (a) and the variation of intensity of ($^5D_3$, $^5D_4$) → $^7F_J$ transitions as a function of $Tb^{3+}$ concentration (b).

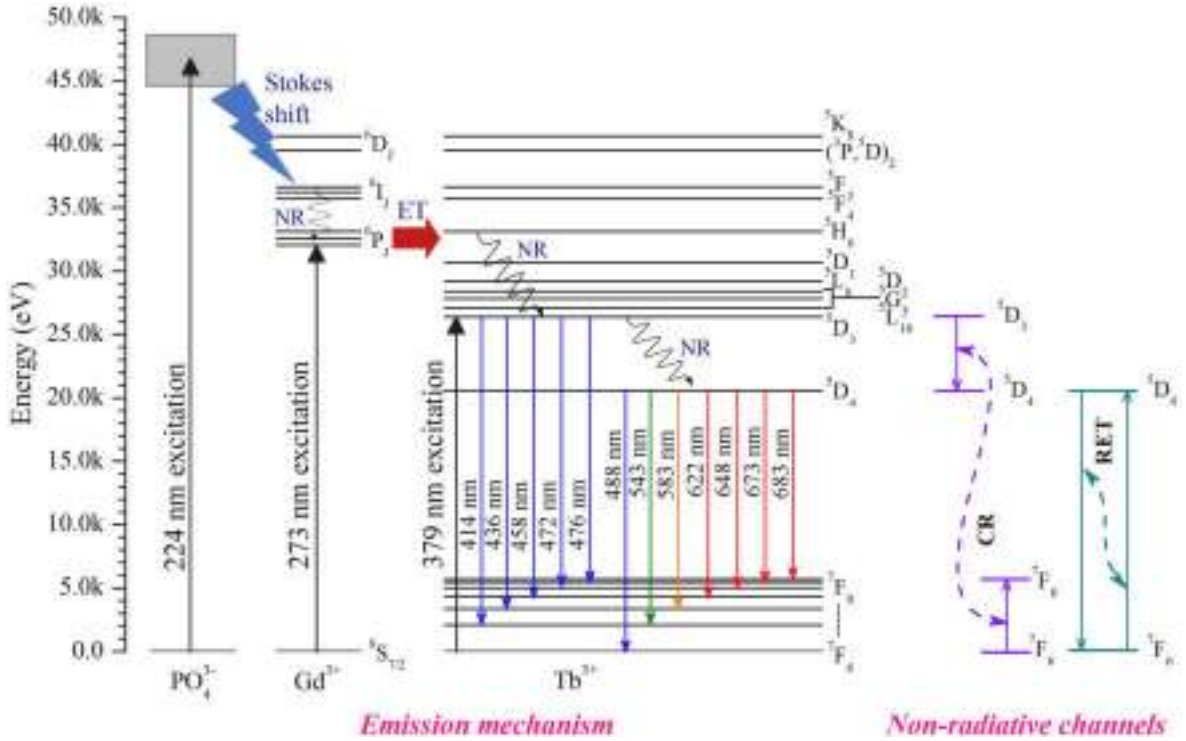



**Fig. 7.** Partial energy-level diagram illustrating emission mechanism of $Tb^{3+}$ ions at 224 nm excitation and possible non-radiative channels responsible for energy transfer in SGPTb*x* phosphors.

transfer takes place causing to improve population densities of $Tb^{3+}$:$^5D_{3,4}$ emission states. Since, the lifetime of $Tb^{3+}$:$^5D_4$ level is relatively higher than that of $Tb^{3+}$:$^5D_3$ level, the population density of $^5D_4$ emission state becomes more furnish to exhibit intense luminescence through $^5D_4 \rightarrow {}^7F_J$ transitions. The emission mechanism of $Tb^{3+}$ ions at 224 nm excitation through Stoke's shift and ET process is illustrated in Fig. 7.

### 3.3. Colour perception analysis

The colour perception of emitted luminescence of SGPTb*x* phosphors has been obtained using Commission International de l'Eclairage (CIE-1931) chromaticity coordinates (x, y). For SGPTb2.0 phosphor, the CIE chromaticity coordinates are found to be (0.282, 0.331), (0.306, 0.338) and (0.311, 0.328) at 224, 273 and 379 nm excitations, respectively. The

**Table 3**
Comparison of CIE coordinates, colour purity and correlated colour temperature (CCT) values of SGPTb*x* phosphors at 224 nm excitation.

| Doping (mol%) | CIE coordinates | colour purity (%) | CCT (K) |
|---|---|---|---|
| $x = 0.1$ | (0.303, 0.289) | 15.0 | 7768 |
| $x = 0.5$ | (0.291, 0.281) | 19.4 | 9198 |
| $x = 1.0$ | (0.286, 0.291) | 19.8 | 9224 |
| $x = 2.0$ | (0.282, 0.331) | 17.4 | 8349 |
| $x = 3.0$ | (0.291, 0.362) | 13.8 | 7314 |
| $x = 5.0$ | (0.301, 0.380) | 10.4 | 6720 |

CIE coordinates of SGPTb*x* phosphors at 224 nm excitation are listed in Table 3. The observed chromaticity coordinates are found close to those reported for SNYPF: $Ce^{3+}$, 0.5%$Tb^{3+}$ phosphors (0.223, 0.387) [32], LGW: 2%$Tm^{3+}$, 4%$Tb^{3+}$ (0.279, 0.418) and LGW: 2%$Tm^{3+}$, 4%$Tb^{3+}$, 5%$Eu^{3+}$ (0.377, 0.296) [33] phosphors. The identification of chromaticity coordinates is illustrated in Fig. 8.

As seen in the chromaticity diagram, it is clear that the coordinates of SGPTb2.0 phosphor at different excitations have been located in greenish-white region [see Fig. 8(a)], while the SGPTb*x* phosphors show a colour tunability at 224 nm excitation. The colour of emitted luminescence has been tuned from bluish-white for $x \leq 1.0$ mol% to greenish-white for $x \geq 2.0$ mol% [see Fig. 8(b)]. The colour purity (CP) and the correlated colour temperature (CCT) rating values of SGPTb*x*

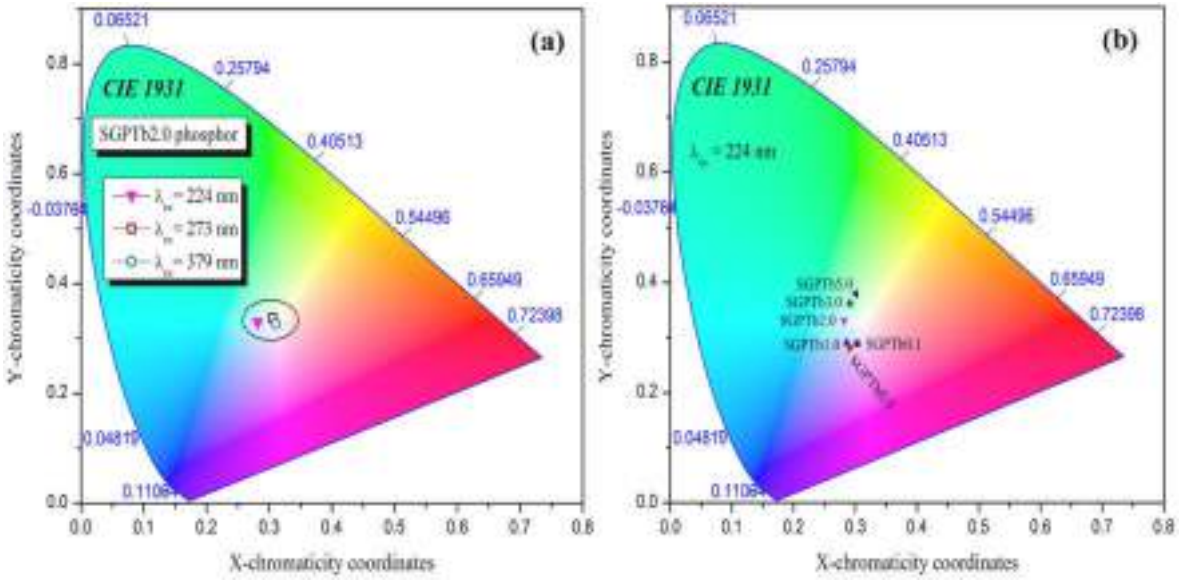



**Fig. 8.** CIE diagram of SGPTb2.0 at different excitations (a) and SGPTb*x* at 224 nm excitation (b).

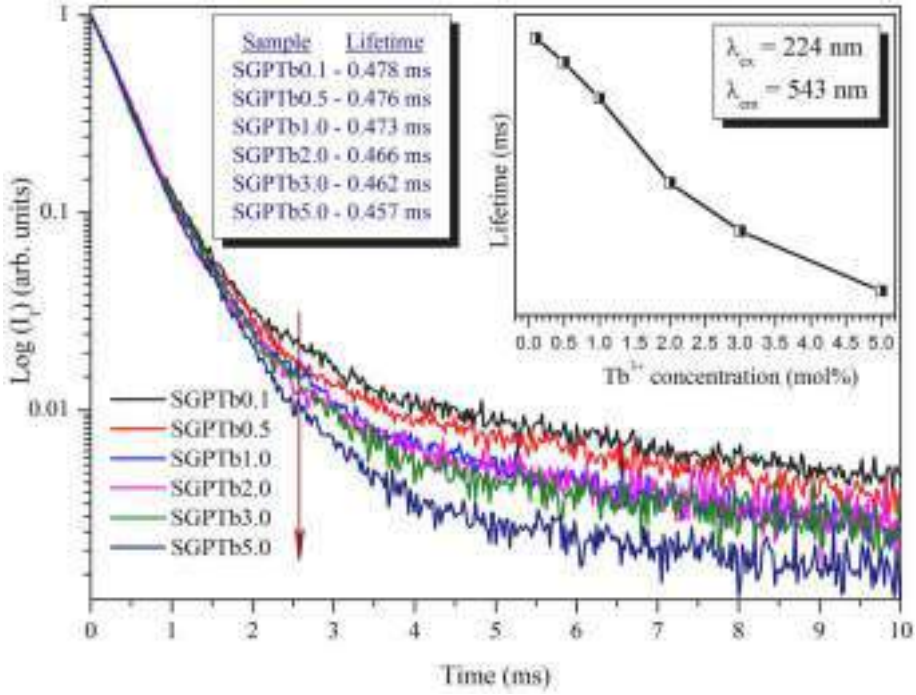



**Fig. 9.** Decay curves of $Tb^{3+}$: $^5D_4$ emission state in SGPTb*x* phosphors. Inset shows the variation of lifetime as a function of $Tb^{3+}$ concentration.

phosphors at 224 nm excitation have been determined following McCamy [34] and they are summarized in Table 3. The CCT rating of 6720 K is close to cool-white light and it has been suitable for lighting applications particularly to illuminate living rooms and lounges [35]. The values of CP for SGPTb2.0 phosphor are found to be 17.4, 9.0 and 7.8% for 224, 273 and 379 nm excitations, respectively. These results show that the percentage of green colour is found higher for SGPTb2.0 phosphor excited at 224 nm.

### 3.4. Luminescence decay analysis

The lifetime of $Tb^{3+}$: $^5D_4$ emission state of SGPTb*x* ($0 \leq x \leq 5.0$ mol %) phosphors has been determined controlling the excitation and emission wavelengths at 224 and 543 nm, respectively and they are described in Fig. 9. All these decay curves are well suited to single exponential function, $I = I_0.e^{-t/\tau}$, where $I_0$ indicates the initial intensity and $\tau$ indicates the lifetime. The values of $\tau$ are found to be 0.478, 0.476, 0.473, 0.466, 0.462 and 0.457 ms for $x = 0.1$, 0.5, 1.0, 2.0, 3.0 and 5.0 mol%, respectively considering the first e-fold times the initial intensity at $t = 0$ s.

The observed values of lifetime decrease gradually with increase of concentration of $Tb^{3+}$ ions confirm the presence of non-radiative (NR) transitions responsible for quenching of lifetime. The variation of lifetime of $Tb^{3+}$: $^5D_4$ emission state as a function of $Tb^{3+}$ concentration is shown in inset of Fig. 9. Since the concentration quenching has not been observed even for $x = 5.0$ mol% for $Tb^{3+}$: $^5D_4 \rightarrow {}^7F_J$ transitions, the exchange interaction mechanism among the excited $Tb^{3+}$ ions at higher concentrations through either cross-relaxation (CR) or resonant energy transfer (RET) or both channels might be responsible for the decrease of lifetime. The possible CR and RET channels responsible for quenching of lifetime at higher $Tb^{3+}$ concentrations are shown below and they are described in Fig. 7.

CR: $[^5D_3, {}^7F_6] \rightarrow [^5D_4, {}^7F_0]$

RET: $[^5D_4, {}^7F_6] \rightarrow [^7F_6, {}^5D_4]$

## 4. Conclusions

A series of SGPTb*x* ($0 \leq x \leq 5.0$ mol%) phosphors have been synthesized via modified citrate-gel combustion method. They have been crystallized into BCC structure with an average size of ~52–55 nm. The presence of different vibrational bonds Sr–O, Gd–O, O–P–O and P–O have been identified using FTIR studies. The HR-SEM image reveals agglomeration and non-uniform distribution of particles. The PLE spectra monitoring the emission at 543 nm ($Tb^{3+}$: $^5D_4 \rightarrow {}^7F_5$) show three kinds of transitions corresponding to $PO_4^{3-}$, $Gd^{3+}$ and $Tb^{3+}$ supporting efficient energy transfer among the excited $Tb^{3+}$ ions. The SGPTb*x* phosphors exhibit strong and intense luminescence when excited at 224 nm ($PO_4^{3-}$) compared to 273 nm ($Gd^{3+}$: $^8S_{7/2} \rightarrow {}^6I_{11/2}$) and 379 nm ($Tb^{3+}$: $^7F_6 \rightarrow {}^5D_3$) excitations due to Stokes shift. Upon these excitations, the $Tb^{3+}$ ions exhibit their characteristic emission bands due to $^5D_3 \rightarrow {}^7F_J$ and $^5D_4 \rightarrow {}^7F_J$ transitions. The colour of emitted luminescence has been tuned from bluish-white for $x \leq 1.0$ mol% to greenish-white for $x \geq 2.0$ mol% at 224 nm excitation. The observed results suggest that the SGPTb5.0 phosphor exhibit great potentiality to be use in the design of lighting devices for living rooms and lounges.

## Conflicts of interest

The authors declare that they have no conflict of interest.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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# Recent Updates on the Bioactive Compounds of Ginger (*Zingiber officinale*) on Cancer: A Study with Special Emphasis of Gingerol and Its Anticancer Potential

## Effect of Ginger and Its Compounds in Cancer Subjects

Handbook of Oxidative Stress in Cancer: Therapeutic Aspects pp 1-18 | Cite as

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## Abstract

Medicinal plants have been used as therapeutic agents since the origin of mankind. Many medicinal plants like *Tinospora cordifolia, Andrographis paniculata, Curcuma longa, Withania somnifera, Zingiber officinale,* etc. are used to treat cancer. Ginger is reported to show anticancer effect in many cancer types like liver cancer, gastric cancer, oral cancer, prostate cancer, breast cancer, and ovarian cancers in animal models and cell lines. To date, over 400 bioactive compounds have been identified in ginger, they are gingerols, shogaols, and paradols. These compounds possess antioxidant, anti-inflammatory, antimicrobial, and anticancer properties. Gingerol especially shows anticancer effects in different cancer subjects. Gingerol

may act on the TNF-α, IL-6, NF-κB, cyclooxygenase-2 (COX-2), and caspase-3, and other tumor-metabolic pathway factors in the prevention of cancer. We hope that this chapter will attract more attention on ginger's therapeutic potential and impact on cancer subjects.

## Keywords

Ginger Bioactive compounds Gingerol Cancer

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# Introduction

The biological term cancer refers to a set of diseases in which the cells of an organ or tissue split uncontrollably and acquire the ability to attack other tissues. Cancer is a global health problem, and it is the top cause of deaths in the world. Cancer occurs through the mutations by stepwise process which results in malignancies. Metastasis is the process whereby cancer cells rupture from a malignant tumor and travel to and invade other tissues in the body (Butt and Sultan 2009).

The most common types of cancer are liver cancer, esophageal cancer, breast cancer, oral cancer, lung cancer, prostate cancer, ovarian cancer, and stomach cancer. According to GLOBOCAN 2020 database in 2020, there were 19.1 million new cases of cancer and 10 million deaths from cancer worldwide, and the new cases will be upto 20 million globally by 2025 (Ferlay et al. 2019). The principle malignant conditions of the cancer are breast cancer (2.26 million cases), lung cancer (2.20 million cases), stomach cancer (1.08 million cases), liver cancer (0.90 million cases), esophagus cancer (0.60 million cases), pancreatic cancer (0.49 million cases), and colorectum cancer (0.73 million cases) in 2020 (Table 1).

**Table 1**

New cancer cases and deaths as per global cancer statistics 2020

| S. no | Cancer type | No of cases (2020) | No of deaths |
|---|---|---|---|
| 1. | Breast cancer | 2,261,419 | 684,996 |
| 2. | Lung cancer | 2,206,771 | 1,796,144 |
| 3. | Prostate cancer | 1,414,259 | 375,304 |
| 4. | Skin cancer | 1,198,073 | 63,731 |
| 5. | Colon cancer | 1,148,515 | 576,858 |
| 6. | Liver cancer | 905,677 | 830,180 |
| 7. | Cervical cancer | 604,127 | 341,831 |
| 8. | Esophageal cancer | 604,100 | 544,076 |
| 9. | Thyroid cancer | 586,202 | 43,646 |
| 10. | Pancreatic cancer | 495,773 | 466,003 |
| 11. | Leukemia | 474,519 | 311,594 |
| 12. | Kidney | 431,288 | 179,368 |
| 13. | Oral cancer | 377,713 | 177,757 |

India has 1.32 lakh new cancer cases in 2020, also the lowest rates of cancer in the world. Breast cancer, oral cancer, cervical cancer, and lung cancer are the top four cancers in India. Cancer deaths in India doubled from 1990 to 2016. It has been reported that genetic mutations, viruses, smoking, heavy metal ingestion, and dietary patterns are actively involved in cancer pathogenesis (Noonan et al. 2007). Despite huge progress and efforts have been made in the field of medicine for the prevention and treatment of cancer for years, cancer still remains the leading cause of deaths around the world (Figure 1).

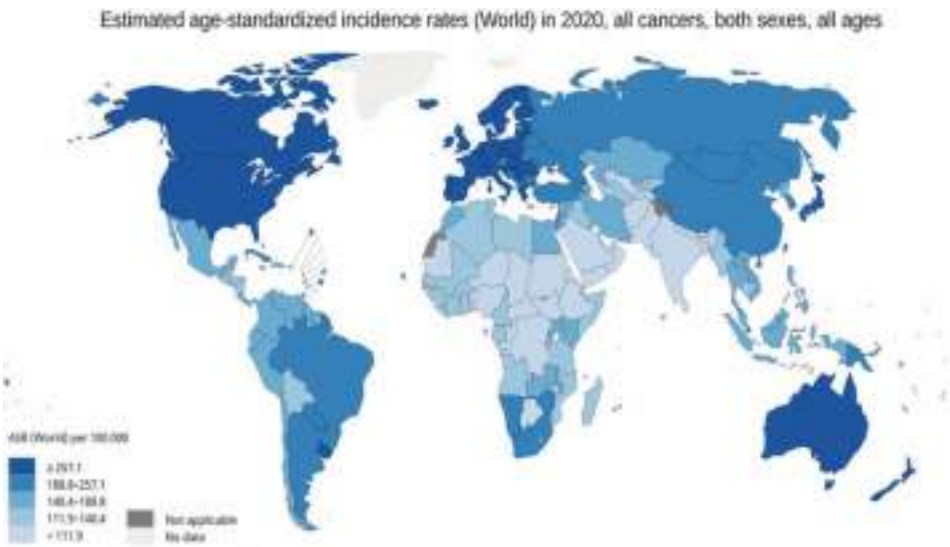



**Figure 1**

Cancer patients in the world as per the Global Cancer report 2020 by WHO. Source:https://www.uicc.org/news/globocan-2020-new-global-cancer-data# (https://www.uicc.org/news/globocan-2020-new-global-cancer-data#)

## Carcinogenesis

Carcinogenesis is the process by which a normal cell is transformed into a tumor cell and its progression to a clinically observable tumor with high probability of metastasis. Cancer is considered a process with three steps: 1. initiation, 2.promotion, and 3. progression (Weston and Harris 2003). This process can vary depending on the etiology of cancer. Normally, cancers are caused by chemical agents, viruses, and others by mutations of DNA, epigenetic changes of DNA (Baylin and Jones 2016).

## Mechanism of Cancer

**Cancer: Reactive Oxygen Species (ROS)**

Cancer is one of the stress-related disorders. During cancer condition, many free radicals or reactive oxygen species (ROS) are produced. The existence of oxidative stress resulting from increased free radicals has been postulated in cancer. Animal models and human studies and *in vitro* experiments suggest a role for oxidative stress, via an increased formation of free radicals in the pathophysiology of many complications, such as neurological, cardiovascular, renal, cancer, rheumatoid arthritis, cancer, and diabetes (Brownlee 2001). According to Sies (Sies et al. 2017), oxidative stress is defined as a shift in balance in cellular oxidation-reduction reactions in favor of oxidation, which leads to damage to the cell and formation of molecular products that are indicators of oxidative stress.

Reactive oxygen species are radicals or ions or molecules that have a one unpaired electron in their outermost shell of electrons. Due to this nature, ROS are highly reactive. Examples of ROS are superoxide ($O_2$-), hydrogen peroxide ($H_2O_2$), hydroxyl radicals (OH), and nitric oxide (•NO). ROS and oxidative stress have been implicated in many diseases like cancer, diabetes, and hepatitis. ROS plays an important role in various cascading of the signals for the cancer cells to survival, proliferation, resistance to apoptosis, neovascularization, invasion, and extravacation. (Cullen et al. 2003). In order to survive from oxidative stress condition, cancer cells adapt and acquire many mechanisms to counteract the potential toxic effects

of ROS stress in order to promote proximal protumorigenic signals. ROS also alters the DNA-binding sites of redox-sensitive transcription factors such as hypoxia-inducible factor-1 alpha (HIF-1α), NFκB, activator protein-1 (AP-1), and p53 (Trachootham et al. 2008). The antioxidant enzymes like SOD, CAT, GPx, GR, and GSH may act on these ROS, and hence these antioxidant enzymes activities are depleted in various cancer subjects.

Warburg (Liberti and Locasale 2016) described about cancer as metabolic alterations that represent a hallmark of cancer cells. Metabolic alterations and redox alterations which are important steps of cancer cell transformation make the mitochondria an attractive therapeutic target. Increased knowledge in the field of redox biology, its reactions, signaling networks, and interplay in disease and physiology has enabled not only a better realization of potential benefits but also grave dangers of ROS with respect to cancer phenotypes and drug resistance.

### Cancer Biomarkers

A thorough understanding of the roles of cancer biomarkers is essential for diagnostic purposes. A biomarker is "a characteristic that is objectively measured and evaluated as an indicator of normal biological processes, pathogenic processes, or pharmacologic responses to a therapeutic intervention." Because early diagnosis of cancer will treat cancer patients early, we can save the patient's life. Cancer biomarkers are produced by tumors or by the body in response to the presence of cancer. Cancer biomarkers can be used to determine the presence of malignancy and for the study of disease transmission. The important cancer biomarkers are Urokinase plasminogen activator (uPA), Carbonic anhydrase XII (CAXII), Cyclooxygenase (COX), Cytochrome P450 (CYP450), Telomerase, and Matrix metalloproteinases (MMPs).

The medical treatments for cancer are surgery, radiotherapy, and chemotherapy. These types of treatment are usually accompanied by a large number of side effects on patient health, like nausea, loss of appetite, weight loss, anemia, spinal cord injury, kidney damage, and mucositis. Hence, there is need for alternative therapy for cancer. So herbal medicine is practiced to treat cancer.

## Medicinal Plants for the Treatment of Cancer

Medicinal plants are used to treat many diseases like diabetes, cancer, epilepsy, alzheimer's, cough, fever, and other diseases. Drugs from medicinal plants focus on the most important active principles in terms of the quantity and the pharmacological actions. The information available on these medicinal plants has allowed the quantification of the active principle and the production of bioactive compounds. The bioactive compounds of medicinal plants have different chemical, pharmacological properties and actions. This has enabled us to evaluate the anticancer drugs from medicinal plants.

Many medicinal plants have been reported to possess anticancer properties. Due to the development of resistance against cancer effects, various plant-derived drugs have gained much attention in the recent years. Hence, it is of importance to focus on medicinal plants with anticancer properties that are easily available, culturally acceptable, and economically free. Herbal medicine has been used for thousands of years to cure cancer. Chemotherapeutic and chemopreventive effects of many herbal plants are attributed to phytochemicals, quinines, which are reported to induce antitumor effects *in vovo* and *in vitro* of cancer cells.

Recently, many well-known plant-derived compounds have been studied in animal models and cell lines. Among the above described plants and their formulations, *Terminalia chebula, Panax ginseng, Arachis hypogaea, Rauwolfia vomitoria, Azadirachta indica, Zingiber officinale, Commiphora mukul,* and *Rosa rugosa* are reported to be beneficial for cancer with less side effects as compared to conventional drugs. Hence, these medicinal plants could be a relatively safer and better therapeutic alternative for cancer treatment (Figure 2).

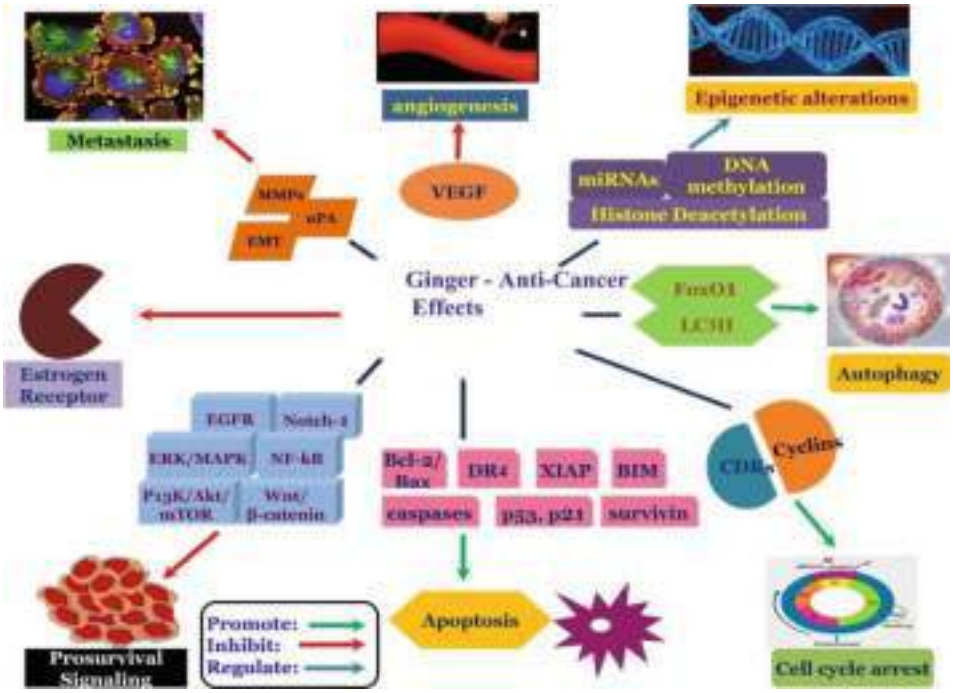



**Figure 2**
Ginger and anticancer mechanism

## Ginger

Ginger is the rhizome of *Zingiber officinale*. Roscoe belongs to the family Zingiberaceae. Ginger has been used as a spice, food, supplement, and flavoring agent. Ginger is used to cure diseases and symptoms, such as headache, nausea, cold, rheumatism, diarrhea, and arthritis. It is also used as a carminative, digestant, and antiflatulent (Ali et al. 2008). Ginger and its compounds are used as medicine in India, China, Burma, Germany, Japan, Indonesia, and the United States.

Ginger is reported to possess various medicinal properties like antibacterial, antiviral, antifungal, antiparasitic, anti-insecticidal, antianalgesic, antimutagen, anticarcinogenic, antispasmolytic, and anti-inflammatory and antioxidant activities (Shanmugam et al. 2021). Ginger have radioprotective, hepatoprotective, gastroprotective, nephroprotective, and neuroprotective properties, and its mechanism of action at the cellular level has been studied by many scientists (Ali et al. 2008; Shanmugam et al. 2009, 2021) (Figure 3).

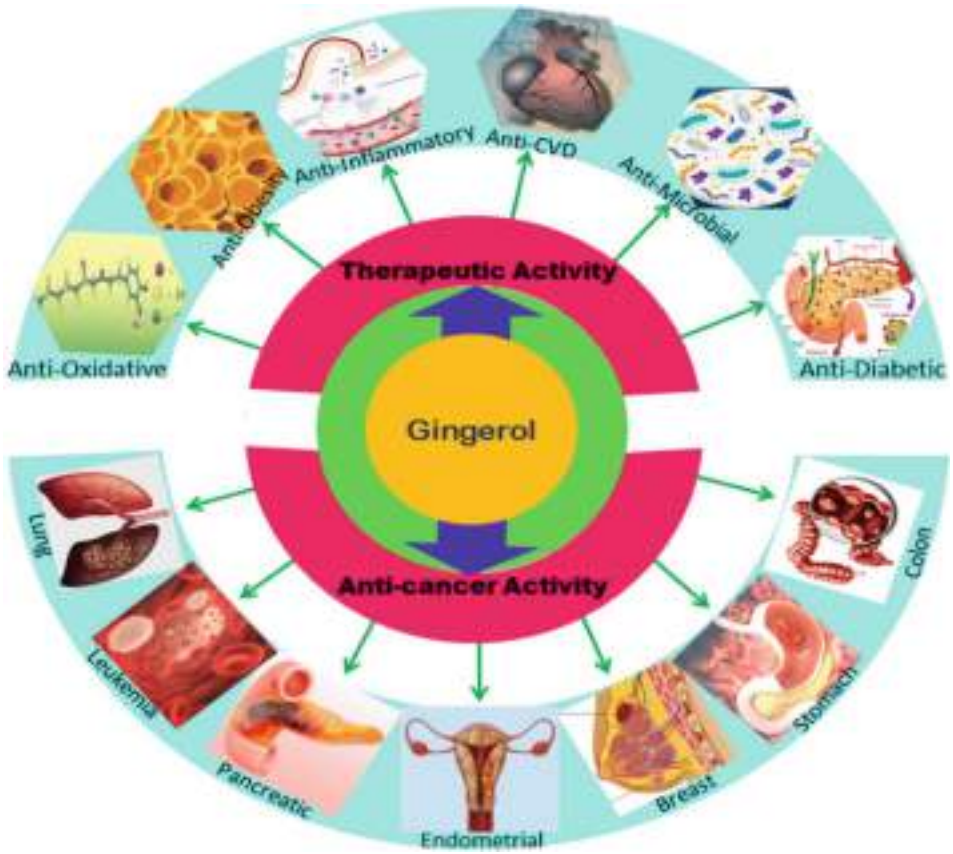



**Figure 3**
Pharmacological and anticancer properties of Gingerol

## Compounds of Ginger

The main constituents in ginger are terpenes, phenolic compounds, carbohydrates (50–70%), and lipids (3–8%). The terpenes (monoterpenes, sesquiterpenes, and sesquiterpene alcohols) are of 20–25%. The terpene compounds of ginger are zingiberene, $\alpha$-farnesene, $\beta$-sesquiphellandrene, $\beta$-bisabolene, and $\alpha$-curcumene. It has been identified that ginger has monoterpenes (such as $\alpha$-pinene, camphene, myrcene, $\alpha$-phellandrene, geranial, citronellal, neral, linalool, borneol, and alpha-terpineol). Phytosterols, amino acids, minerals, proteins, vitamins (vitamin A and nicotinic acid), and raw fiber, ash, are present in ginger (Shukla and Singh 2007).

The phenolic compounds of ginger are gingerol, shogaol, and paradols. In ginger, gingerols are in higher concentration. Ginger-specific smell and odor are due to the presence of gingerol and shogaols. The other compounds of ginger are 6-paradol, 1-dehydrogingerdione, 8-gingerdiol, 10-gingerdiol, 4-gingerdiol, 6-gingerdiol, 6-gingerdione, and 10-gingerdione. Ginger also contains diterpenes, galanolactone, diterpenoid, and ginger glycolipids (Yeh et al. 2014). Ginger has ascorbic acid, alkaloids, beta-carotene, and polyphenols. Ginger also has key volatile oils such as oleoresins, bisabolene, cineol, phellandrene, citral, borneol, and citronellol, vitamin B6, vitamin c, and linoleic acid. As per the available information, there are more than 400 bioactive compounds in ginger (Shukla and Singh 2007) (Figure 4).

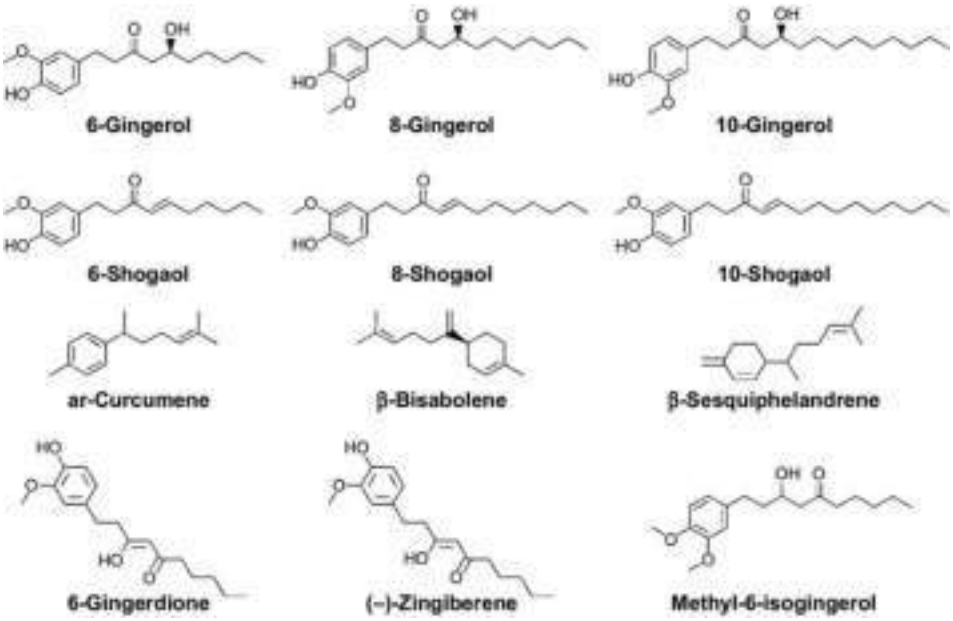



**Figure 4**
Compounds of Ginger

## Anticancer Effects of Ginger

Ginger has anticancer properties. In the methanolic, ethanolic, aqueous, n-hexane, and ethyl acetate, benzene extracts of ginger, many bioactive compounds are present which show antiproliferative, cytotoxic, and antiangiogenic activities. These pharmacological effects are due to bioactive compounds of ginger, which show antioxidant, anti-inflammatory, antioxidant, antihyperglycemic, antitumorigenic, and antilipidemic activities. These compounds may modulate the genetic expression and cause induction of apoptosis in cancer cells.

The anticancer effect of ginger may be due to the reduction of initiation, promotion, and progression. Hence, ginger can be used as anticancer agent (Zhang et al. 2017). Ginger has been reported to show its positive effects against many cancers, like liver cancer, gastric cancer, pancreatic cancer, breast cancer, prostate cancer, and other types of cancers. Ginger also has anticancer effects in different cancer cell lines in vitro, like lung, ovarian, liver, colon, cervical, and prostate cancer, through the stimulation of apoptosis and the reticence of cell proliferation (Zhang et al. 2017) (Table 2).

**Table 2**
Effect of ginger and its compounds on different cancer subjects

| S. no. | Ginger extract/compounds of ginger | Study type | Subjects | Dose | Potential mechanisms | Referen |
|---|---|---|---|---|---|---|
| 1 | Ginger ethanolic extract | *In vivo* | Wistar rats | 50 mg/kg | NADH dehydrogenase activity elevated | Ali et al. 2008) |
| 2 | Ginger extract | *In vitro* | HepG2 human hepato-cellular carcinoma cells | 1.11 mg/mL | Increasing the level of ROS levels increased and elevated p53 levels, thus promoting apoptosis | Li et al. ( 2013) |
| 3 | 6-gingerol | *In vitro* | He La human adenocarcinoma cervical cells | 60, 100, and 140μM | Cyclin A, cyclinD1, and cyclin E1 levels decreased, and caspase levels increased | Zhang et al. (2017 |
| 4 | 10-gingerol | In vitro | Human and mouse breast carcinoma cells | 50, 100, and 200μM | Cell growth and cell division are reduced | Bernard et al. ( 2017) |
| 5 | 6-gingerol,10-gingerol,6-shogaol, and 10-shogaol | *In vitro* | PC-3 human prostate cancer cells | 1,10, and 100μM | Inhibiting prostate cancer decreased, and the expression of MRP1 and GSTπ are lowered | Liu et al. (2017) |

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| 6 | 6-shogaol | *In vitro* | LNCaP, DU145, and PC-3 human prostate cancer cells | 10, 20, and 40μM | Cyclin D1, surviving, c-Myc, and Bcl2 expression are decreased Inhibition of STAT3 and NF-κB signals | Saha et al. (2014 |

Ginger has an antitumor activity by modulating of genetic pathways. It helps for the activation of suppressing gene of the tumor. Furthermore, ginger can inhibit the vascular endothelial growth factors and modulate apoptosis; thus, ginger supplementation can reduce cancer. Ginger extract prevents the initial stage of colon cancer. Supplementation of ginger to the mice with carcinogen 1,2-dimethylhydrazine (DMH) inhibited the levels of tissue cholesterol, HMG CoA reductase, free fatty acids, and triglycerides (Manju et al. 2006). Hence, ginger treatment reduces the risk of cancer by antioxidative compounds.

For instance, it has been identified that the terpenoids, compound of ginger, induce apoptosis in uterus cancer cells via the activation of tumor protein p53. Water and organic solvent extracts of ginger reported to show anticancer activities in THP-1 AMoL cells in vitro. These reports show that ginger has anticancer activity (Prasad and Tyagi 2015).

Ginger constituents ([6]-gingerol, [10]-gingerol, [6]-shogaol, and zerumbone) show anticancer effects. They are effective against many cancers (Habib et al. 2008). Habib et al. (2008) reported that ginger extract inhibits liver carcinogenesis in wistar rat through the downregulation of elevated NF-$\kappa$B and TNF-$\alpha$. Hence, ginger may act as an anticancer agent, which may be helpful in treatment of cancer subjects. Ginger ingredients inhibit the development of diethylnitrosamine-(DEN-) induced premalignant phenotype in rat hepato-carcinogenesis. It has been reported that supplementation of ginger prevented decrease of the content of metallothionein and endostatin in the liver and elevated the growth factors induced by the carcinogen in wistar albino rats. Ginger also reverses the altered serum-hepatic tumor markers (Mansour et al. 2010).

Wang et al. (2008) reported that beta-elemenean compound of ginger induces caspase-3, −7, −9 activities, decreases Bcl-2 expression, which releases cytochrome c, and elevated the levels of cleaved caspase-9 and poly (ADP-ribose) polymerase in cells. Application of ginger extract to mouse skin afforded significant inhibition of TPA-caused epidermal edema (56%) and hyperplasia (44%) (Katiyar et al. 1996). Kim et al. ( 2005) also reported that ginger induces programmed cell death in cell lines. Ethanol extract of ginger has antitumor-promoting effects in mouse skin tumorigenesis model, and it was concluded that animals pretreated with ginger showed depleted tumor compared with unginger-treated rats.

Zingerone with a dose of 100 mg mL suppressed LPS-induced NF-kB activities in cells. Dietary zingerone reduces proinflammatory cytokines. This study reports zingerone anti-inflammatory activity due to suppressing the activation of NF-kB, production of IL-1b, and the infiltration of inflammatory cells (Ganaie et al. 2019). Ganaie et al. (2019) also reported the anticancer effect of zingerone due to activation of cytochrome P4502E1 and suppression of NF-kB-p65, iNOSCOX-2, and PCNA in cancer subjects.

Zerumbone, seen in ginger, shows antiproliferative and anti-inflammatory effects and mediates its activity through the modulation of NF-kB activation (Takada et al. 2005). Zerumbone also inhibits the activation of NF-kB, and this inhibition may provide basis for the prevention and treatment of cancer. The antihepato-carcinogenic effect of zerumbone was due to suppression of PCNA and elevation of Bax and depletion of Bcl-2 protein expression (Gross et al. 1998). Hence, zerumbone may act as anticancer agent in liver cancers

(Fuzer et al. 2017). Fuzere et al. (2017) reported that zerumbone induces the phase II detoxification enzymes depletion in rat liver epithelial cell line RL34. Hence, Zerumbone may act as a potential activator for the Nrf2-dependent detoxification pathway and provides a new insight into cancer management (Tsuboi et al. 2014) (Figure 5).

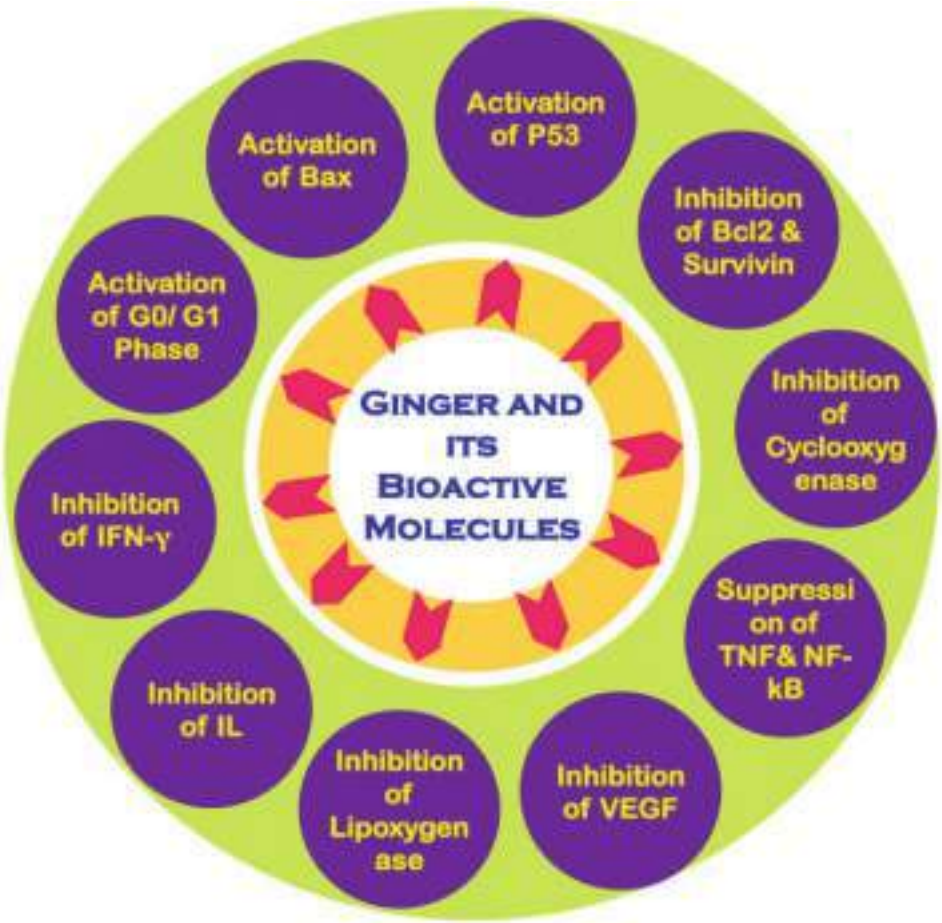



**Figure 5**
Suppression of tumors markers by ginger and its compounds

## Ginger-Bioactive Compound: Gingerol and Its Anticancer Effects

Gingerols are part of the phenolic compounds and volatile organic compounds of ginger. 4-, 6, 8-, 10-, and 12-gingerol are types of gingerol. 6-gingerol is the main compound which is responsible for the strong aroma of ginger. The biological properties of gingerols are antimicrobial, anticancer, antioxidant, anti-inflammatory, and antiallergic (Akinyemi et al. 2015).

6-gingerol has been identified to show anticancerous effects. Gingerol helps in the suppression of the hyperproliferation, inflammatory processes, and transformation that engaged in various steps of angiogenesis and metastasis. For instance, through the activation of CD8+ T cells, it inhibited B16F10 melanoma cells of pulmonary metastasis in mice. Antitumoral activity showed by 6-gingerol through induction of reactive oxygen species (ROS) which, trigger p53 activation, apoptosis, and arrest the cell cycle (Lee et al. 2008). The study found that 6-G induced arrest of the cell cycle in both cell lines by reducing the expression of cyclin A and CDKA. In addition, Radhakrishnan et al. (2014) reported that 6-G induced cell death by apoptosis in the cell line with the mutated p53 gene. [6]-gingerol stimulated death receptor-mediated apoptosis in glioblastoma cells or p53-mediated apoptosis in skin tumor cells (Nakamura et al. 2004).

6-gingerol demonstrates an important potential to treat pancreatic cancer and has been shown to have a potential inhibitor of metastasis in *in vitro* and *in vivo* studies by different mechanisms, including a reduction in the expression of MMP and inhibiting angiogenesis (Kim et al. 2005). 6-gingerol targets many cellular molecules which promote cancer, for cell survival, cell proliferation, invasion, and angiogenesis. 6-Gingerol supplementation alters STAT3, NF-κB, Rb, MAPK, Akt, ERK, PI3K, and caspase-3/7, cIAP1. Thus, gingerol treatment may modulate molecular targets of cancer components, so gingerol may have the therapeutic potential for preventing and treating many cancers.

*In vitro* and *in vivo* analysis of [10]-gingerol has been reported against the metastatic triple negative breast cancer (TNBC) [97]. In addition, it was experimented that 10-gingerol inhibits cervical cancer (Zhang et al. 2017). A study carried out by Martin et al. (2017) showed the anticancer activity of 10-G *in vivo* and *in vitro* in triple negative breast cancer models through proapoptotic activity and the inhibition of metastasis. The activity of 10-G in vitro was dose dependent, finding that at the highest concentration (100μM) colony formation was completely inhibited and extensive cell death occurred. 10-gingerol caused a considerable upsurge in the initiation of caspase-3 and inhibited orthotopic tumor growth of spontaneous breast cancer metastasis. Zhang et al. (2017) reported that 10-gingerol inhibits metastasis to multiple organs like lung, bone, and brain.

## Therapeutical Potential of Gingerol and Its Effect on Metabolic Pathways in Cancer

Anticancer mechanisms of gingerol include free radical scavenging effect, antioxidant effect, modulation of various enzymes of inflammation, modulation of cell cycle proteins, induction of apoptosis, and arrest the cell cycle at G2/M phase in carcinoma which will provide basis for inhibition of tumor progression in experimental animals. TNF-α, IL-6, NF-κB, cyclooxygenase-2 COX-2, and caspase-3 are the most important cancer metabolic factors.

### Free Radical Scavenging and Antioxidant Activity of Gingerol

Gingerol possesses antioxidant activity due to their free radical scavenging activity. It has been investigated that gingerol may modulate the antioxidant enzymes and suppress the lipid peroxidation products in cancer subjects. Hence, gingerol may prevent the pathogenesis of cancer-related disorders by its free radical scavenging activity. Alsahli et al. (2021) reported anticancer activity of gingerol in colon cancer, breast cancer, by elevating antioxidant enzymes and depleting lipid peroxidation in cancer condition.

### Effect of Gingerol on Apoptotic Genes

Apoptosis is one of the prerequisites to maintain the normal and healthy internal milieu. Alteration in the normal process of apoptosis may raise cell survival and support the tumor growth and progression (Kim et al. 2005). Gingerol plays a vital role in the elevation of different proapoptotic genes and at the same time depletion of the antiapoptotic genes and by this way balances the apoptosis process. An interesting study showed that gingerol induces apoptosis in scleroderma lung fibroblasts without affecting normal lung fibroblasts. Furthermore, gingerol has shown an antitumor activity and was involved in the apoptosis induction and the modulation of key apoptotic proteins such as Bax and bcl-2 (Yu et al. 2011).

A study has reported that growth arrest and apoptosis of B cell lymphoma occur through the downregulation of c-myc, bcl-XL, and p53 with the treatment of gingerol. Another report in human breast cancer cell line showed that CD437 induces G0-G1 arrest and apoptosis via regulation of p21WAFI/CIPI, Bcl-2, and Bax in a p53-independent manner after treatment with gingerol. Another study on p53-null cells, as well as TR9-7 cells, reported that gingerol induces apoptosis in tumor cells via a p53-dependent pathway, and Bax acts as downstream effectors of p53.Gingerol induces apoptosis in a range of tumor cell lines through activation of caspase-3, cytochrome c release, and depletion of bcl-2 (de Lima et al. 2018).

Gingerol has shown an apoptotic effect by inhibiting various genes such as proteintyrosine kinase, protein kinase C, c-myc mRNA expression, and bcl-2 mRNA expression and also mitochondrial pathway. Earlier studies have shown that gingerol possesses an apoptotic activity in different types of cancer cells such as human colon cancer cells, stomach, and skin tumors, breast cancer cells, and prostate cancer cells (Nakamura et al. 2004). Gingerol may lower the incidence of various cancers and also induce apoptosis in MBT-2 cells and G2/M arrest of T24 cells (Park et al. 2014). Experimental studies showed that the downregulation of the expression of antiapoptotic protein occurs with gingerol treatment (Nakamura et al. 2004).

### Effect of Gingerol on Tumor-Suppressor Genes

Tumor-suppressor genes play a vital and significant role in the inhibition of cancer formation and its progression. An alteration or mutations may occur in a gene, then tumor suppressor gene loses its ability to perform normal function and it transforms into tumor gene. p53 is one of the important suppressor genes, and it is the guardian of all genes and regulates the various cellular and molecular pathways and prevents the formation of cancer.

Numerous *in vivo* and *in vitro* reports showed that gingerol has a significant role in cancer prevention or inhibition. Another study showed that gingerol downregulates the expression of p53, as well as the survival genes egr-1,c-mycandbcl-XL in B cells. Another report also indicated that gingerol inhibits cell cycle progression of immortalized human umbilical vein-endothelial cells via upregulating the CDK inhibitors p21WAF1/CIP1, p27KIP1, and p53 (Park et al. 2014).

Another tumor-suppressor gene, phosphatase and tensin homolog deleted on chromosome ten (PTEN), has a role in the progression of the cell cycle and apoptosis. The alteration or mutation of PTEN gene has been noticed in several types of cancers. A study of the gingerol has shown that PTEN increases the gingerol-induced apoptosis, whereas inactive PTEN decreases/inhibits the gingerol-induced apoptosis.

In mice, [6]-gingerol suppressed the promotion of skin cancer. Park et al. (Park et al. 2014) reported that [6]-gingerol inhibited TPA skin tumor promotion in addition to the inhibition of epidermal ornithine decarboxylase activity in ICR mice. In a study, Surh et al. [1999] reported antitumor-promoting properties of both [6]-gingerol and [6]-paradol. [6]-gingerol treatment attenuated the skin papilloma genesis and inhibited the tumor-promoter genes, TNF-alpha production, and activation of epidermal ornithine decarboxylase in ICR mice (Nakamura et al. 2004).

### Effect of Gingerol on Cycloxygenase Enzyme

COX is an inducible enzyme in the conversion of arachidonic acid to prostaglandins (PGs). There are two types of cyclooxygenase COX-1 that play a vital role in physiological functions and COX-2, an enzyme responsible for inflammation and pain. COX-2 is upregulated or overexpressed in various types of cancers (Pournaderi et al. 2017). It was previously stated that gingerol inhibits the critical stage of tumor initiation and promotion stages and COX inhibition. Gingerol also inhibits the COX2 expression on colon cancer cell lines (Nonn et al. 2007). Previous reports states that gingerol plays an important role in the downregulation of the expression of COX-2 and finally suppresses the cancer progression (Kim et al. 2005). Gingerol plays a significant role in the cancer prevention via controlling the activities of various genes in the initiation, promotion, and progression stage of tumor development and progression.

### NF-$\kappa$B and Gingerol in Cancer Prevention

NF-$\kappa$B family of transcription factors shows an important role in immune, inflammatory response and also stimulates the development and progression of cancer. In this regard, an important study demonstrated that gingerols have anticancer, antioxidant, and anti-inflammatory effects via the downregulation of the transcription factors NF-$\kappa$B, AP-1, and Egr-1 (Han et al. 2002) and repression of the genes for cell adhesion molecules (chemokines, TNF, Cox-2, and MMP-9). Another study showed that gingerol has been involved in the suppression of NF-$\kappa$B activation and NF-$\kappa$B gene products (Plummer et al. 1999). An important study in pancreatic cancer cells reported that gingerol shows a vital role in the suppression of NF-$\kappa$B activation by inhibiting I$\kappa$B kinase, ultimately induces I$\kappa$B$\alpha$ phosphorylation, and inhibits the NF-$\kappa$B downstream gene expression. [6]-gingerol inhibited both the vascular endothelial growth factor (VEGF) and basic fibroblast growth factor(b-FGF)-induced proliferation of human endothelial cells and caused cell cycle arrest in the G1 phase (Vijaya Padma et al. 2007). Recently, anticancer and anti-inflammatory potential of 6-gingerol was reported by inactivating NF-kB through the suppression of the proinflammatory TNF-alpha (Kim et al. 2005 ; Habib et al. 2008). Numerous studies have shown that gingerol is a potent inhibitor of NF-$\kappa$B activation.

Kim et al. (2005) reported that 6-gingerol regulates tight junction-related proteins and suppresses invasion and metastasis of pancreatic cancer cells. 6-gingerol mediated through NF-$\kappa$B inhibition via inhibition of the extracellular signal-regulated kinases (ERK) pathway. Thus, 6-gingerol suppresses the invasive activity of PANC-1 cells.

### Impact of Gingerol on Angiogenesis

Angiogenesis is a complex process involving widespread interaction between the cells, soluble factors, and ECM components. During cancer development, tumor growth is triggered by many signals in chain reaction manner. In cancer formation, there are stages and angiogenic factors such as vascular endothelial growth

factor (VEGF), basic fibroblast growth factor (bFGF), angiogenin, transforming growth factor (TGF-$\alpha$, TGF-$\beta$), and epidermal growth factors, which play vital role in tumor angiogenesis through cancerous tumor cells by releasing molecules and sending signals to surrounding normal host tissue. VEGF is a crucial survival factor for endothelial cells in the process of physiological, tumor angiogenesis, and it induces the expression of antiapoptotic proteins in the endothelial cells (Shukla and Singh 2007). Many reports showed that many medicinal plants suppress the VEGF and other factors of cancer. We also reported that gingerol is best inhibitor of VEGF in different types of cancer (Weng et al. 2010).

*In vitro* studies on hepatic cancer cell lines conducted so far have demonstrated that ginger suppressed the growth of human hepatic cancer cell lines by inhibiting the phosphorylation of tyrosine-kinase receptor IGF-1R, inducing apoptosis by activating Caspase 9 and downregulating Bcl-2 and cyclooxygenase-2 (COX-2), modulating the levels of VEGF and its receptor (VEGFR-2), NF-κB, p53, and extracellular signal-regulated kinase 1/2 (ERK1/2), reducing the expression of lipogenic enzymes, certain types of RTKs, and their downstream pathways, and activating adenosine monophosphate-activated protein kinase (AMPK) and ROS-mediated lysosomal membrane permeabilization. Based on various liver carcinogenesis animal models with the intake of ginger, the inhibition of hepatoma growth, restriction of hepatic cancer cell line progression, and activation of apoptosis were observed; the probable mechanisms behind might be associated with suppression of hepatocyte progenitor cell/stem cell population, activation of AMPK protein in the liver, and modulation of self-renewal pathways and their related genes. *In vitro* and *in vivo* studies reported that gingerol suppresses the proliferation of human vascular endothelial cells and also abrogates the FGF-2-induced angiogenic response. Moreover, gingerol has the ability to inhibit both VEGF and its receptor in various cancer types; it might be useful as an antiangiogenic agent. Hence, gingerol acts as anticancer agent against many cancers through suppressing proliferation, angiogenesis, NF-$\kappa$B, and NF-$\kappa$B-regulated gene products.

# Conclusion and Future Perspectives

Cancer is one of the deadliest diseases and a major health problem in the world. The present modes of treatments like chemotherapy and radiotherapy are very expensive and also exhibit many side effects in cancer patients. Ginger and its bioactive compounds are used to treat cancer. Gingerol a bioactive compound of ginger has been shown to target multiple signaling molecules in cancer metabolism and provides a basis for its therapeutic applications for cancer subjects. Moreover, most of the known activities of gingerol are based only on *in vitro* and *in vivo* studies, and some clinical studies in human subjects. Therefore, more extensive and well-controlled animal and human studies are required to demonstrate efficacy of gingerol and other compounds of ginger against cancer.

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# Recent Updates on the Bioactive Compounds of Ginger (*Zingiber officinale*) on Cancer: A Study with Special Emphasis of Gingerol and Its Anticancer Potential

## Effect of Ginger and Its Compounds in Cancer Subjects

Kondeti Ramudu Shanmugam, Bhasha Shanmugam, Gangikunta Venkatasubbaiah, Sahukari Ravi, and Kesireddy Sathyavelu Reddy

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**Abstract**

Medicinal plants have been used as therapeutic agents since the origin of mankind. Many medicinal plants like *Tinospora cordifolia, Andrographis paniculata, Curcuma longa, Withania somnifera, Zingiber officinale,* etc. are used to treat cancer. Ginger is reported to show anticancer effect in many cancer types like liver cancer, gastric cancer, oral cancer, prostate cancer, breast cancer, and ovarian cancers in animal models and cell lines. To date, over 400 bioactive compounds have been identified in ginger, they are gingerols, shogaols, and paradols. These compounds possess antioxidant, anti-inflammatory, antimicrobial, and anticancer

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properties. Gingerol especially shows anticancer effects in different cancer subjects. Gingerol may act on the TNF-α, IL-6, NF-κB, cyclooxygenase-2 (COX-2), and caspase-3, and other tumor-metabolic pathway factors in the prevention of cancer. We hope that this chapter will attract more attention on ginger's therapeutic potential and impact on cancer subjects.

**Keywords**

Ginger · Bioactive compounds · Gingerol · Cancer

## Introduction

The biological term cancer refers to a set of diseases in which the cells of an organ or tissue split uncontrollably and acquire the ability to attack other tissues. Cancer is a global health problem, and it is the top cause of deaths in the world. Cancer occurs through the mutations by stepwise process which results in malignancies. Metastasis is the process whereby cancer cells rupture from a malignant tumor and travel to and invade other tissues in the body (Butt and Sultan 2009).

The most common types of cancer are liver cancer, esophageal cancer, breast cancer, oral cancer, lung cancer, prostate cancer, ovarian cancer, and stomach cancer. According to GLOBOCAN 2020 database in 2020, there were 19.1 million new cases of cancer and 10 million deaths from cancer worldwide, and the new cases will be upto 20 million globally by 2025 (Ferlay et al. 2019). The principle malignant conditions of the cancer are breast cancer (2.26 million cases), lung cancer (2.20 million cases), stomach cancer (1.08 million cases), liver cancer (0.90 million cases), esophagus cancer (0.60 million cases), pancreatic cancer (0.49 million cases), and colorectum cancer (0.73 million cases) in 2020 (Table 1).

**Table 1** New cancer cases and deaths as per global cancer statistics 2020

| S. no | Cancer type | No of cases (2020) | No of deaths |
|---|---|---|---|
| 1. | Breast cancer | 2,261,419 | 684,996 |
| 2. | Lung cancer | 2,206,771 | 1,796,144 |
| 3. | Prostate cancer | 1,414,259 | 375,304 |
| 4. | Skin cancer | 1,198,073 | 63,731 |
| 5. | Colon cancer | 1,148,515 | 576,858 |
| 6. | Liver cancer | 905,677 | 830,180 |
| 7. | Cervical cancer | 604,127 | 341,831 |
| 8. | Esophageal cancer | 604,100 | 544,076 |
| 9. | Thyroid cancer | 586,202 | 43,646 |
| 10. | Pancreatic cancer | 495,773 | 466,003 |
| 11. | Leukemia | 474,519 | 311,594 |
| 12. | Kidney | 431,288 | 179,368 |
| 13. | Oral cancer | 377,713 | 177,757 |

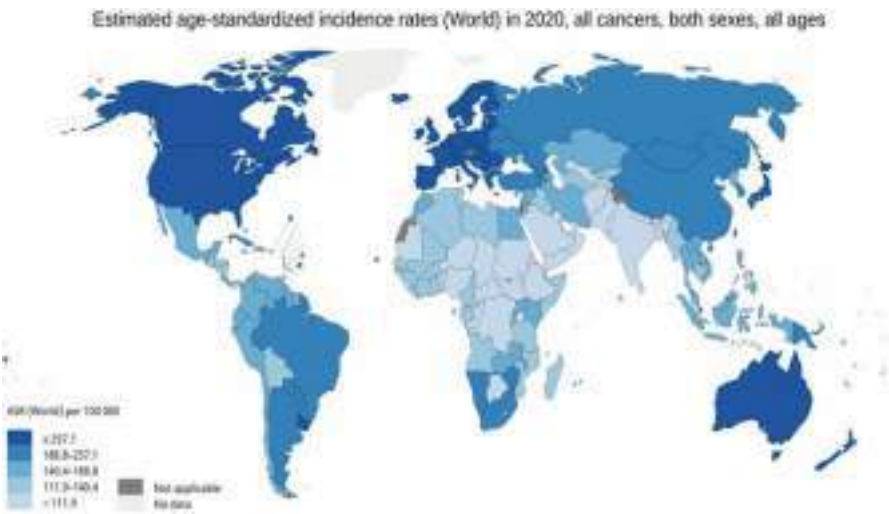



**Figure 1** Cancer patients in the world as per the Global Cancer report 2020 by WHO. Source: https://www.uicc.org/news/globocan-2020-new-global-cancer-data#

India has 1.32 lakh new cancer cases in 2020, also the lowest rates of cancer in the world. Breast cancer, oral cancer, cervical cancer, and lung cancer are the top four cancers in India. Cancer deaths in India doubled from 1990 to 2016. It has been reported that genetic mutations, viruses, smoking, heavy metal ingestion, and dietary patterns are actively involved in cancer pathogenesis (Noonan et al. 2007). Despite huge progress and efforts have been made in the field of medicine for the prevention and treatment of cancer for years, cancer still remains the leading cause of deaths around the world (Figure 1).

## Carcinogenesis

Carcinogenesis is the process by which a normal cell is transformed into a tumor cell and its progression to a clinically observable tumor with high probability of metastasis. Cancer is considered a process with three steps: 1. initiation, 2.promotion, and 3. progression (Weston and Harris 2003). This process can vary depending on the etiology of cancer. Normally, cancers are caused by chemical agents, viruses, and others by mutations of DNA, epigenetic changes of DNA (Baylin and Jones 2016).

## Mechanism of Cancer

### Cancer: Reactive Oxygen Species (ROS)

Cancer is one of the stress-related disorders. During cancer condition, many free radicals or reactive oxygen species (ROS) are produced. The existence of oxidative

stress resulting from increased free radicals has been postulated in cancer. Animal models and human studies and *in vitro* experiments suggest a role for oxidative stress, via an increased formation of free radicals in the pathophysiology of many complications, such as neurological, cardiovascular, renal, cancer, rheumatoid arthritis, cancer, and diabetes (Brownlee 2001). According to Sies (Sies et al. 2017), oxidative stress is defined as a shift in balance in cellular oxidation-reduction reactions in favor of oxidation, which leads to damage to the cell and formation of molecular products that are indicators of oxidative stress.

Reactive oxygen species are radicals or ions or molecules that have a one unpaired electron in their outermost shell of electrons. Due to this nature, ROS are highly reactive. Examples of ROS are superoxide ($O_2$-), hydrogen peroxide ($H_2O_2$), hydroxyl radicals (OH), and nitric oxide (•NO). ROS and oxidative stress have been implicated in many diseases like cancer, diabetes, and hepatitis. ROS plays an important role in various cascading of the signals for the cancer cells to survival, proliferation, resistance to apoptosis, neovascularization, invasion, and extravacation. (Cullen et al. 2003). In order to survive from oxidative stress condition, cancer cells adapt and acquire many mechanisms to counteract the potential toxic effects of ROS stress in order to promote proximal protumorigenic signals. ROS also alters the DNA-binding sites of redox-sensitive transcription factors such as hypoxia-inducible factor-1 alpha (HIF-1α), NFκB, activator protein-1 (AP-1), and p53 (Trachootham et al. 2008). The antioxidant enzymes like SOD, CAT, GPx, GR, and GSH may act on these ROS, and hence these antioxidant enzymes activities are depleted in various cancer subjects.

Warburg (Liberti and Locasale 2016) described about cancer as metabolic alterations that represent a hallmark of cancer cells. Metabolic alterations and redox alterations which are important steps of cancer cell transformation make the mitochondria an attractive therapeutic target. Increased knowledge in the field of redox biology, its reactions, signaling networks, and interplay in disease and physiology has enabled not only a better realization of potential benefits but also grave dangers of ROS with respect to cancer phenotypes and drug resistance.

## Cancer Biomarkers

A thorough understanding of the roles of cancer biomarkers is essential for diagnostic purposes. A biomarker is "a characteristic that is objectively measured and evaluated as an indicator of normal biological processes, pathogenic processes, or pharmacologic responses to a therapeutic intervention." Because early diagnosis of cancer will treat cancer patients early, we can save the patient's life. Cancer biomarkers are produced by tumors or by the body in response to the presence of cancer. Cancer biomarkers can be used to determine the presence of malignancy and for the study of disease transmission. The important cancer biomarkers are Urokinase plasminogen activator (uPA), Carbonic anhydrase XII (CAXII), Cyclooxygenase (COX), Cytochrome P450 (CYP450), Telomerase, and Matrix metalloproteinases (MMPs).

The medical treatments for cancer are surgery, radiotherapy, and chemotherapy. These types of treatment are usually accompanied by a large number of side effects on patient health, like nausea, loss of appetite, weight loss, anemia, spinal cord

injury, kidney damage, and mucositis. Hence, there is need for alternative therapy for cancer. So herbal medicine is practiced to treat cancer.

## Medicinal Plants for the Treatment of Cancer

Medicinal plants are used to treat many diseases like diabetes, cancer, epilepsy, alzheimer's, cough, fever, and other diseases. Drugs from medicinal plants focus on the most important active principles in terms of the quantity and the pharmacological actions. The information available on these medicinal plants has allowed the quantification of the active principle and the production of bioactive compounds. The bioactive compounds of medicinal plants have different chemical, pharmacological properties and actions. This has enabled us to evaluate the anticancer drugs from medicinal plants.

Many medicinal plants have been reported to possess anticancer properties. Due to the development of resistance against cancer effects, various plant-derived drugs have gained much attention in the recent years. Hence, it is of importance to focus on medicinal plants with anticancer properties that are easily available, culturally acceptable, and economically free. Herbal medicine has been used for thousands of years to cure cancer. Chemotherapeutic and chemopreventive effects of many herbal plants are attributed to phytochemicals, quinines, which are reported to induce antitumor effects *in vovo* and *in vitro* of cancer cells.

Recently, many well-known plant-derived compounds have been studied in animal models and cell lines. Among the above described plants and their formulations, *Terminalia chebula, Panax ginseng, Arachis hypogaea, Rauwolfia vomitoria, Azadirachta indica, Zingiber officinale, Commiphora mukul,* and *Rosa rugosa* are reported to be beneficial for cancer with less side effects as compared to conventional drugs. Hence, these medicinal plants could be a relatively safer and better therapeutic alternative for cancer treatment (Figure 2).

## Ginger

Ginger is the rhizome of *Zingiber officinale.* Roscoe belongs to the family Zingiberaceae. Ginger has been used as a spice, food, supplement, and flavoring agent. Ginger is used to cure diseases and symptoms, such as headache, nausea, cold, rheumatism, diarrhea, and arthritis. It is also used as a carminative, digestant, and antiflatulent (Ali et al. 2008). Ginger and its compounds are used as medicine in India, China, Burma, Germany, Japan, Indonesia, and the United States.

Ginger is reported to possess various medicinal properties like antibacterial, antiviral, antifungal, antiparasitic, anti-insecticidal, antianalgesic, antimutagen, anticarcinogenic, antispasmolytic, and anti-inflammatory and antioxidant activities (Shanmugam et al. 2021). Ginger have radioprotective, hepatoprotective, gastroprotective, nephroprotective, and neuroprotective properties, and its

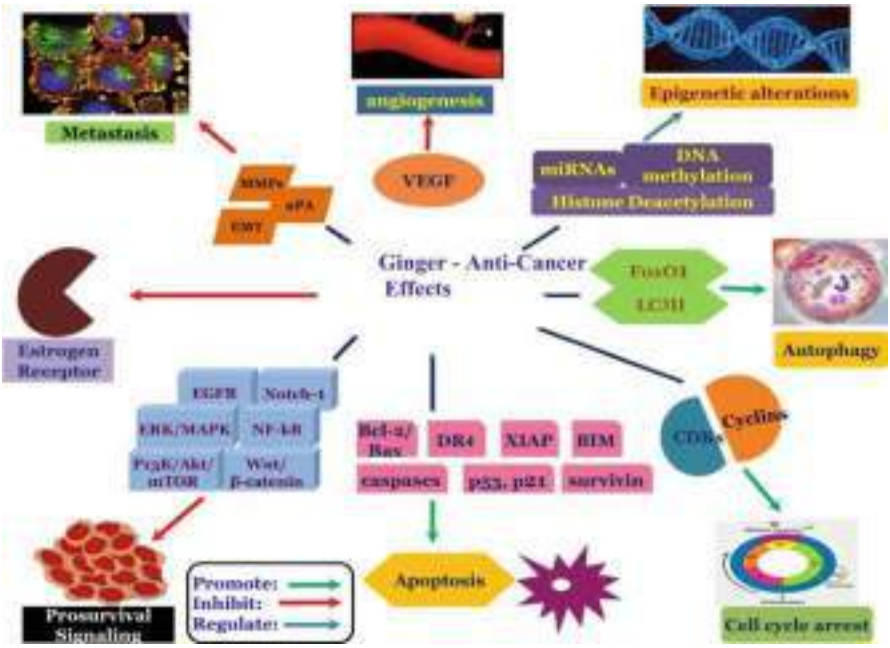



**Figure 2** Ginger and anticancer mechanism

mechanism of action at the cellular level has been studied by many scientists (Ali et al. 2008; Shanmugam et al. 2009, 2021) (Figure 3).

## Compounds of Ginger

The main constituents in ginger are terpenes, phenolic compounds, carbohydrates (50–70%), and lipids (3–8%). The terpenes (monoterpenes, sesquiterpenes, and sesquiterpene alcohols) are of 20–25%. The terpene compounds of ginger are zingiberene, α-farnesene, β-sesquiphellandrene, β-bisabolene, and α-curcumene. It has been identified that ginger has monoterpenes (such as α-pinene, camphene, myrcene, α-phellandrene, geranial, citronellal, neral, linalool, borneol, and alpha-terpineol). Phytosterols, amino acids, minerals, proteins, vitamins (vitamin A and nicotinic acid), and raw fiber, ash, are present in ginger (Shukla and Singh 2007).

The phenolic compounds of ginger are gingerol, shogaol, and paradols. In ginger, gingerols are in higher concentration. Ginger-specific smell and odor are due to the presence of gingerol and shogaols. The other compounds of ginger are 6-paradol, 1-dehydrogingerdione, 8-gingerdiol, 10-gingerdiol, 4-gingerdiol, 6-gingerdiol, 6-gingerdione, and 10-gingerdione. Ginger also contains diterpenes, galanolactone, diterpenoid, and ginger glycolipids (Yeh et al. 2014). Ginger has ascorbic acid, alkaloids, beta-carotene, and polyphenols. Ginger also has key volatile oils such as




**Figure 3** Pharmacological and anticancer properties of Gingerol

oleoresins, bisabolene, cineol, phellandrene, citral, borneol, and citronellol, vitamin B6, vitamin c, and linoleic acid. As per the available information, there are more than 400 bioactive compounds in ginger (Shukla and Singh 2007) (Figure 4).

## Anticancer Effects of Ginger

Ginger has anticancer properties. In the methanolic, ethanolic, aqueous, n-hexane, and ethyl acetate, benzene extracts of ginger, many bioactive compounds are present which show antiproliferative, cytotoxic, and antiangiogenic activities. These pharmacological effects are due to bioactive compounds of ginger, which show antioxidant, anti-inflammatory, antioxidant, antihyperglycemic, antitumorigenic, and antilipidemic activities. These compounds may modulate the genetic expression and cause induction of apoptosis in cancer cells.

The anticancer effect of ginger may be due to the reduction of initiation, promotion, and progression. Hence, ginger can be used as anticancer agent (Zhang et al. 2017). Ginger has been reported to show its positive effects against many cancers,

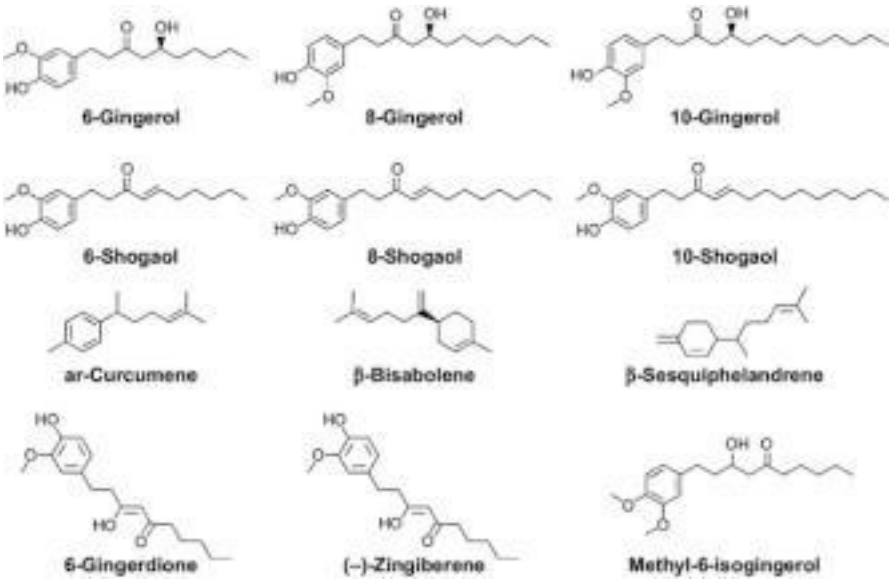



**Figure 4** Compounds of Ginger

like liver cancer, gastric cancer, pancreatic cancer, breast cancer, prostate cancer, and other types of cancers. Ginger also has anticancer effects in different cancer cell lines in vitro, like lung, ovarian, liver, colon, cervical, and prostate cancer, through the stimulation of apoptosis and the reticence of cell proliferation (Zhang et al. 2017) (Table 2).

Ginger has an antitumor activity by modulating of genetic pathways. It helps for the activation of suppressing gene of the tumor. Furthermore, ginger can inhibit the vascular endothelial growth factors and modulate apoptosis; thus, ginger supplementation can reduce cancer. Ginger extract prevents the initial stage of colon cancer. Supplementation of ginger to the mice with carcinogen 1,2-dimethylhydrazine (DMH) inhibited the levels of tissue cholesterol, HMG CoA reductase, free fatty acids, and triglycerides (Manju et al. 2006). Hence, ginger treatment reduces the risk of cancer by antioxidative compounds.

For instance, it has been identified that the terpenoids, compound of ginger, induce apoptosis in uterus cancer cells via the activation of tumor protein p53. Water and organic solvent extracts of ginger reported to show anticancer activities in THP-1 AMoL cells in vitro. These reports show that ginger has anticancer activity (Prasad and Tyagi 2015).

Ginger constituents ([6]-gingerol, [10]-gingerol, [6]-shogaol, and zerumbone) show anticancer effects. They are effective against many cancers (Habib et al. 2008). Habib et al. (2008) reported that ginger extract inhibits liver carcinogenesis in wistar rat through the downregulation of elevated NF-κB and TNF-α. Hence, ginger may act as an anticancer agent, which may be helpful in treatment of cancer subjects. Ginger ingredients inhibit the development of diethylnitrosamine-(DEN-)

**Table 2** Effect of ginger and its compounds on different cancer subjects

| S. no. | Ginger extract/ compounds of ginger | Study type | Subjects | Dose | Potential mechanisms | Reference |
|---|---|---|---|---|---|---|
| 1 | Ginger ethanolic extract | *In vivo* | Wistar rats | 50 mg/kg | NADH dehydrogenase activity elevated | Ali et al. (2008) |
| 2 | Ginger extract | *In vitro* | HepG2 human hepato-cellular carcinoma cells | 1.11 mg/mL | Increasing the level of ROS levels increased and elevated p53 levels, thus promoting apoptosis | Li et al. (2013) |
| 3 | 6-gingerol | *In vitro* | He La human adenocarcinoma cervical cells | 60, 100, and 140μM | Cyclin A, cyclinD1, and cyclin E1 levels decreased, and caspase levels increased | Zhang et al. (2017) |
| 4 | 10-gingerol | In vitro | Human and mouse breast carcinoma cells | 50, 100, and 200μM | Cell growth and cell division are reduced | Bernard et al. (2017) |
| 5 | 6-gingerol,10-gingerol,6-shogaol, and 10-shogaol | *In vitro* | PC-3 human prostate cancer cells | 1,10, and 100μM | Inhibiting prostate cancer decreased, and the expression of MRP1 and GSTπ are lowered | Liu et al. (2017) |
| 6 | 6-shogaol | *In vitro* | LNCaP, DU145, and PC-3 human prostate cancer cells | 10, 20, and 40μM | Cyclin D1, surviving, c-Myc, and Bcl2 expression are decreased Inhibition of STAT3 and NF-κB signals | Saha et al. (2014) |

induced premalignant phenotype in rat hepato-carcinogenesis. It has been reported that supplementation of ginger prevented decrease of the content of metallothionein and endostatin in the liver and elevated the growth factors induced by the carcinogen in wistar albino rats. Ginger also reverses the altered serum-hepatic tumor markers (Mansour et al. 2010).

Wang et al. (2008) reported that beta-elemenean compound of ginger induces caspase-3, −7, −9 activities, decreases Bcl-2 expression, which releases cytochrome c, and elevated the levels of cleaved caspase-9 and poly (ADP-ribose) polymerase in cells. Application of ginger extract to mouse skin afforded significant inhibition of TPA-caused epidermal edema (56%) and hyperplasia (44%) (Katiyar et al. 1996). Kim et al. (2005) also reported that ginger induces programmed cell death in cell lines. Ethanol extract of ginger has antitumor-promoting effects in mouse skin tumorigenesis model, and it was concluded that animals pretreated with ginger showed depleted tumor compared with unginger-treated rats.

Zingerone with a dose of 100 mg mL suppressed LPS-induced NF-kB activities in cells. Dietary zingerone reduces proinflammatory cytokines. This study reports zingerone anti-inflammatory activity due to suppressing the activation of NF-kB, production of IL-1b, and the infiltration of inflammatory cells (Ganaie et al. 2019). Ganaie et al. (2019) also reported the anticancer effect of zingerone due to activation of cytochrome P4502E1 and suppression of NF-kB-p65, iNOSCOX-2, and PCNA in cancer subjects.

Zerumbone, seen in ginger, shows antiproliferative and anti-inflammatory effects and mediates its activity through the modulation of NF-kB activation (Takada et al. 2005). Zerumbone also inhibits the activation of NF-kB, and this inhibition may provide basis for the prevention and treatment of cancer. The antihepato-carcinogenic effect of zerumbone was due to suppression of PCNA and elevation of Bax and depletion of Bcl-2 protein expression (Gross et al. 1998). Hence, zerumbone may act as anticancer agent in liver cancers (Fuzer et al. 2017). Fuzere et al. (2017) reported that zerumbone induces the phase II detoxification enzymes depletion in rat liver epithelial cell line RL34. Hence, Zerumbone may act as a potential activator for the Nrf2-dependent detoxification pathway and provides a new insight into cancer management (Tsuboi et al. 2014) (Figure 5).

## Ginger-Bioactive Compound: Gingerol and Its Anticancer Effects

Gingerols are part of the phenolic compounds and volatile organic compounds of ginger. 4-, 6, 8-, 10-, and 12-gingerol are types of gingerol. 6-gingerol is the main compound which is responsible for the strong aroma of ginger. The biological properties of gingerols are antimicrobial, anticancer, antioxidant, anti-inflammatory, and antiallergic (Akinyemi et al. 2015).

6-gingerol has been identified to show anticancerous effects. Gingerol helps in the suppression of the hyperproliferation, inflammatory processes, and transformation that engaged in various steps of angiogenesis and metastasis. For instance, through the activation of CD8+ T cells, it inhibited B16F10 melanoma cells of pulmonary

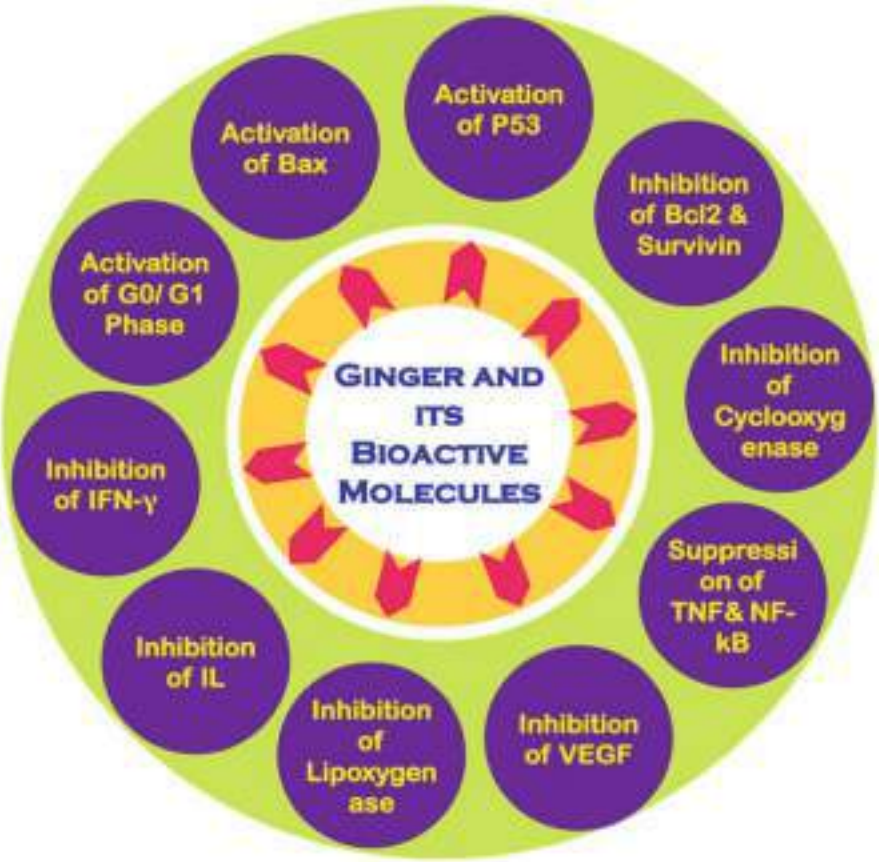



**Figure 5** Suppression of tumors markers by ginger and its compounds

metastasis in mice. Antitumoral activity showed by 6-gingerol through induction of reactive oxygen species (ROS) which, trigger p53 activation, apoptosis, and arrest the cell cycle (Lee et al. 2008). The study found that 6-G induced arrest of the cell cycle in both cell lines by reducing the expression of cyclin A and CDKA. In addition, Radhakrishnan et al. (2014) reported that 6-G induced cell death by apoptosis in the cell line with the mutated p53 gene. [6]-gingerol stimulated death receptor-mediated apoptosis in glioblastoma cells or p53-mediated apoptosis in skin tumor cells (Nakamura et al. 2004).

6-gingerol demonstrates an important potential to treat pancreatic cancer and has been shown to have a potential inhibitor of metastasis in *in vitro* and *in vivo* studies by different mechanisms, including a reduction in the expression of MMP and inhibiting angiogenesis (Kim et al. 2005). 6-gingerol targets many cellular molecules which promote cancer, for cell survival, cell proliferation, invasion, and angiogenesis. 6-Gingerol supplementation alters STAT3, NF-κB, Rb, MAPK, Akt, ERK,

PI3K, and caspase-3/7, cIAP1. Thus, gingerol treatment may modulate molecular targets of cancer components, so gingerol may have the therapeutic potential for preventing and treating many cancers.

*In vitro* and *in vivo* analysis of [10]-gingerol has been reported against the metastatic triple negative breast cancer (TNBC) [97]. In addition, it was experimented that 10-gingerol inhibits cervical cancer (Zhang et al. 2017). A study carried out by Martin et al. (2017) showed the anticancer activity of 10-G *in vivo* and *in vitro* in triple negative breast cancer models through proapoptotic activity and the inhibition of metastasis. The activity of 10-G in vitro was dose dependent, finding that at the highest concentration (100μM) colony formation was completely inhibited and extensive cell death occurred. 10-gingerol caused a considerable upsurge in the initiation of caspase-3 and inhibited orthotopic tumor growth of spontaneous breast cancer metastasis. Zhang et al. (2017) reported that 10-gingerol inhibits metastasis to multiple organs like lung, bone, and brain.

## Therapeutical Potential of Gingerol and Its Effect on Metabolic Pathways in Cancer

Anticancer mechanisms of gingerol include free radical scavenging effect, antioxidant effect, modulation of various enzymes of inflammation, modulation of cell cycle proteins, induction of apoptosis, and arrest the cell cycle at G2/M phase in carcinoma which will provide basis for inhibition of tumor progression in experimental animals. TNF-α, IL-6, NF-κB, cyclooxygenase-2 COX-2, and caspase-3 are the most important cancer metabolic factors.

### Free Radical Scavenging and Antioxidant Activity of Gingerol

Gingerol possesses antioxidant activity due to their free radical scavenging activity. It has been investigated that gingerol may modulate the antioxidant enzymes and suppress the lipid peroxidation products in cancer subjects. Hence, gingerol may prevent the pathogenesis of cancer-related disorders by its free radical scavenging activity. Alsahli et al. (2021) reported anticancer activity of gingerol in colon cancer, breast cancer, by elevating antioxidant enzymes and depleting lipid peroxidation in cancer condition.

### Effect of Gingerol on Apoptotic Genes

Apoptosis is one of the prerequisites to maintain the normal and healthy internal milieu. Alteration in the normal process of apoptosis may raise cell survival and support the tumor growth and progression (Kim et al. 2005). Gingerol plays a vital role in the elevation of different proapoptotic genes and at the same time depletion of the antiapoptotic genes and by this way balances the apoptosis process. An interesting study showed that gingerol induces apoptosis in scleroderma lung fibroblasts without affecting normal lung fibroblasts. Furthermore, gingerol has shown an antitumor activity and was involved in the apoptosis induction and the modulation of key apoptotic proteins such as Bax and bcl-2 (Yu et al. 2011).

A study has reported that growth arrest and apoptosis of B cell lymphoma occur through the downregulation of c-myc, bcl-XL, and p53 with the treatment of gingerol. Another report in human breast cancer cell line showed that CD437 induces G0-G1 arrest and apoptosis via regulation of p21WAFI/CIPI, Bcl-2, and Bax in a p53-independent manner after treatment with gingerol. Another study on p53-null cells, as well as TR9-7 cells, reported that gingerol induces apoptosis in tumor cells via a p53-dependent pathway, and Bax acts as downstream effectors of p53.Gingerol induces apoptosis in a range of tumor cell lines through activation of caspase-3, cytochrome c release, and depletion of bcl-2 (de Lima et al. 2018).

Gingerol has shown an apoptotic effect by inhibiting various genes such as proteintyrosine kinase, protein kinase C, c-myc mRNA expression, and bcl-2 mRNA expression and also mitochondrial pathway. Earlier studies have shown that gingerol possesses an apoptotic activity in different types of cancer cells such as human colon cancer cells, stomach, and skin tumors, breast cancer cells, and prostate cancer cells (Nakamura et al. 2004). Gingerol may lower the incidence of various cancers and also induce apoptosis in MBT-2 cells and G2/M arrest of T24 cells (Park et al. 2014). Experimental studies showed that the downregulation of the expression of antiapoptotic protein occurs with gingerol treatment (Nakamura et al. 2004).

### Effect of Gingerol on Tumor-Suppressor Genes

Tumor-suppressor genes play a vital and significant role in the inhibition of cancer formation and its progression. An alteration or mutations may occur in a gene, then tumor suppressor gene loses its ability to perform normal function and it transforms into tumor gene. p53 is one of the important suppressor genes, and it is the guardian of all genes and regulates the various cellular and molecular pathways and prevents the formation of cancer.

Numerous *in vivo* and *in vitro* reports showed that gingerol has a significant role in cancer prevention or inhibition. Another study showed that gingerol downregulates the expression of p53, as well as the survival genes egr-1,c-mycandbcl-XL in B cells. Another report also indicated that gingerol inhibits cell cycle progression of immortalized human umbilical vein-endothelial cells via upregulating the CDK inhibitors p21WAF1/CIP1, p27KIP1, and p53 (Park et al. 2014).

Another tumor-suppressor gene, phosphatase and tensin homolog deleted on chromosome ten (PTEN), has a role in the progression of the cell cycle and apoptosis. The alteration or mutation of PTEN gene has been noticed in several types of cancers. A study of the gingerol has shown that PTEN increases the gingerol-induced apoptosis, whereas inactive PTEN decreases/inhibits the gingerol-induced apoptosis.

In mice, [6]-gingerol suppressed the promotion of skin cancer. Park et al. (Park et al. 2014) reported that [6]-gingerol inhibited TPA skin tumor promotion in addition to the inhibition of epidermal ornithine decarboxylase activity in ICR mice. In a study, Surh et al. [1999] reported antitumor-promoting properties of both [6]-gingerol and [6]-paradol. [6]-gingerol treatment attenuated the skin

papilloma genesis and inhibited the tumor-promoter genes, TNF-alpha production, and activation of epidermal ornithine decarboxylase in ICR mice (Nakamura et al. 2004).

### Effect of Gingerol on Cycloxygenase Enzyme

COX is an inducible enzyme in the conversion of arachidonic acid to prostaglandins (PGs). There are two types of cyclooxygenase COX-1 that play a vital role in physiological functions and COX-2, an enzyme responsible for inflammation and pain. COX-2 is upregulated or overexpressed in various types of cancers (Pournaderi et al. 2017). It was previously stated that gingerol inhibits the critical stage of tumor initiation and promotion stages and COX inhibition. Gingerol also inhibits the COX2 expression on colon cancer cell lines (Nonn et al. 2007). Previous reports states that gingerol plays an important role in the downregulation of the expression of COX-2 and finally suppresses the cancer progression (Kim et al. 2005). Gingerol plays a significant role in the cancer prevention via controlling the activities of various genes in the initiation, promotion, and progression stage of tumor development and progression.

### NF-κB and Gingerol in Cancer Prevention

NF-κB family of transcription factors shows an important role in immune, inflammatory response and also stimulates the development and progression of cancer. In this regard, an important study demonstrated that gingerols have anticancer, antioxidant, and anti-inflammatory effects via the downregulation of the transcription factors NF-κB, AP-1, and Egr-1 (Han et al. 2002) and repression of the genes for cell adhesion molecules (chemokines, TNF, Cox-2, and MMP-9). Another study showed that gingerol has been involved in the suppression of NF-κB activation and NF-κB gene products (Plummer et al. 1999). An important study in pancreatic cancer cells reported that gingerol shows a vital role in the suppression of NF-κB activation by inhibiting IκB kinase, ultimately induces IκBα phosphorylation, and inhibits the NF-κB downstream gene expression. [6]-gingerol inhibited both the vascular endothelial growth factor (VEGF) and basic fibroblast growth factor (b-FGF)-induced proliferation of human endothelial cells and caused cell cycle arrest in the G1 phase (Vijaya Padma et al. 2007). Recently, anticancer and anti-inflammatory potential of 6-gingerol was reported by inactivating NF-kB through the suppression of the proinflammatory TNF-alpha (Kim et al. 2005; Habib et al. 2008). Numerous studies have shown that gingerol is a potent inhibitor of NF-κB activation.

Kim et al. (2005) reported that 6-gingerol regulates tight junction-related proteins and suppresses invasion and metastasis of pancreatic cancer cells. 6-gingerol mediated through NF-κB inhibition via inhibition of the extracellular signal-regulated kinases (ERK) pathway. Thus, 6-gingerol suppresses the invasive activity of PANC-1 cells.

### Impact of Gingerol on Angiogenesis

Angiogenesis is a complex process involving widespread interaction between the cells, soluble factors, and ECM components. During cancer development, tumor growth is triggered by many signals in chain reaction manner. In cancer formation, there are stages and angiogenic factors such as vascular endothelial growth factor (VEGF), basic fibroblast growth factor (bFGF), angiogenin, transforming growth factor (TGF-α, TGF-β), and epidermal growth factors, which play vital role in tumor angiogenesis through cancerous tumor cells by releasing molecules and sending signals to surrounding normal host tissue. VEGF is a crucial survival factor for endothelial cells in the process of physiological, tumor angiogenesis, and it induces the expression of antiapoptotic proteins in the endothelial cells (Shukla and Singh 2007). Many reports showed that many medicinal plants suppress the VEGF and other factors of cancer. We also reported that gingerol is best inhibitor of VEGF in different types of cancer (Weng et al. 2010).

*In vitro* studies on hepatic cancer cell lines conducted so far have demonstrated that ginger suppressed the growth of human hepatic cancer cell lines by inhibiting the phosphorylation of tyrosine-kinase receptor IGF-1R, inducing apoptosis by activating Caspase 9 and downregulating Bcl-2 and cyclooxygenase-2 (COX-2), modulating the levels of VEGF and its receptor (VEGFR-2), NF-κB, p53, and extracellular signal-regulated kinase 1/2 (ERK1/2), reducing the expression of lipogenic enzymes, certain types of RTKs, and their downstream pathways, and activating adenosine monophosphate-activated protein kinase (AMPK) and ROS-mediated lysosomal membrane permeabilization. Based on various liver carcinogenesis animal models with the intake of ginger, the inhibition of hepatoma growth, restriction of hepatic cancer cell line progression, and activation of apoptosis were observed; the probable mechanisms behind might be associated with suppression of hepatocyte progenitor cell/stem cell population, activation of AMPK protein in the liver, and modulation of self-renewal pathways and their related genes. *In vitro* and *in vivo* studies reported that gingerol suppresses the proliferation of human vascular endothelial cells and also abrogates the FGF-2-induced angiogenic response. Moreover, gingerol has the ability to inhibit both VEGF and its receptor in various cancer types; it might be useful as an antiangiogenic agent. Hence, gingerol acts as anticancer agent against many cancers through suppressing proliferation, angiogenesis, NF-κB, and NF-κB-regulated gene products.

## Conclusion and Future Perspectives

Cancer is one of the deadliest diseases and a major health problem in the world. The present modes of treatments like chemotherapy and radiotherapy are very expensive and also exhibit many side effects in cancer patients. Ginger and its bioactive compounds are used to treat cancer. Gingerol a bioactive compound of ginger has been shown to target multiple signaling molecules in cancer metabolism and provides a basis for its therapeutic applications for cancer subjects. Moreover, most of

the known activities of gingerol are based only on *in vitro* and *in vivo* studies, and some clinical studies in human subjects. Therefore, more extensive and well-controlled animal and human studies are required to demonstrate efficacy of gingerol and other compounds of ginger against cancer.

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# Effect of Bioactive Compound (-)-Epicatechin of *Phyllanthus Niruri* on Hepatic Stress Markers and Lipid Metabolic Profiles in D-galactosamine Induced Hepatitis in Aged Rats

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## ABSTRACT

*The present study was designed to explore the hypolipidemic and hepatoprotective effects of Phyllanthus Niruri (PN) bioactive compound (-)-Epicatechin in D-galactosamine induced hepatitis in rats. Rats were distributed into normal controls (NC), (-)-epicatechin treated (Et), hepatitis control (Hc), hepatitis+ (-)-epicatechin (H+Et), hepatitis+silymarin treated (H+St). After 21 days of treatment, lipid peroxidation (MDA), total cholesterol (TC), triglyceride (TG), low-density lipoprotein cholesterol (LDL), very low-density lipoprotein cholesterol (VLDL), high-density lipoprotein cholesterol (HDL), bilirubin (BL), urea (UR), creatinine (CR) are estimated in serum. In D–galactosamine-induced hepatitis rats, we observed increased levels of MDA, TC, TG, LDL, VLDL, BL, and decreased levels of HDL, UR, CR. However (-)-epicatechin supplementation normalized all the lipid metabolic profiles and also hepatic stress*

*markers. Furthermore, histopathological examinations have also proved that (-)-epicatechin pre-treatment decreased the tissue damage in hepatitis conditions. This is the first reported data on the hypolipidemic activity of (-)-epicatechin. Our experimental findings indicate the potential benefits of (-) epicatechin in hepatitis conditions.*

**Keywords**: (-) Epicatechin, Hepatitis, Hypolipidemic activity, Hepatic damage, Rats.

Ageing is characterized by reduced skeletal muscle mass and increased adiposity. Physiological ageing is characterized by a gradual loss of cognitive performance, expressed as a decline in memory, reasoning, mental capacity, and spatial ability. In addition, age-related changes in body composition intrinsically connect with the biology of ageing resulting in frailty, dementia, Alzheimer's, diabetes, cardiovascular diseases, liver-related disorders. The proportion of the population over 65 years has been increasing worldwide, and low birth rate and longevity have contributed to this growth of the aged population. According to a report by United Nations, in the next 35 years, the number of people aged 60 and above around the world is projected to get more than double, reaching almost 2.1 billion people. Demographic projections also suggest that the world's 60+ population is expected to be around 2 billion by 2030, up from 900 million in 2015.

Hepatitis is a major cause of liver disease leading to many health consequences, like liver cirrhosis and hepatic carcinoma. There is also a global concern due to its high impact on the older population´s health in terms of mortality and morbidity (Fyiad *et al.,* 2012). World Health Organization reported 130 to 150 million people infected with hepatitis worldwide representing a global prevalence of 3 per cent (WHO, 2014).

A recent estimation showed that hepatitis infection was the tenth leading cause of death and accounted for 7,86,000 deaths each year around the world but the death rate for older people is higher when compared to younger people. (GBD, 2013). During hepatitis condition, several organs appear affected in aged people and liver being the worst affected organ. Hepatitis also alters protein, lipid, and

antioxidant enzyme systems. Hence, hepatitis remains a serious clinical challenge and a health problem of major concern.

There are several traditional medicines recommended for the treatment of hepatitis. It has been reported that many herbs and their bioactive compounds possess hypolipidemic, hepatoprotective, and other beneficial substances. In the present study, we selected *Phyllanthus niruri* as a therapeutic plant against hepatitis in old rats. PN contains a series of phenols, alkaloids, terpenoids, and tannins (Shanmugam *et al*., 2017), which are reported to show hepatoprotective, anti-hepatitis, anti-inflammatory, antidiabetic, antiviral, and other properties. (Baiguera *et al.,* 2018). PN contains many compounds like phyllanthin, hypophyllanthin, quercetin, geraniin, fraternusterol, gallocatechin, limonene, lupeol, phyllnirurin, cymene, estradiol, niranthin, mirphyllinastragalin, catechin, (+), (-)-epicatechin, catechin–3-o-gallate, epicorilagin, etc. Our study demonstrated that the administration of (-)-epicatechin may improve the damaged liver tissue in hepatitis rats. Interestingly, (-)-epicatechin treatment in aged rats ameliorated the hepatic tissue in hepatitis rats.

(-)-Epicatechin is a flavonol belonging to the group of flavonoids. (-)-Epicatechin is present in many plants. High quantities can be found in cocoa, tea, grapes, and phyllanthus. The present study was designed to explore the hypolipidemic and hepatoprotective effect of (-)-epicatechin in D-galactosamine-induced hepatitis in aged rats. This is the first study of the hypolipidemic and hepatoprotective effect of (-)-epicatechin in hepatitis-induced rats of the senile age group.

## Materials and Methods

### *Chemicals*

D-galactosamine were purchased from Sigma Chemical Co. (St. Louis, MO, USA) and all other chemicals obtained from Fisher Scientific (Pittsburg, PA, USA), Merck (Mumbai, India), Ranbaxy (New Delhi, India) and Qualigens (Mumbai, India).

### *Animals and Experimental Design*

Male Wistar rats (3000 ± 20 g) obtained from Indian Institute of Science, Bangalore, were kept under standard laboratory conditions (temperature (27 ± 2°C), natural light-dark cycle (photoperiod of 12 h light and 12 h), and humidity 55–60 per cent. The rats were maintained on a standard pellet diet (M/s Hindustan Lever Ltd., Mumbai) and provided access to water *ad libitum*. The study design was approved by the animal ethical committee (Resolution No. 10/08/a/CPCSCA/IAEC/SVU/09–10/ZOOL/KRS/Dt.25.09.2009). After 7 days of acclimatization, animals were divided into five groups of six rats each.

*Group I Normal Control (NC):* Old rats received saline for 21 days and served as normal control.

*Group II Bioactive ((-)-Epicatechin) compound control treatment (Et):* old rats were given bioactive compound of *Phyllanthus niruri* ((-)-epicatechin–50 mg/kg b/w) for 21 days.

*Group III Hepatitis Control (Ht):* A single injection of D-galactosamine (800 mg/kg b/w) was given intraperitoneally to the old rats for the induction of hepatitis 48 hours before sacrifice.

*Group IV Hepatitis + Bioactive compound ((-)-Epicatchin–50mg/Kg b/w) treatment (H+Et):* Pre-treatment of (-)-epicatechin was administered orally to the old rats for 21 days and a single injection of D-galactosamine (800 mg/kg b/w) was given intraperitoneally for the induction of hepatitis 48 hours before sacrifice.

*Group V Hepatitis + Silymarin treatment (H+St):* Pre-treatment of standard drug silymarin (100 mg/kg b/w) was administered orally to the old rats for 21 days and a single injection of D-galactosamine (800 mg/kg b/w) was given intraperitoneally for the induction of hepatitis 48 hours before sacrifice.

After 21 days of treatment, all the aged rats were sacrificed for blood sampling and serum was separated and frozen at –80EC for further analysis.

### *Estimation of Lipid Metabolic Profiles*

Total cholesterol, triglyceride, low-density lipoprotein cholesterol, very-low-density lipoprotein cholesterol, and high-density lipoprotein cholesterol were estimated in the serum using kit methods.

### *Estimation of the thiobarbituric acid reactive substances TBARS*

The extent of serum lipid peroxidation in terms of thiobarbituric acid reactive substance formation was measured as described by Ohkawa *et al.,* (1979).

### *Estimation of Serum Markers*

The biochemical parameters like bilirubin (BL), urea (UR), creatinine (CR) were measured in serum by using commercially available kits following the manufacturer′s protocol.

### *Protein Estimation*

Protein content was estimated by the method of Bradford, (1976).

### *Statistical Analysis*

Results are expressed as means ± standard deviation (SD). Variance analysis was done with Duncan's multiple comparison Tests on data were carried out using the SPSS (Version 15; SPSS Inc., Chicago, IL, USA) and M.S. Office, excel software for the significance of the main effects (factors), and treatments along with their interactions. Statistical significance was set at $P < 0.05$. The p-values are presented with obtained data.

## Results

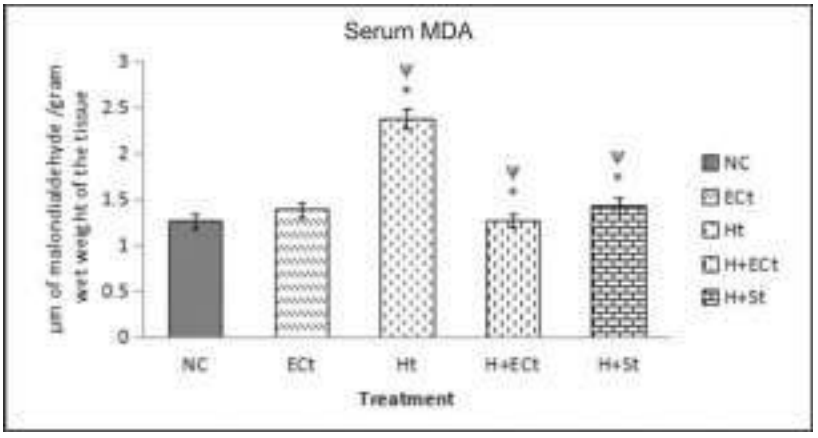
### *Effect of (-)-Epicatechin on Lipid metabolic Profiles*

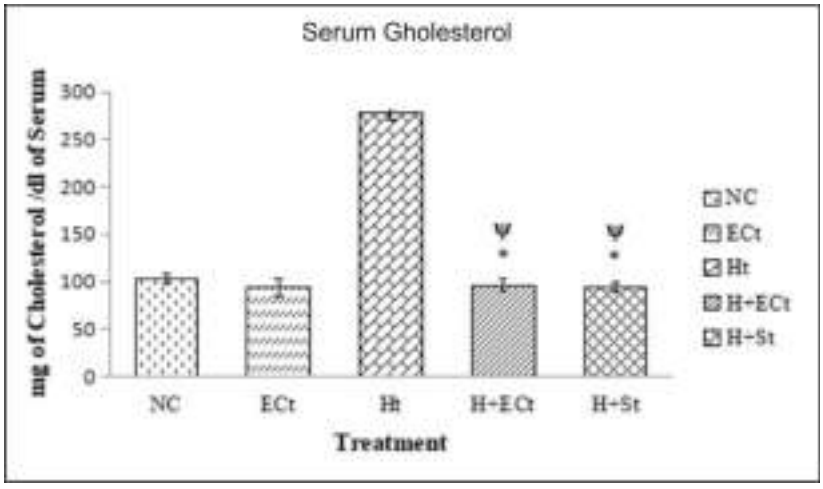
In this study, the lipid metabolic profiles total cholesterol, triglycerides, LDL, VLDL levels are increased and HDL levels are decreased in the serum of aged hepatitis subjects. However, with (-)-epicatechin pre-treatment in old-aged hepatitis rats, these lipid metabolic profile levels came near to normal levels. (Figure 1). Insert here

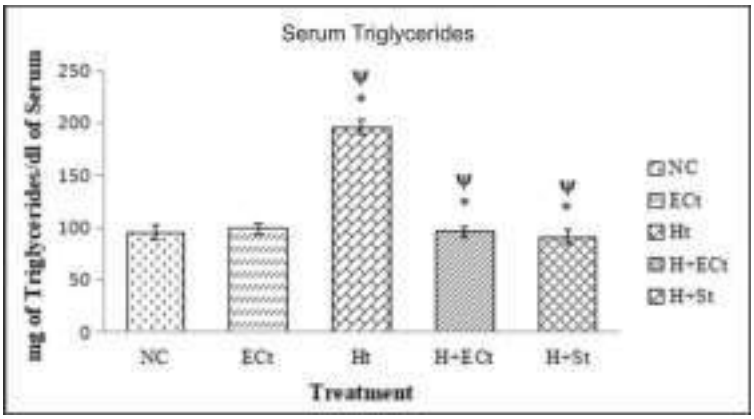
MDA levels are also upregulated in aged hepatitis rats. However with (-)-epicatechin supplementation MDA level downregulated in aged hepatitis rats. (Figure 1).

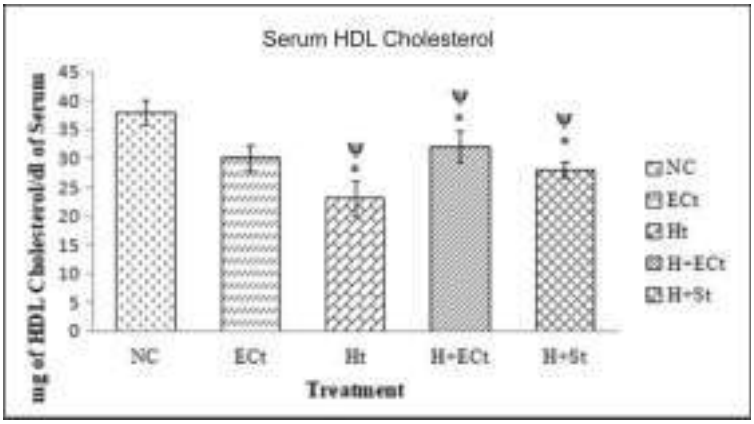
**Figure 1**

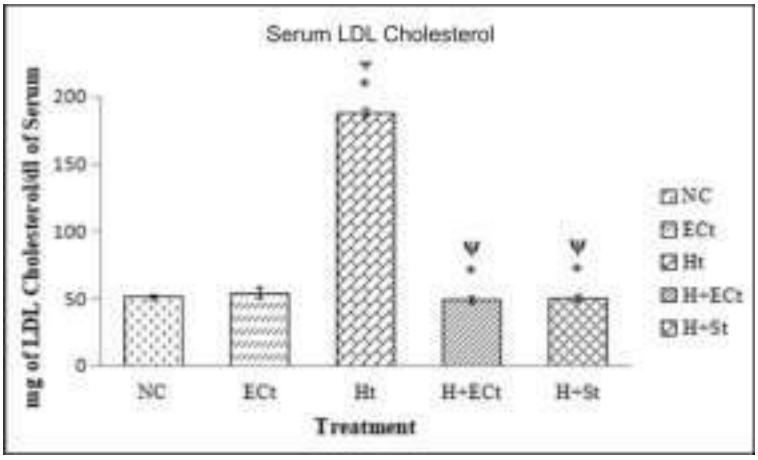
*Effects of (-)-Epicatechin and silmyrin on Lipid Metabolic Profiles (MDA, Cholesterol, Triglycerides, HDL, LDL & VLDL) levels in the serum of aged hepatitis rats. Data are expressed as means ± SD (n = 6). * The values are significant compared to the following: control (* p < 0.001), hepatitic (*p < 0.01) (Dunnett's multiple comparison test).*

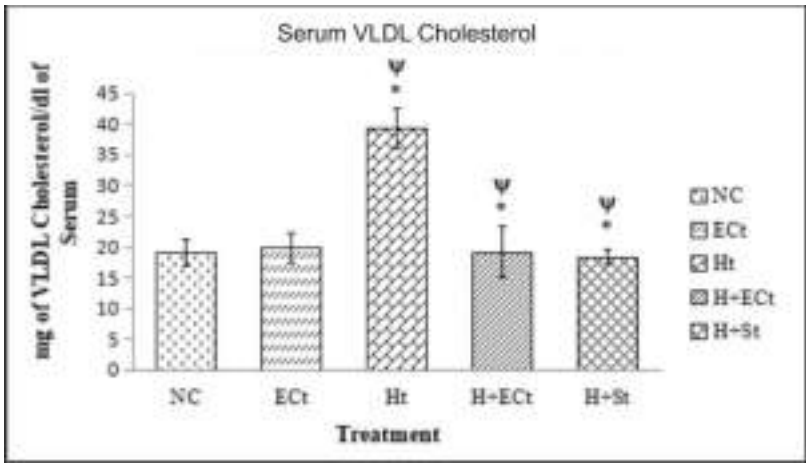



Serum Triglycerides
mg of Triglycerides/dl of Serum
250
200
150
100
50
0
NC
ECt
Ht
H+ECt
H+St
Treatment
NC
ECt
Ht
H+ECt
H+St


Serum HDL Cholesterol
mg of HDL Cholesterol/dl of Serum
45
40
35
30
25
20
15
10
5
0
NC
ECt
Ht
H+ECt
H+St
Treatment
NC
ECt
Ht
H+ECt
H+St


Serum LDL Cholesterol
mg of LDL Cholesterol/dl of Serum
200
150
100
50
0
NC
ECt
Ht
H+ECt
H+St
Treatment
NC
ECt
Ht
H+ECt
H+St




### *Effect of (-)-Epicatechin on BL, UR & CR in Hepatitis Rats*

In the present investigation, urea (UR) and creatinine (CR) levels decreased and bilirubin (BL) levels increased in aged hepatitis rats. Whereas with (-)-epicatechin supplementation in old hepatictic rats, we observed elevated levels of UR & CR and depleted levels of BL suggestive of hepatoprotective effect of (-)-epicatechin.

**Table 1**

*Effect of (-)-Epicatechin on Serum markers (BL, Urea, Creatinine) in aged hepatitis rats*

| *Groups* | *Bilirubin (mg/dL)* | *Urea (mg/dL)* | *Creatinine (mg/dL)* |
|---|---|---|---|
| Group I (NC) | 0.62 | 36 | 0.23 |
| | (±0.2) | (±6.24) | (±0.02) |
| Group II (Et) | 0.68 | 42 | 0.28 |
| | (±0.2) | (±3.05) | (±0.106) |
| Group III (Ht) | 3.2* | 28 | 0.102 |
| | (±0.48) | (±5.49) | (±0.046) |
| Group IV (H+Et) | 0.54* | 38 | 0.26 |
| | (±0.62) | (±4.26) | (±0.049) |
| Group V (H+St) | 0.68* | 32 | 0.24 |
| | (±0.024) | (±3.92) | (±0.063) |

All the values are means ± SD of six individual observations.
* Significant at $p < 0.001$ with respect to normal control.

## Discussion

Increasing evidence indicates that oxidative stress causes liver injury, cirrhosis development, and carcinogenesis (Farzaei *et al*., 2018). The present study was focused on investigating the hypolipidemic role of (-)-epicatechin against D-galactosamine-induced hepatitis and finding its possible mode of action in aged hepatitis rats.

The liver is the major site of cholesterol and phospholipid synthesis and metabolism. Lipid-related abnormalities are most common in hepatitis conditions. Alterations in lipid metabolism have been reported in D-GalN induced hepatitis conditions in rats. In this study, we observed elevated levels of MDA, total cholesterol, triglycerides, LDL, VLDL, and reduced levels of HDL in old hepatitis rats, when compared to control rats. These lipid disorders are due to alterations in lipid metabolism in hepatitis.

Malondialdehyde (MDA) is a natural metabolic product of lipid peroxidation. In this study, we observed higher levels of MDA in old hepatitis rats. But pre-treatment with the (-)-epicatechin protected the liver from D-galactosamine-induced hepatitis. This may be due to the suppression of toxic free radical production during hepatitis conditions. Hence, with (-)-epicatechin pre-treatment, MDA levels decreased in old hepatitis rats. This is the first reported data on the effect of (-)-epicatechin on MDA in aged hepatitis rats.

Higher levels of LDL, VLDL are due to decreased activity of lipoprotein lipase. Increased VLDL levels in old hepatitis rats are due to the increased concentration of free fatty acids. These lipid abnormalities in hepatitis rats may be due to alterations in lipid metabolism. Numerous studies have reported the increased levels of LDL, VLDL, and reduction in the HDL levels during D-galactosamine-induced liver injury (Arain *et al.,* 2017). Lipid disorders, most often encountered in liver diseases also include increased levels of LDL and VLDL (Arain *et al.,* 2017). (-) Epicatechin may reduce the activity of lipoprotein lipase in old hepatitis conditions. This may cause a reduction in LDL, VLDL levels in hepatitis rats. (-)-Epicatechin treatment has a profound effect on the lipid and lipoprotein metabolism in aged hepatitis rats. So, LDL, VLDL decreased with (-)-epicatechin in old-aged hepatitis rats.

HDL one of the beneficial lipoprotein (Brown *et al.*, 2010), could be helped through the scavenging of cholesterol from the extrahepatic tissues. In our study, we reported decreased levels of HDL in old hepatitis rats. HDL depletion might be attributed to an alteration in lipoprotein lipase and LCAT activity during hepatitis conditions. However, with (-)-epicatechin pre-treatment HDL levels are increased in old hepatitis rats. These alterations may be due to the hypolipidemic effect of (-)-epicatechin. Hence, all the lipid metabolic profiles MDA, TC, TG, LDL, VLDL, HDL are normalized with (-)-epicatechin supplementation in hepatitis condition.

Bilirubin, urea, and creatinine are indicators of liver function because a majority of proteins are synthesized in the liver. In this study, we reported that urea, creatinine levels are decreased and total bilirubin levels increased in old hepatitis rats. It shows the hepatotoxicity in hepatitis rats, supporting the previous study of Arvind Kumar and Sangeeta 2017. In hepatitis condition, the liver cell is unable to excrete bilirubin, urea, creatinine and therefore all these substances are mixed in the serum (Ibid.). So, higher total bilirubin (BL) levels are reported in hepatitis rats.

An increase in BL in hepatitis rats appears indicative of hepatic cell damage and disturbance of hepatocellular functions. As a result, BL levels increased in aged rats in contrast to decreased CR level and UR levels. Depletion in CR levels might be due to increased production of free radicals and a decrease in the breakdown of creatinine phosphate during the hepatitis condition. UR levels might have decreased due to the failure of the liver to convert amino acids and ammonia to urea. There are several reports on the depletion of urea during hepatitis conditions (Glavind *et al.*, 2016). D-galactosamine induction may alter the urea cycle and lead to depletion of urea in hepatitis rats. Whereas (-)-epicatechin pre-treatment urea, creatinine levels elevated and bilirubin levels depleted in old hepatitis rats. This may be due to the modulation of serum markers by (-)-epicatechin in old hepatitis rats. (Table 1).

## Conclusion

This is the first reported data on the hypolipidemic and hepatoprotective effect of (-)-epicatechin in hepatitis conditions. In

conclusion, (-)-epicatechin bioactive compound isolated from *Phyllanthus niruri* shows hypolipidemic and hepatoprotective effects against hepatitis in aged rats. But, the mechanism of its protective and hypolipidemic action is not known. Further studies are, therefore needed to know the mechanism and other related metabolic pathways alterations by (-)-epicatechin in aged hepatitis condition.

**Acknowledgments**: The authors are grateful to the Department of Science and Technology (DST), New Delhi, India for the sanction of Young Scientist Fast Track Project No. SERC/LS–387/2012, dated 02/09/2014.

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Original Article

# Effect of *Ocimum sanctum* in Sodium fluoride (NaF) induced Fluorosis in Rats: A Study with Respect to Antioxidant Enzymes and Fluorosis Markers

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## ABSTRACT

**Introduction:** Fluoride contamination was observed in groundwater's of India, Pakistan, China, Indonesia and several other countries. In India the states like Andhra Pradesh, Telangana, Rajasthan, Haryana etc are contaminated with fluoride. Approximately 68 million people are suffering from fluorosis in India. The current study was done to know the antioxidant effect, anti-fluorosis and free radical scavenging property of *Ocimum sanctum* (OS). **Methods:** Superoxide dismutase (SOD), glutathione peroxidase (GPx), glutathione (GSH), glutathione reductase (GR), glutathione-s-transferase (GST), catalase (CAT), malondialdehyde (MDA), alanine aminotransferase (AAT), alkaline phosphatase (ALKP), aspartate aminotransferase (AST) and flurosis markers phosphorus ($P_4$) and calcium (Ca) are estimated in all groups. 1,1-diphenyl-2-picryl hydrazyl radical (DPPH), hydroxyl radical, hydrogen peroxide ($H_2O_2$), Gas chromatography–mass spectrometry (GC-MS) was analyzed in methanolic extract of *Ocimum sanctum*. **Results:** SOD, GR, GSH, GPx CAT, activities and Ca levels are decreased in sodium fluoride (NaF) intoxicated rats. Whereas MDA, ALKP AST, AAT, and $P_4$ levels are increased in NaF rats. However, *Ocimum* phenolic fraction treatment normalized the antioxidant enzymes, hepatic markers and flurosis markers in NaF intoxicated rats. DPPH, $H_2O_2$ and hydroxyl radical of ocimum posses potent free radical scavenging activities. GC – MS studies of *Ocimum sanctum* showed the presence of many bioactive compounds like Caryophyllene oxide, 2-(2-Propenyl)-m-anisidine, 2H-Pyan-2-one, 5,6-Dihydro-4-(2-methyl-3-methylene-1-buten-4-yl etc. Further, histopathological observations prove that ocimum protects the hepatic tissue from NaF intoxication. **Conclusion:** Our study proves that *Ocimum sanctum* phenolic fraction protects the hepatic tissue from Na F induced fluorosis in rats.
**Key words:** *Ocimum sanctum*, Antioxidant Enzymes, Fluorosis markers, Liver markers, GC-MS analysis, Rats.

## INTRODUCTION

Fluorosis is a worldwide health problem resulting from excess consumption of fluoride through food products, ingesting water, and industrial contaminants over a long period. Fluorosis affects teeth, liver, bone, kidney and other parts of human body.[1,2] The major complications of fluorosis are dental fluorosisand skeletal fluorosis.

The practice of herbs to cure diseases was observed, since the dawn of civilization. Plant derived drugs are used to treat diseases like cancer, hepatitis, diabetes etc. The World Health Organization reported that traditional medicines like Ayurveda, sidda, unani use plant drugs to treat many health problems, because they are cheap and have no side effects.[3,4]

*Ocimum sanctum* is known as Tulasi. *Ocimum sanctum* has antiseptic, antimicrobial, anti-bactericidal, anti-inflammatory, antioxidant, antiulcer, anti-diarrheal and anti-diabetic

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properties.[5-8] However, no study was carried on the anti-fluorosis property of *Ocimum sanctum*.

The aim of current study was to explore the anti-fluorosis, antioxidant activity of phenolic fraction of *Ocimum sanctum* in NaF toxicity rats. Our study is the first reported research investigation on the effect of phenolic fraction of *Ocimum sanctum* in fluorosis intoxicated rats.

## MATERIALS AND METHODS

### Collection of plant material and Preparation of extracts

Fresh and good *Ocimum sanctum* leaves are collected from Tirupati, A. P, India. The methanol extract of OS leaves are prepared as per the experimental protocol and was used for the study of free radical scavenging assay and GC MS analysis.

### Chemicals and reagents

The chemicals are purchased from Himedia, Merck and Sigma–Aldrich.

### Extraction of Phenols from *Ocimum Sanctum*

Phenolic fraction was extracted from *Ocimum sanctum* by the method of Magalhães *et al.* 2010.[9]

### Treatment Groups

The young rats are divided into five groups.

**Normal Control - Group I (NC):** Six rats were treated with saline (0.9% NaCl) for the period of 60 days.

**Ocimum Control - Group II (Ot):** Six rats were treated with *Ocimum sanctum* phenolic fraction (100mg/kgBW) for the period of 60 days.

**NaF treatment - Group III (Na F):** Six rats were treated with sodium fluoride (10mg/kgBW) dissolved in water for the period of 60 days.

**NaF + Ocimum treatment - Group IV (NaF+Ot):** Six rats were treated with fluoride and Ocimum phenolic fraction for the period of 60 days.

**Na F+ Vitamin treatment - Group V (NaF+Vit C):** Six rats were treated with fluoride and Vitamin C for the period of 60 days.

After completion of last treatment i,e after sixty days treatment the rats are sacrificed by cervical dislocation and the liver tissue was collected in ice cold condition at 4°C. The liver tissues are stored in deep freezer at -80°C and later liver tissue was used for the estimation of antioxidant enzymes and other parameters. Blood sample was collected and used for analysis of liver markers and fluorosis makers.

### Estimations of Antioxidant Enzymes

The antioxidant enzymes like superoxide dismutase (SOD), glutathione reductase (GR), glutathione –s–transferase (GST), glutathione (GSH), catalase (CAT), glutathione peroxidase (GPx), activities, and MDA levels were estimated by the methods of Misra and Fridovich,[10] Carlberg and Mannervik,[11] Akerboom and Sies,[12] Habig *et al.*,[13] Aebi,[14] Flohe and Gunzler,[15] Ohkawa *et al.*,[16] respectively.

Liver markers AST, ALT and ALP activities and Fluorosis markers Calcium, phosphorus levels are measured by standard kits.

### Estimation of Free radical scavenging activity

DPPH, hydroxyl radical and hydrogen peroxide ($H_2O_2$) radical activities of ocimum are estimated by the methods of Koleva *et al.*,[17] Halliwell *et al.*[18] and Rosen and Rauckman.[19]

### GC-MS Analysis for Bioactive compounds in *Ocimum sanctum*

The phytochemical compounds like polar, semi polar, nonpolar and other compounds are present in *Ocimum sanctum* are recognized by GC- MS instrument. Gas Chromatography (GC) peaks obtained for compounds in this study are coupled with Mass Spectroscopy (MS) and compound structures present in ocimum are searched in National Institute of Standard and Technology (NIST) library and their structures are drawn by using Marvin Sketch a Chemo informatics (*in silico*) tool.

### Histopathological studies

Liver tissue was immediately fixed in 4 % paraformaldehyde phosphate buffer solution, after collection and process, it is used to assess the histopathology.

### Statistical study

The results of our study are expressed as mean values ± standard deviation. Statistical comparison was carried with five groups by using one-way ANOVA with Dunnett's multiple comparison Test. Differences are considered significant at $p < 0.01$.

## RESULTS

### Free radical scavenging assay of *Ocimum sanctum*

DPPH activity expressed by methanolic extract and ascorbic acid are depicted in Figure 1. In the current study, *Ocimum* at the estimated concentrations showed significant DPPH scavenging activity, which shows free radical scavenging activity of *Ocimum sanctum*.

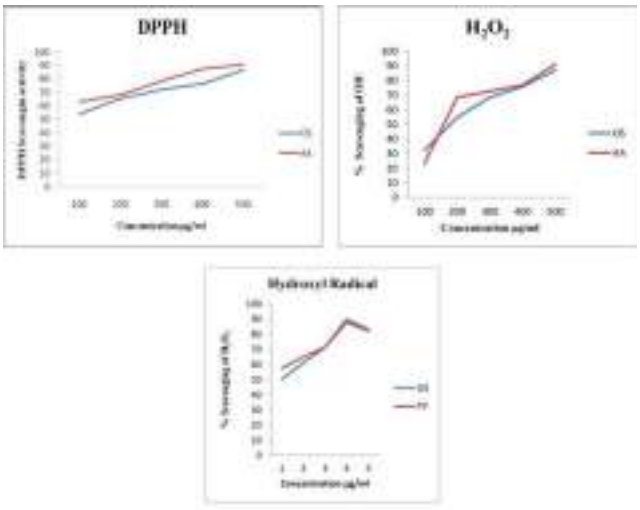



**Figure 1: Free radical scavenging activity (DPPH, Hydrogen peroxide and Hydroxy Radicals) of metaholic extract of *Ocimum sanctum* with ascorbic acid and α tocopherol as standards.**

The deoxyribose assay is a used to determine the hydroxyl radical activity of OS at different concentrations. (Figure 1). In the current study *Ocimum sanctum* at different concentrations posses significant hydroxyl radical scavenging potential.

Our results represents that the $H_2O_2$ scavenging activity of OS decreases than that of α-tocopherol. Hydrogen peroxide converts to water due to the antioxidant compounds in the methanolic extract of OS.

## GC–MS Analysis for phytochemical profile identification

GC–MS can discover many chemical compounds in the plants, food, and other samples. GC–MS analyse the structure of different bioactive compounds. In our analysis, we reported 14 compounds in *Ocimum sanctum* methanolic extract. GC–MS chromatogram reported the presence of bioactive compounds like 2H-Pyan-2-one, 5,6-Dihydro-4-(2-methyl-3-methylene-1-buten-4-yl, Tricyclo[6.3.3.0] tetradec-4-ene, 10,13-dioxo, Perhydrohistrionicotoxin, 2-methylthio-2-depentyl,Trans-Z-à-Bisaboleneepoxide,2-(2-Propenyl)-m-anisidine, Patchoulene, 1,2,4-Triazol-4-amine 5-methyl-3-(3,5-dimethylpyrazol-1-yl)-Naphthalene,1,2,3,4,4a,5,6,8a-octahydro-4a,8-dimethyl-2-(1-methylethenyl-, [2R-(2à,4aà,8aà)], Caryophyllene oxide, 9-Octadecenoic acid [Z], (tetrahydro-3-furanyi)methyl ester, 5-methyl-3-(3,5-dimethylpyrazol-1-yl), 7,10-Octadecadienoic acid, methyl ester, Z-10-Methyl-11-tetradecen-1-ol propionate, Nonadecanoic acid, 18-oxo-, methyl ester, 4-Piperi-dineacetic acid, 5-ethylidene-2-[3-(2-hydroxyethyl)-1H-indol-2-yi]-à methylene-, methyl ester, [2S-(2à, 4à, 5E)]. (Figure 2, 3 and Table 1).

## Effect of Phenolic fraction of *Ocimum* on Hepatic antioxidant enzymes in Sodium Fluoride treatment rats

In the current investigation, SOD, GPx, GR, CAT, activities, GSH levels are decreased in NaF intoxicated rats. However, with phenolic fraction of Ocimum supplementation in Na F rats, we observed significant elevation. But MDA content and GST activity are significantly increased in NaF intoxicated rats, however Ocimum supplementation decreased GST activity and MDA content in NaF rats. This shows the potential antioxidant effect of *Ocimum* (Figure 4).

## Effect of Phenolic fraction of *Ocimum* on Serum and Fluorosis markers in Fluorosis rats

In the present study, AST, ALT, ALP activities and phosphorus levels are elevated in sodium fluoride intoxicated rats. But Calcium levels depleted in NAF rats. This indicates severe liver injury in Fluorosis condition. However phenolic fraction of Ocimum for 60 days supplementation significantly altered all the liver parameters and fluorosis markers in fluorosis rats. (Table 2).

## Effect of Phenolic fraction of Ocimum on Liver tissue in Fluorosis rats

In this study, liver of normal rats and *Ocimum* treated rats exhibited normal central vein, hepatocytes and sinusoids. Where as in NaF rats, degeneration of central vein, hepatocytes and sinusoids are observed. However with Ocimum treatment for 60 days regenerated the central vein, hepatocytes and sinusoids in NaF toxicity rats. This study showed the hepatoprotective effect of Ocimum. (Figure 5).

# DISCUSSION

The current investigation was carried to know the pharmacological effect *of Ocimum sanctum* phenolic faction in NaF induced fluoosis in rats.

DPPH activity is one of the important free radical scavenging assay which actually depend on the 1,1-diphenyl-2-picrylhydrazyl, which decolorize in presence of antioxidants, such asantioxidant compounds in *Ocimum sanctum*.[20] The antioxidant compounds in *Ocimum sanctum* reacts with DPPH and convert it into1-1-diphenyl-2-picrylhydrazine and this scavenging activity was mainly depends on decolourization potential of methanolic extract of *Ocimum sanctum*. This assay have been used to estimate the free radical scavenging effect of

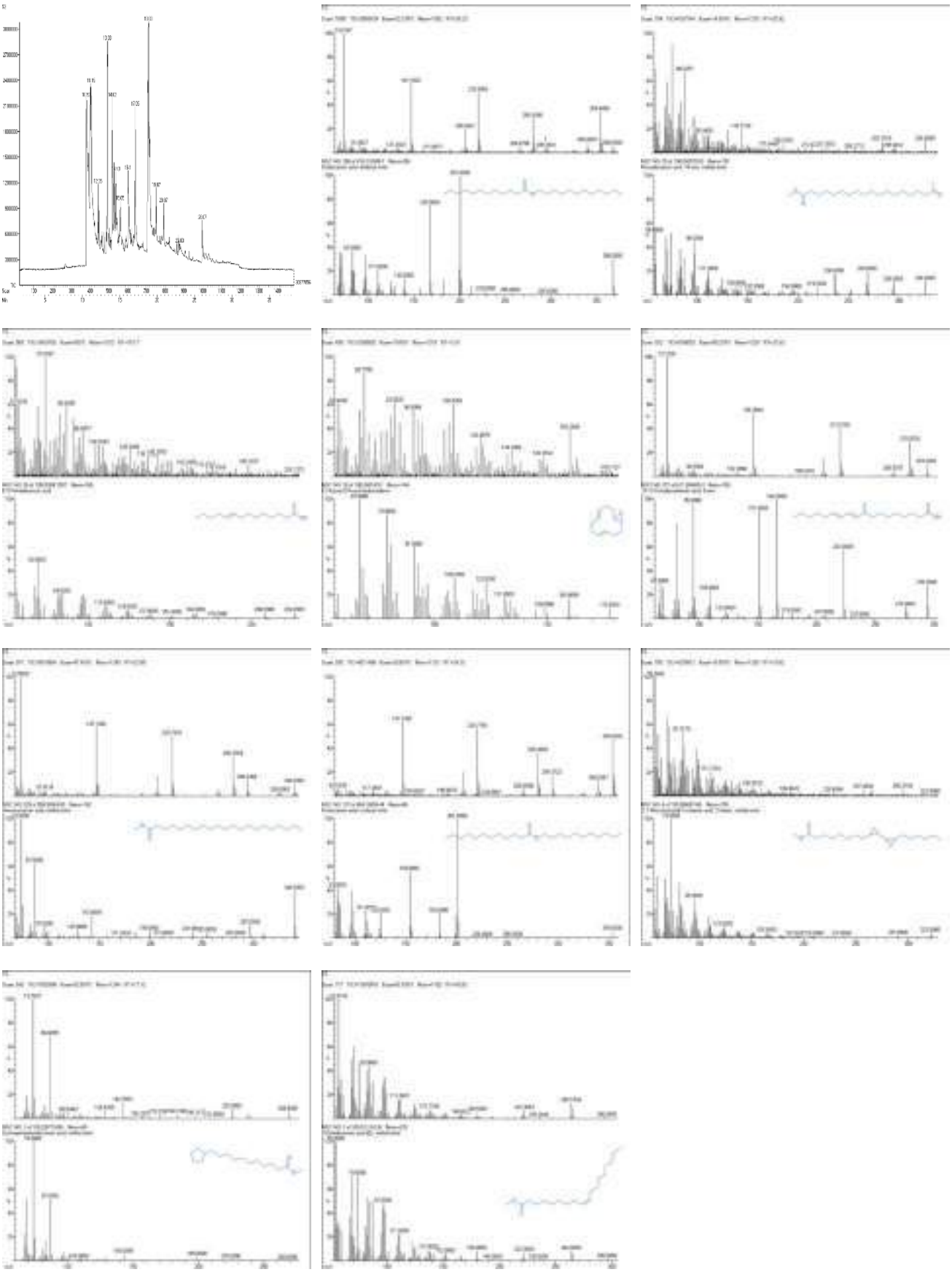


**Figure 2: Pictographic Diagram of GC-MS Analysis of *Ocimum sanctum***

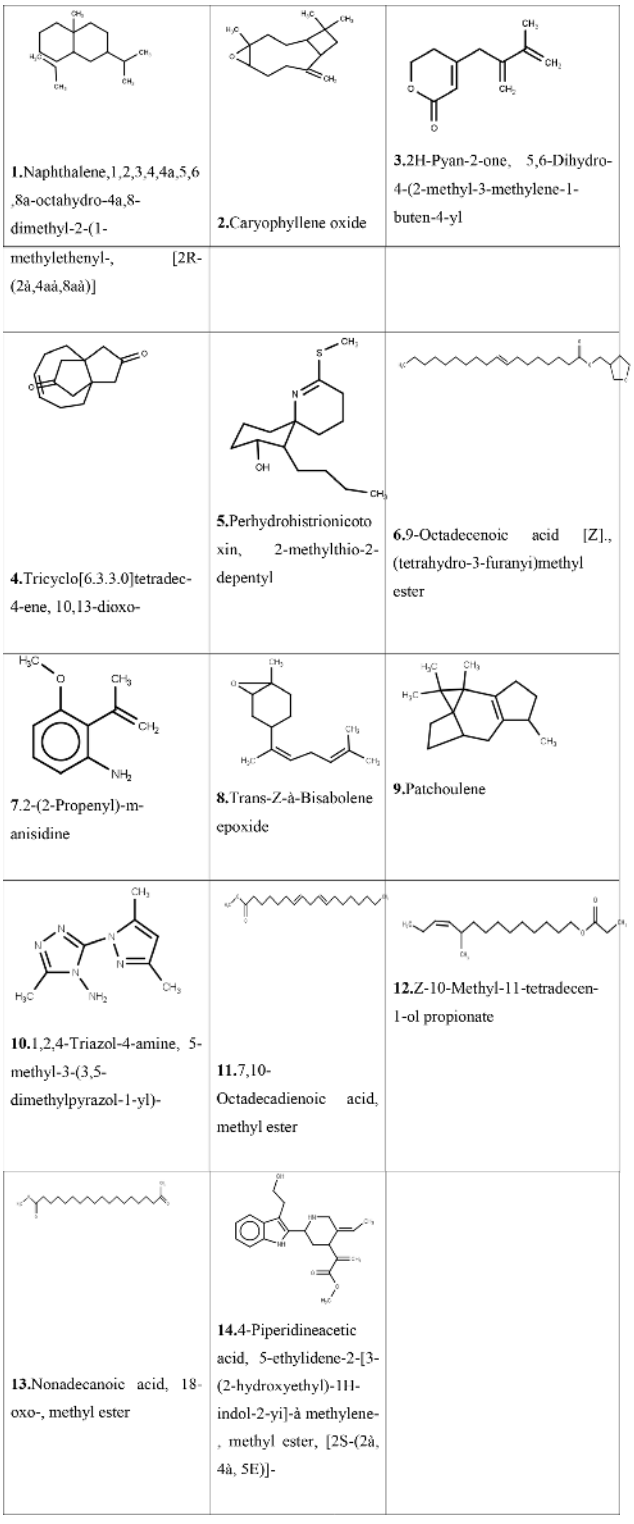



**Figure 3: Chemical structures of the Bioactive compounds of *Ocimum sanctum.***

many medicinal plants.[21] Antioxidant activity of *Ocimum sanctum* have been reported by many researchers.[22,23] The standard ascorbic acid exhibits significant DPPH activity than OS methanolic extract.

**Table 1: GC-MS Analysis of *Ocimum sanctum* showing the Bioactive compounds and their Molecular weights.**

| S.NO | Name of the Bioactive Compounds | R TIME | Molecular Weights |
|---|---|---|---|
| 1 | Naphthalene,1,2,3,4,4a,5,6,8a-octahydro-4a,8-dimethyl-2-(1-methylethenyl-, [2R-(2à,4aà,8aà)] | 12.05 | 238.459 |
| 2 | Caryophyllene oxide | 13.33 | 220.356 |
| 3 | 2H-Pyan-2-one, 5,6-Dihydro-4-(2-methyl-3-methylene-1-buten-4-yl | 11.15 | 178.231 |
| 4 | Tricyclo[6.3.3.0]tetradec-4-ene, 10,13-dioxo- | 14.02 | 218.296 |
| 5 | Perhydrohistrionicotoxin, 2-methylthio-2-depentyl | 17.05 | 269.45 |
| 6 | 9-Octadecenoic acid [Z]., (tetrahydro-3-furanyi)methyl ester | 26.08 | 366.586 |
| 7 | 2-(2-Propenyl)-m-anisidine | 10.55 | 163.220 |
| 8 | Trans-Z-à-Bisabolene epoxide | 14.43 | 220.356 |
| 9 | Patchoulene | 15.05 | 216.368 |
| 10 | 1,2,4-Triazol-4-amine, 5-methyl-3-(3,5-dimethylpyrazol-1-yl)- | 16.1 | 192.226 |
| 11 | 7,10-Octadecadienoic acid, methyl ester | 18.83 | 294.479 |
| 12 | Z-10-Methyl-11-tetradecen-1-ol propionate | 19.87 | 282.468 |
| 13 | Nonadecanoic acid, 18-oxo-, methyl ester | 20.87 | 326.521 |
| 14 | 4-Piperidineacetic acid, 5-ethylidene-2-[3-(2-hydroxyethyl)-1H-indol-2-yi]-à methylene-, methyl ester, [2S-(2à, 4à, 5E)]- | 23.03 | 354.450 |

Hydrogen peroxide involves in various important physiological processes of cells.[24] Methanolic extract of *Ocimum sanctum* convert the hydrogen peroxide to water. *Ocimum sanctum* showed potent $H_2O_2$ scavenging activity at different concentrations.[18] DPPH, $H_2O_2$ and hydroxyl radical scavenging activity of methanolic extract of *Ocimum sanctum* showed lower effect than standard. The standards i,e ascorbic acid and alpha tocopherol are completely independent compounds hence, they posses good antioxidant effect at different concentrations than methanolic extract of *Ocimum sanctum*. (Figure 1). Free radical scavenging effects are due the presence of phytochemicals and secondary metabolites like phenolic, flavonoids, and other compounds[25] in *Ocimum sanctum*. The importance of free radical scavenging activity is to estimate the antioxidant effect because *Ocimum sanctum* has many antioxidant compounds.[26]

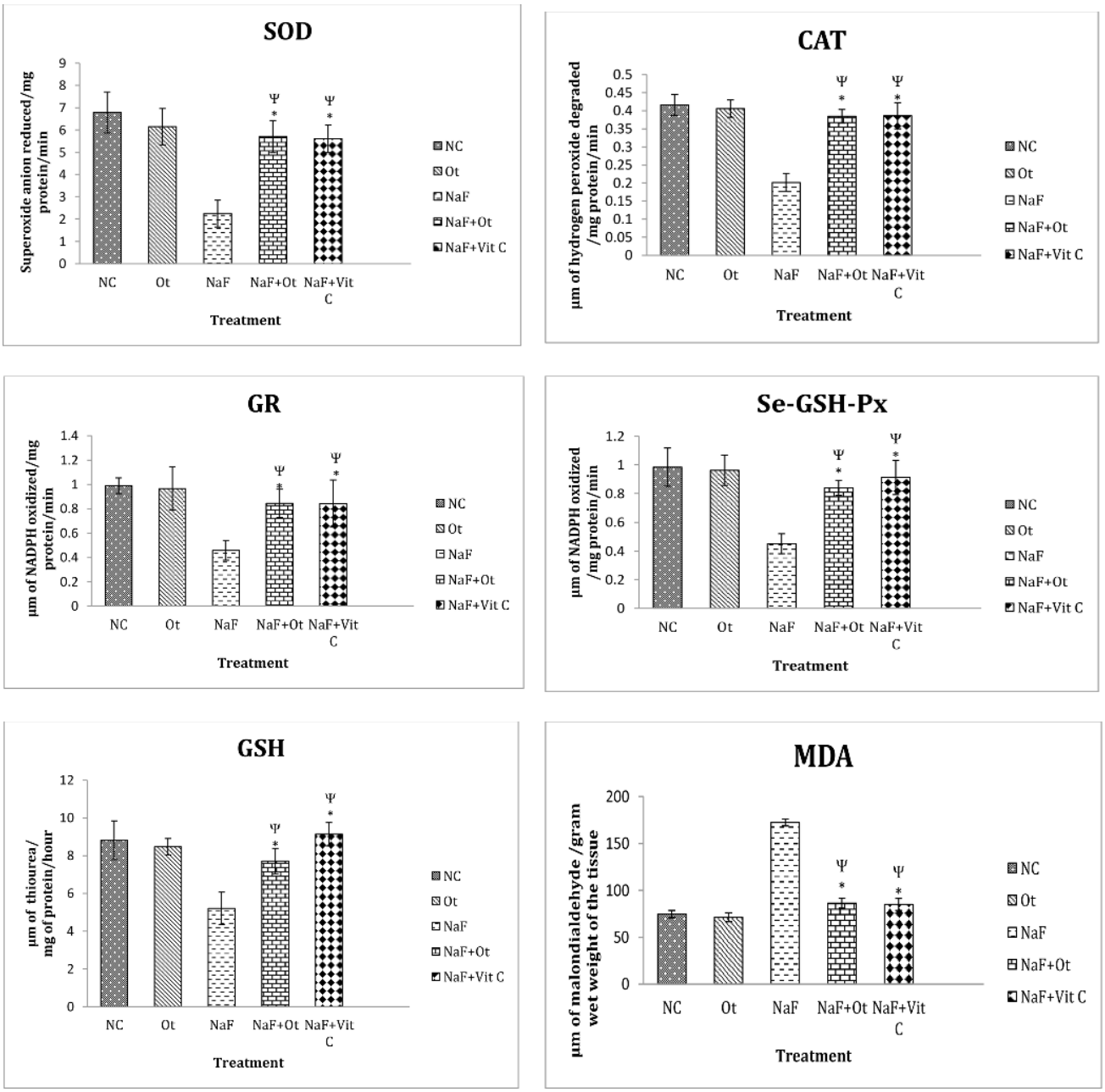



**Figure 4: Impact of *Ocimum sanctum* phenolic fraction on SOD, CAT, GR, GPx, activities and GSH, MDA levels in the liver tissues of Normal and Fluorosis rats. Data are expressed as means ± SD (*n* = 6). * The values are significant compared to the following: control (* *p* < 0.01), Fluorosis (**p* < 0.01) (Dunnett's multiple comparison tests).**

In our study GC-MS analysis of *Ocimum sanctum* reports many bioactive compounds. These bioactive compounds were recognized through mass spectrum analysis connected with GC. The unknown peaks obtained from the chromatogram are examined with the database of known spectrum of components kept in GC-MS library. The bioactive compounds, which are detected by the GC-MS are shown in Table 1.

In our analysis, we have identified 14 compounds in *Ocimum sanctum* methanolic extract. The compounds are 5-methyl-3-(3,5-dimethylpyrazol-1-yl)-Naphthalene, [2R-(2à,4aà,8aà)],Caryophylleneoxide,5,6-Dihydro-4-(2-methyl-3-methylene-1-buten-4-yl, 9-Octadecenoic acid [Z], (tetrahydro-3-furanyi)methyl ester, 2H-Pyan-2-one, Tricyclo[6.3.3.0] tetradec-4-ene, 10,13-dioxo, Perhydrohistrionicotoxin, 2-methylthio-2-depentyl,Trans-Z-à-Bisabo leneepoxide,2-(2-Propenyl)-m-anisidine, Patchoulene, 1,2,4-Triazol-4-amine, 5-methyl-3-(3,5-dimethylpyrazol-1-yl), 1,2,3,4,4a,5,6,8a-octahydro-4a,8-dimethyl-2-(1-methyl ethenyl-,7,10-Octadecadienoic acid, methyl ester, Z-10-

| Table 2: Effect of *Ocimum sanctum* Phenolic fraction on Serum markers in NaF rats. | | | | | |
|---|---|---|---|---|---|
| **Groups** | **AST (IU/L)** | **ALT (IU/L)** | **ALP (IU/L)** | **Ca (IU/L)** | **PP (mg/dL** |
| Group I | 586.82 | 94.12 | 414 | 11.31 | 14.24 |
| (NC) | (±12.48) | (±6.68) | (±8.26) | (±1.69) | (±1.24) |
| Group II | 435 | 92.535 | 285 | 11.82 | 13.84 |
| (Ot) | (±12.46) | (±10.14) | (±10.42) | (±1.46) | (±1.16) |
| Group III | 606.442* | 101.642* | 614* | 8.2* | 16.82* |
| (NaFt) | (±18.48) | (±8.68) | (±11.28) | (±1.72) | (±1.36) |
| Group IV | 72.267* | 67.348* | 180* | 10.2* | 13.26* |
| (NaF+Ot) | (±4.62) | (±4.52) | (±8.42) | (±1.82) | (±1.32) |
| Group V | 66.731* | 51.189* | 151* | 11.22* | 13.86* |
| (NaF+Vit C) | (±3.14) | (±4.12) | (±6.14) | (±1.12) | (±1.64) |

All the values are means ± SD of six individual observations.
* Significant at $p < 0.001$ with respect to normal control.

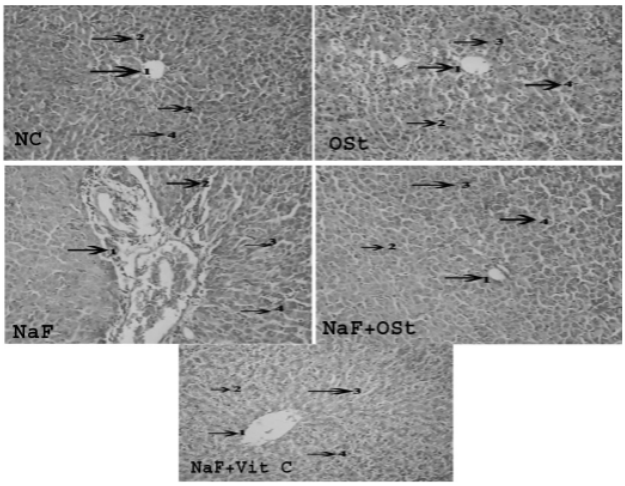



**Figure 5: Impact of Ocimum on Liver tissue in NaF intoxicated Fluorosis rats.**

**1. Normal Control (Nc).** 1. Normal central vein, 2. Normal hepatocytes, 3.Normal sinusoids, 4. Normal nucleus. **2. Ocimum treatment (OSt):** 1.Nomal cenntral vein, 2. Normal hepatocytes, 3. Normal sinusoids, 4. Normal nucleus. **3.Sodium fluoride (NaF)** 1. Degeneration of central vein, 2. Degeneration of hepatocytes, 3. Degeneration of sinusoids, 4. Degeneration of nucleus. **4. Sodium fluoride + Ocimum treatment (NaF+OSt)** showed 1. Regeneration of central vein, 2. Regeneration of hepatocytes, 3.Regeneration of sinusoids, 4. Regeneration of nucleus. **5. Sodium fluoride +Vitamin C treatment (NaF+Vit C)** 1. Regeneration of central vein, 2. Regeneration of hepatocytes, 3.Regeneration of sinusoids, 4. Regeneration of nucleus.

Methyl-11-tetradecen-1-ol propionate, Nonadecanoic acid, 18-oxo-, methyl ester, 4-Piperidineacetic acid, 5-ethylidene-2-[3-(2-hydroxyethyl)-1H-indol-2-yi]-à methylene-, methyl ester, [2S-(2à, 4à, 5E)]-These compounds may have pharmacological properties, which are unexplored (Figure 2,3 and Table 1).

In the present investigation, the antioxidant enzymes like SOD, GPx, GR, CAT, GSH are depleted in sodium fluoride induced fluorosis rats. Our study reported that depletion of these antioxidant enzymes in Na F treatment rats. This may be due to the oxidative stress and excess free radicals production in NaF intoxicated rats. However, OS phenolic fraction treatment in NaF rats for 60 days reversed these antioxidant enzymes. Ocimum has many pharmacological properties like antioxidant, hepatoprotective and antimicrobial and other properties. *Ocimum* has many bioactive and pharmacological compounds, these may be responsible for the up regulation of antioxidant enzymes in NaF rats. Ocimum treatment considerably recovered the activities of antioxidant enzymes in NaF intoxicated rats. (Figure 4).

Oxidative stress is reported to be associated with more than 100 diseases like cancer, diabetes and hepatitis. There is a strong relationship between TBA (thiobarbituric acid-reactive substances) and products that reflect oxidative damage to DNA. MDA levels depleted in NaF rats, but with Ocimum treatment reversed back MDA levels, near to normal. This shows the antiperoxidative activity. Hepato toxicity is the condition of oxidative stress in liver generating reactive oxygen species as a result, liver MDA levels increased in NaF rats. However, Ocimum treatment, MDA levels decreased in hepatitis rats. (Figure 4).

In rats, which received NaF for 60 days, showed liver damage and also disturbance of liver cell metabolism which lead to alterations in the activities of many enzymes. Serum enzymes AST, ALP and ALT are markers of liver toxicity and their higher levels are representation of cellular damages and loss of hepatic

cell membrane. In the current study, we reported elevation in AST, ALT and ALP activities in NaF intoxicated rats. Our report showed fluorosis leads to hepatic cellular dysfunction, which results in the upregulation of liver markers. However with Ocimum supplementation these serum markers are depleted in NaF rats. Based on our results, the *Ocimum sanctum* methanolic extract have hepatoprotective potential. OS may reduce the formation of toxic free radicals and reduces the hepatocellular injury in NaF rats (Table 2).

Calcium and Phosphorus are important to humans, because, they help in the formation of bone. In the present study, we observed depleted calcium levels and elevated phosphorus levels in sodium fluoride intoxicated rats. These alterations in calcium and phosphorus levels are due changes in the metabolism of phosphorus and calcium. Whereas Ocimum treatment in NaF rats, for 60 days, these fluorosis markers normalized to near normal levels. (Table 2).

In the current investigation, we reported that in normal control rats, *Ocimum* treated rats the liver architecture is normal. Whereas in fluorosis rat liver, degeneration of central vein, hepatocytes, sinusoids and blood coagulation are observed. But with Ocimum treatment in fluorosis rats, regeneration of central vein, hepatocytes and sinusoids are observed. Histopathological studies also prove that the hepatoprotective effect of Ocimum in NaF rats. (Figure 5).

## CONCLUSION

The current study proved that phenolic fraction of *Ocimum sanctum* protects the hepatic tissue from sodium fluoride intoxication in albino rats. We also reported that antioxidant enzymes, hepatic markers and flurosis markers are normalized with *Ocimum* treatment in Fluorosis rats. GC-MS analysis reported many bioactive compounds in *Ocimum sanctum* and these compounds may responsible for anti-fluorosis effect and antioxidant effects. This is the first study on the effect of phenolic fraction of *Ocimum sanctum* in fluorosis rats.

## ACKNOWLEDGEMENT

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## CONFLICT OF INTEREST

The authors declare that there is no conflict of interest.

## ABBREVIATIONS

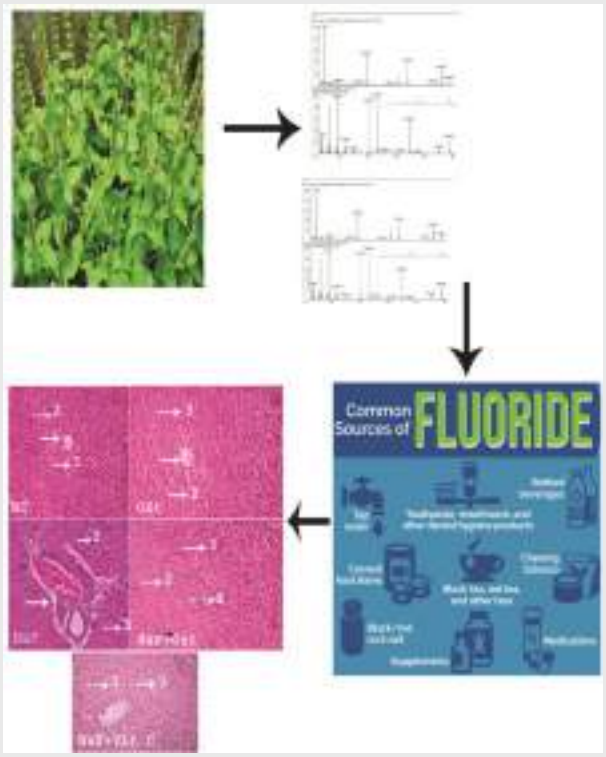
**OS:** *Ocimum sanctum*; **SOD:** Superoxide dismutase; **GPx:** Glutathione peroxidase; **GSH:** Glutathione; **GR:** Glutathione reductase; **GST:** Glutathione-s-transferase; **CAT:** Catalase; **MDA:** Malondialdehyde; **AAT:** Alanine aminotransferase; **ALKP:** Alkaline phosphatase; **AST:** Aspartate aminotransferase; **P4:** Phosphorus; **Ca:** Calcium; **DPPH:** 1,1-diphenyl-2-picryl hydrazyl radical; **$H_2O_2$:** Hydrogen peroxide; **GC-MS:** Gas chromatography–mass spectrometry; **MS:** Mass Spectroscopy; **NIST:** National Institute of Standard and Technology; **TBA:** thiobarbituric acid-reactive substances.

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## PICTORIAL ABSTRACT




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# Pharmacological evaluation of *Strychnos colubrina* L., an endangered medicinal plant

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**Abstract**
Plants have been used since ancient times to cure diseases and to improve health and wellbeing of the populations. Plant diversity is a great source of medicines, while it provides direct economic benefits in the form of timber, food, fibre, industrial enzymes, flavours, cosmetics, emulsifiers, dyes, plant growth regulators, bio-pesticides and biofertilizers etc. The secondary metabolites, alkaloids, saponins, quinones, indoles, anthraquinones, terpenoids, flavonoids, phenolic compounds and amino acids are localised in cells. These have therapeutic properties and responsible for phytochemical markers to identify the genuine drug. *Strychnos colubrina* L. was screened for the presence of secondary metabolites using standard protocols as given by Harborne (1973),Gibbs(1974), Kokate (2001)and Khandelwal (2006), followed by pharmacological evaluation. Methanolic leaf extracts are tested for antioxidant and antimicrobial activities. The results were expressed as standard ± mean deviation (SD) of five replicates. Where ever applicable, the data were subjected to one-way and 2-way ANOVA and differences between samples were determined by with Scheffe's post hoc test, Dunnet's test using the program Statistical Analysis System (SASS V25). P Values < 0.05 were regarded as significant. In the preliminary phytochemical studies, the tannins, phenolic compounds, Alkaloids, flavonoids, Saponins, fats, oils, terpenoids have *shown positive test in Strychnos colubrina.* Glycosides, Lignins, Quinones, Anthraquinones, Anthocyanides, Coumarins, Carbohydrates, reducing sugars and Aminoacids are found to be absent. Sterols are absent in *Strychnos colubrina.* Administration of methanolic leaf extracts of *Strychnos colubrine* (200mg/kg) to have significant detrimental effect on one of 3 bacterial strains used i.e, *Staphylococcus aureus* and it has no effect on other 3 microbes namely, *Bacillus subtilis, Pseudomonas aeruginosa* and a fungal strain namely *Candida albicans.* Methanolic extract of plant leaves of *Strychnos colubrina* has not earlier been reported to have anti-microbial activity. The statistical analysis of the DPPH and $NO_3$ free radical tests with the *Strychnos colubrina* methanol extract has shown significant difference in results with the control groups in both the comparisons. The extracts solution exhibited significant anti-oxidant properties in the both tests Present study is significant and fills the gap in the ethno-medico-botanical repository of Andhra Pradesh.

**Keywords:** methanolic extract, snake wood tree, phytochemicals, antioxidant, antimicrobial, scheffe's post hoc test, dunnet's test

## Introduction

Plants have been used since ancient times to heal and cure diseases and to improve the health and the wellbeing of the populations. Products made out plants for therapeutic or other human health benefits contain either raw or processed ingredients from one or more plants, is the focus of this research. The plant diversity is a great source of medicines, provides direct economic benefits in the form of timber, food, fibre, industrial enzymes, flavours, fragrance, cosmetics, emulsifiers, dyes, plant growth regulators, bio-pesticides and biofertilizers. The biochemicals present in vast majority of the plant species are the great reservoirs of new and potential drugs. They can be used for monitoring the environmental changes. They are the key resources for new genes and biotechnological valuable compounds (Marotrao Dalvi, 2010). Parts of any plant that are used for therapeutic purpose or used a precursor for making a useful drug. This makes it possible to differentiate between medicinal plants whose therapeutic properties and constituents have been established scientifically, and plants that are considered as medicinal but which have not yet been subjected to a thorough scientific study (Sofowora *et al.,* 2013). Medicinal plants are important constitute of flora and are widely distributed in India. The importance of medicinal plants and traditional health systems to solve healthcare problems of the world is gaining increasing attention. Because of this resurgent interest, the research on plants of medicinal importance is growing phenomenally across the world, often to the detriment of natural habitats and mother populations in the countries of origin. In most of the developing countries traditional medical practices have adopted as an integral part of their culture. Medicinal plants form an important pool for the identification of novel drug leads which have proven their value as a source of molecules with therapeutic potential since ancient time (Atanasov *et al.,* 2015). According to Harshberger (1896) the study on ethnobotany has now become a critical need of time.

### India-An 'Emporium of Ethnomedicinal Plants'.

India has been one of the oldest countries having well-orchestrated medical practices based on plant resources. So

far on the globe about 4, 80, 000 plant species are discovered. India is known as an 'Emporium of Medicinal Plants' due to occurrence of more than 48,000 plant taxa, of which 18,000 are flowering plants, among these 10,000 plant species are estimated to be used by 4635 ethenic communities for human and veterinary health care.

The plant materials and recipes from herbs used traditionally by various human societies is a challenging field of research in ethnobotanical studies. The indigenous systems of medicine have their roots in folk medicine still practiced in remote tribal and rural areas and aboriginal societies where modern civilization has not yet made in roads. There are some miraculous medicines known to the tribals and rural folk and much acquired knowledge through experience of ages is usually passed on from one generation to other generation as a guarded secret of certain families. Recent studies have shown that groups having common or similar climate and environments but different ethnic and /or religion backgrounds have a very different knowledge and use of medicinal plant. It is not yet clear what factors influence this diversity in utilization.



**Fig 1:** Strychnos colubrina Plant

## Materials and Methods

Leaves of *Strychnos colubrina* were collected from Penchalakona forest of Nellore district Andhrapradesh, India. The plants were identified by comparing with herbarium specimens. The plant material was purified with distilled water and was shade dried for one month. Leaf sample of the material was ground into fine powder and stored in air tight containers at room temperature. The powdered material was then extracted using solvent, methanol in the ratio 1:10 using Soxhlet apparatus. (Khan *et al*., 1988). The solvent was evaporated under reduced pressure in rotatory evaporator to get methanol and ethanol extracts. After extracting all colouring material, the solvent was removed by evaporating in a water bath, which gave rise to a solid isolate of extract used for antimicrobial and antioxidant activities along with phytochemical analysis.

**I. Phytochemical analysis:** The phytochemical analysis of the leaves was done to find out the presence of bioactive compounds with the help of standard qualitative protocols. (Harborne, 1973 and Gibbs, 1974, Kokate, 2002.)

**Tests performed for the presence of phytochemicals**

**A. Tests for Flavonoids**

- **Shinoda test (Magnesium hydrochloride reduction test):** To the test solution few fragments of magnesium ribbon and concentrated hydrochloric acid were added drop wise and reddish to pink colour was resulted.
- **Zinc Hydrochloride reduction test:** To test the sample solution for the flavonoids added a mixture of zinc dust and concentrated hydrochloric acid results in red colour.
- **Lead acetate test:** When aqueous basic lead acetate was added to test sample produces reddish brown precipitate.

**Ferric chloride test:** To few ml of test samples taken separately, few drops of ferric chloride were added which resulted in the formation of blackish red precipitate.

- **Alkaline reagent test**: To detect the presence of flavonoids, sodium hydroxide solution is added to turn the test sample solution green. When few drops of diluted acid is added the solution turns colourless to indicate the presence of flavonoids.

**B. Tests for Saponins**

- Foam test: 5ml of extract was vigorously shaken to obtain a stable froth, which was added with olive oil (3 drops). Presence of emulsion indicates the existence of saponins.

**C. Tests for Glycosides**

- **Kellar Kiliani test:** 1ml of concentrated sulphuric acid was taken in a test tube then 5ml of extract and 2ml of glacial acetic acid and ferric chloride (one drop) and observed for blue color formation.
- **Raymond's test:** Test solution when treated with dinitrobenzene in hot methanolic alkali giving a violet colour.
- **Molisch test:** Alpha naphthol with conc.H2SO4 when added to test sample gives reddish violet ring at the junction of 2 layers.
- **Conc.H2SO4 test:** Conc.H2SO4 was added to test sample which resulted in appearance of reddish colour.
- Legal's test: The test samples when treated with pyridine and sodium nitroprusside solution blood red colour will be developed.
- **Bromine water test:** When bromine solution is added the test solution gives yellow precipitate.

**Tests for Alkaloids**

- **Dragendorff's test:** 1 ml of the sample solution is taken in a test tube, and few drops of potassium bismuth iodide solution (Dragendorff's reagent) was added. The presence of alkaloids was determined by the appearance of reddish-brown precipitate.
- **Meyer's test:** 1ml of the sample solution is added with few drops of potassium mercuric chloride solution (Meyer's reagent). A creamy white precipitate was formed indicating the presence of alkaloids.
- **Hager's test:** To 1 ml of each of the sample few drops of Hager's reagent (Picric acid) was added. Yellow precipitate was formed reacting positively for alkaloids.
- **Tannic acid test:** When few ml of 10% Tannic acid was added to 1ml of each sample, a buff colour precipitate was formed giving positive result for alkaloids.

- **FeCl 3 test:** One drop of FeCl 3solution was added to each of the test sample, formation of yellow precipitate was resulted reacting positively for alkaloids.

**D. Tests for Sterols**

- **Libermann-Buchard test:** When few drops of acetic anhydride and few drops of concentrated sulphuric acid were added to the test samples if a brown ring shows up at the junction of two layers, it indicates presences of steroids. 2. Salkowski test: The presence of sterols can be detected by adding few drops of concentrated sulphuric acid to the test samples in chloroform, the lower layers of solution turns green on sterols presence.

**E. Tests for Tannins and Phenolic Compounds**

- **Gelatin test:** When gelatine and water were added to test samples formation of white precipitate was resulted.
- **Lead acetate:** Few ml of test samples were taken in different test tubes followed by the addition of aqueous basic lead acetate. It results in the formation of reddish brown bulky preceipitate.
- **Alkaline reagent:** The test solution will give a yellowish red precipitate when sodium hydroxide solution was added.
- **Ellagic acid test:** Presence of phenols in the test solution can be detected by adding 5% each of glacial acetic acid and Sodium Nitrite. If the solution turn Niger brown colour, it indicates phenols in solution.

**F. Tests for Fats and Oils**

- **Stain test:** when we a small quantity of extract between two filter papers, the stain on filter papers gives the presence of the oils.
- **Saponification test:** Added a few drops of 0.5N alcoholic potassium hydroxide to various extracts with a drop of phenolphthalein separately and heat on water bath for 1-2hours. If the solution produces soap or partial neutralization of alkali, it's a sign of presence of oils and fats.

**G. Tests for Lignins**

- **Labat test:** The test sample turns olive green colour on addition of gallic acid when lignins are present.
- **Furfuraldehyde test:** The test sample turns red colour on addition of fur furaldehyde when lignins are present.

**H. Tests for Quinones**

- **Alcoholic KOH test:** When alcoholic KOH was added to the test samples red to blue colour appears reacting positively for quinones.

**I. Terpenoids and steroids test**

- 50% $H_2SO_4$ is added along the sides of the test tube containing a mixture of methanolic HCl and acetic anhydride. If there is any change in color, from green to blue-green (sometimes via red or blue) indicates the presence of terpenoids and steroids Anthraquinones test
- 5 g plant powder was shaken with 20 ml of benzene and filtered. To the filtrate 5 ml of 10% ammonium hydroxide solution was added and shaken well. Presence of pink red or violet color, in the ammonical phase indicates the presence of free anthroquinones (Fransworth, 1966).

**J. Anthocyanidin test**

- To the plant extract was added equal volume of methanolic HCl. Appearance of red or purple color indicates the presence of anthocyanidins.

**K. Coumarin test**

- When few drops of sodium hydroxide are added to the methanolic extracted test solution, if the solutions turning yellow indicates presence of coumarins.

**L. Proteins test (Millions test)**

- 2 ml of methanolic extract was boiled with a few drops of Million's reagent (Millions reagent is a solution of mercuric nitrate in nitric acid) results in the formation of red color indicates the presence of proteins.

**M. Carbohydrate test (Molish test)**

- To the methanolic extract, c-naphthol solution (1gm dissolved in 100 ml of ethanol w/v) was added. Then conc. $H_2SO_4$ is added gently along the walls of the inclined test tube. Appearance of a red to violet color at the interface is taken as a positive reaction.

**N. Indole test**

- If a violet color was developed on adding Ehrlich reagent to the alcoholic extract, it is considered as a positive reaction for indoles.

**O. Test for reducing sugars**

- To the 5 ml of methanolic extract, 5 ml of Benedict's reagent was added in a boiling test tube. The test tubes were incubated in boiling on water bath for 15-30 minutes. The formation of an orange red precipitate indicated the presence of reducing sugars.

**P. Test for amino acids**

- To the methanolic extract, was added few drops of Ninhydrin solution and boiled. The formation of violet colour indicates the presence of amino acids.

**Determination of In vitro Antioxidant Activity of *Strychnos colubrina* methanolic leaf extracts Using DPPH Scavenging Method, Nitric oxide radical scavenging method.**

**A. DPPH (1, 1-Diphenyl-2picrylhydrazyl) free radical scavenging activity**:(**Blois, 1958)**

1. The ability of the sample to scavenge DPPH radicals were determined
2. 0.5 ml of aliquot of test at different concentrations (100 µg/ml and 200 µg/ml) in methanol was taken and to this, 100mM methanolic solution (0.5 ml) of 1, 1-Diphenyl-2picryl hydrazyl (DPPH) was added.
3. The mixture was incubated for 30 min in darkness and at ambient temperature.
4. Absorbance was recorded at 517 nm.

**B. Nitric oxide radical scavenging activity: (Ganesh *et al.*, 2004).**

- The standard used here was Ascorbic acid. 100 µg/ml and 200 µg/ml solution of standard in methanol and ethanol were used for assay.
- Sample solution was prepared by dissolving the sample in methanol and ethanol

- 10 mg of each extract were dissolved in methanol and ethanol and solutions of 100 µg/ml and 200 µg/ml concentrations were prepared.
- In this assay 0.5 ml of Sodium nitro prusside (Ganesh *et al*., 2004). (5 mmol) in phosphate buffered saline pH 7.4, was mixed with different concentration of the sample and incubated at 25°C for 3 hrs.
- A control without the test compound, but an equivalent amount of methanol and ethanol were taken. Buffer solution containing tube is acted as control.
- Then 1.5 ml of Griess reagent (1% sulphonyl amide, 2% phosphoric acid and 0.1% N-1-naphthyl ethylene diamine dihydrochloride) was added and incubated for 30 minutes.
- The absorbance of the chromophore formed during diazotization of nitrite ions with suphanilic acid and its subsequent coupling with Napthyl ethyl enediamine was read at 546 nm. The experiment was repeated in triplicate.
- Absorbance was measured at 546 nm and the percentage scavenging activity was measured.

$$\text{Percentage inhibition} = \frac{\text{Absorbance of Control} - \text{Absorbance of Test X 100}}{\text{Absorbance of Control}}$$

- The percentage of inhibition for each reaction was then calculated, and EC50 values (µg/mL) were calculated from the linear equation from the curve between the percentage of inhibition and the solution's concentration. Each experiment was conducted in triplicate. The EC50 value of each extract was expressed as the mean˘SD. The assays were performed as previously described.

**Determination of Antibacterial Activity activity of *Strychnos colubrina* methanolic leaf extracts using Disc Diffusion Assay**

Kirby-Bauer method (Bauer *et al* 1966) was followed to perform sensitivity test using disc diffusion with standard antibiotics. The assessment of antimicrobial activity was done based on the measure of diameter of inhibition zones, Sensitivity tests were performed by disc diffusion (*NCCLS, 1998*). The assays were performed against three clinically pathogenic bacteria *Bacillus subtilis MTCC 441, Staphylococcus aureus MTCC 737, Pseudomonas aeruginosa MTCC 1035* and a fungal pathogen *Candida albicans MTCC 3018.* Each extract was dissolved in 95% Methanol or sterile water at different concentrations (250, 500 and 1000 mg/mL). Then each solution was impregnated on to a small disc of filter paper and placed on the top of agar containing 100 µL of bacterial solution at a concentration of 1.5ˆ108 CFU/mL per plate (adjusted by comparing to 0.5 McFarland). In the same manner each plate has carried a blank disk by keeping solvent control only in the centre, and antibiotic discs (6mm diam) of 20 µg/ml, Streptomycin sulphate (for bacteria) and Nystatin 20 µg/ml, (for fungal) were used as positive control. All of the plates were incubated at 37°C for 18 hours for bacteria and at 28°C for 48 hours for fungi. The zones of growth inhibition around the discs were measured after 18 hours of in incubation at 37°C for bacteria and 48 hours for fungi at 28°C, respectively. The size of inhibitory zone is taken as a measure of sensitivity of micro-organism to the plant extract.

**Statistical Analysis**

Each test is conducted in three sets. The average value is calculated duly following statistical methods. Experimental results were expressed as standard ± mean deviation (SD) of five replicates.

Where ever applicable, the data were subjected to one-way analysis of variance (ANOVA), 2-way analysis of variance (ANOVA) methods and differences between samples were determined by with Scheffe's post hoc test, Dunnett's post hoc test using the Statistical Analysis System (SAS, 1999) programme. P Values < 0.05 were regarded as significant.

## Results

**Phytochemical studies**

**Table 1:** Analysis of Phytochemicals from methanolic leaf extracts of *Strychnos colubrina.*

| S. NO. | Name of the phytochemical | Name of the test | Methanolic leaf extract of *Strychnos columbrina* |
|---|---|---|---|
| 1. | Flavonoids | Shinoda test | + |
| | | Zn-HCl reduction test | + |
| | | Lead acetate test | - |
| | | $Fecl_3$ test | + |
| | | Alkaline reagent test | + |
| 2 | Saponins | Frothing test/Foam test | + |
| 3 | Glycosides | Keller-Kilianii test | - |
| | | Raymond's test | - |
| | | Molisch test | - |
| | | Conc.$H_2SO_4$ test | - |
| | | Legal's test | - |
| | | Bromine water test | - |
| 4 | Alkaloids | Dragendorff test | + |
| | | Mayer's test | - |
| | | Wagner's test | + |
| | | Hager's test | - |
| | | Tanicacid test | + |
| | | $Fecl_3$ test | + |
| 5 | Sterols | Lieberman Burchardt test | + |
| | | Salkowski test | + |

| | | | |
|---|---|---|---|
| 6 | Tannins and Phenolic Compounds | $FeCl_3$ test | + |
| | | Gelatin test | - |
| | | Lead acetate test | + |
| | | Alkaline reagent test | - |
| | | Mitchell's test | + |
| | | Elagic acid test | + |
| 7 | Fats and Oils | Stain test | + |
| | | Saponification test | + |
| 8 | Lignins | Labat test | - |
| | | Lignin(furfuraldehyde) test | - |
| 9 | Quinones | Alcoholic KOH test | - |
| 10 | Terpenoids | 50% $H_2SO_4$ Test | + |
| 11 | Anthraquinones | Benzene+ammonium hydroxide test | - |
| 12 | Anthocyanides | Methanolic HCl test | - |
| 13 | Coumarins | Alcoholic Sodium hydroxide | - |
| 14 | Proteins | Million's test | - |
| 15 | Carbohydrate test | Molish test | - |
| 16 | Indole test | Ehrlich reagent +alcoholic extract | - |
| 17 | Reducing sugars | Benedict's reagent test | - |
| 18 | Aminoacids | Ninhydrin test | - |

'+' Present, '--' Absent

## Anti-oxidant properties of *Strychnos colubrine*

### DPPH Method

**Table 2:** DPPH Mean values for Anti-oxidant properties of *Strychnos colubrine*

| Treatments | Concentration (µg/ml) | Absorbance at 517 nm | % Absorbance at 517 nm |
|---|---|---|---|
| Control | - | 1.68 ± 0.03 | 0.00% |
| Standard(Ascorbic acid) | 100 | 0.78 ± 0.03 | 53.57% |
| | 200 | 0.47 ± 0.06 | 72.02% |
| Methanolic Leaf extract of *Strychnos columbrina* | 100 | 0.82 ± 0.03 | 51.19% |
| | 200 | 0.57 ± 0.03 | 66.07% |

**Table 3:** One-way Anova of DPPH for Anti-oxidant property of *Strychnos colubrine*

| ANOVA | | | | | |
|---|---|---|---|---|---|
| Absorbance Value | | | | | |
| | **Sum of Squares** | **df** | **Mean Square** | **F** | **Sig.** |
| Between Groups | 2.734 | 4 | .684 | 490.579 | .000 |
| Within Groups | .014 | 10 | .001 | | |
| Total | 2.748 | 14 | | | |

**Table 4:** Dunnett's Post Hoc Test Analysis for DPPH of *Strychnos colubrine*

| Multiple Comparisons | | | | | |
|---|---|---|---|---|---|
| Dependent Variable: Absorbance Value | | | | | |
| Dunnett t (<control)[a] | | | | | |
| **(I) Treatment** | **(J) Treatment** | **Mean Difference (I-J)** | **Std. Error** | **Sig.** | **95% Confidence Interval** |
| | | | | | **Upper Bound** |
| Standard (Absrobic Acid ) 100 | Control - DPPH solution | -.89667* | .03048 | .000 | -.8215 |
| Standard (Absrobic Acid ) 200 | Control - DPPH solution | -1.20667* | .03048 | .000 | -1.1315 |
| strychnos columbrina 100 mg | Control - DPPH solution | -.86000* | .03048 | .000 | -.7849 |
| strychnos columbrina 200 mg | Control - DPPH solution | -1.10667* | .03048 | .000 | -1.0315 |
| *. The mean difference is significant at the 0.05 level. | | | | | |
| a. Dunnett t-tests treat one group as a control, and compare all other groups against it. | | | | | |

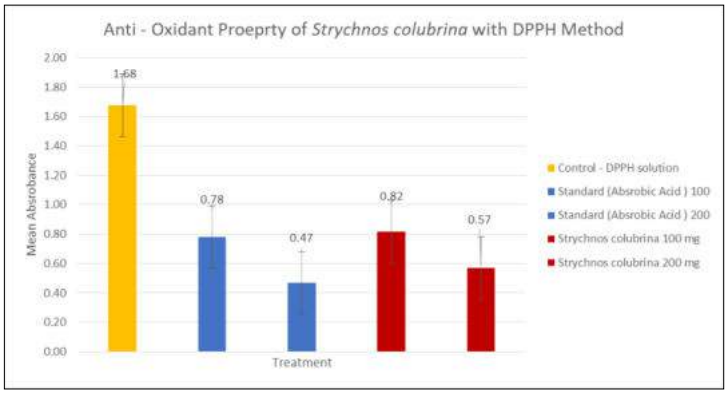



**Fig 2:** For DPPH method for Anti-oxidant property of *Strychnos colubrina*

### Nitric Oxide ($NO_3$) free radicals absorption method

**Table 5:** Mean values for $NO_3$ Free radical scavenging of *Strychnos colubrine*

| Treatments | Concentration (µg/ml) | Absorbance at 546 nm | % Absorbance at 546 nm |
|---|---|---|---|
| Control | - | 1.5 ± 0.03 | 0.00% |
| Standard (Ascorbic acid) | 100 | 0.63 ± 0.06 | 58.00% |
| | 200 | 0.34 ± 0.04 | 77.33% |
| Methanolic Leaf extract of *Strychnos columbrina* | 100 | 0.66 ± 0.06 | 56.00% |
| | 200 | 0.42 ± 0.04 | 72.00% |

**Table 6:** Anova of NO3 free radical scavenging test of *Strychnos colubrine*

| ANOVA | | | | | |
|---|---|---|---|---|---|
| Absorbance Value | | | | | |
| | **Sum of Squares** | **df** | **Mean Square** | **F** | **Sig.** |
| Between Groups | 2.550 | 4 | .638 | 289.829 | .000 |
| Within Groups | .022 | 10 | .002 | | |
| Total | 2.572 | 14 | | | |

**Table 7:** Dunnett's Post Hoc Analysis of NO3 test of *Strychnos colubrine*

| Multiple Comparisons | | | | | |
|---|---|---|---|---|---|
| Dependent Variable: Absorbance Value | | | | | |
| Dunnett t (<control)[a] | | | | | |
| **(I) Treatment** | **(J) Treatment** | **Mean Difference (I-J)** | **Std. Error** | **Sig.** | **95% Confidence Interval** |
| | | | | | **Upper Bound** |
| Standard (Absrobic Acid ) 100 | Control -nitric oxide | -.87333* | .03830 | .000 | -.7789 |
| Standard (Absrobic Acid ) 200 | Control -nitric oxide | -1.15667* | .03830 | .000 | -1.0622 |
| strychnos columbrina 100 mg | Control -nitric oxide | -.84000* | .03830 | .000 | -.7456 |
| strychnos columbrina 200 mg | Control -nitric oxide | -1.07667* | .03830 | .000 | -.9822 |
| *. The mean difference is significant at the 0.05 level. | | | | | |
| a. Dunnett t-tests treat one group as a control, and compare all other groups against it. | | | | | |

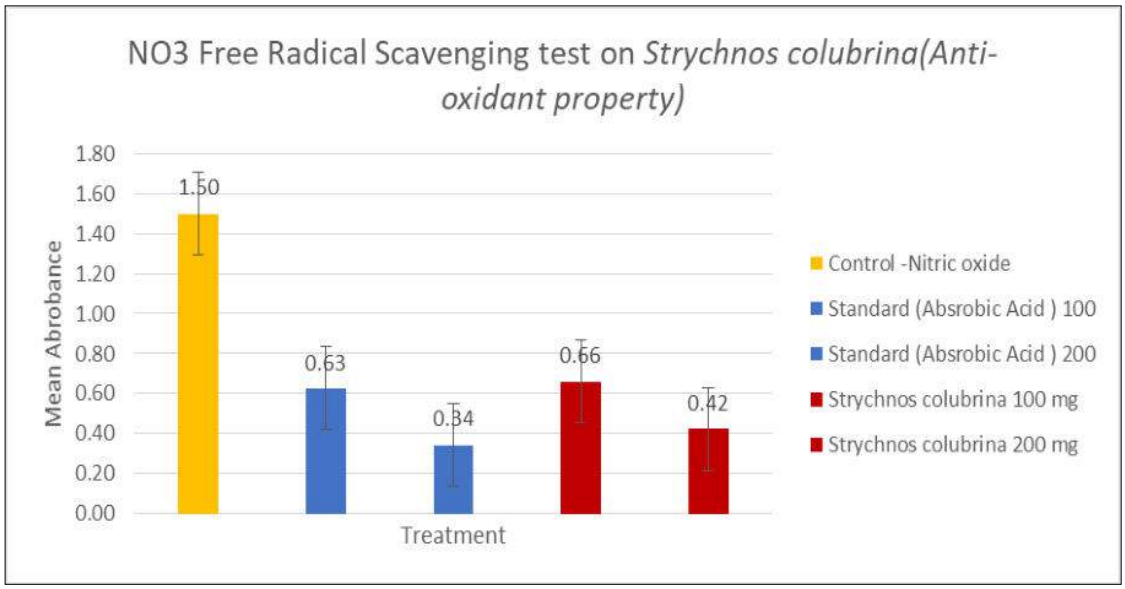



**Fig 3:** For NO3 Free Radical scavenging test of *Strychnos colubrina*

### Anti-microbial activity of and *Strychnos Columbrina*

**Table 8:** Anti-microbial property of *Strychnos Colubrina*

| Solvent extracts | Zone of inhibition in mm | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Names of microbes | | | | | | | | | | | |
| | ***Bacillus subtilis* (MTCC 441)** | ***Staphylococcus Aureus* (MTCC 737)** | ***Pseudomonas aeruginosa* (MTCC 1035)** | | | | | | | ***Candida albicans*** | | |
| Quantity (Micrograms) | 1000 | 500 | 250 | 1000 | 500 | 250 | 1000 | 500 | 250 | 1000 | 500 | 250 |
| Methanolic extract of *Strychnos Columbrina* | -N- | -N- | -N- | 17.7 ± 1.2 | 16.5 ± 0.5 | 15.5 ± 0.4 | -N- | -N- | -N- | -N- | -N- | -N- |

**Table 9:** 2-way Anova of Anti-microbial property of *Strychnos Colubrina*

| Tests of Between-Subjects Effects | | | | | |
|---|---|---|---|---|---|
| **Dependent Variable: Zone of Inhibition in mm** | | | | | |
| **Source** | **Type III Sum of Squares** | **df** | **Mean Square** | **F** | **Sig.** |
| Corrected Model | 1867.310[a] | 11 | 169.755 | 1055.474 | .000 |
| Intercept | 620.010 | 1 | 620.010 | 3854.984 | .000 |
| Dosage | 1.820 | 2 | .910 | 5.658 | .010 |
| Microbe | 1860.030 | 3 | 620.010 | 3854.984 | .000 |
| dosage * microbe | 5.460 | 6 | .910 | 5.658 | .001 |
| Error | 3.860 | 24 | .161 | | |
| Total | 2491.180 | 36 | | | |
| Corrected Total | 1871.170 | 35 | | | |
| a. R Squared =. 998 (Adjusted R Squared =. 997) | | | | | |

**Table 10:** 2-Scheffe's Post Hoc analysis of Anti-microbial property of *Strychnos Colubrina*

| Multiple Comparisons | | | | | | |
|---|---|---|---|---|---|---|
| **Dependent Variable: Zone of Inhibition in mm** | | | | | | |
| **Scheffe** | | | | | | |
| **(I) microbe** | **(J) microbe** | **Mean Difference (I-J)** | **Std. Error** | **Sig.** | **95% Confidence Interval** | |
| | | | | | **Lower Bound** | **Upper Bound** |
| Bacillus subtilis | Staphylococcus aureus | -16.6000* | .18905 | .000 | -17.1680 | -16.0320 |
| | Pseudomonas aeruginosa | .0000 | .18905 | 1.000 | -.5680 | .5680 |
| | Candida albicans | .0000 | .18905 | 1.000 | -.5680 | .5680 |
| Staphylococcus aureus | Bacillus subtilis | 16.6000* | .18905 | .000 | 16.0320 | 17.1680 |
| | Pseudomonas aeruginosa | 16.6000* | .18905 | .000 | 16.0320 | 17.1680 |
| | Candida albicans | 16.6000* | .18905 | .000 | 16.0320 | 17.1680 |
| Pseudomonas aeruginosa | Bacillus subtilis | .0000 | .18905 | 1.000 | -.5680 | .5680 |
| | Staphylococcus aureus | -16.6000* | .18905 | .000 | -17.1680 | -16.0320 |
| | Candida albicans | .0000 | .18905 | 1.000 | -.5680 | .5680 |
| Candida albicans | Bacillus subtilis | .0000 | .18905 | 1.000 | -.5680 | .5680 |
| | Staphylococcus aureus | -16.6000* | .18905 | .000 | -17.1680 | -16.0320 |
| | Pseudomonas aeruginosa | .0000 | .18905 | 1.000 | -.5680 | .5680 |
| Based on observed means. The error term is Mean Square (Error) =. 161. | | | | | | |
| *. The mean difference is significant at the. 05 level. | | | | | | |

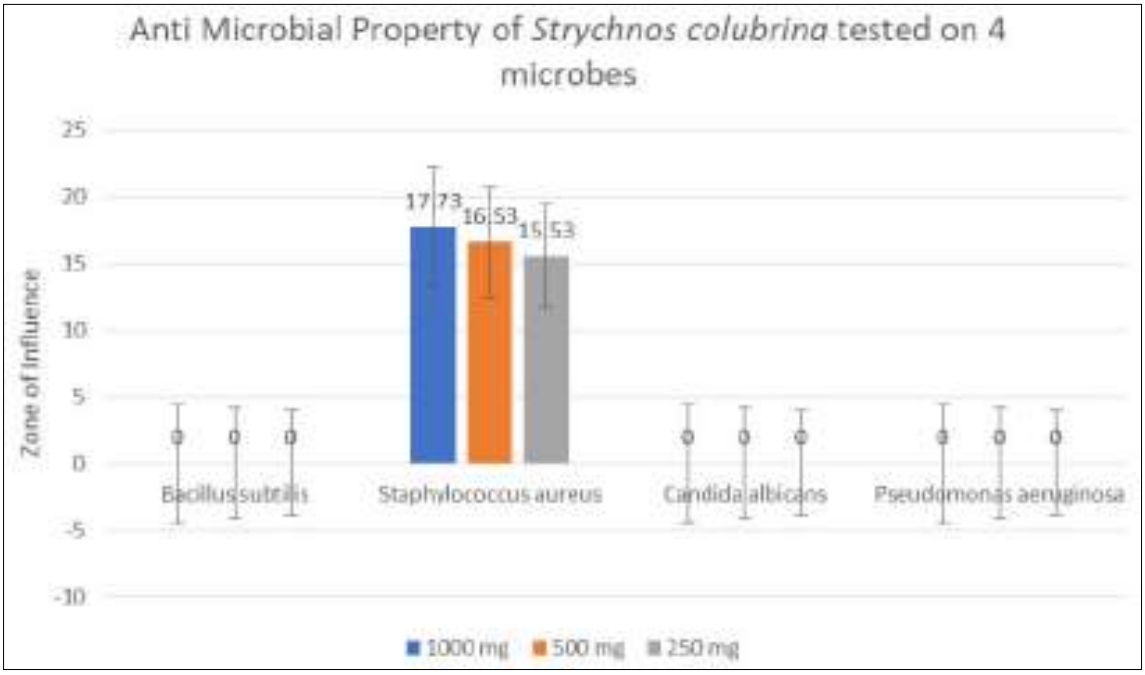



**Fig 4:** Anti-microbial property of *Strychnos Colubrina*

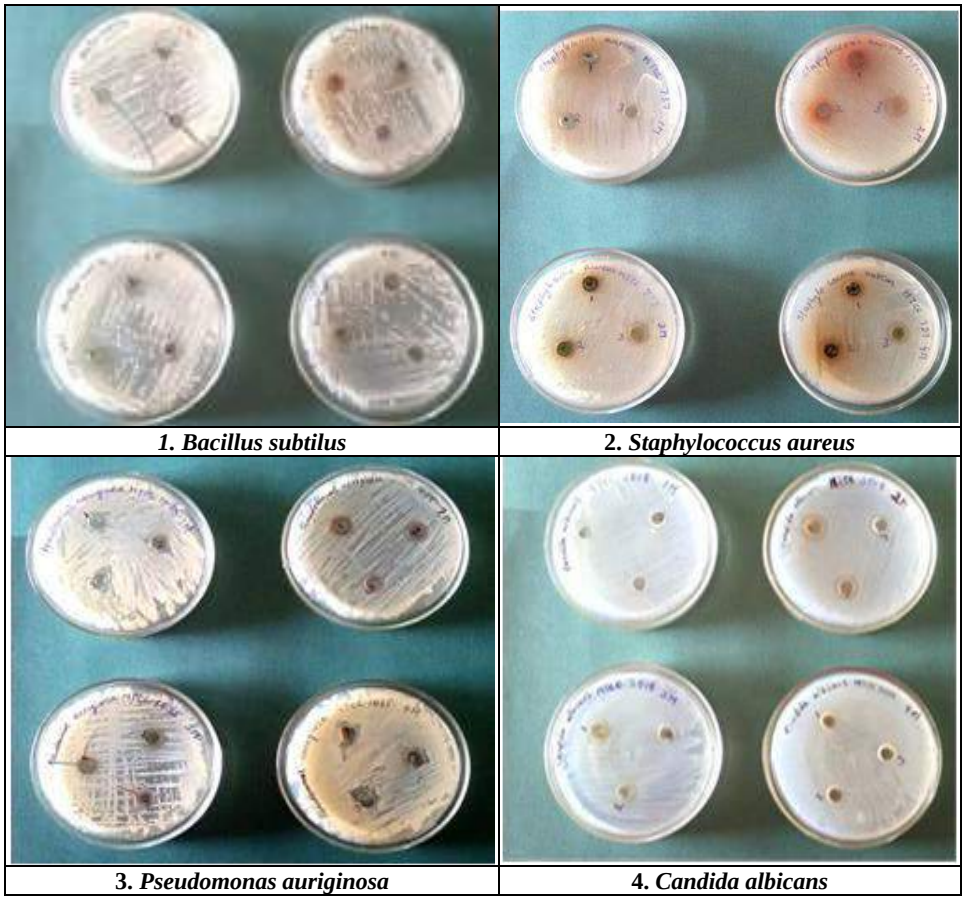



**Fig 5:** Plates with Anti-microbial activity

## Conclusion

**The phytochemical studies:** These studies have been carried out during the present study for preliminary screening of secondary metabolites and qualitative analysis of whether these compounds are present or not in various taxa. These studies act as an identification marker of genuine plant-based drugs. In the preliminary phytochemical studies, the tannins, phenolic compounds, alkaloids, flavonoids, saponins, fats, oils, terpenoids are known to present in *Strychnos colubrina.* Whereas glycosides, lignins, quinones, anthraquinones, anthocyanides, coumarins, carbohydrates, reducing sugars and aminoacids and Sterols are found to be absent in this plant

**The anti-oxidant activity of *Strychnos Colubrina:*** Phytochemical analysis of the extracts has shown the presence of some flavonoids and phenolics. These compounds give antioxidant effect, and this can be used for drug extractions from *Strychnos colubrina* in the future. Quantitative analysis of these bio-active constituents in *Strychnos colubrina* leaves have to be further investigated in the future. They can become potent antioxidants.

**Anti-microbial activity of *Strychnos Colubrina:*** The present study reveals that *Strychnos Colubrina* leaf extracts have significant detrimental effect on one of three bacterial strains used i.e, *Staphylococcus aureus* and it shows no effect on other two bacteria namely, *Bacillus subtilis, Pseudomonas aeruginosa* and a fungal strain namely *Candida albicans.* Methanolic plant extract generally contain various potent phytochemicals in mixed form. This may be the reason for the lesser inhibitory effect shown by leaf extract when compared to that exerted by proven antibiotics. For the study of plant extracts, the number of microbial strains was reduced in accordance with their known function as food destroying agents and human pathogens. The methanolic extract of plant leaves of *Strychnos colubrina* has not earlier been reported to have anti-microbial activity.

As discussed above, medicinal plants are at the mainstay in the treatment of diseases for the vast majority of tribal and rural people. As the present study reveals the potential of these medicinal plants, further research can be directed to probe into the structure and mechanism of action of the bioactive therapeutic principles for development of drugs to treat various diseases that affect the mankind. Phytochemical screening of ethno-medico-botanical species indicated the presence of numerous potential chemical constituents which have high therapeutic value. Thus, the phytochemical studies of this species may lead for further investigations to find out drugs of importance. The present study concludes that the plant species with numerous highly effective phytochemical compounds like saponins, alkaloids, terpenoids, steroids, lignins, tannins, indoles, anthroquinones and several types of anthocyanidins, phenolic compounds, flavonoids and lipid compounds having many medicinal applications, used in wide range of formulations, commercial, higher therapeutic and economic values. Biological activity conducted in screening the medicinal properties of selected plant material of methanolic extracts of leaves of *Strychnos colubrina* has proven as antibacterial and anti-oxidant, agent. It is, therefore, implied that the isolation and proper characterization of the active

constituents from the extracts of the select plant species as possible antioxidant, antimicrobial agent is possible. Quantitative analysis of the active compounds in *Strychnos colubrina L.* leaf extracts should be further studied. Hence this report provides insights into the therapeutic potential of the phytomedicine and scope for further research on these drugs. Further investigations must be carried out from this research for the benefit of human welfare. The present screening may also be useful for continuing, future research mainly in the field of pharmaco toxicology.

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# The Role of Implementing Deep Learning applications in enhancing health care services during COVID-19

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**ABSTRACT**
*Due to the sudden pandemic outbreak across the globe, global physicians have witnessed the necessity of implementing Deep Learning Applications to save a life more quickly and efficiently. Researchers in the research study have pointed out the implementation of deep learning applications from an effective angle. Researchers have outlined a series of relevant survey questions to gather and understand almost 60 participants' perspectives about the utilization of deep learning methods in healthcare more accurately. It has been observed that deep learning can be highly used to satisfy the growing requirements for diagnosis and medicines during the pandemic outbreak. However, by applying a positivism research philosophy, researchers have effectively conducted the primary analysis through a probability data sampling technique. From the research findings, it can be analyzed that around 60% of the participants strongly support the idea of utilizing deep learning for mitigating more error percentages while predicting necessary treatment procedures. On the other hand, around 57% of the people can be traced to highly support the implementation of deep learning approaches for enhancing overall industrial efficiency during the time of crisis. Moreover, around 25% of the participants also can be spotted who only agreed with the use of DL approaches in medical imaging for better patient-care approaches. From the survey results, it can be determined that selected participants possess a lack of proper understanding regarding the beneficial use of deep learning applications in enhancing future healthcare practices in the post-COVID situation.*
***Keywords:*** *Deep-learning applications, patient-care, global pandemic, healthcare survey, researchers, participants, and efficiency.*

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## INTRODUCTION

Modern-day medical science has witnessed several benefits in patient-care facilities after utilizing machine learning and deep learning applications. Detecting critical symptoms of diseases, predicting proper treatment procedures and medical image recognition have become easier than before with the applications of deep learning approaches [1]. During the time of the global pandemic, the demand for deep learning applications has increased for evaluating the accurate medical history of patients, detecting symptoms of diseases, and necessary tests [2]. Researchers have investigated that Natural language processing through DL language offers better insights regarding relevant clinical information during the virus outbreak to determine the most accurate clinical treatments. It has been highly observed that deep learning approaches can quickly acquire COVID-affected patient insights that at once provide utter benefits to the healthcare industry while discovering major aspects across patient care.

The ML-based deep learning algorithms played a major role in enhancing the overall efficiency of the UK-based healthcare industry, by almost 89.97% from 2019 to 2021 [3]. Regarding the harmful effects of the pandemic outbreak, numerous online surveys, as well as clinical resources, have been gathered from various patient-care sectors of the UK. During the past few years, the entire world has experienced a strong blow from the COVID-19 global pandemic. Surveys and reports reflected that the rapidly spreading virus at once raised the death rate to around 82.83% across entire Europe during the time [4]. Besides,

deep learning alos helps in corona virus imaging from the large medical image database. Moreover, the DL applications can raise the overall efficiency of patient-care facilities during the virus outbreak that leads to an almost ***80%*** drop in the global economy over those years [5].

**LITERATURE REVIEW**

Researchers opine that only the effective applications of the DL approaches can remove around ***37%*** of the economic slump due to the uncertainty that has engulfed the healthcare sector [6]. Moreover, the application of AI-based machine learning approaches also helped physicians to conduct proper tests and diagnose Corona virus's effects in the host's body. Various researches conducted across the UK-based healthcare industry reflect that around ***78%*** of the medical practitioners strongly support the implementation of DL insights in analyzing relevant clinical information [7]. In order to undertake proper diagnosis and treatment procedures for patients' easy recovery, DL approaches provide utter assistance to global healthcare professionals.

Scientists have discovered various applications of deep learning in global healthcare practices while tracking essential medical devices and equipment. During the time of the global pandemic, physicians widely utilized deep learning applications to predict the level of patients' illness through COVID tests [8]. Apart from this, DL approaches also aided physicians to undertake proper treatment methods by keeping the patient in isolation and providing him with necessary clinical assistance [9]. The disease can spread with high contacts, so physicians use deep learning techniques while sanitizing and providing COVID-affected patients with proper medical help.

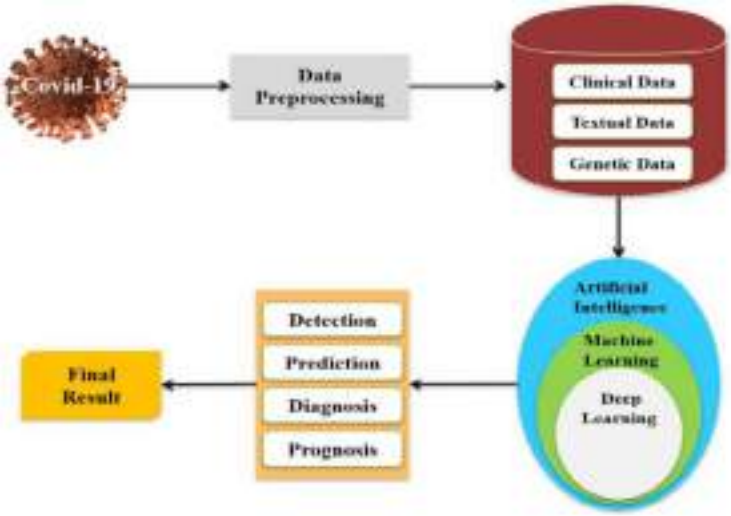



**Figure 1: Deep learning framework for detecting and diagnosing Corona virus syndromes**[9]

On the other hand, medical scientists have placed their opinions and research findings on the use of ML and DL approaches for offering people vaccines to combat the harmful virus. Based on their decade-covering research findings, researchers have come to a satisfactory point that deep learning approaches can be highly used in the vaccination and immunization process. As a result, accurate use of DL techniques can enhance the overall efficiency rate of the healthcare industry by around ***91.26%*** in the sustainable future [10]. With the proper use of DL algorithms, physicians can easily predict the reasons and symptoms of population health threats by determining the virus' patterns (Fig. 2). On the contrary, deep learning can also help doctors to treat the ways of mitigating the high risk of surfacing rates towards a pandemic disease progression in the future patient-care delivery.

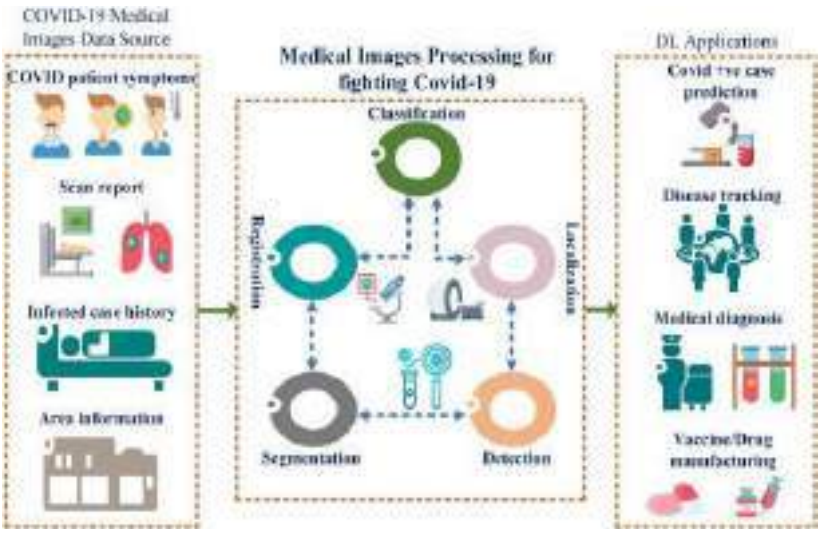



**Figure 2: Medical image processing by using deep learning methods during the pandemic**[10]

Effective use of DL techniques at once leads the entire healthcare industry towards a more accurate predictive analysis that can mitigate the death rate by ***41%*** more in the upcoming years [11]. The growing implementations of DL learning during the years ***2019-2021***, aided healthcare practitioners to recover ***52.83%*** of the pandemic loss more efficiently [12]. With the growing cases of Corona, physicians feel a need to conduct more innovation, development, and improvement in the application procedures of deep learning in the recent era (Fig. 3). During the detection and diagnosis of COVID-19 disease syndromes, ***63.85%*** of scientists and doctors prefer the use of relevant wearable clinical technology incorporated with AI systems [13]. From a remote place and with the help of neural networks across the vast Internet, efficient healthcare practices can be easily regulated by DL algorithms.

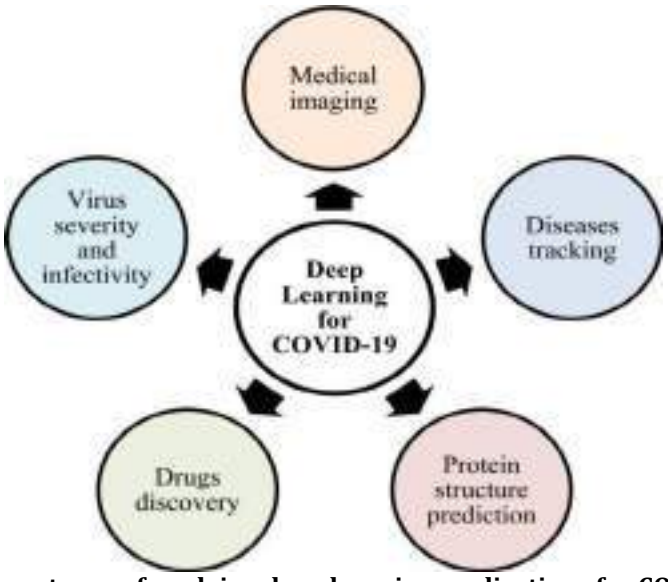



**Figure 3: Importance of applying deep learning applications for COVID-19**[13]

However, to serve patients in a better way during the global crisis, deep learning offers physicians the acquisition of meaningful as well as long-lasting language-based learning [14]. Apart from this, deep learning also enhances critical disease diagnosis operations at cheaper expenses during the global pandemic [15]. As a result, researchers show genuine interest to examine the role of DL applications in treating Corona cases more precisely besides offering more personalized patient care during the current era.

## MATERIAL AND METHODS

It has been also observed that proper use of deep learning has escalated the entire economic growth by ***47%*** much bigger than the COVID-years' revenue collection [16]. Researchers in this research paper thus

utilized various effective research methodological approaches to determine the role played by DL in enhancing patient care during the pandemic period. Researchers while scrutinizing the research study have undertaken a Primary Quantitative method for relevant medical collection for understanding the current research topic more clearly.

Researchers have applied quantitative methods for both collecting and analyzing current medical records to get an idea about the harmful impacts of the Corona virus [17]. In order to investigate more on the usefulness of using DL approaches during pandemic times, researchers have framed relevant survey questions by incorporating a positivism research philosophy in the research paper. They have also applied a deductive research method while gathering authentic and valid clinical data. On the other hand, during carrying out relevant research on the use of DL in healthcare, researchers have also pointed out the significance of incorporating a descriptive research design to collect and evaluate necessary patient-care records related to the research topic more accurately. However, the primary data involvement would be highly beneficial for conducting the research by reducing relevant challenges faced by the researchers during the global pandemic crisis.

After collecting relevant opinions from physicians, clinical practitioners, patient-care professionals, healthcare staff, and hospital nurses, researchers focused much on comprehending the consequences of implementing DL for acquiring more proper results. Researchers have focused much on collecting relevant responses from around 70 participants through survey analysis. However, around 10 participants did not help researchers during the conduction of the research study regarding the role of the DL approach for increasing better healthcare deliveries through virtual mediums. Researchers have outlined three important survey questions while collecting virtual binary responses through options from around 60 participants. Besides, the detailed survey analysis at once involves the accuracy as well as the relevance connection with the use of DL approaches in healthcare during the pandemic outbreak. Researchers have performed probability methods during gathering sampling. However, all opinions of the participants have been gathered and analyzed through undertaking a random selection of people directly linked with the topic of the research. After collecting their responses, all the survey outcomes have been analyzed in detail by the researchers.

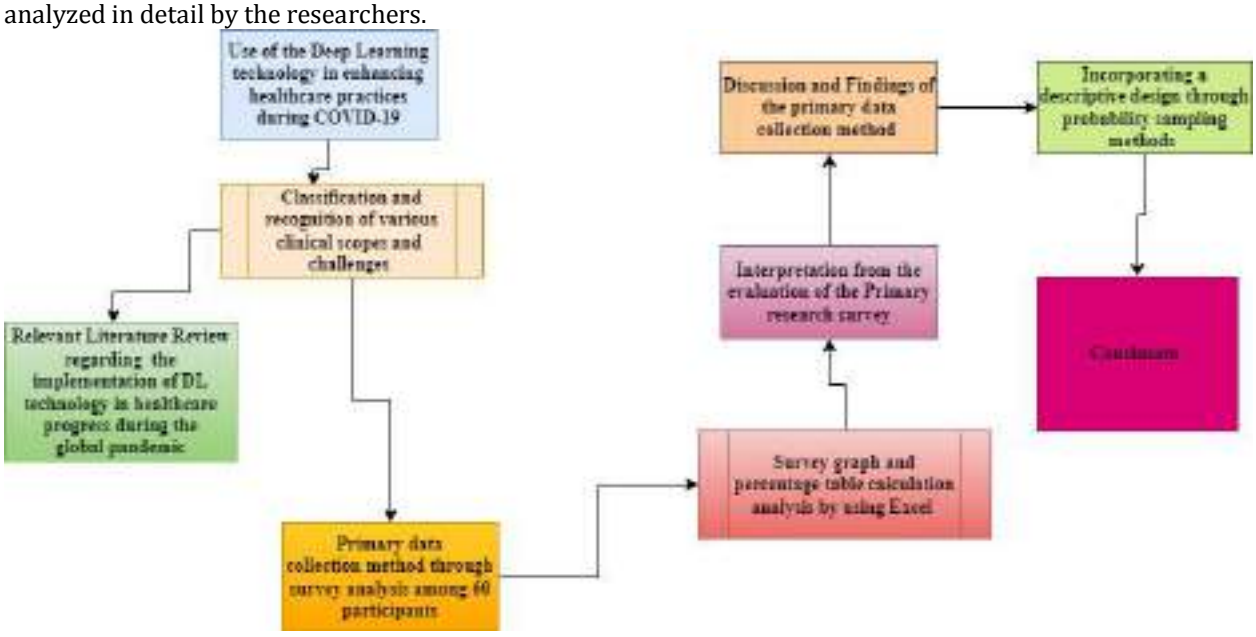



**Figure 4: Flowchart diagram of the research**

## RESULTS

Researchers have focused on acquiring relevant medical records by applying probability techniques while comprehending the necessities of analyzing participants' responses from an effective perspective. Apart from the survey questionnaires, researchers have framed two additional research questions for evaluating all the survey outcomes more efficiently. The important questions created by the researchers regarding the particular topic are-

- What are the benefits and scopes offered by deep learning approaches towards increasing the efficiency rate of better healthcare services during the global pandemic?

- How can deep learning applications enhance the accuracy detecting rate in healthcare by mitigating errors and risks in the sustainable future?

***Survey-related questions***

**Q1.** Do you think that deep learning applications can reduce error percentage rates during predicting treatment analysis regarding Corona virus detection across the healthcare industry?

**TABLE I. ERROR MITIGATION RATE CALCULATION IN HEALTHCARE BY USING DL TECHNIQUES**

(SOURCE: CREATED BY THE RESEARCHERS)

| Participants' choice | Overall Participants | Response gathered | Percentage |
|---|---|---|---|
| **Strongly Agreed** | 60 | 19 | 31.66 |
| **Supported** | 60 | 17 | 28.33 |
| **Remained Neutral** | 60 | 3 | 5 |
| **Disagreed** | 60 | 11 | 18.33 |
| **Disagreed Strongly** | 60 | 10 | 16.66 |

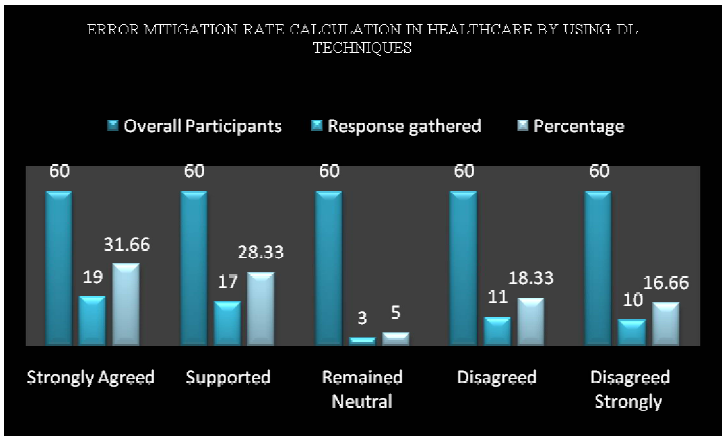



**Figure 5: Error mitigation rate calculation in efficient healthcare practices during the pandemic by using DL approaches**

Researchers have analyzed the first survey question by evaluating all the collected responses from the ***60 participants***. From the above percentage table, it can be highly evident that around ***31.66%*** of the people have strongly supported the validity of the question. Besides, around ***28.33%*** of the participants positively supported this approach. However, only ***5%*** of the people remained neutral regarding the error mitigation rate measurement due to deep learning approaches in healthcare. During the time of the global pandemic, it has been found that around ***18.33%*** of the participants denied the idea of using DL approaches in detecting Corona virus by eliminating the conventional process. On the contrary, researchers have traced around ***16.66%*** of people who strongly disagreed with the relevancy of the first survey question. Relevant calculation gaps and percentage differences have been highly evaluated from the calculation table.

**Q2.** Do you support that accurate application of deep learning can enhance the overall efficiency of healthcare towards improved patient care during the pandemic outbreak?

**TABLE II. HEALTHCARE EFFICIENCY RATE MEASUREMENT BY APPLYING DEEP LEARNING**

| Options of the Participants | Total Participants | Response Collected | Percentage |
|---|---|---|---|
| **Strongly Supported** | 60 | 21 | 35 |
| **Agreed** | 60 | 13 | 21.66 |
| **Stayed Neutral** | 60 | 5 | 8.33 |
| **Disagreed** | 60 | 12 | 20 |
| **Strongly Disagreed** | 60 | 9 | 15 |

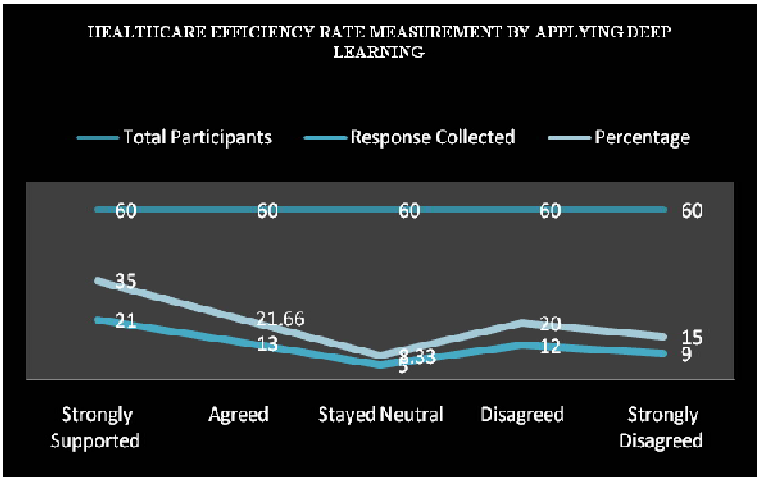



**Figure 6: Healthcare efficiency rate measurement in healthcare during the COVID outbreak by applying deep learning techniques**

In order to discuss the role of deep learning in increasing the overall effectiveness of the healthcare sectors, researchers have focused more on analyzing the second survey question. After analyzing participants' responses regarding the particular survey question, researchers have pointed out that around ***35%*** of the people strongly support the use of DL technology in mitigating corona virus-related death risks. On the other hand, among *60 potential participants*, around ***21.66%*** of the people supported the idea of the second survey topic. However, from the table, it can be highlighted that only ***8.33%*** of the participants did not provide any positive response regarding the use of DL techniques for better patient-care approaches. Apart from this, researchers have also spotted almost ***20%*** of the people who disagreed with the relevancy of the second question. Further, among the participants, almost ***15%*** of people can be identified who strongly rejected the validity of the second survey question related to the research topic. All the major percentage gaps can be minutely analyzed from the percentage calculation table to understand the importance of applying deep learning approaches in healthcare aspects.

**Q3.** Will proper deep learning implementation help in better corona virus disease imaging from large datasets for more improved patient-care service delivery?

**TABLE III. MEDICAL IMAGING EFFICIENCY RATE CALCULATION BY USING DEEP LEARNING**

| Participants' options | Total number of Participants | Collected Opinions | Percentage |
|---|---|---|---|
| **Supported Strongly** | 60 | 8 | 13.33 |
| **Supported** | 60 | 7 | 11.66 |
| **Neutral** | 60 | 4 | 6.66 |
| **Did not support** | 60 | 23 | 38.33 |
| **Disagreed Strongly** | 60 | 18 | 30 |

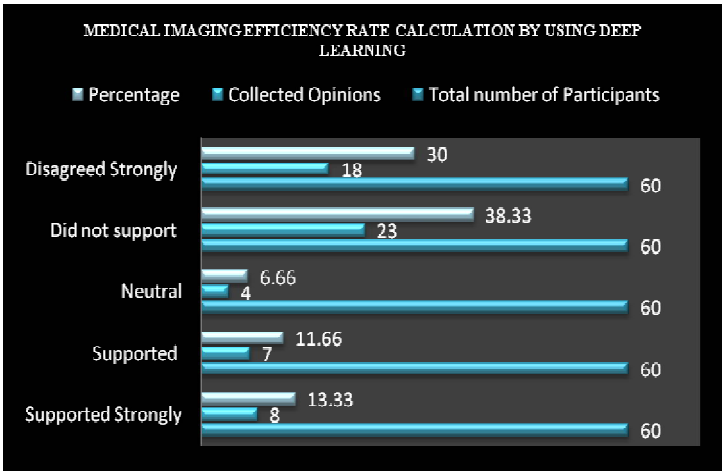



**Figure 7: Medical imaging rate measurement during the pandemic outbreak by using DL methods**

While analyzing the third survey question, researchers have experienced a sudden shift in the opinions of participants from a positive angle to a negative point. In order to investigate the role of DL approaches in combating COVID syndromes, researchers have collected and evaluated opinions from ***60 participants*** regarding the efficient conduction of clinical images. From the above analysis, it can be stated that around ***13.33%*** of the participants have strongly supported the idea of using DL approaches for more accurate medical imaging. Besides, almost ***11.66%*** of the people can be highlighted from the participants who positively agree with the third relevant survey question. However, researchers have pointed out only ***6.66%*** of the participants did not provide any responses positively or negatively related to the research topic. On the contrary, researchers have spotted almost ***38.33%*** of the people who provided negative responses regarding the relevance of the third research question. Moreover, around ***30%*** of the participants strongly denied the usefulness of the third survey topic in healthcare sectors. From the above growth and percentage calculation table, all the key differences can be highly observed to a great extent.

**DISCUSSION**

From the survey findings, it can be analyzed that researchers have successfully analyzed all the perspectives of almost 60 potential participants for understanding the research topic more clearly. After evaluating all the 3 survey results, researchers examined that participants have different changing opinions regarding the scopes offered by deep learning approaches. However, during the pandemic outbreak, all the responses regarding healthcare practices have been conducted effectively through online and contactless mediums. The result from the first question related to the survey at once reflects that almost 60% of the participants agreed with the usefulness of the DL application for more error reduction practices and obtaining more accurate results from a positive approach. With the effective solutions of Deep learning Applications, healthcare professionals can effectively deliver personalized facilities of patient care. Moreover, researchers have also determined that with the growing utilization of deep learning algorithms in healthcare, the overall growth is expected to be around 98% within the year 2026 [18].

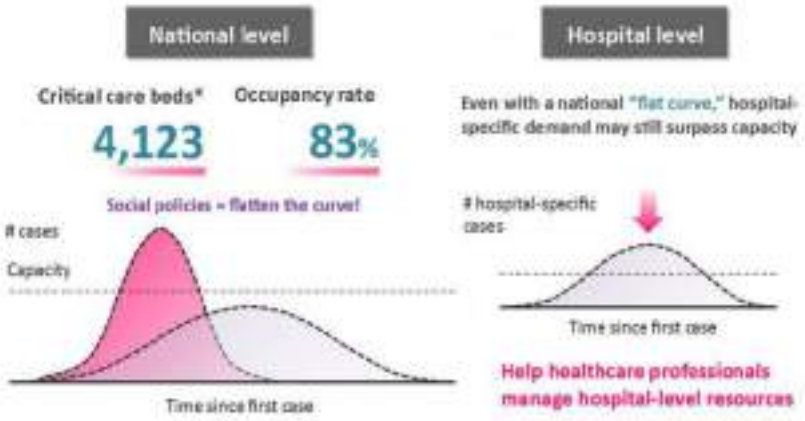



**Figure 8: Graph reflecting the use of deep learning approaches during the global pandemic for better healthcare supports**[18]

On the other hand, from the analysis of the second survey question, researchers can highly identify the causes of applying deep learning. However, in the diagnosis of COVID-related diseases, DL approaches at once can increase the efficiency of the entire industry by almost ***51.26%*** in the sustainable future. It has been analyzed from the second survey outcome that around ***57%*** of the people have supported the idea of utilizing deep learning for better healthcare conduction in the post-COVID future. Scientists have identified that to eradicate life threats and infection risks due to the Corona virus, DL applications can at once be highly beneficial for life-saving clinical practices [19]. Towards enhancing more accurate and beneficial healthcare services across the globe, deep learning benefits at once inspire scientists to investigate more on satisfying the growing demands for medicines.

**TABLE IV: ANALYSIS OF THE SURVEY OUTCOMES REGARDING THE APPLICATIONS OF DEEP LEARNING IN PATIENT-CARE PRACTICES**

| *Topic Discussed* | *Supported* | *Neutral* | *Disagreed* |
|---|---|---|---|
| (a) Deep learning is essential for mitigating error percentage while undertaking relevant healthcare decisions during COVID-19. | **60%** | **13%** | **27%** |
| (b) Relevant use of deep learning can at once increase the overall efficiency of healthcare practices. | **57%** | **9%** | **34%** |
| (c) During the time of the pandemic outbreak, deep learning has helped physicians in detecting proper medical imaging of coronavirus disease. | **25%** | **15%** | **60%** |

From the third survey question analysis, researchers can at once conclude that during the outbreak of the global pandemic, deep learning assisted healthcare practices to some extent. As people have no accurate understanding of the technical implications of deep learning in medical image processing, a large shift from positivity can be seen while collecting participants' opinions. After analyzing the validity of the third survey question, researchers have pointed out that only ***25%*** of the people have shared their positive responses along with the third survey opinion [20]. The deep learning approaches in healthcare practices can help medical professionals to evaluate big medical data sets consisting of patients' history and essential data records. While treating the corona virus syndromes, doctors widely used deep learning medical imaging techniques to pull together the affected person's insights [21]. Deep learning algorithms at once enable healthcare professionals to offer personalized healthcare facilities to global patients by examining a patient's clinical history and records [22]. With the implementation of the deep learning approaches, detecting corona virus symptoms has been more efficient these days. Moreover, the entire evaluation of survey results shows the significant applications of deep learning in increasing more sustainable patient-care practices during the global pandemic outbreak.

## CONCLUSION

Nowadays, machine learning, transfer learning, and deep learning approaches are being broadly used in global healthcare sectors by medical scientists. Previously, physicians faced a lot of challenges while detecting diseases and conventionally predicting necessary treatment procedures. However, with the advent of various AI-based technological approaches, the healthcare industry has experienced huge progress while monitoring patients across the globe. People started being widely affected by the attack of Coronavirus and as a result, the global healthcare industry was adversely affected during the year ***2019-21***. Scientists and physicians have investigated minutely the medical uses of DL applications while detecting proper COVID syndromes or predicting necessary diagnostic procedures [23].

Researchers have identified that with the proper utilization of deep learning algorithms, the overall healthcare efficiency could be amplified much better during the period of the global pandemic. Maintaining proper AI-based deep learning approaches can help physicians to conduct improved patient-care facilities in the sustainable future. However, to combat the global disease, researchers have witnessed the need for applying deep learning language in healthcare practices. However, researchers have gathered and interpreted all the outcomes of COVID-related clinical records through primary sources. Researchers by presenting three relevant survey questions to the participants have asked their opinions about COVID-related medical practices. Survey researchers have submerged themselves into evaluating all the responses collected from the participants for determining accurate results and incorporating them into the study.

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ORIGINAL ARTICLE

# Extraction of novel biosilica from finger millet husk and its coconut rachilla-reinforced epoxy biocomposite: mechanical, thermal, and hydrophobic behaviour

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## Abstract

High-toughness epoxy biocomposites are made in the current work employing coconut rachilla fibre and biosilica particles recovered from finger millet husk (FMH) for lightweight and affordable technological applications. The purpose of this study is to determine the impact of FMH biosilica particles added at various concentrations on the mechanical and wear properties, as well as the thermal and hydrophobic behaviour, of epoxy composites made from coconut rachilla fibre. The combination of 3 vol.% FMH biosilica particle with surface-treated palmyra sprout fibre as a reinforcing material has the highest tensile strength, impact strength, flexural strength, and hardness with 155 MPa, 6.17 J, 183 MPa, and 92 D-shore, respectively. The coconut rachilla fibre and FMH biosilica-generated epoxy composite have the lowest specific wear rate and coefficient of friction (COF) of 0.006 $mm^3$/Nm and 0.42, respectively, with the addition of 5 vol% FMH biosilica particles. These composites also exhibit excellent thermal properties having maximum first decomposition temperature of 342 °C and glass transition temperature of 102 °C. Additionally, these composites keep their hydrophobic properties indefinitely, and the ERB3 composite has the lowest contact angle at 81°. These epoxy composites having improved mechanical, thermal, and wear properties may be helpful in a range of engineering applications that can use for high load bearing capacity and biodegradability, such as sporting goods, automobiles, home furnishings, food packaging, transport, and aircraft.

**Keywords** Composites · Natural fibre, Biomass, Filler · Mechanical properties · Hydrophobicity

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## 1 Introduction

In recent years, demand for natural fibres and composites made from them has increased significantly for new advance materials for engineering. Natural fibres are employed primarily for the reason that they are affordable, lightweight, simple to produce, renewable, recyclable, need less energy from fossil fuels, and most importantly they have a high specific strength to weight ratio [1, 2]. Growing demand for environmentally friendly materials has caused a paradigm change in favour of natural fibres alternative to synthetic fibres and culminating in the creation of these materials [3, 4]. Being versatile, the natural fibre composites are particularly desirable in many sectors like automobile, drug or food storing, sporting goods, and light weight applications [5, 6].

However, due to the hydrophilic nature of natural fibres and hydrophobic nature of resin does not yield suitable outcomes in natural fibre polymer composites [7]. As a result, the surface of the natural fibres might be surface treated before being incorporated into the polymer as a main reinforcement. Natural fibres can have their loosely bound cellulose and hemicellulose removed through surface treatment. To improve the quality of the fibre-polymer matrix interface, a variety of chemical processes are used to modify the surface of natural fibres, including alkali treatment, benzoyl peroxide treatment, silane treatment potassium permanganate treatment, acetic acid treatment, isocyanate treatment, bleaching, and graft copolymerization treatment, which will improve the fibre's interface interaction with the matrix [8]. The most used chemical treatment for natural fibres is alkali treatment and silane treatment [9]. Alkali treatment removes the lignin, hemicellulose, wax, and other natural impurities, while during silane treatment, the silane molecules attached to the cellulose improves the interaction between the polymer matrix and fibre by increasing reaction sites and surface roughness [10]. In this research work, the combined alkali-silane treatment is used for the surface treatment of fibre. Researchers have looked into using natural plant fibres such as jute, sisal, bamboo, flax, cornhusk, banana, and ramie as a reinforcement material in composites [11, 12].

Murugan et al. [13] studied the silane-treated aloe vera/hemp/flax-reinforced epoxy composite. They demonstrated that the addition of silane-treated hybrid fibre has the highest normalised strength of 98% and low velocity impact damage. Arun Prakash et al. [14] examined the silane-treated *Caryota urens* fibre as a reinforced material in epoxy composite and study their mechanical, thermal, and fatigue behaviour. They found that the incorporation 30vol% fibre in the resin shows the highest fatigue cycle of 18,315 for 25% of maximum tensile stress and highest interlaminar shear strength of 28 MPa. Likewise, to these natural lignocellulosic fibres, coconut rachilla fibre is a new entry which basically obtained from stem of coconut plant and potentially used as reinforcement material in a polymer composite. Akter et al. [15] investigated the mechanical properties of coconut spathe fibre-reinforced HDPE composite. They revealed that tensile strength, flexural strength, impact strength, and hardness of HDPE are enhanced by 5% with the incorporation of coconut spathe fibre.

Furthermore, in order to achieve the appropriate properties for polymer composites, particle reinforcing may be just as important as fibre reinforcement. The particles might improve the composite distinctive properties such as mechanical, thermal, wear properties, and damping properties. Numerous ceramics, nanoparticles, and metallic particles are frequently employed to form composites; however, innovative bio-based particle types are gaining popularity for usage in multi-dimensional composites [16]. Bio-based particles produced from domestic, animal, or marine waste may also be used as filler in composites [17]. These agricultural wastes might be transformed into beneficial bioceramics, which would minimise pollution, increase process economy, and help with solid waste management [18]. Poomathi et al. [19] conducted a study on red matta rice husk ash-extracted biosilica particles' derived epoxy composites. They found that with incorporation of biosilica particles, there is improvement of mechanical and fatigue behaviour of composite. Jayabalakrishnan et al. [20] evaluated the mechanical, dielectric, and hydrophobic behaviour of epoxy composites fabricated with biochar particle extracted from coconut shell. They found that composites with 5vol.% biochar particles has maximum mechanical strength. While the composite with 7 vol.% has highest dielectric constant with 6.2 and high hydrophobic contact angle of 70°. Similarly, Gairola et al. [21] explore the crop residual waste extracted from finger millet husk (FMH) and barnyard millet husk (BMH) and its potential in thermoplastic composites. They demonstrated the FMH-reinforced composite exhibits better mechanical properties as compared to BMH-reinforced composites.

The objective of the current study is to determine the advantages of employing biosilica extracted from finger millet husk and the development of a unique fibre made from coconut rachilla as a reinforcement material. The main objective of the current study is to determine how the high-performance epoxy composite's mechanical, wear, thermal, and hydrophobic behaviour is affected by coconut rachilla fibre and FMH biosilica particles.

## 2 Material and methods

### 2.1 Materials

As reinforcements, coconut rachilla fibre with dimensions of 300–400 mm in length, 0.2 µm in diameter, and 0.94 g/cc is acquired from regional farms in Tamil Nadu, India. Fig. 1

shows how coconut rachilla fibre is prepared. Usually the green coconut rachilla was soaked in the water for 2 weeks. Then, it was dried in sun light for easy removal of fibre. The top thick lignin layer is removed in the soaking period and the fibre bundle alone remains. Finally the fine fibre was extracted using hammering process. The prepared fibre contains cellulosic content of 30–38%, semi-cellulosic content of 13–18%, holo-cellulose of 8–16%, lignin of 28–38%, and wax content of 1–3%. This fibre has tensile strength of 380 MPa, young's modulus of 9.3GPa, and density of 1.35 g/cc, whereas the other peer group natural fibres such as cotton, flax, hemp, jute, and kenaf have lesser physical properties than this fibre [22]. Finger millet husk is also collected from the local market for preparation of biosilica particles. Huntsman, India Pvt. Ltd. supplied the Araldite Epoxy Resin of grade LY556 and the hardener of grade HY591 used as the resin system. 3-Aminopropyletriethoxysilanesilane is used as a surface enhancer procured from Sigma-Aldrich by the USA (APTES). Another chemical like NaOH, HCl is provided by MERCK India Ltd.

## 2.2 Preparation of biosilica from finger millet husk

The finger millet husk (FMH) biosilica is synthesized using a thermo-chemical process. The FMH biosilica particles are prepared in two stages. The FMH are initially interlaced and lit using a separate air supply mechanism at 750 °C in a thermal reactor. The by-product of burning is FMH ash which has high biosilica content and very few contaminants. Cleaning the FMH ash contaminants is the second stage. To manufacture sodium silicate solution, the produced FMH ash is combined with various concentrations of NaOH solution at 80 °C and continuously agitated for 1 h. To remove sodium silicate, the solution is filtered using filter paper (Whatman grade 41). The sodium silicates are titrated once more in the 1 N (normality) HCl solution at a pH of 7. The silica gels are gathered when the mixing procedure is finished and aged for 24 h. Silica gels will be washed with distilled water to create a silica slurry. This silica slurry is heated in a beaker for roughly 20 h at 70 °C after being periodically rinsed. To obtain a finer particle size, the created xerogel silica is subsequently mashed in a mortar for a number of hours. The FMH biosilica that is obtained has a density of 2.7 g/cc with a simple cubic structure and a diameter of 1–3 µm. The prepared biosilica particles are then surface treated with silane as same as fibre treatment. SEM image of FMH biosilica and coconut rachilla fibre is shown in Fig. 2.

## 2.3 Surface treatment of coconut rachilla fibre

The palmyra sprout fibre is first given an alkali base treatment. Prior to the alkali treatment, the fibres are dried for 2 h at 100 °C in an oven. For alkali treatment, fibres are steeped for 3 h at room temperature in a 1 N NaOH solution using a 1:20 ML ratio. After the procedure, the samples are thoroughly neutralized by being rinsed with water to get rid of any remaining NaOH. The samples are dried for 24 h at room temperature before being oven dried for 2 h at 100 °C [23].

## 2.4 Composite preparation

The epoxy biocomposites are created utilising a rubber mould by hand lay-up approach. Prior to moulding, a consistent volume of epoxy resin is combined with three distinct FMH biosilica particle concentrations (1 vol. %, 3 vol. %, and 5 vol. %), and the mixtures are continually stirred until homogeneous. Then, hardener is added to the epoxy resin and biosilica particle mixture with ratio of 10:1. After precisely measuring out 20 vol. % and 40 vol. % of coconut rachilla fibres, the epoxy resin mixture is then poured into the mould. Cover the mould with a top plate to get rid of any leftover resin. The resin can then




**Fig. 1** Extraction step-by-step process of preparation of coconut rachilla fibre

**Table 1** Composition and designation of composite fabricated

| Composite designations | Epoxy resin (vol.%) | Rachilla fibre (vol.%) | Biosilica (vol.%) |
|---|---|---|---|
| E | 100 | - | - |
| ER1 | 80 | 20 | - |
| ER2 | 60 | 40 | - |
| ERB1 | 59 | 40 | 1 |
| ERB2 | 57 | 40 | 3 |
| ERB3 | 55 | 40 | 5 |

be post-cured for 12 h at 120 °C after curing for 24 h at room temperature [24]. Table 1 shows the composition and designation of composites fabricated.

## 3 Characterizations

According to ASTM D638 and D790, the tensile and flexural properties of composite materials are assessed using a universal testing machine (UTM), INSTRON 4855, UK, with a 10-ton loading capability. All samples are tested at a transverse speed of 1.1 mm/sec. A micro-impact tester made by Crystal Equipments India Pvt. Ltd. with a maximum energy reading scale of 20 J is used to assess impact toughness. The Shore-D durometer from Bluesteel India is used to measure the microhardness of composites in accordance with ASTM D 2240, 2016. The wear characteristics of epoxy and its composites are examined using the ASTM G99-compliant dry pin-on-disc technique (Magnum, India). The test conditions include a standard weight of 10 kg, a disc speed of 800 rpm, and a worn track diameter of 100 mm. The mass polymer composites lost with the temperature change are examined by thermogravimetric analysis. To conduct the thermogravimetry experiment on epoxy composite, TGA, thermo-scanner from NETZSCH STA Jupiter, 409 PL Luxx, Germany, is used. The temperature raise was controlled as 10 °C/min at $N_2$ gas environment. The glass transition behaviour and thermal stability of composites are investigated using differential temperature analysis. According to ASTM D 2578, contact angle measurement is used to assess the hydrophobicity (sessile drop test) of an epoxy composite coating (Holmarc, India). This included using a high-performance, aberration-corrected CMOS lens to place a water drop on the composite and determine the contact angle between the drop and the composite. Finally, a scanning electron microscope is used to study the epoxy composite micrographs (Hitachi-1500, Japan).

**Table 2** Mechanical properties of epoxy and its derived composites

| Composite designations | Tensile strength (MPa) | Tensile modulus (GPa) | Flexural strength (MPa) | Flexural modulus (GPa) | Izod impact (J) | Hardness (Shore-D) |
|---|---|---|---|---|---|---|
| E | 61 | 2.361 | 94 | 3.832 | 0.38 | 86 |
| ER1 | 94 | 3.845 | 136 | 5.384 | 3.74 | 86 |
| ER2 | 128 | 4.872 | 152 | 6.175 | 4.28 | 87 |
| ERB1 | 136 | 5.278 | 168 | 6.329 | 5.62 | 89 |
| ERB2 | 155 | 6.335 | 183 | 6.819 | 6.17 | 92 |
| ERB3 | 138 | 5.261 | 162 | 6.194 | 6.04 | 94 |

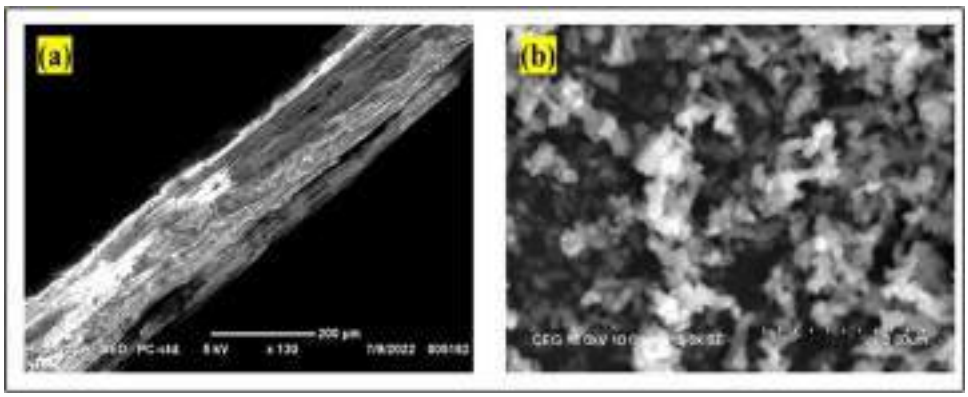



**Fig. 2** SEM image of **a** coconut rachilla fibre and **b** FMH biosilica particles

## 4 Result and discussion

### 4.1 Mechanical properties

The mechanical characteristics of epoxy composites made with coconut rachilla fibre and FMH biosilica particles are listed in Table 2. The neat epoxy resin has the tensile strength, tensile modulus, flexural strength, flexural modulus, Izod impact toughness, and hardness of 61 MPa, 2.361 MPa, 94 MPa, 3.83 MPa, 0.38 J, and 86 Shore-D, respectively. According to ASTM standard test specimen, the values are almost closer and produced repeatability. Because of its brittle nature, epoxy matrix resin has poor mechanical qualities. The mechanical characteristics of composites improve by 54.1%, 62.8%, 44.6%, 26.1%, 884.2%, and 1.16%, respectively, when coconut rachilla fibre is added, as shown in Table 2. While there is further enhancement observed in mechanical properties when volume percentage of fibre is increased [25], on comparison with the previous article [25], the mechanical properties are improved significantly. The fibre acts as a load-bearing capacity in the composite and is equally disseminated throughout the epoxy matrix resin, which lowers the stress intensity factor and so improves mechanical qualities. Additionally, by lowering the fibre's moisture absorption, surface treatment of the palmyra fibre enhances the contact between the hydrophobic matrix and hydrophilic fibre. Alkali-silane-treated fibre thereby improves the interfacial interaction between the matrix and fibre at the interface, resulting in high adhesion to the resin system and the epoxy matrix. Additionally, it is clear from Fig. 3a that the silane group and epoxy matrix resin have a chemical link that makes the reactive phase of the alkali-silane-treated fibre more compatible with the matrix resin.

Additionally, the mechanical properties of coconut rachilla-reinforced epoxy composites are improved by the dispersion of FMH biosilica particles. The distribution of biosilica particles has a substantial impact on the initial and maximum debonding loads of palmyra sprout fibres from the epoxy matrix. Figure 3 illustrates the rather smooth pull-out behaviour of fibre from the epoxy matrix during the failure of ERB composites. This can be due to a strong chemical link between the alkali-silane-treated fibre and FMH biosilica particles that results in good adhesion between the epoxy matrix resin and coconut rachilla fibre. The composite with the designation ERB2 exhibits the greatest increase in mechanical characteristics. This betterment is due to strong bonding between matrix resin and fibre because of high concentration of biosilica particles as shown in Fig. 3c. It is also interesting to notice that, aside from hardness, the mechanical properties of the biocomposites drastically decrease as the concentration of FMH biosilica particles rises by 5vol%. This is due to the agglomeration that takes place at large biosilica particle volumes, and the voids the agglomerates create have a significant impact on tensile strength as shown in Fig. 3d.

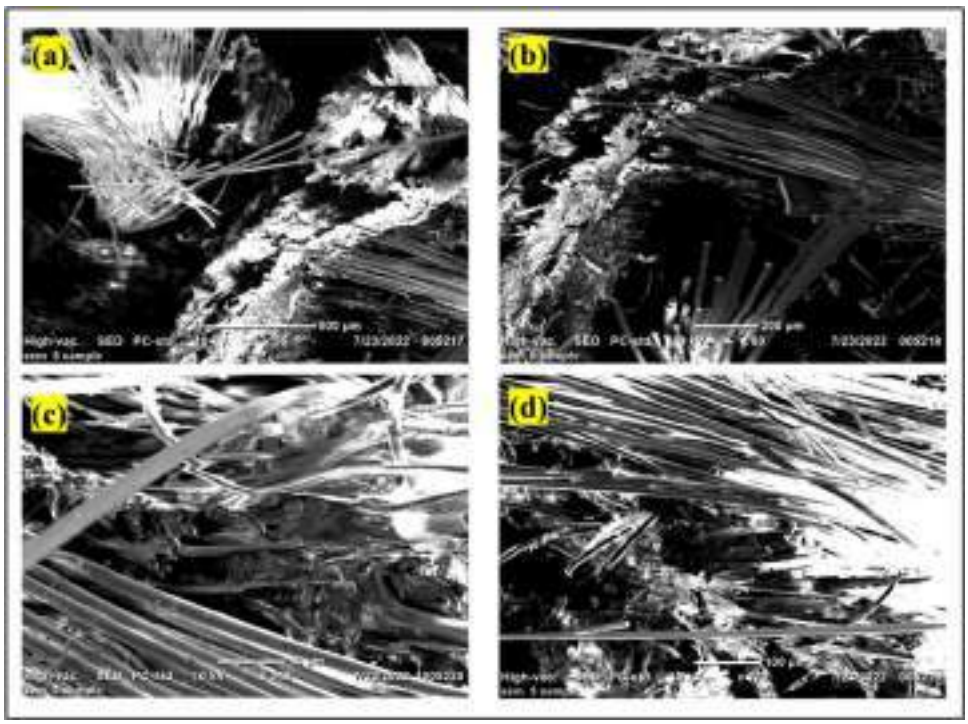



**Fig. 3** SEM images of tensile fractured composite samples: **a** ER2, **b** ERB1, **c** ERB2, and **d** ERB3

### 4.2 Wear properties

Figure 4 demonstrates the wear characteristics of composites made from epoxy reinforced with coconut rachilla fibre and FMH biosilica particles. The increased wear attributes of coconut rachilla fibre-reinforced composites are comparable to the mechanical properties. The specific wear rate and coefficient of friction of pure epoxy resin are 0.028 $mm^3$/Nm and 0.74, respectively, higher than those of other composites. On comparison with the ASTM standard test specimen, the COF and specific wear rate are deviated with 0.02%. The high specific wear rate and coefficient of friction cause a rise in abrasion and adhesion wear loss. Epoxy resin's molecular structure is sticky and adheres to the abrasion disc, removing a lot of material from the work piece in the process. This substance re-adhered to the abrasion disc and provided increased two-body and three-body abrasion [26]. Additionally, a portion of the material is released from the work piece as a result of high frictional heat during a major run in the material, increasing wear loss.

By improving the epoxy system with coconut rachilla fibre, wear loss is reduced. However, wear loss is decreased even further when FMH biosilica particles are added to composites. Both the COF and the specific wear rate decrease as FMH biosilica particle concentration increases. The ERB3 composite has the lowest COF of 0.42 and the lowest specific wear rate of 0.006 $mm^3$/Nm. This significant improvement in wear characteristics results in the strong interfacial adhesion behaviour of the biosilica particles. By reducing adhesion with the abrasion disc, FMH biosilica particles improve the sliding behaviour of composite surfaces. The previous article reported lesser wear resistance of 0.014 $mm^3$/Nm for composite they prepared. However, the present composite holds higher wear resistance. The biosilica particles are converted into cellulose flakes when the biosilica dispersed epoxy composite is abraded in the friction disc. Acting as solid lubricant packets in between the abrasion discs, these flakes lessen wear loss. Additionally, because there is less friction between the surfaces, the rate of heat dissipation is higher [27]. The epoxy resin composite's biosilica particles work as a heat absorber to stop erosion and adhesion wear, lowering the wear rate and COF as a result.

### 4.3 Thermal properties

The TGA and relative DSC arrived Tg values of epoxy and its coconut rachilla fibre and FMH biosilica particles generated composite are shown in Fig. 5. It should be mentioned that the pure resin had a Tg value of 63 °C and breakdown temperatures of 295 °C, 374 °C, and 483 °C at the beginning, middle, and end of the process, respectively. The chemically reacted secondary side polymer branches and the highly cross-linked epoxy molecular structure are the reason for greater Tg and reasonable mass loss stability. Since the primary and secondary molecules of epoxy resin are very reactive, it takes a lot of heat energy for them to move around, which increases the heat flow and raises the Tg as well as mass loss stability [28]. However, it should be emphasised that the Tg and thermal stability at the beginning, middle, and final stages are only little altered by the addition of coconut rachilla fibre alone in to the resin. The Tg and thermal stability of an ER2 composite designated with high concentration of fibre are increased, which might prevent the early evaporation of large amount of fibre molecules when the temperature is raised, is a result of this enhancement.

Additionally, it should be noticed that the incorporation of FMH biosilica particles added to the resin improved the thermal stability as well as Tg. Due to the creation of nanocomposite materials, the softening temperature has

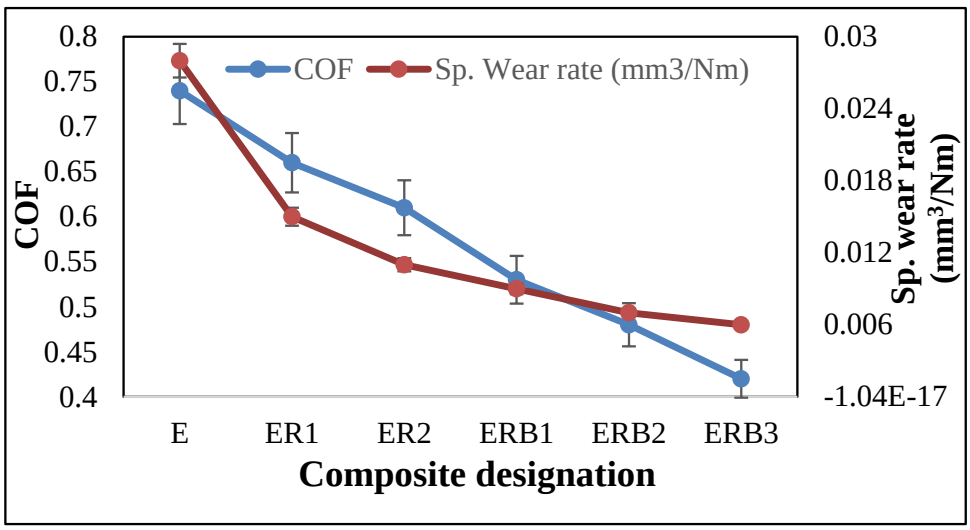



**Fig. 4** Wear properties of epoxy and its derived composites

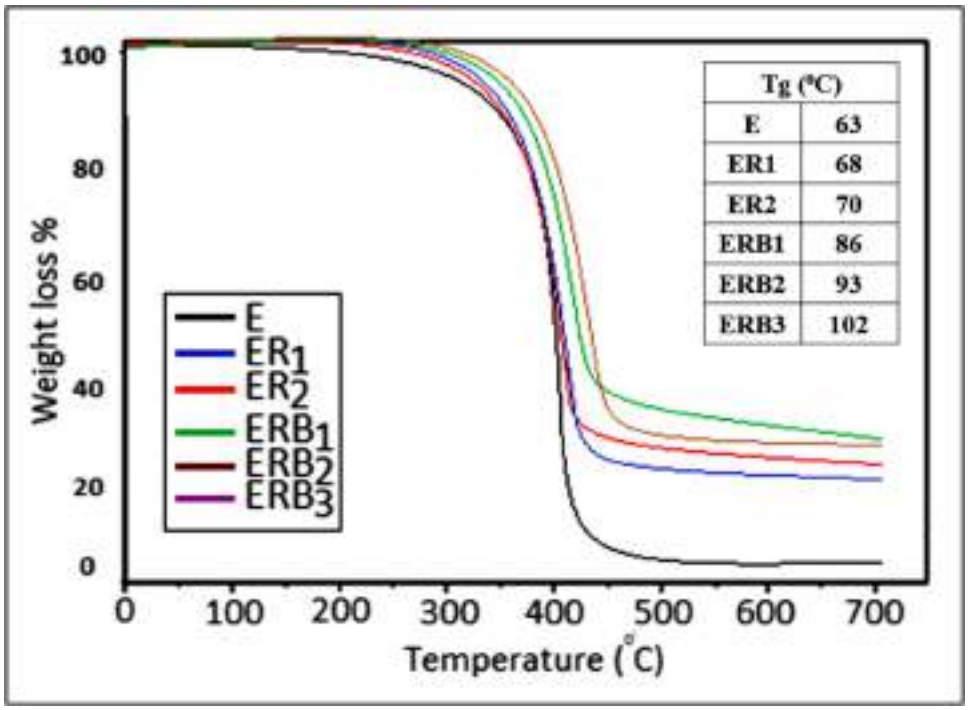



**Fig. 5** Thermal behaviour of epoxy and its derived composites

increased, which has improved heat energy absorption. Biosilica additives neatly filled in the gaps left by the polymer and increased the heat capacity. The unit length and weight of the polymer chain has risen as a result of the additional FMH particle reacting with the multiple polymer chains. Therefore, weight gain in chain during heating may take a lot of energy to rotate itself around the core C–C chain [29]. As a result, the increased Tg is seen. The stability of mass loss is also increased by this improved Tg. The initial, middle, and final decomposition temperatures are raised for the FMH biosilica particle-added composite designations ERB1, ERB2, and ERB3. For EFP3 composite designation, a maximum first decomposition temperature of 336 °C is reported; this represents a 13.8% improvement over the neat epoxy resin system. Suganya et al. [29] reported the thermal stability of composites with an improvement of 8.4% on compare with neat epoxy resin. However, this present composite produced extra 5.4% of improvement.

## 4.4 Hydrophobic behaviour

Figure 6 shows the hydrophobic contact angle of composites made with FMH biosilica and coconut rachilla fibre-reinforced epoxy. Pure epoxy resin has been shown to have the largest contact angle, measuring 102°. High contact angle happens as a result of the free, unsaturated OH molecules in the epoxy primary chain's capacity to fend off water molecules and maintain low surface activation energy. Due to the addition of coconut rachilla fibre by 20 vol%, contact angle is drop by 3.9% because of high water permeability of

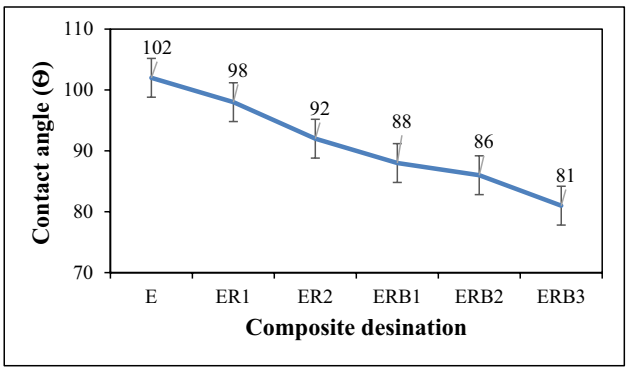



**Fig. 6** Hydrophobic behaviour of epoxy and its derived composites

fibre and hence increases water absorption. Natural fibres are cellulosic; hence, coconut rachilla fibres are incredibly vulnerable to water absorption. With increasing concentration of fibre, contact angle decreases. Also, it is interesting to note that the contact angle continues to decrease with the addition of biosilica particles. Low contact angle is observed as a result of this behaviour, which is brought on by the FMH biosilica particle's high active surface energy and high water permeability. Alshahrani et al. [30] also reported similar effects when adding biosilica particle into the epoxy resin. With a contact angle of 81°, the composite with the designation ERB3 has the lowest value. As a result, despite the addition of natural fibre and biosilica particles, the composite retains its hydrophobic properties indefinitely and does not become more hydrophilic [31 and 32].

## 5 Conclusions

In this study, the role of FMH biosilica and coconut rachilla fibre in the creation of incredibly durable epoxy composites is examined. According to results it is noted that the composite containing 3vol% of FMH biosilica exhibits maximum enhancement and surpasses conventional composites in terms of tensile strength, tensile modulus, flexural strength, flexural modulus, Izod impact strength, and hardness. The mechanical properties of the biocomposite are diminished as a result of the agglomeration caused by the high concentration of biosilica particles (5 vol. %) in the material. The biocomposite contains 5 vol. % of biosilica particle, which has the lowest specific wear rate and COF of 0.003 $mm^3$/Nm and 0.42, respectively. Additionally, it also exhibits the greatest weight loss percentage with temperature and glass transition temperature with 102 °C; hence, it has outstanding thermal properties. These composites also do not become more hydrophilic when natural fibre and biosilica are added, thus maintaining their hydrophobic properties indefinitely. Therefore, for engineering applications, including high load bearing applications as well as in automobiles, the alkali-silane-treated coconut rachilla fibre-reinforced FMH biosilica particle-toughened epoxy composites could be helpful.

**Author contribution** P. Sivamurugan: research
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M. Pandian: research
Mohd.ShaikhulAshraf: research and drafting
Inavolu Srinivasa Chakrapani: research
A. Thanikasalam: testing and drafting
P. Roshith: research and characterization
K. Ramesh: research and finance
B. Ramesh: research

**Data availability** All data within manuscript.

## Declarations

**Ethical approval** Not applicable.

**Competing interests** The authors declare no competing interest.

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# NOVEL COMPUTATIONAL APPROACHES FOR INVESTIGATING BACTERIAL INHIBITORS FROM MALABAR NUT PLANT

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**Abstract:** The issue of bacterial diseases is spreading throughout the globe. It is now recognised that bacterial diseases kill more people each year than malaria. Ayurvedic medicine was among the most effective treatments for bacterial infections in antiquity. It was discovered that the plant Malabar nut has a variety of pharmacological qualities after studying the most recent survey on the plant with antibacterial activity. The plant, which is an Acanthaceae member and was endemic to India, was known by the common name Adusa. Through a review of the literature, 102 phytochemical components from the Malabar nut plant were found for the present study project. Only 84 substances have their two-dimensional structure determined using PubChem databases. These compounds were subjected to virtual screening, the results of which indicated that only 28 compounds would be found to contain active drug molecules. Most of the bacterial illnesses that affected humans were brought on by the bacterial protein Cytochrome P450 14-alpha-sterol demethylases (CYP51). The three-dimensional protein structure was acquired from PDB databases and then utilised for the docking procedure. Using docking tools, only 1 chemical, out of 28, predicted the optimal binding relationship with the protein.

***Keywords:*** *Malabar nut, Antibacterial activity, Phytochemical, Protein Cytochrome P450 14-alpha-serol demethylases, Docking*

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## 1. Introduction

Bacterial pathogens have a significant impact on public health. Any part of the body can develop disease, and it can be brought on by the organism itself or by the body's reaction to its existence[1]. Humans can contract bacteria via the air, water, food, or living things. The main means of bacterial infection transmission are contact, aerosol, droplet, vectors, and moving vehicles[2]. Morbidity and mortality are significantly impacted by preventive strategies. As we encroach into new environments, new species and novel variations of well-known species continue to be discovered[3]. Disease-causing pathogenic microorganisms have properties that enable them to sidestep the body's defenses and utilize its resources4. Last but not least, virulence refers to an organism's potential to spread disease through traits including invasiveness and toxin production[5]. In determining whether a disease will spread after a bacterial agent has been transmitted, host factors are crucial[6]. These variables include genetic make-up, nutritional status, age, length of organism exposure, and co-occurring diseases. Antibiotic resistance among bacteria is a rising issue that necessitates careful usage of antibiotics[7,8].

*Adhatoda vasica* Nees (Acanthaceae), sometimes referred to as Adusa or the Malabar nut tree[9]. The Assam, Bangladesh, India, Nepal, and Sri Lankan subcontinents, Laos, and Myanmar make up the natural range of the Malabar nut[10]. Many alkaloids, phenolics, flavonoids, sterols, and their glycoside derivatives have been identified from the well-known medicinal herb Malabar nut. Its wide range of therapeutic effects include hepatoprotective, antimicrobial, antitussive, abortifacient, antitubercular, antimutagenic, antiulcer, antiasthmatic and cardiovascular protection[11,12]. It is commonly used in South-East Asian traditional and folk medical systems, and it is also a well-known plant medication in Ayurvedic and Unani medicine[13]. The protein that was found to cause of the bacterial infections in human was Cytochrome P450 14-alpha-sterol demethylases (CYP51) are important enzymes in sterol in plants biosynthesis and cholesterol biosynthesis in humans[14]. In the pathways leading to the synthesis of ergosterol in fungus, various forms of sterols in plants, and cholesterol in humans, the demethylated products of the CYP51 reaction are essential intermediates[15]. These sterols are found in cells plasma membranes, where they serve a crucial structural function in the control of membrane permeability and fluidity[16]. They also have an impact on the activity of enzymes, ion channels, and other embedded cell components. In an effort to find novel ways to cure bacterial infections, drug researchers have started focusing on the 14-demethylase enzyme in bacteria[17]. By inhibiting the bacteria's production of ergosterol, the pathogen is killed since the breakdown of the plasma membrane causes cellular leakage[18]. The CYP51 family is an intriguing subject for fundamental P450 structure/function studies and is also an important clinical drug target[19]. *In silico* screening, large libraries of drug-like compounds that are commercially accessible are computationally screened against targets of known structure, and those that are predicted to bind well are experimentally tested[20]. Virtual Screening of the compound was excluded by Molinspiration software[21]. The software predicts the calculations of leading molecular properties as well as calculation of bioactivity score for the most important drug targets[22]. Docking method is one of the most important and frequently used methods in structural-based drug designing, which predict the

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binding affinity of small molecules to their applicable target binding sites there by inhibiting the target functions[23].

## 2. Materials and Methods

### Ligand selection

Through literature study, 102 phytochemicals were identified from the plant Malabar nut for computational analysis. From the Pubchem database, 2D structures were retrieved for 84 compounds and for remaining 18 compounds, 2D structures was not available in the database.

### Prediction of oral drug activity using Molinspiration server

By using Molinspiration server, the drug likeness filter test was conducted for above 84 phytochemicals. Molinspiration expressed 6 rules (logP, Topological Polar Surface Area (TPSA), Molecular weight (MW), number of hydrogen bond acceptor (No.HA), number of hydrogen bond acceptor No.HD, and volume (Vol)) to determine whether a compound could be orally consummate. The compounds which clear the oral drug properties were further, analyzed for its biological properties using Molinspiration bioactivity server. Bioactivity predicts the 6 properties including GPCR ligand, Ion channel modulator, Kinase inhibitor, nuclear receptor ligand, Protease inhibitor, Enzyme inhibitor. The compound which satisfies all the biological properties could be taken for further docking process.

### Accession of target protein

The protein cytochrome P450 14-alpha-sterol demethylases (CYP51) were found to be most important bacterial protein. The three dimensional structure (1EA1) of that protein was retrieved using Protein Databank database which was resolute by experimental studies through X-Ray Diffraction with the Resolution of 2.21 Å.

### Analysis of target active binding sites

The Binding sites of small molecules present in the protein structure were recognized by SCFBio - Supercomputing Facility for Bioinformatics and Computational Biology (http://www.scfbio-iitd.res.in/dock/ActiveSite.jsp). SCFBioActive Site prediction server which will predict the active site in the 3 dimensional structure of the protein for the binding of the ligand.

### Molecular Docking Interactions using Argus Lab

The docking studies were performed to analyze the structural relationship between receptor and ligand using Argus Lab 4.0.1 docking software program28. The following factors were set for docking process: Population size, Grid resolution, Binding site box size, Maximum generation, Crossover rate, Mutation rate, Elitism, Dock engine used Lamarckian Genetic Algorithm. For the docking calculations, docking mode should be was set as “Dock” and “Flexible” ligand for each docking runs.

### Visualization of docking interaction using PyMol

The best docking result were analyzed using PyMol which is an open source molecular visualization tool to view the hydrogen bond interactions between the protein and ligand and also predict the distance of hydrogen formation between them.

## 3. Results and Discussions

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**Preparation of small molecules:**

Through literature survey, totally 102 phytoconstituents were identified from plant Malabar nut. The virtual screening was carried out for 84 phytoconstituents using Molinspiration server. From the result of Drug likeness properties revealed that only 38 compounds pass the Drug likeness screening test (Table 1). Further these compound were screened for its bioactivity test, the result proved that out of 38, only 28 compounds satisfies the oral drug properties (Table 2).

**Table 1: The phytochemical compounds which satisfy the drug likeness properties**

| Compound | Pubchem ID | LogP | TPSA | MW | No. HA | No. HD | Vol |
|---|---|---|---|---|---|---|---|
| 2-Glycylaminobutyric acid | 86878 | 2.62 | 92 | 160 | 5 | 4 | 149 |
| Anisotine | 442884 | 2.99 | 73 | 349 | 6 | 1 | 312 |
| Apigenin | 5280443 | 2.46 | 90 | 270 | 5 | 3 | 224 |
| Betaine | 247 | 5.41 | 40 | 117 | 3 | 0 | 119 |
| 42752-07-8 | 206 | 2.64 | 110 | 180 | 6 | 5 | 51 |
| Deoxyvasicine Hydrochloride | 3046290 | 1.95 | 15 | 172 | 2 | 0 | 165 |
| Deoxyvasicinone | 68261 | 1.47 | 34 | 186 | 3 | 0 | 167 |
| 2-Aminoacetic acid | 750 | 2.55 | 63 | 75 | 3 | 3 | 67 |
| 4-Heptanone | 31246 | 2.36 | 17 | 114 | 1 | 0 | 131 |
| Hydroxychalcone | 97765 | 3.57 | 37 | 24 | 2 | 1 | 209 |
| Kaempferol | 5280863 | 2.17 | 111 | 86 | 6 | 4 | 232 |
| 178740-33-5 | 21769547 | 0.49 | 64 | 32 | 5 | 1 | 201 |
| 77500-13-1 | 110349 | 3.76 | 66 | 319 | 5 | 2 | 344 |
| 147-85-3 | 145742 | 1.72 | 49 | 115 | 3 | 2 | 108 |
| Quercetin | 5280343 | 1.68 | 131 | 02 | 7 | 5 | 240 |
| 2-Amino-3-hydroxypropanoic acid | 617 | 1.67 | 83 | 105 | 4 | 4 | 92 |
| 2-amino-3-methylbutanoic acid | 1182 | 1.91 | 63 | 17 | 3 | 3 | 117 |
| Peganine | 72610 | 1.04 | 35 | 88 | 3 | 1 | 173 |
| Vasicinone | 442935 | 0.48 | 55 | 02 | 4 | 1 | 175 |
| Benzenamine | 626005 | 3.33 | 18 | 291 | 3 | 0 | 282 |
| Vasicolinon | 627712 | 2.91 | 38 | 305 | 4 | 0 | 285 |
| 2-(3'-hydroxy-2'-oxopyrrolidinomethyl) aniline | 14285793 | 0.02 | 66 | 06 | 4 | 3 | 91 |
| Vasicinolone | 13970119 | 0.03 | 75 | 218 | 5 | 2 | 183 |
| Vasicinol | 4486241 | 0.53 | 56 | 204 | 4 | 2 | 181 |
| Vasnetine | 9997066 | 3.03 | 73 | 335 | 6 | 1 | 296 |
| Erythorbic acid | 54675810 | 1.40 | 107 | 176 | 6 | 4 | 139 |
| 2,4-Dimethyl-2,4-Heptadiene | 572949 | 3.93 | 10 | 24 | 0 | 0 | 150 |
| Methyl 4-hydroxycinnamate | 5319562 | 2.05 | 46 | 178 | 3 | 1 | 164 |

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|---|---|---|---|---|---|---|---|
| 5,5-Dimethyl-1,3-Dioxane-2-Ethanol, Tert-Butyldimethylsilyl Ether | 91714410 | 4.24 | 27 | 274 | 3 | 0 | 91 |
| 5-Isopropyl-1,3-Cyclohexanedione | 566106 | 1.57 | 34 | 154 | 2 | 0 | 156 |
| 16688-21-4 | 595376 | 1.72 | 67 | 351 | 6 | 1 | 318 |
| STK766913 | 5292275 | 4.53 | 72 | 370 | 6 | 1 | 288 |
| Syringic Acid | 10742 | 1.20 | 76 | 198 | 5 | 2 | 170 |
| Methyl 4-hydroxy-3-methoxy-cinnamate | 16830 | 1.86 | 55 | 208 | 4 | 1 | 189 |
| 1151-93-5 | 2825054 | 3.55 | 29 | 255 | 3 | 0 | 245 |
| 1-Cyclohexylsilatrane | 208266 | 1.87 | 30 | 257 | 4 | 0 | 251 |
| Hydroquinone | 785 | 0.98 | 40 | 110 | 2 | 2 | 100 |
| Dibutyl Phthalate | 3026 | 4.43 | 52 | 278 | 4 | 0 | 273 |

**Table 2: The phytochemical compounds which satisfy the bioactivity properties**

| ***S.No*** | ***Pubchem ID*** | ***GPCR Ligand*** | ***Ion Channel Modulator*** | ***Kinase Inhibitor*** | ***Nuclear Receptor Ligand*** | ***Protease Inhibitor*** | ***Enzyme Inhibitor*** |
|---|---|---|---|---|---|---|---|
| 1. | 86878 | -0.30 | 0.05 | -1.25 | -1.16 | 0.04 | -0.02 |
| 2. | 442884 | -0.14 | -0.31 | -0.19 | -0.37 | -0.41 | -0.08 |
| 3. | 247 | -2.53 | -1.79 | -3.50 | -3.75 | -3.47 | -2.12 |
| 4. | 3046290 | -0.26 | 0.09 | -0.83 | -1.22 | -0.91 | 0.03 |
| 5. | 68261 | -0.98 | -0.92 | -0.75 | -1.39 | -1.22 | -0.09 |
| 6. | 750 | -3.45 | -3.11 | -3.71 | -3.55 | -2.95 | -3.29 |
| 7 | 31246 | -3.17 | -2.75 | -3.66 | -2.91 | -3.06 | -2.63 |
| 8. | 97765 | -0.34 | -0.17 | -0.54 | -0.30 | -0.51 | -0.05 |
| 9. | 21769547 | -0.24 | -0.43 | -0.44 | -0.67 | -0.86 | 0.07 |
| 10. | 145742 | -2.15 | -1.54 | -3.08 | -3.07 | -1.72 | -1.85 |
| 11. | 617 | -2.66 | -2.54 | -3.34 | 3.34 | -2.36 | -2.38 |
| 12. | 1182 | -2.66 | -2.11 | -3.40 | -3.04 | -2.12 | -2.18 |
| 13. | 627712 | -0.40 | -0.35 | -0.53 | -0.85 | -0.97 | 0.03 |
| 14. | 442935 | -0.04 | -0.26 | -0.21 | -0.35 | -0.48 | -0.01 |
| 15. | 14285793 | -0.13 | 0.04 | -0.29 | -0.52 | 0.14 | 0.16 |
| 16. | 13970119 | -0.26 | -0.25 | -0.33 | -0.51 | -0.87 | 0.15 |
| 17. | 9997066 | -0.24 | -0.40 | -0.26 | -0.43 | -0.50 | -0.08 |
| 18. | 54675810 | -0.53 | -0.24 | -1.09 | -1.01 | -0.81 | 0.20 |
| 19. | 572949 | -2.13 | -1.14 | -2.53 | -1.39 | -2.35 | -1.03 |
| 20. | 5319562 | -0.71 | -0.35 | -0.92 | -0.30 | -0.87 | -0.28 |
| 21. | 566106 | -0.91 | -0.38 | -1.74 | -0.67 | -0.73 | -0.32 |
| 22. | 595376 | 0.01 | -0.29 | -0.32 | -0.12 | -0.36 | 0.12 |

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| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 23. | 5292275 | -0.58 | -1.01 | -0.37 | -0.99 | -0.66 | -0.46 |
| 24. | 10742 | -0.65 | -0.28 | -0.69 | -0.44 | -0.82 | -0.15 |
| 25. | 16830 | -0.58 | -0.35 | -0.72 | -0.26 | -0.78 | -0.21 |
| 26. | 2825054 | -0.14 | -0.13 | -0.06 | 0.00 | -0.39 | -0.04 |
| 27. | 785 | -3.02 | -2.48 | -3.07 | -2.84 | -3.20 | -2.66 |
| 28. | 3026 | -0.16 | -0.09 | -0.27 | -0.12 | -0.25 | -0.07 |

### 3.1 Preparation of protein

The 3D structure of protein (1EA1) was retrieved using Protein Data Bank database. The possible binding site sites of the protein Cytochrome P450 14-alpha-sterol demethylases (CYP51) were predicted using SCFBio. The secondary structure, name, position and of the amino acid present in the protein are as follows: Alpha Helix - SER260, THR261 and PHE399: Coil- GLY94, PRO319, ILE322, GLY388, ARG391, CYS394 and ALA397.

### 3.2 Docking analysis

The predicted 10 active residues were used as the binding sites for 28 natural compounds from the plant Malabar nut for docking studies. The results of the binding interaction between the active site residues of target protein Cytochrome P450 14-alpha-sterol demethylases (CYP51) and 28 compounds were shown in the Table 3.

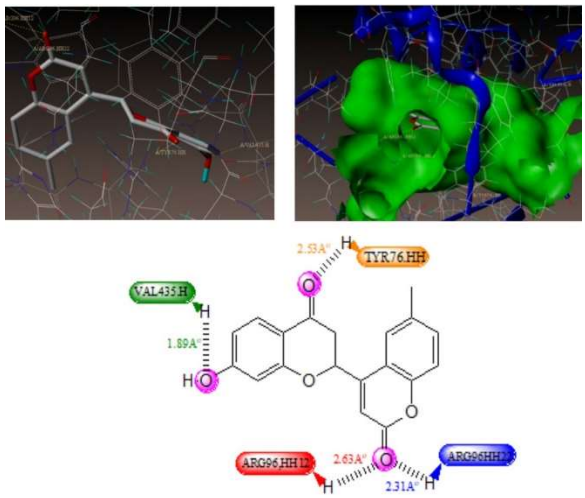
**Table 3: Molecular Docking between Phytochemical Compounds and the Protein (1EA1)**

| ***Compound*** | ***Binding Affinity*** | ***Compound*** | ***Binding Affinity*** |
|---|---|---|---|
| Hydroxychalcone | -8.9 Kcal/Mol | Dibutyl Phthalate | -7.4 Kcal/Mol |
| Methanone [4-(Dimethylamino)Phenyl] (4-Methoxyphenyl) | -8.7 Kcal/Mol | Methyl 3-(4-Hydroxy-3-Methoxyphenyl)Prop-2-Enoate | -7 Kcal/Mol |
| 5-Isopropyl-1,3-Cyclohexanedione | -7 Kcal/Mol | 2,4-Dimethyl-2,4-Heptadiene | -5.5 Kcal/Mol |
| Syringic Acid | -6.5 Kcal/Mol | Hydroquinone | -5.3 Kcal/Mol |
| 4-Heptanone | -5.2 Kcal/Mol | Amino-N Butyric Acid | -5.1 Kcal/Mol |
| D-Erythro-Hex-2-Enonic Acid, Gamma-Lactone | -4.7 Kcal/Mol | Glycine | -4 Kcal/Mol |

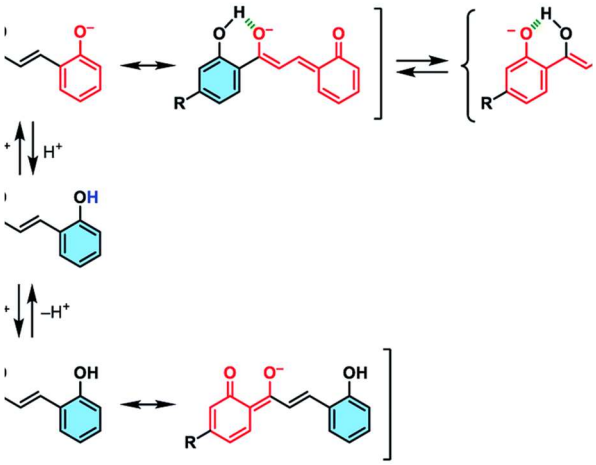
By analyzing the docking result, 2 compounds: Hydroxychalcone and Methanone [4-(Dimethylamino) Phenyl] (4-Methoxyphenyl) were found to have the highest inhibitory activity of -8.9 Kcal/Mol and -8.7 Kcal/Mol when compared with 10 other compounds which showed the inhibitory activity of $< -8$ Kcal/mol. The remaining 16 compounds do not exhibit any inhibitory activity between protein Cytochrome P450 14-alpha-sterol demethylases (CYP51).

**Table 4: Docking interactions between hydroxychalcone – 1EA1**

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Best docking interactions between Hydroxychalcone - 1EA1




Hydrogen distance between Hydroxychalcone - 1EA1

The latest docking study on 1EA1 protein revealed that same binding inhibitory activity towards compounds Emodin when compared with the existing drugs[24]. From the current docking results, it was clearly conveyed that among the 28 plant compounds, Hydroxychalcone exhibits the best binding interaction with the Protein Cytochrome P450 14-alpha-sterol demethylases (CYP51) and further this study could be useful in designing of new preventive and therapeutic drug against bacterial infection.

## Conclusion

The development of novel natural compounds with pharmacological activity is an urgent need in designing effective drug towards bacterial infections. In the present study, docking results revealed the binding interactions between protein Cytochrome P450 14-alpha-sterol demethylases (CYP51) and 28 natural flavonoid compounds. Among those compounds, Hydroxychalcone were found to have the best binding energy of -8.9 Kcal/mol and also satisfies the pharmacological properties which provide the strong recommendation for the compound to be considered for an oral drug. On the whole, this study could be concluded that compound Hydroxychalcone could be potent anti-bacterial drugs activity against the protein Cytochrome P450 14-alpha-sterol demethylases (CYP51). Further In vivo investigations are needed to enrich the bacterial activity of the Hydroxychalcone compound from Malabar nut to determine the dosage for the safety levels.

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# Integrated network pharmacology and zebrafish model to investigate effects components of Origanum valgare for treating Alzheimers Disease



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## Abstract

Origanum vulgare ssp. hirtum is a medicinal herb that promotes antioxidants, anti-inflammatory, antibacterial, and its neuroprotective effects. Here the research investigates the preventative impacts and the procedure of O. vulgare ssp. hirtum essential oil (OEO) on the impairment of cognitive and brain oxidative stress in a scopolaminedecreased uneasy-like behaviour and enhanced mental capacity. Our findings show that exposure to Sco (100 M) causes problems with anxiety, spatial memory, and novelty response. The OEO injection also lessened the impact of Sco on antioxidant stress and acetylcholinesterase (AChE).

The OEO mix was perceived by the gas chromatography-mass being thymol (27.83%), p-cymene (19.22%), and -terpinene (20.59%). These results point to OEO's potential to reverse the cognitive deficiencies caused by Sco by reactivating the cholinergic procedure and boosting brains antioxidant levels. OEO could therefore be employed as a possible source of bioactive chemicals that exhibit beneficial biological actions and have the potential for medicinal usage.

**Keywords:** Zebrafish model, Guiera senegalensis**,** Alzheimers Disease, Origanum valgare

**DOI Number: 10.14704/nq.2022.20.13.NQ88175 Neuro Quantology 2022; 20(13):1391-1400**

## Overview

Aromatherapy is the supervise application of herbal essential oils that have been condensed, flowers, and other plant materials for therapeutic or preventative purposes. The three primary routes by which essential oils are delivered are orally, topically (aromatherapy massage), and olfactorily (direct and indirect inhalation). Essential oils' antifungal, antiviral, antibacterial, and antioxidant properties are their main pharmacological advantages. Numerous authors have recently emphasised the advantages of aromatherapy for reducing stress, restoring mental well-being, and relieving anxiety and despair.

Origanum majorana L. (Lamiaceae), also known as marjoram, is a herb that is native to the Mediterranean region and is grown in many countries in, North Africa,Europe and Asia.

Popular spice marjoram has a powerful & alluring scent. Asthma, dyspepsia, headaches, and rheumatism are just a few of the diseases for which this herb has been used in folk medicine. Numerous authors have discussed marjoram's impact on various illnesses as well as its antibacterial, antiviral, antioxidant, anti-acetylcholinesterase (AChE), anti-metastatic, and anti-tumor growth properties. Recent research has revealed that Origanum majorana essential oil (OmEO) can mimic the effects of antidepressants by modulating the noradrenergic, dopaminergic, and serotonergic systems. Another group of researchers discovered that OmEO helped bruxism patients feel less anxious, and they hypothesised that this essential oil would be a safe alternative to benzodiazepines in the treatment of bruxism. O. majorana also possesses anti-inflammatory properties. [21].

The structural and functional similarity between the blood-brain & barrier (BBB) of the zebrafish and mammals, as well as the existence of many proteins that are related to human assisted neurodegenerative diseases in the zebrafish, highlight the possibility of molecular cellular features that are easily observable being conserved. Other significant benefits of this animal model are also present.

Zebrafish embryos serve as evidence that mobility is a complex habit, as they continue to posses a foundational capability to swim long after the hatching. The neocortex is deficient in the zebrafish, yet the synapse structures are as yet unblemished and are believed to be engaged with the transmission cycle as well as learning and memory. Even if there is a significant association between the various brain regions' functioning in zebrafish, this is nonetheless the case.

It is generally known that cholinergic signaling contributes to both memory and learning consolidation. Scopolamine (Sco), a nonselective muscarinic acetylcholine receptor antagonist, reduces learning and short-time memory and causes amnesia. In the object identification test, Sco reduces the ability of rodents to establish memories and weakens their cognitive abilities. Zebrafish, who are likewise entirely powerless against Sco, show amnesic impacts in the clever item acknowledgment (NOR) and Y-labyrinth tests. Sco-instigated amnesia models are thusly ordinarily used to assess the potential for neuroprotection of related substances and regular items.

The bulk of the Origanum species are indigenous to the Mediterranean, North Africa and Eurasia and are used in classical medications to cure gastrointestinal, respiratory, and cold-related conditions. The Origanum genus is a part of the Lamiaceae family. O. syriacum L. has been demonstrated to have neuroprotective properties and to be advantageous in the treatment of a range of ailments that impact numerous body systems, including the respiratory, cardiovascular, and neurological systems. Additionally, it improves memory and learning in mouse models of AD. The antioxidant, antibacterial, and anti-inflammatory capabilities of origanum's phenolic parts were traditionally thought to be responsible for the therapeutic actions of the herb in conventional medicine. O. vulgare's anti-inflammatory features have been investigated in numerous studies utilizing two of them cell and animal-based modelling. Avola et al. represented the anti-inflammatory and wound-healing properties of O. vulgare L. essential oil in a person keratinocyte cell culture. Han and Parker have provided affirmation of the anti-inflammatory, tissues re-modelling. Studies into the antioxidant benefits of O. vulgare, especially those of its essential oil derivatives, have been extensive. The chemical combination of O. vulgare essential oil contains carvacrol (35.00%) and thymol (35.19%), which is primarily to blame for Kakhri's demonstration of the oil's highest antioxidant activity.

## Materials and Methods

### Using and Extracting Plant Material

In the Touloum area, fresh Guiera senegalensis leaves were picked in June 2021. (Far North,Cameroon). The plant was identified botanically by comparison to a botanically sample of Sabatié B. No. 698, which was discovered and got registered under No. 49838/HNC, at the National Herbarium of Cameroon.

The extraction process was followed exactly as Imam et al. [40] had previously reported.

Fresh G. senegalensis leaves were reduced to a fine powder after being dried in the shade for 1 week. The powder in result, 300 g, was macerated for 74 hours in a solvent made up of 80% ethanol and 25% distilled water. Whatman paper was used to filter the mixture. The final product was evaporated at 80°C in a rotating vapor to eliminate the ethanol and at 50°C for 45hours in an oven to remove the water. 7.67% (v/v) of the hydroethanolic extraction yield was obtained.

**High-Performance Liquid Chromatograph (HPLC-PDA)**

The extracts was initially diluted in a 3:7 methanol to H2O solution to create a stock solution with an initial concentration of 5 mg/mL. Clarifying the solutions required the use of a 0.2 m Millipore filter

The quaternary pump produced the mobile phase throughout the analysis by combining The sample analysis was done at a rate of flow 0.9 mL/min. Utilizing aliquots, the diluted extract was delivered in linearity gradients. For alignment bends with connection coefficients more noteworthy than 0, standard stock . Identification was done by comparing UV spectra and retention times, taking into account a match index of at least 950/1000. Sigma Aldrich provided all of the HPLC solvents and quality standards (Darmstadt, Germany).

**Treatment and Animal**

Adult fish received commercial flake fish feed twice daily (Gadstrup, Norwin Noryitall, Norwin, Denmark). Prior to the start of the study, fish was acclimated for 1 week.

Before the commencement of the behavioural tests, a 500 mL glass containing GS (1, 4, and 8 g/L) and Sco (100 M) was immersed once daily for an hour All strategies and conventions including the consideration and utilization of lab creatures have been supported by the Workforce of Science's Creature Exploration Morals Board of trustees at Alexandru Ioan Cuza College of Iaşi, Romania (No. 15308/30.07.2019), which found that they completely conformed to Order 2010/64/EU of the European Parliament and Gathering of September 22, 2010 on the insurance of creatures. The utilization of creatures was diminished to a base, and endeavors to improve

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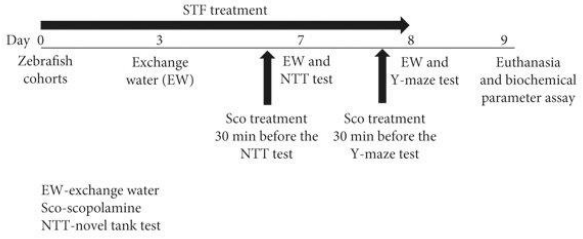



Figure 1: Design Procedure of experiment

**Novel Tank Diving Test (NTT)**

According to Cachat, the NTT is a specialized test utilized to measure zebrafish locomotor activity and anxiety reaction. The NTT was a 1.4 L trapezoidal tank (14.1 x 25.8 x 5.1 cm) with top and bottom parts separated by a virtually horizontal line. Zebrafish were evaluated one at a time for 6 minutes. Distance walked and average speed were the locomotor activity endpoints (measured in m and m/s, respectively). The quantity of passages to the top, time spent at the top (s), normal passage length (s), absolute distance went in the top (m), and freeze term (s) endpoints were evaluated to recognize tension like way of behaving.

**Y-Maze Test**

To find out how the zebrafish would react in an unknown setting, the Y-maze test was utilised. Zebrafish were put in the novel arm of a Y-shaped glass tank to test their recall (27 8 15 cm for each arm, 4 L). The "start" arm, "other" arm (which was consistently open), and "new" arm were the names of the Y-labyrinth arms (obstructed in instructional meeting and opened in test meeting). The fish were each independently positioned in the start arm, and the new arm was shut, for the term of the preparation (5 minutes). The fish were set in the beginning arm once more, yet this time the new arm was opened, and testing for five minutes began following an hour. Outright distance traveled (m) and turn point () were used to evaluate locomotor activity, while time spent in the sharp arm (% of hard and fast arm time) was utilized to survey the reaction to interest.

### Novel Object Detection Test

The NOR, a behavioral experiment, is often used to study the memory function of zebrafish. Zebrafish were introduced to the novel tank for a total of 5 minutes over the course of 3 days without the objects (30 cm filled with 6 cm of water). Zebrafish were exposed for ten minutes on the fourth day to two similar objects (training phase).

## Results and Discussion

### Extract from Guiera senegalensis: Chemical Makeup

The study was done to determine the chemical composition of the GS extract. According to the findings, several flavonoids and polyphenolic acids were identified. The following quantities were discovered: rutoside (204.81 g/g of dry extract), quercetin (305.6 g/g of dry extract), quercetin3-O-arabinoside (312.40 g/g of dry extracts), catechin (108.54 g/g of dry extracts), and luteolin-7-Oglucoside (55.35 g/g of dry extracts).

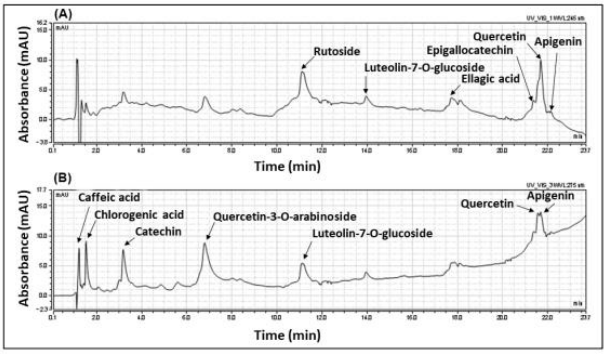
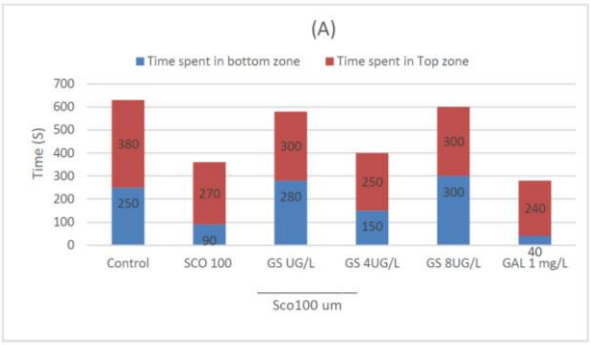



Figure 2: LC-PAD chromatography profile

Various distributions have exhibited that the vegetal material from G. senegalensis utilized in traditional medication contains in excess of 46 mixtures. According to earlier published data, chemicals that are similar to those in our results have been discovered in the leaves of G. senegalensis. In any case, most of the ongoing information just gives a conventional distinguishing proof without the measurements of these mixtures. Extractability is connected with the plant material, the solvent, and the preparation process. The most common combinations described included different polyphenolic acids, flavonoids, and gallic acid derivatives. As per the synthetic arrangement, the examined remove gives off an impression of being rich in polyphenols (flavonoids, catechins, and polyphenolic acids), which are referred to work as normal cell reinforcements. The free hydroxyl moieties likewise enact a safeguard component against free radicals in addition to connecting with cell layers. Additionally, quercetin, apigenin, and catechin derivatives inhibit oxidative enzymes like lipoxygenases to stop the denaturation of cells.

### Impact of the NOR, Y-Maze and NTT Tests on Zebrafish Anxious Behavior and Spatial Memory

Zebrafish are in many cases utilized in the new tank plunging test (NTT) to analyze the impacts of uneasiness. The GS treatment brought about huge changes in the top/base proportion, complete distance went in the top zone, number of sections to the top, and time spent in the highest point of the tank, as per the one-way of ANOVA. Following Sco treatment, there was a sensational decline (p 0.0001) in how much time spent in the top zone of the tank, the top/base proportion, the distance went in the top zone, and the quantity of doorways to the top contrasted with the benchmark group (p 0.0001). Furthermore, the Sco-organization diminished the locomotory design in contrast with the benchmark group. For contrast, GS treatment had anxiolytic-like effects in Sco zebrafish at all dosages (1 g/L, 4 g/L, and 8 g/L). Iripramine (IMP), a favourable reference drug, showed anxiolytic effects.



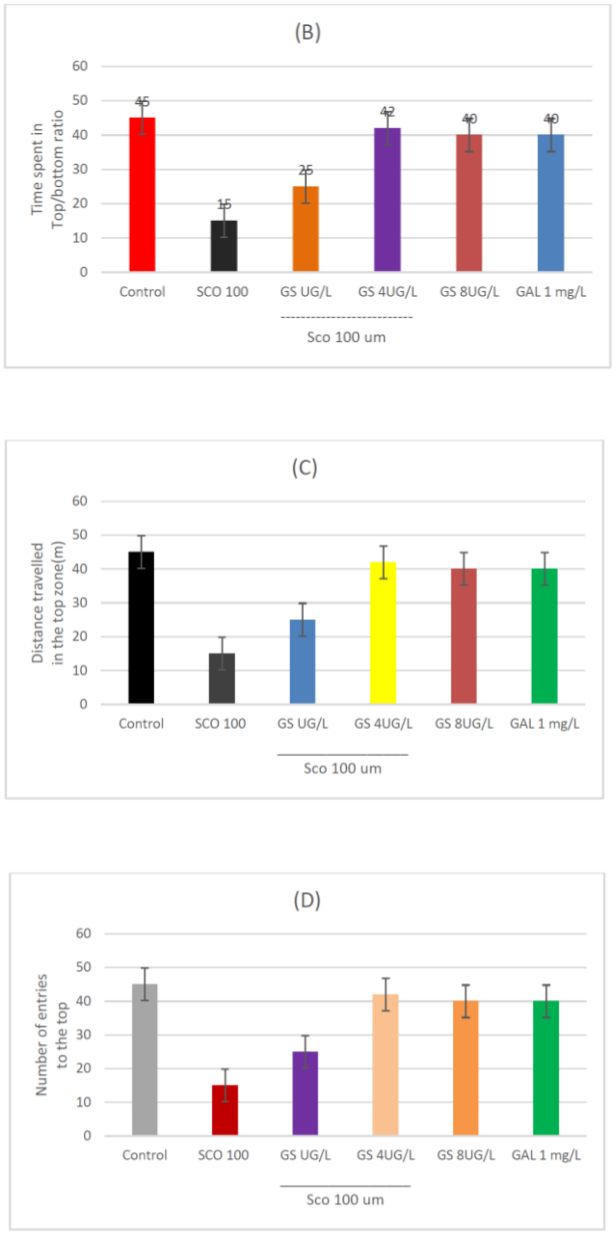



Figure 3: Guiera senegalensis hydroethanolic extract

Our findings confirm past research suggesting GS may have a neuroprotective effect. Sombie suggests a new possible source of naturally occurring neuroprotective and antioxidant components: the galls from G. senegalensis.

Additionally, Somewhat's exploration uncovered that G. senegalensis is as a treatment mental and neuropsychiatric sicknesses in the Hauts-Bassins locale of Burkina Faso. As per the creators, the advantages were achieved by the presence of the neuroprotective mixtures.

These results suggest that GS may be considered a therapeutic medication with a high potential for enhancing cognitive impairments. In fact, we demonstrated that GS has cognitive-improving and anxiolytic properties using the Sco zebrafish model.

**Impact on AChE Activity in the Brain**

AChE activity was investigated to learn more about the GS mechanism in the Sco zebrafish model. In mild cognitive impairment, AChE activity represented cholinergic status. When processing memories, the cholinergic system is crucial, and cholinergic neurons are destroyed. Acetylcholine levels fall as a result of AChE, which causes the learning and memory impairments associated with AD. Additionally, AChE inhibitors are implied in AD therapy, which improves cholinergic neurotransmission.

The AChE activity in the zebrafish treated with Sco was extremely higher than in the control group (p 0.0002). Additionally, the GS treatment significantly decreased the Sco-mediated AChE aggravation at all dosages (p 0.0001). The GS has cholinesterase inhibitory potential, which is connected to zebrafish with superior memory capacity, according to the results of the NTT, Y-maze, and NOR tests. Inhibiting AChE can be used to treat dementia caused by Alzheimer's disease, Parkinson's disease, senile dementia.

Particularly at low doses, GS dramatically reduced the In the zebrafish brain, Sco causes a rise in AChE. Since it modifies mental capability, hippocampal Hurt is a significant supporter of dementia-related cognitive declines and the fundamental component of mental problems..

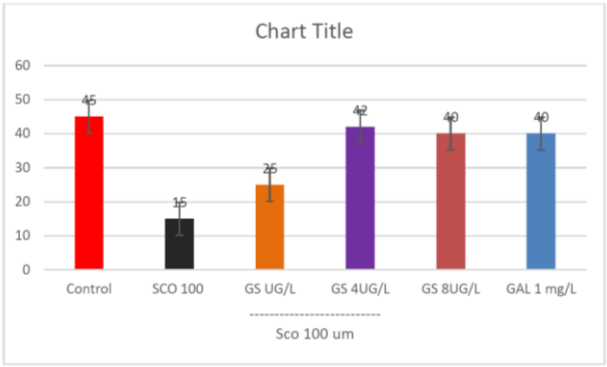



Figure 4: Impact of Guiera senegalensis hydroethanolic extract

**Brain antioxidant capacity effects**

The oxidative stress indicators were assessed to see if GS boosts antioxidant capability in vivo. Following exposure to Sco, Superoxide dismutase (SOD), catalase (CAT), glutathione peroxidase (GPX), total reduced glutathione (GSH), as well as protein carbonyl (p 0.0001) and lipid peroxidation (malondialdehyde—MDA) activities, all extremely decreased (p 0.0003).

Additionally, GS treatment (1 g/L, 4 g/L, and 8 g/L) significantly reversed the fall in CAT,SOD specific activity, GPX, and the overall amount of reduced GSH (p 0.001, 0.0001, and 0.0004, respectively) (p 0.0001). In addition, animals treated with Sco had extremely lower levels of protein carbonyl (p 0.0001) and MDA (p 0.001) after receiving GS therapy, which in turn decreased protein and lipid peroxidation.

**Conclusions**

In this work, the chemical composition of OmEO was first determined, then the proteomes of AD model rats were analysed to look for any molecular alterations. This approach indicated four biological processes as potential OmEO side effects that might affect rat brain (hippocampi) performance: apoptosis, oxidative stress, neuriinflammation and cognitive processes mediated by neurotrophins.

Testing corresponding targets—recognized representatives of the biological processes of interest—led to the determination of the relevance of the biological processes in question. In this work, we discovered that OmEO improved cognition in rats treated with A1-42 and decreased brain oxidative stress. In order to demonstrate that OmEO improves memory performance in rats given A1-42 treatment, we finally connected the cellular and molecular findings with behavioural data.

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# Cardioprotective Effects of 6-Gingerol against Alcohol-Induced ROS-Mediated Tissue Injury and Apoptosis in Rats

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**Abstract:** The present study investigated the cardioprotective properties of 6-gingerol against alcohol-induced ROS-mediated cardiac tissue damage in rats. Experiments were conducted on 4 groups of rats, orally treated with control, 6-gingerol (10 mg/kg body weight), alcohol (6 g/kg body weight) and combination of 6-gingerol plus alcohol for two-month. In the results, we found 6-ginger treatment to alcohol-fed rats substantially suppressed ROS production in cardiac tissue. Alcohol-induced elevated 8-OHDG and protein carbonyls which represent oxidative modification of DNA and proteins were completely reversed by 6-gingerol. This was further endorsed by restored superoxide dismutase and catalase activities with 6-gingerol against alcohol-induced loss. The elevated cardiac biomarkers (CK-MB, cTn-T, cTn-I) and dyslipidemia in alcohol-intoxicated rats was significantly reversed by 6-gingerol. Furthermore, alcohol-induced apoptosis characterized by overexpression of cytochrome C, caspase-8 and caspase-9 was diminished with 6-gingerol treatment. Transmission electron microscope images conferred the cardioprotective properties of 6-gingerol as we have seen less structural derangements in mitochondria and reappearance of myofilaments. Our findings conclude that 6-ginger effectively protect alcohol-induced ROS-mediated cardiac tissue damage, which may be due to its potent antioxidant efficacy. Therefore, 6-gingerol could be a potential therapeutic molecule that can be used in the treatment of alcohol-induced myocardial injury.

**Keywords:** apoptosis; ROS; oxidative stress; protein carbonyl; gingerol; ethanol

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## 1. Introduction

Chronic alcohol consumption is implicated in risk of developing various diseases, including cardiovascular diseases (CVD), and leads to alcohol-related morbidity and mortality [1]. Alcohol and its metabolites can cause mild to severe tissue injuries, mainly due to impaired antioxidant status and oxidative stress [2,3]. The highly unstable free radicals or reactive oxygen species (ROS) that are produced during alcohol metabolism ruins the defensive antioxidant status, and cause destructive damage to cardiac tissue [4]. Excessive accumulation of ROS disrupts the redox homeostasis and leads to the oxidative modification of vital biomolecules, including proteins, lipids and DNA [5–7]. Oxidative stress is considered to be an important factor to promote cell death in response to a variety of signals and pathophysiological situations. Excessive alcohol consumption is linked with abrupt apoptosis of cardiomyocytes via various signaling pathways [8,9]. A study found that alcohol induced mitochondrial apoptosis in cardiomyocytes through stimulated oxidative stress [5,10]. Alcohol-induced cardiac tissue damage was further witnessed by elevated cardiac biomarkers, such as creatine kinase-MB (CK-MB), cardiac troponin-T (cTn-T) and

cardiac troponin-I (cTn-I) in rats [11]. Although ROS scavengers have been shown to inhibit alcohol-induced cardiac tissue damage [11], the mechanism and involved molecules behind this phenomenon remain elusive.

The rhizome of *Zingiber officinale*, known as 'ginger', has been consumed worldwide as a spice and herbal medicine, and cultivated in most tropical regions of the world. Ginger has vital non-volatile pungent phytochemicals, such as gingerols, shogaols, paradols and zingerone, which have shown biological activities [12]. Among them, 6-gingerol (Figure 1A), a phenol phytochemical constituent of fresh ginger, has been reported to possess several pharmacological efficacies, including anticancer, antioxidant, anti-inflammation, anti-platelet aggregation and antifungal [11,13,14]. Sampath et al. reported that 6-gingerol prevents atherosclerosis by inhibiting the oxidative stress biomarkers [15]. Another study showed that 6-gingerol treatment improves antioxidant status and prevents myocardial injury induced by doxorubicin [16]. The protective effects of 6-gingerol against myocardial fibrosis possibly associated with increased antioxidant capacity, decreased inflammation and apoptosis in mice [17].

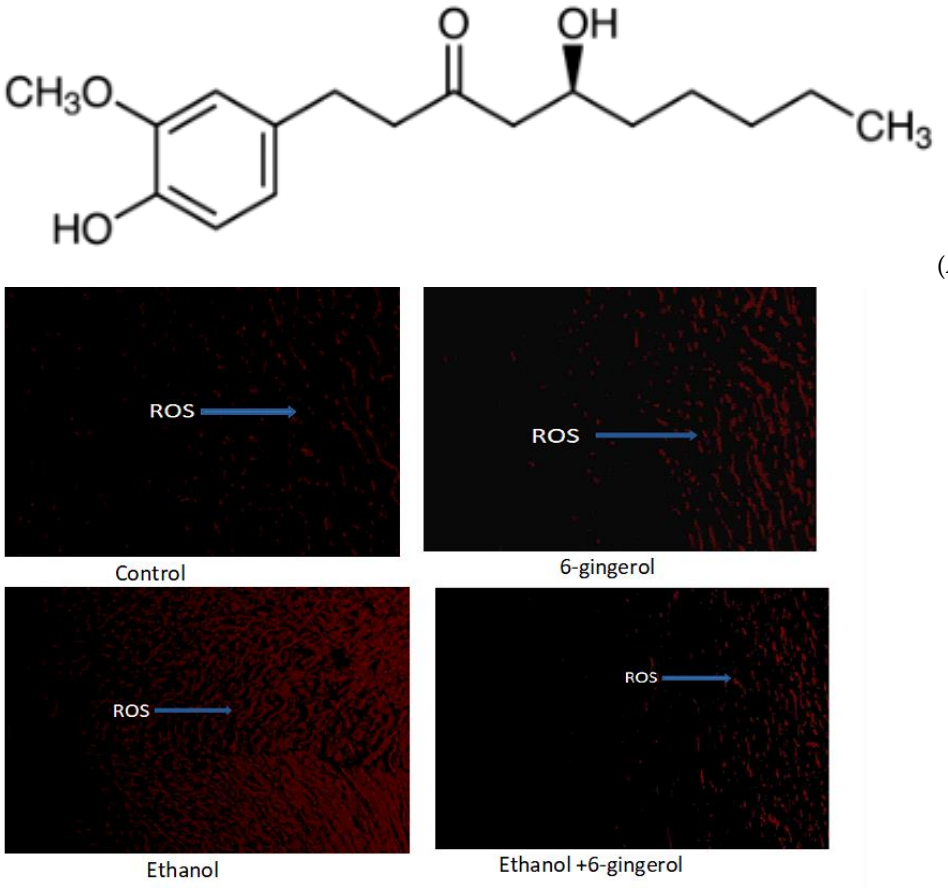



**Figure 1.** (**A**) Chemical structure of 6-gingerol. (**B**) Changes in intracellular ROS production in control, 6-gingerol, ethanol and 6-gingerol plus alcohol-fed rats.

Although previous studies have revealed the pharmacological efficacies of 6-gingerol against oxidative stress and inflammation, the function of 6-gingerol against alcohol-induced myocardial injury and oxidative stress has not yet been established. Therefore, in this study, we investigated the cardioprotective properties of 6-gingerol against alcohol-induced myocardial damage in rats. We examined the changes in key biomarkers that are involved in regulation of antioxidant status, oxidative stress and apoptosis with or without 6-gingerol treatment in alcohol-fed rats.

## 2. Results

### *2.1. Six-Gingerol Suppress ROS Production in Alcohol-Fed Rats*

ROS, which play a crucial role in provocation of oxidative stress, were determined in cardiac tissues of all experimental groups by dihydroethidium (DHE) fluorescent dye. We found ROS distribution in a small area of cardiac tissue in control and 6-gingerol-treated rats (Figure 1B). By contrast, ROS were found in large areas of cardiac tissue in alcohol-treated rats, detected by red fluorescent dye (DHE) under the fluorescent microscope. However, 6-gingerol treatment in combination with alcohol substantially suppressed the ROS generation in cardiac tissue (Figure 1B). These findings reveal that occurrence of ROS-mediated myocardial damage in alcohol-fed rats could be attenuated by 6-gingerol treatment.

### *2.2. Treatment of 6-Gingerol Restores Antioxidant Enzymes against Alcohol-Induced Loss*

The concentrations of intracellular ROS typically dictate the tissue antioxidant status. Therefore, we examined the changes of primary antioxidant enzyme activities in response to alcohol and gingerol treatments. In the results, we found a significant decrease of both superoxide dismutase (SOD) and catalase (CAT) activities in cardiac tissue of alcohol-fed rats (Figure 2A,B). Nevertheless, gingerol treatment considerably restored the SOD ($p < 0.05$) and CAT ($p < 0.05$) activities against alcohol-induced loss. The restored antioxidant enzyme activities with gingerol treatment were further witnessed in the inhibition of excessive ROS production.

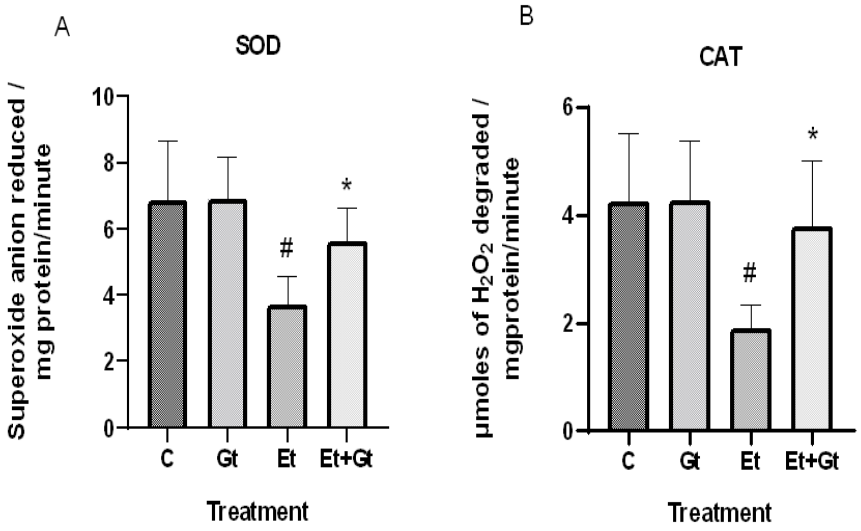



**Figure 2.** Changes in superoxide dismutase (**A**) and catalase (**B**) activities in cardiac tissue of control (C), 6-gingerol (Gt)-, ethanol (Et)- and ethanol + 6-gingerol (Et + Gt)-treated rats. The data were expressed as mean ± standard deviation (SD). $^{\#}$ $p < 0.05$ compared with control and * $p < 0.05$ compared with ethanol treated groups.

### *2.3. Gingerol Treatment Reverses Elevated 8-Hydroxyguanosine (8-OHDG) and Protein Carbonyls*

We next determined the levels of oxidative damage to DNA and proteins in alcohol- and gingerol-treated groups. Our results showed a considerable DNA oxidative damage in cardiac tissue by alcohol intoxication, which was represented by elevated 8-OHDG levels. This was about 3-fold higher compared with normal control (Figure 3A). It is worth noting that gingerol treatment substantially ($p < 0.05$) inhibited the elevated 8-OHDG levels, indicating the protective effects of gingerol against DNA damage.

Furthermore, we found that alcohol intoxication led to oxidative modification of cardiac proteins, which was evidenced by increased protein carbonyl levels. However, gingerol treatment to alcohol-fed rats significantly ($p < 0.05$) suppressed protein carbonyl content in the myocardial tissue (Figure 3B). Taken together, gingerol is able to protect the cardiac tissue by inhibiting the oxidative modification of DNA and proteins against alcohol intoxication.

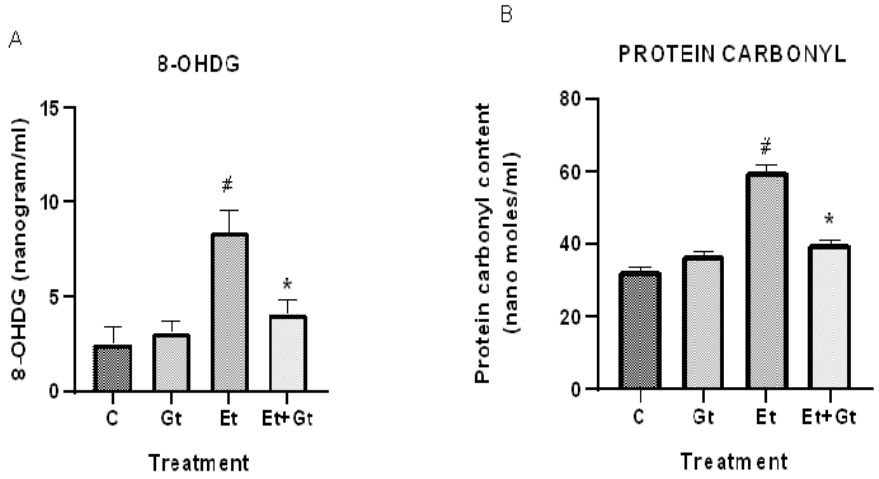



**Figure 3.** Gingerol treatment suppressed 8-OHDG (**A**) and protein carbonyls (**B**). Assessments were done in control (C), 6-gingerol (Gt)-, ethanol (Et)- and ethanol plus 6-gingerol (Et + Gt)-treated rats. The data were expressed as mean ± SD. # $p < 0.05$ compared with control and * $p < 0.05$ compared with ethanol-treated groups.

### *2.4. Antilipidemic Properties of 6-Gingerol in Alcohol-Fed Rats*

To elucidate the antilipidemic effects of gingerol, we measured the changes of total cholesterol (TC), triglyceride (TG), low-density lipoprotein (LDL) and high-density lipoprotein (LDL) levels in all experimental groups. We found that circulating total cholesterol, TG and LDL were significantly increased, while HDL levels were significantly decreased following alcohol drinking. In contrast to these, gingerol treatment to alcohol-fed rats significantly decreased the total cholesterol, TG and LDL levels and restored the HDL levels (Table 1).

**Table 1.** Alcohol-induced dyslipidemia reversed by 6-gingerol. Data were expressed as mean ± SD (N = 6). # $p < 0.005$ compared with control * $p < 0.05$ compared with ethanol groups. Values were shown in control (C), 6-gingerol (Gt)-, ethanol (Et)- and ethanol plus 6-gingerol (Et + Gt)-treated groups.

| Lipid Profile (mg/dL) | Groups | | | |
|---|---|---|---|---|
| | C | Gt | Et | Et + Gt |
| TG | 38.83 ± 5.05 | 39.38 ± 4.17 | 89.20 ± 6.08 # | 44.17 ± 4.98 * |
| TC | 66.94 ± 4.12 | 64.24 ± 5.13 | 119.86 ± 5.45 # | 72.45 ± 6.13 * |
| HDL | 25.13 ± 2.36 | 24.51 ± 2.08 | 12.62 ± 3.06 # | 21.33 ± 1.94 * |
| LDL | 40.48 ± 2.11 | 38.73 ± 1.91 | 109.11 ± 2.37 # | 56.77 ± 1.98 * |

### *2.5. Gingerol Prevents Alcohol-Induced Elevation of Cardiac Biomarkers*

The protective effects of gingerol against alcohol-induced cardiac tissue injury was determined by measuring the important cardiac biomarkers, including CK-MB, cTn-T and cTn-I. As we assumed, alcohol intoxication significantly elevated the circulating levels of CK-MB ($p < 0.05$), cTn-T ($p < 0.05$) and cTn-I ($p < 0.05$), which indicates the cardiac tissue damage (Figure 4A,B,C). Six-gingerol treatment prevents the alcohol-induced cardiac damage through suppressed cardiac biomarkers ($p < 0.05$). The suppressed levels of cTn-T, cTn-I and CK-MB with gingerol treatment were 41.5%, 40.26% and 42.38%, respectively, compared to alcohol-induced elevation (Figure 4). These results revealed the potential cardioprotective effects of 6-gingerol against alcohol intoxication.

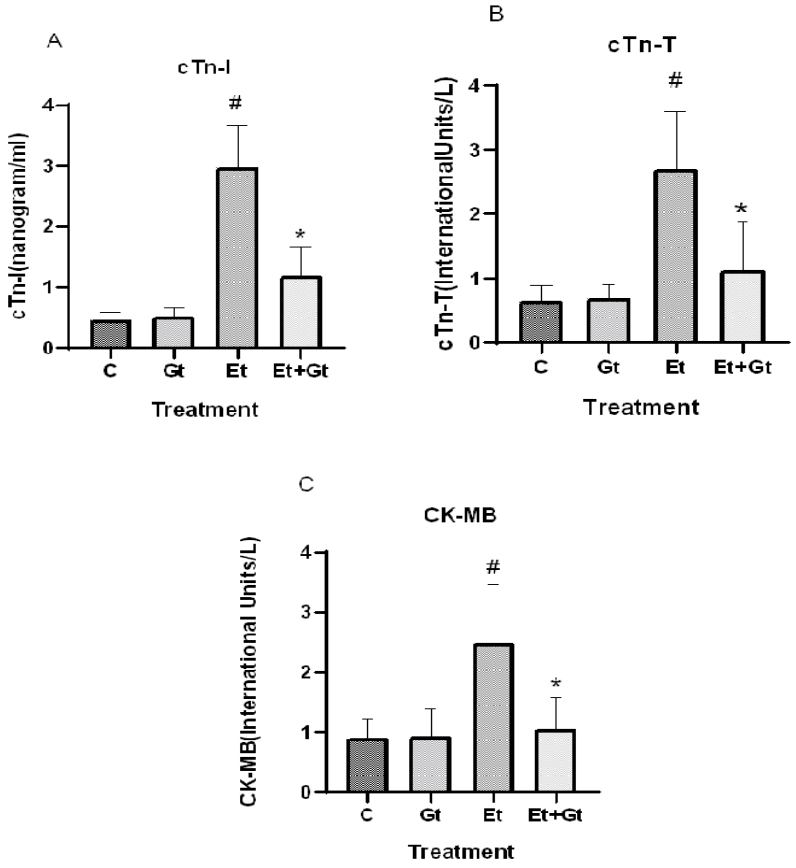



**Figure 4.** Changes in cTn-I (**A**), cTn-T (**B**) and CK-MB (**C**) levels in plasma of control (C), 6-gingerol (Gt)-, ethanol (Et)- and ethanol plus 6-gingerol (Et + Gt)-treated groups. The data are expressed as mean ± SD. # $p < 0.05$ compared with control and * $p < 0.05$ compared with ethanol-treated groups.

### *2.6. Gingerol Treatment Attenuates Upregulated Apoptotic Markers in Alcohol-Fed Cardiac Tissue*

We extended our studies to evaluate the anti-apoptotic properties of 6-gingerol against alcohol-induced induction of apoptosis in cardiac tissue. The studied key apoptotic makers through immunohistochemistry visualized that alcohol drinking triggered the expression of cytochrome C, caspase-8 and caspase-9 in cardiac tissue. Interestingly, 6-gingerole treatment for 60 days along with alcohol diminished the overexpression of cytochrome C, caspase-8 and caspase-9 in cardiac tissue. These findings evidenced that alcohol-induced initiation of apoptosis could be attenuated by 6-ginferol treatment (Figure 5). Similar to antioxidant enzyme activities, the immunohistochemistry images also showed restored expression of SOD and CAT with 6-gingerol co-administration with alcohol (Figure 6A,B).

### *2.7. Transmission Electron Microscopy (TEM) Demonstrates Cardioprotective Effects of Gingerol*

Subsequently, TEM was performed to assess the cardioprotective efficacies of 6-gingerole. As shown in the images, control heart was characterized by typical symmetric myofibrils comprised of Z lines with sarcomeres. Furthermore, packed mitochondria adjacent to the fibers were evidenced in the control group. Gingerol alone treated rats shown mitochondria slightly deviated from the fibers remaining myofibril structure intact. However, alcohol alone treated group represented with altered myofibril structure, disappearance of Z lines, derangement of sarcomeres and mitochondrial swelling. All these destructive features imply the mitochondrial apoptosis with alcohol intoxication. It should be noted that gingerol treatment prominently attenuated these structural derangements. These protective effects were evidenced by less structural alterations in mitochondria, reappearance of myofilaments and Z lines (Figure 7).

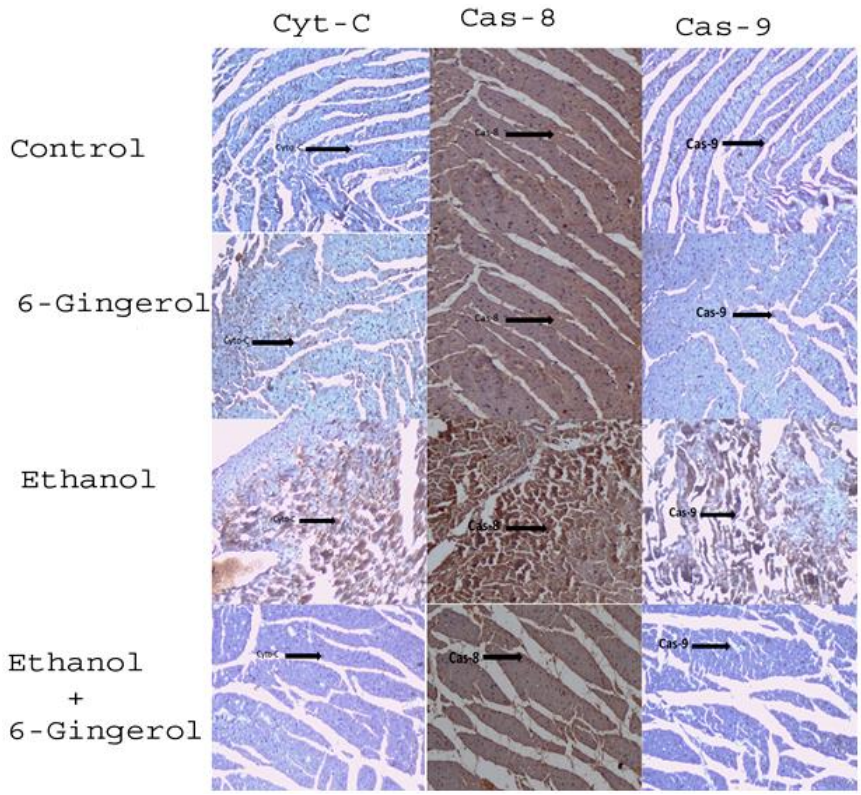



**Figure 5.** Six-gingerol regulates ethanol induced ROS-mediated apoptosis in cardiac tissue. Expressions of mitochondrial cytochrome C, caspase-8 and caspase-9 in cardiac tissues of control, 6-gingerol, ethanol and ethanol plus 6-gingerol groups. The arrow in each panel indicates the expressions of cytochrome C, caspase-8 and caspase-9 in respective groups.

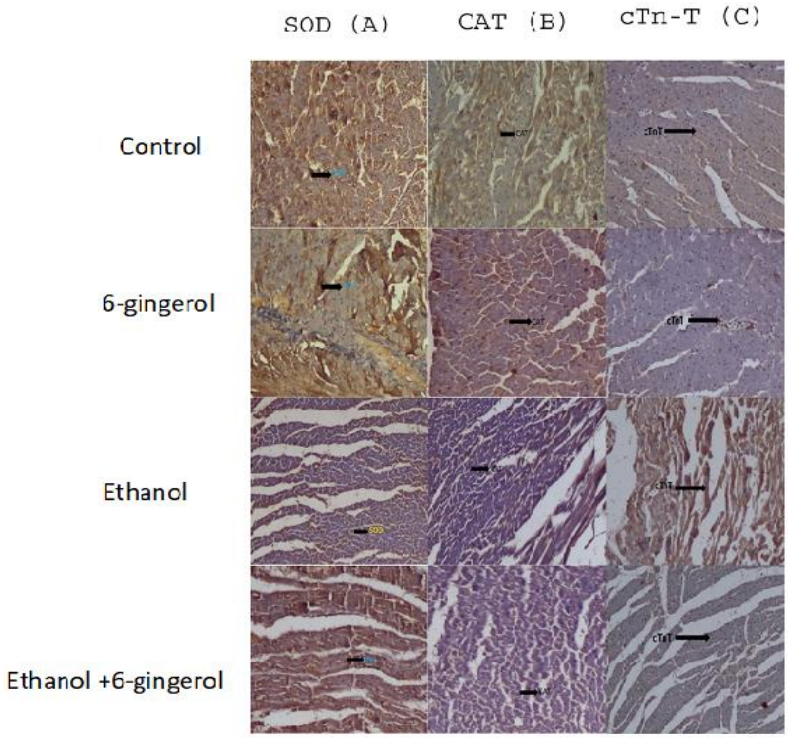



**Figure 6.** Immunohistochemistry images of SOD (**A**), CAT (**B**) and cTn-T (**C**) in all experimental groups. The arrow in each panel indicates the expressions of SOD, CAT and cTn-T in respective groups.

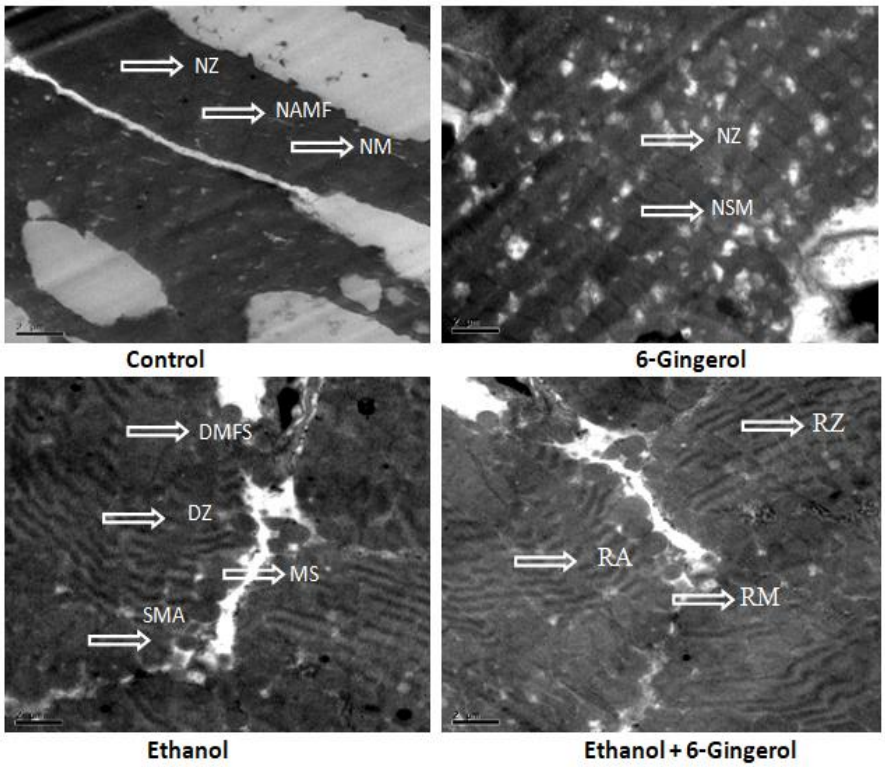



**Figure 7.** Transmission electron microscopy images of cardiac tissue display alcohol-induced tissue damage and 6-gingerol mediated recovery. The arrow indicates normal structure of Z line (NZ), normal architecture of myofibril (NAMF), normal mitochondria (NM) and normal sarcomere (NSM) in control or 6-gingerol groups. The arrow indicates, degeneration of myofibril structure (DMFS), degeneration of Z lines (DZ), sarcomere alteration (SMA) and mitochondria swelling (MS) in ethanol group. The arrows in ethanol plus 6-gingerol group indicate regeneration of Z line (RZ), regeneration of mitochondria (RM) and reappearance of sarcomere (RA).

## 3. Discussion

In this study, for the first time we have demonstrated that 6-gingerol substantially alleviated the alcohol-induced oxidative damage, myocardial injury and apoptosis. Experimental evidence shows that 6-gingerol treatment suppressed alcohol-induced ROS production in cardiac tissue. This therapeutic effect was accompanied by restored myocardial antioxidant status, and decreased DNA oxidative damage and protein carbonyls. In addition, alcohol-induced elevated cardiac biomarkers (CK-MB, cTn-T, cTn-I) and dyslipidemia were significantly reversed by gingerol. Histopathological evidence further confirmed the tissue protective effects of 6-gingerol against alcohol-induced myocardial injury and apoptosis. Since alcohol is typically involved in impairing of antioxidant homeostasis and myocardial injuries, supplementation of antioxidant rich molecules like 6-gingerol could possibly alleviate the myocardial damage. The calculated 6-gingerol dose from our rat model (10 mg/kg) is ~97 mg per adult with an average weight of 60 kg [18]. This dose might be feasible to humans, as a previous study reported no serious adverse effects of 6-gingerol with dose ranges from 100 mg to 2000 mg per adult [19].

It has been documented that alcohol intake, either chronic or acute, alters the cardiomyocyte and whole organ functioning of the heart [20]. ROS or free radicals that are generated during alcohol metabolism are crucially involved in the onset of myocardial disturbances possibly through ruining of intracellular antioxidant homeostasis [21,22]. Accumulations of highly reactive ROS destabilize the myocardial contractility, cause myocardial tissue injury, and induce myocyte apoptosis [23]. In agreement with these findings, we also noticed excessive production of ROS and subsequent myocardial injury in alcohol-fed rats. However, 6-gingerol treatment to alcohol-fed rats for a period of 2 months considerably inhibited

the ROS production in cardiac tissue. Previous studies have shown that 6-gingerol is able to decrease ROS-mediated oxidative stress in the liver [24], and its antioxidant property reduces acute renal toxicity [25]. Our previous in vitro findings also demonstrated the free radical scavenging ability of 6-gingerol [26]. A recent study reported that only 7 days of 6-gingerol treatment to arsenic trioxide injected mice significantly decreased ROS production in heart [27]. These findings indicate that 6-gingerole is able to inhibit intracellular ROS production during ethanol metabolism.

Oxidative stress is an imbalance between the amount of intracellular ROS and antioxidant defense status. Alcohol intoxication is characterized by elevated oxidative stress and decreased antioxidant enzyme status in various tissues, including liver and heart of rodents [6,11,28]. Here, we found alcohol-induced oxidative damage of DNA and proteins as reported by elevated 8-OHDG and protein carbonyl levels, respectively. Chronic ethanol consumption in rats has been shown to increase protein oxidation in parallel with increased free radicals [29]. The uncontrolled-highly unstable ROS that are generated during alcohol metabolism eventually affect the function of cardiomyocytes/heart through irreversible damage of mitochondria, DNA and proteins. These events are clinically associated with pathogenesis of cardiomyopathy [5,30]. Therefore, controlling alcohol-induced oxidative stress by known antioxidants is necessary to prevent the progression of cardiomyopathy. We found that gingerol treatment along with alcohol tremendously inhibited the formation of 8-OHDG and protein carbonyls. Due to their highly reactive nature, hydroxyl radicals or singlet oxygen hydroxylate the deoxyguanosine and formed 8-hydroxy-2′deoxyguanosine. Decreased 8-OHDG levels with 6-gingerol explains that gingerol molecules possibly inhibit the production of intracellular hydroxyl radical and/or singlet oxygen against alcohol toxicity and thereby prevent the oxidative damage to DNA and proteins. Our present findings and previous reports also confirmed the potent free radical scavenging activity or ROS inhibitory efficacy of 6-gingerol [26]. An in vitro study reported that 6-gingerol possess a strong protective ability against the DNA damage caused by mono (2-ethylhexyl) phthalate in human endothelial cells, and the mechanism may be due to its antioxidant activity [31].

Decreased intracellular ROS production or oxidative stress in any context could possibly explained by the antioxidant status of a tissue. Therefore, we determined the primary antioxidant enzyme activities in the heart of alcohol and 6-gingerol-treated rats. In accordance with elevated oxidative stress and ROS production, the primary radical scavenging enzymes SOD and CAT were significantly decreased following alcohol intoxication. Decreased antioxidant enzyme activities with alcohol drinking were repeatedly confirmed by several previous studies [3,5]. Persistent lower grade antioxidant capacity and subsequent oxidative stress perhaps contributes to morphological changes and malfunctioning of cardiac tissue [5]. The important finding in our study is that the decreased SOD and CAT activities were restored with 6-gingerol treatment. In a rat model, 6-gingerol was reported to increase antioxidant enzyme activities and protect the intestinal barrier from ischemia/reperfusion-induced damage [32]. Various doses of gingerol fraction was reported to improve the renal antioxidant enzyme activities and decrease the lipid peroxidation against gentamicin-induced nephrotoxicity in rats [25]. Another study demonstrated that cotreatment of 6-gingerol and ethanol significantly restored the antioxidant enzyme activities against ethanol-induced loss in cultured mouse embryos [33]. Taken together, our findings provided additional knowledge that 6-gingerol treatment for a period of 2 months could protect the cardiac tissue against alcohol-induced oxidative damage through improved antioxidant status.

Chronic alcohol consumption not only impairs the redox homeostasis, but also causes dyslipidemia, a major risk factor for developing cardiovascular diseases. Dyslipidemia is typically represented by abnormal increase of circulating lipid profiles; including TG, TC and LDL, while HDL levels are decreased. Alcohol administration to rats resulted in increased TG, TC and LDL levels and decreased HDL, which confirmed the dyslipidemia status. In our study, 6-gingerol treatment to alcohol-fed rats reversed the dyslipidemia as shown by decreased TG, LDL, and TC levels along with increased HDL levels. Clinical

studies have shown that increasing TG, LDL and TC increases the risk of non-ischemic heart failure, while decreasing serum lipids can reverse the heart dysfunction [34]. In this context, decreased levels of TG, LDL and TC with 6-gingerol treatment perhaps improved the heart function which was deteriorated by alcohol intoxication in rats. Saravanan and colleagues also reported that oral administration of gingerol for 30 days contributed to a significant decrease of lipid profile in obese rats [35]. Another study reported that 6-gingerol treatment for 12 days significantly decreased plasma TG, LDL, and free fatty acid concentrations in db/db mice. This lipid-lowering effect of 6-gingerol was accompanied by an increased antioxidant enzyme activities and suppressed ROS generation in db/db mice [36]. These findings reveal that 6-gingerol is a considerable molecule to lower the lipid profile and prevent the lipid-associated cardiac dysfunction.

Circulating cardiac biomarkers are novel quantitative measures which shed light on occurrence of cardiac pathophysiology [37]. The biomarker troponin I (cTn-I/cTn-T) is a sensitive and specific marker for myocardial injury, which is widely used to diagnose the myocardial infarction [38]. In our study, alcohol-induced elevation of clinical cardiac biomarkers in plasma is another evidence of cardiac tissue damage in alcohol-fed rats. There was a substantial correlation between elevated lipid profile and increased release of cardiac biomarkers in plasma by damaged cardiac cell under ethanol intoxication [11]. In agreement with previous findings, our results also revealed that ethanol intoxication increase the cardiac biomarkers, including CK-MB, cTn-T and cTn-I in plasma. A previous study reported a several-fold rise in serum troponin, myoglobin and CK-MB concentrations after alcohol septal ablation for the treatment of hypertrophic cardiomyopathy [39]. Based on the cardiac biomarker data, a community-based cohort study reported even modest habitual alcohol intake was associated with an increased risk of atrial fibrillation [37]. These results indicate that controlling of cardiac biomarkers is essential in treating the myocardial injuries. Nevertheless, 6-gingerol treatment along with alcohol exerts the cardioprotective effects by diminishing the elevated CK-MB, cTn-T and cTn-I levels. A study by Ren et al., demonstrated that various concentrations of 6-gingerol protects cardiomyocytes from hypoxia-induced injury by suppressing the release of lactate dehydrogenase (LDH) and apoptosis [40]. Cotreatment of ginger to alcohol-fed rats also reported decreased concentrations of cTn-T, LDH and CK-MB in rats [11]. Pretreatment of 6-gingerol has been shown to improve the cardiac function by decreasing the cTnT and CK-MB expressions in ischemia/reperfusion (I/R)-induced myocardial injury model [41]. Lipid-lowering effect and/or improved antioxidant status by gingerol possibly contributed to attenuate the alcohol-induced elevation of cardiac biomarkers.

It has been speculated that overwhelming production of ROS intrinsically involved in initiation and progression of cardiac myocytes apoptosis under chronic ethanol intoxication [42]. Several studies have shown that chronic alcohol consumption promptly associated with occurrence of cardiomyocytes apoptosis by alterations in mitochondria membrane potential [43,44]. Although we haven't detected the mitochondrial membrane potential, the apoptotic proteins in implicated in mitochondrial apoptosis was determined through immunohistochemistry. Our results showed that the apoptotic biomarkers, such as cytochrome C, caspase-9 and caspase-8, were highly expressed in alcohol-intoxicated hearts. Furthermore, elevation of apoptotic proteins were accompanied by decreased cardiac SOD and CAT expressions with alcohol. At molecular levels, ethanol may initiate the apoptosis in cardiac tissue by both intrinsic and extrinsic pathways. In the cascades of apoptosis, ethanol-induced ROS accumulation and decreased antioxidant defense mechanism may play a major role in the expression of caspase-8. Triggering of cytochrome C release by alteration in mitochondrial membrane permeability led to activation of caspase-9 [45,46]. Meanwhile, 6-gingerol treatment profoundly inhibited the apoptosis in cardiac tissue by suppressing the overexpressed cytochrome C, caspase-9 and caspase-8, while restoring the tissue antioxidant status. The earlier reports have shown that ROS scavengers or inhibitors can control the alcohol-induced apoptosis in cardio myocytes [47]. In this context, 6-gingerol was reported to decrease the formation of apoptotic proteins that reserved the myocardial

apoptosis under hypoxia condition [40]. 6-gingerol administration to isoproterenol-treated mice (14-day) resulted in a significant reduction of caspase-3, Bax protein expressions and Bax/Bcl-2 ratio, indicating attenuation of cardiac apoptosis. This anti-apoptotic property of gingerol was accompanied by inhibition of oxidative stress and inflammatory biomarkers [17]. It has been reported that 6-gingerol metabolites may stay about 12 h in the body after oral administration [48]; therefore, we assume that the bioavailability of gingerol may be responsible for its therapeutic efficacies under stress. Taken together, our results suggest that 6-gingerol can inhibit the apoptosis under ethanol intoxication through reduction of ROS production and improvement of antioxidant defense mechanism.

Another important finding of this study is that TEM analyses provided additional convincing evidences that 6-gingerol is a potent tissue protective molecule. TEM visuals demonstrated that ultra-structural derangement in cardiac tissue following ethanol intoxication. We further noticed intense lysis of myofibrils with disruption of Z lines and sarcomere structure, mitochondrial swelling and damage, which collectively results in myocardium apoptosis in ethanol-intoxicated rats. It is worth noting that 6-gingerol attenuate all these destructive changes and retained the ultra-structure of myocardium against cardiotoxic effect of ethanol. In I/R-induced myocardial injury model, 6-gingerol pretreatment to rats reduce myocardial infarction area and degree of cardiac pathological injury followed by lower levels of myocardial enzyme and inflammatory mediators [41]. Some studies have shown that food-based formulations that contain ginger could promote alcohol metabolism and alleviate the alcohol hangover effects [49]. In such case, we assume that 6-gingerol may be involved in rapid alcohol metabolism, which facilitates lower accumulation of toxic alcohol metabolites and then results in less cardiac tissue damage. Despite the lack of experimental evidence to reveal this phenomenon, this is the first report to demonstrate the cardioprotective effects of 6-gingerol against ethanol-induced cardiac tissue damage in rats.

## 4. Materials and Methods

### *4.1. Chemicals and Reagents*

The phytochemical compound, 6-gingerol (purity: >98.0%) was purchased from TCI chemicals (India) Pvt. Ltd. Both dihydroethidium fluorescent dye and SOD primary antibody were obtained from the Sigma-Aldrich (St. Louis, MO, USA). Catalase, caspase-9 and -8, cytochrome C primary antibodies and secondary antibody horseradish peroxidase (HRP)-conjugated goat anti-rabbit IgG were purchased from Invitrogen (Waltham, Thermo Scientific, MA, USA). Troponin-T primary antibody was obtained from Abcam (Cambridge, UK). Creatine kinase–MB (CK-MB), cardiac troponin-T (cTn-T) and cardiac troponin-I (cTn-I) ELISA kits were purchased from the Biocheck, South San Francisco, USA. Triglyceride (TGs), total cholesterol (TC), high-density lipoprotein (HDL) and low-density lipoprotein (LDL) colorimetric kits were obtained from the Merck (Rathway, NJ, USA). All other chemicals and reagents were analytical reagent grade and purchased from Sigma-Aldrich.

### *4.2. Experimental Animals*

A total of 24 Wister strain male albino rats, weighing 200 ± 30 g, were obtained from the Indian Institute of Science, Bangalore, India. All rats were housed in standard polypropylene transparent cages at a controlled temperature (23–27 °C) and humidity (50% ± 5%) with a 12 h light/dark cycle. Rats had free access to food and water. The experimental design and protocols were approved by the Institutional Animal Ethics Committee (IAEC) of Sri Venkateswara University, India, with (10/i/a/CPCSEA/IAEC/SVU/KSR-GVS/dt 15 November 2010).

### *4.3. Animal Grouping and Treatment*

After a week of adaptation to the laboratory conditions, the rats were randomly assigned into 4 groups, control (C), 6-gingerol (Gt), ethanol (Et) and combination of both ethanol plus 6-gingerol (Et + Gt) groups, with 6 rats in each. Rats in the control group received 0.9% saline solution, rats in the Gt group received 6-gingerol by gavage (10 mg/kg

bodyweight, oral administration) and rats in the Et group received ethanol by gavage (20%, 6 g/kg bodyweight, oral administration). The remaining rats in the Et + Gt group received both ethanol and 6-gingerol as described in respective groups. The treatment was given once a day for all groups, and the whole treatment lasted for 2 months. The selective dosage of alcohol and 6-gingerol used in this study was well established by previous studies [11,16]. Blood samples were collected at 10 am into a sterile heparinized tube from the retro-orbital plexus of rats at the end of the treatment period, and plasma was collected by centrifugation at 2000 rpm for 10 min at 4 °C and then stored at −20 °C for further analysis. The heart tissues were isolated from rats after cervical dislocation and immediately washed with ice cold saline and kept on a chilled glass plate. One part of the heart tissue was stored at −20 °C for further biochemical assays, and the remaining was fixed in 4% formaldehyde for histopathological studies.

### *4.4. ROS Detection by Dihydroethidium (DHE) Fluorescent Dye*

ROS in the cardiac tissue was detected using DHE dye as described by Carter et al., (1994) method [50]. Cryostat sections of cardiac tissue was cut into 10 µm thick and incubated with 5M DHE dye at 37 °C for 30 min. The DHE is oxidized by ROS to produce fluorescent ethidium that subsequently binds to nucleic acids, further staining the nucleus a bright fluorescent red. The red fluorescent from DHE was detected by fluorescent microscope.

### *4.5. Determination of 8-Hydroxydeoxyguanosine (8-OHDG)*

Wash solution (20×) in a volume of 15 mL was diluted with 285 mL of distilled water and prepared 1x assay buffer by 14 mL of assay buffer was added to 56 mL of distilled water. To each well, cardiac tissue samples or standard 50 µL and 75 µL of conjugate was added. With the exception of NSB wells, 25 µL of 8-hydroxydeoxyguanosine antibody was added, and then the side of the plate was tapped to mix and incubated for 2 h at room temperature and 100 µL of TMB substrate was added to each well. The substrate solution began to turn blue, was incubated for 30 min at room temperature without shaking, 50 µL of stop solution was added to each well and the absorbance was read at 450 nm. The plate reading was completed within 10 min after adding the stop solution.

### *4.6. Estimation of Protein Carbonyl Content*

Protein carbonyl content in the cardiac tissue was estimated by commercial kit (Sigma-Aldrich). Briefly, 200 mg of tissue was homogenized in 1 mL of tris buffer and centrifuge at 10,000× *g* for 15 min at 4 °C, and the supernatant was stored on ice. A 200 µL sample was added to 800 µL of DNPH, incubated for 1 h in dark at room temperature, and each tube was vortexed briefly for every 15 min during incubation, 1 mL of 20% TCA was added to each tube, and the tubes were vortexed, placed on ice, incubated for 15 min and centrifuged at 10,000× *g* for 10 mint at 4 °C. The supernatant was discarded, the pellet was re-suspended in 1 mL of TCA and the tubes were placed on ice for 5 min and centrifuged at 10,000× *g* for 10 min. The supernatant was discarded, and the pellet was resuspended in 1 mL of (1:1) ethanol and ethyl acetate mixture, then centrifuged at 10,000× *g* for 10 min at 4 °C (Remi C-24 BL/CPR 24 Cooling centrifuge, Mumbai, India). A 220 µL sample was added to each well, and the absorbance was measured at 360–385 nm (Simadzu, UV1800 Spectrophotometer, Kyoto, Japan).

### *4.7. Assessment of Superoxide Dismutase and Catalase Activities*

Changes in SOD activity in the mitochondrial fraction was assessed by the method of Misra and Fridovich (1972) [51] at 480 nm for 4 min on a Simadzu, UV1800 Spectrophotometer (Kyoto, Japan). Activity was expressed as the amount of enzyme that inhibits the oxidation of epinephrine by 50%, which is equal to 1 U per milligram of protein. We then determined the CAT activity at room temperature using the modified version of Aebi [52]. The absorbance of the sample was measured at 240 nm for 1 min in a UV-Spectrophotometer

(Simadzu, UV-Spectrophotometer, Kyoto, Japan). One-unit activity is equal to the moles of $H_2O_2$ degraded/mg protein/min.

### *4.8. Estimation Cardiovascular Risk Factors*

Widely considered lipid based cardiovascular risk factors, including triglyceride (TGs), total cholesterol (TC), high density lipoprotein (HDL) and low-density lipoprotein (LDL) levels, were measured in plasma by commercially available kits (Merck, Rathway, NJ, USA).

### *4.9. Evaluation of Cardiac Biomarkers*

The isoenzyme creatine kinase–MB (CK-MB) levels in plasma were estimated using a commercially available kit (Biocheck, ELISA kit, South San Francisco, CA, USA) in all experimental groups. The absorbance of the sample was measured at 340 nm using iMark Microplate reader (Bio-Rad, Hercules, CA, USA). CK-MB levels were described as international units per liter. Next, changes in cardiac troponin–T (cTn-T) and cardiac troponin–I (cTn-I) in plasma were determined by commercially available kits (Biocheck ELISA kit, South San Francisco, CA, USA) in all experimental groups. The sample absorbance was measured at 450 nm in an iMark Microplate absorbance reader (Bio-Rad, Hercules, CA, USA). The units of cTn-T and cTn-I levels were described as grams per milliliter.

### *4.10. Immunohistochemistry*

Immunohistochemistry study was performed according to the study by Liu et.al., [53]. Briefly, the sections were collected on 3-aminopropyltriethoxysilane (APES)-coated slides, and xylene was added and kept for 15 min. For each slide, alcohol was added in descending concentrations (100–70%), and after 1 min, the slides were washed in tap water for 10 min and distilled water for 5 min. Further, the slides were kept in a presser cooker in 1 mM of citrate buffer (pH 6). After leaving the pressure cooker, placed in sink water for cooling at room temperature, the samples were washed in distilled water for 5 min and with 5 mM of TBS buffer (pH 7.6) twice for 5 min each time. The samples were blocked with peroxidase for 10–15 min, washed three times with TBS buffer and drained. The section was covered with concerned primary antibodies (caspase-8, caspase-9 and cytochrome C) for 1 h (1:1000). Further, the samples were washed three times with TBS buffer for 5 min, andthen incubated with the HRP-conjugated secondary antibody (1:1000). The color was developed within 5–8 min with the use of 3,3′-diaminobenzidine. The samples were washed with TBS buffer three times for 5 min, then incubated in hematoxylin for 1 min. Finally, samples were kept in tap water for 5 min. In the same way, the antioxidants enzymes, such as SOD and CAT, and cardiac biomarkers, such as cTn-T were also assessed in the cardiac tissues of all experimental groups. A microscope (BX51; Olympus, Tokyo, Japan) was used to capture the images of the sections.

### *4.11. Transmission Electron Microscopy*

Heart tissue excised from the rats was perfused with 0.1 M sodium phosphate buffer (pH 7.4) solution containing 2.5% glutaraldehyde and 2% formalin for 15 min at 48 °C according to the protocol described by Watanabe and Yamada [54]. Then the tissue was kept for 2 h at 48 °C in 1% osmium tetroxide contained buffer solution for post fixation. After dehydration, the heart tissue with a various concentration series of alcohol (70–100%), embedded in spurr1 resin. Reichert Ultracut 1 microtome was used for cut the heart tissue with 90 nm thickness. The grids were counterstained with 4% uranyl acetate and 0.4% lead citrate solutions and examined in a Jeol JEM 1010 transmission electron microscope (Peabody, MA, USA) at 80 kV. This assay was performed at the Centre for Cellular and Molecular Biology, Hyderabad, India.

### *4.12. Statistical Analysis*

The experimental data was expressed as means ± standard deviation (SD). One-way analysis of variance (ANOVA) was conducted followed by Duncan's test using SPSS version

19.0 software (Armonk, New York, NY, USA). Statistical significance was considered at $p < 0.05$. Graphs were prepared using GraphPad Prism (Version 5.00, GraphPad Software Inc., San Diego, CA, USA).

## 5. Conclusions

For the first time, our findings demonstrated the potential cardioprotective properties of 6-gingerol against alcohol-induced oxidative stress, apoptosis and architectural damage. The underlying phenomenon may be due to an effective suppression of alcohol-induced ROS protection and/or antioxidant efficacy of gingerol. Further evidence showed that gingerol cotreatment suppressed vital biomarkers of apoptosis and cardiac injury followed by recovered tissue architectural damages. Our findings suggest that 6-gingerol could be a potential therapeutic molecule to use in the treatment of alcohol-induced myocardial injury.

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**Institutional Review Board Statement:** The study was carried in accordance with the Institutional Instructions on Animal Care and Use Committee, Sri Venkateswara University, India. The designing of project and protocols which was used the project reviewed and follow the Institutional animal ethical committee (10/i/a/CPCSEA/IAEC/SVU/KSR-GVS/dt 15 November 2010).

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**Data Availability Statement:** The data which were submitted to this journal is available with corresponding author and first author.

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**Sample Availability:** The samples are available with the first and corresponding authors at the Department of Zoology, Sri Venkateswara University, India.

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# Minimax Multi objective Fractional Programming with B-(p, r)-Invexity with Non differentiable functions

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**Abstract:** In this paper, we derive some theorems and duality theorems on non differentiable Multiobjective Fractional Minimax Programming Under B-(p, r)-Invexity functions.

**Keywords:** B-(p, r)-invex function and Duality.

## Introduction

The necessary and sufficient conditions for generalized minimax programming were first developed by Schmitendorf [1]. Tanimoto [9] applied these optimality conditions to define a dual problem and derived duality theorems. Bector and Bhatia relaxed the convexity assumptions in the sufficient optimality condition in [1] and also employed the optimality conditions to construct several dual models which involve pseudo-convex and quasi-convex functions, and derived weak and strong duality theorems. Yadav and Mukherjee [16] established the optimality conditions to construct the two dual problems and derived duality theorems for differentiable fractional minimimax programming.

Convexity plays an important role in deriving sufficient conditions and duality for non linear programming problems Karush-Kuhn-Tucker type sufficient optimality conditions for nonlinear programming problems. Generalized invexity and duality for multiobjective programming problems are discussed in [5], and inseparable Hilbert spaces are studied by Soleimani-Damaneh [3]. Soleimani-Damaneh [4] provides a family of linear infinite problems or linear semi-infinite problems to characterize the optimality of nonlinear optimization problems. Recently, optimality conditions for a class of generalized fractional minimax programming problems involving B(p, r)-invexity functions and established duality theorems for various duality models.

This paper is organized as follows. In section 2, we give some preliminaries. An example which is B-(1, 1)-invex but convex. In section 3, we establish the sufficient optimality conditions. Duality results are presented in section4 by developing some theorems and duality theorems in non differentiable minimax multi objective fractional programming with B-(p, r)-invexity.

## Notations and Preliminaries

**Definition:** 1. Let $f : X \to R$ ( where $X \subseteq R^n$ ) be differentiable function, and let p, r be arbitrary real numbers. Then f is said to be (p, r)-invex (strictly (p, r)-invex) with respect to $\eta$ at $u \in X$ on X if there exists a function $\eta : X \times X \to R^n$ such that, for all $x \in X$, the inequalities.

$$\frac{1}{r}e^{r(f(x))} \geq \frac{1}{r}e^{r(f(u))}\left[1+\frac{r}{p}\nabla f(u)\left(e^{p\eta(x,u)}-1\right)\right] (>\text{if } x \neq u) \text{ for } p \neq 0,\ r \neq 0$$

$$f(x)-f(u) \geq \frac{1}{p}\nabla f(u)\left(e^{p\eta(x,u)}-1\right) (>\text{if } x \neq u) \text{ for } p \neq 0,\ r = 0 \qquad f(x)-f(u) \geq \nabla f(u)\ \eta(x,u)$$

$(>\text{if } x \neq u)$ for $p = 0,\ r = 0$ hold.

**Definition 2 :** The differentiable function $f : X \to R$ (where $X \subseteq R^n$) is said to be (strictly) B-(p, r)-invex with respect to $\eta$ and b at $u \in X$ on X if there exists a function $\eta : X \times X \to R^n$ and a function $b : X \times X \to R_+$ such that, for all $x \in X$, the following inequalities.

$$\frac{1}{r} b(x, u)\left(e^{r(f(x)-f(u))} - 1\right) \geq \frac{1}{p} \nabla f(u)\left(e^{p\eta(x, u)} - 1\right) (> \text{if } x \neq u) \text{ for } p \neq 0,\ r \neq 0$$

$$\frac{1}{r} b(x, u)\left(e^{r(f(x)-f(u))} - 1\right) \geq \nabla f(u)\, \eta(x, u) (> \text{if } x \neq u) \text{ for } p = 0,\ r = 0$$

$$b(x, u)\left(f(x) - f(u)\right) \geq \frac{1}{p} \nabla f(u)\left(e^{p\eta(x, u)} - 1\right) (> \text{if } x \neq u) \text{ for } p \neq 0,\ r = 0$$

$b(x, u)\left(f(x) - f(u)\right) \geq \nabla f(u)\ \eta(x, u)\ (> \text{if } x \neq u)$ for $p = 0,\ r = 0$ hold. f is said to be (strictly) B-(p, r)-invex with respect to $\eta$ and b on X if it is B-(p, r)-invex with respect to same $\eta$ and b at each $u \in X$ on X.

In this paper, we consider the following non differentiable minimax fractional programming problem:

(FP)

$$\min_{x \in R^n} \sup_{y \in Y} \frac{l_i(x, y) + (x^T Dx)^{\frac{1}{2}}}{m_i(x, y) - (x^T Ex)^{\frac{1}{2}}}$$

Subject to $g(x) \leq 0, \quad x \in X$

where Y is a compact subset of $R^m$, $l(\cdot,\cdot): R^n \times R^m \to R$, $m(\cdot,\cdot): R^n \times R^m \to R$ and $C^1$ functions on $R^n \times R^m$ and $g(\cdot): R^n \times R^p$ is $C^1$ function on $R^n$, D and E are $n \times n$ positive semidefinite matrices.

Let $S = \{x \in X : g(x) \le 0\}$ denote the set of all feasible solutions of (FP)

Any point $x \in S$ is called the feasible point of (FP)

For each $(x, y) \in R^n \times R_m$, we define

$$\Phi(x, y) = \frac{l_i(x, y) + (x^T Dx)^{\frac{1}{2}}}{m_i(x, y) - (x^T Ex)^{\frac{1}{2}}}$$

such that for each $(x, y) \in S \times Y$,

$$l_i(x, y) + (x^T Dx)^{\frac{1}{2}} \ge 0 \quad and \quad m_i(x, y) - (x^T Ex)^{\frac{1}{2}} > 0$$

For each $x \in S$, we define

$$H(x) = \{h \in H : g_h(x) = 0\},$$

where $Y(x) = \left\{ y \in Y : \frac{l_i(x, y) + (x^T Dx)^{\frac{1}{2}}}{m_i(x, y) - (x^T Ex)^{\frac{1}{2}}} = \underset{Z \in Y}{Sup} \frac{l_i(x, z) + (x^T Dx)^{\frac{1}{2}}}{m_i(x, z) - (x^T Ex)^{\frac{1}{2}}} \right\}$

$$k(x) = \Big\{ (s, t, \bar{y}) \in N \times R_+^s X_R^{ms} : 1 \le s \le n+1,\ t = (t_1, t_2, ..... t_{s+}) \in R_+^s$$

with $\sum_{i=1}^{s} t_i = 1, \bar{y} = (\bar{y}_1, \bar{y}_2, ....., \bar{y}_s)\ \bar{y}_i \in Y(x)\ (i = 1, 2, ..., s) \Big\}$

Since $l_i$ and $m_i$ are continuously differentiable and Y is compact in $R^m$, it follows that for each $x^* \in s, Y(x^*) \neq \phi$, and for any $\bar{y}_i \in Y(x^*)$, we have a positive constant.

$$k_0 = \phi\left(x^*, \bar{y}_i\right) = \frac{l_i(x^*, \bar{y}_i) + (x^{*T} Dx^*)^{\frac{1}{2}}}{m_i^*(x^*, \bar{y}_i) - (x^{*T} Ex^*)^{\frac{1}{2}}}$$

**Generalized Schwartz Inequality**

Let A be a positive-semi definite matrix of order n. Then, for all $x, w \in R^n$,

$$x^T Aw \leq (x^T Ax)^{\frac{1}{2}} (w^T Aw)^{\frac{1}{2}} \qquad 1)$$

Equality holds if for some $\lambda \geq 0$

$$Ax = \lambda Aw$$

Evidently, if $(w^T Aw)^{\frac{1}{2}} \leq 1$, we have

$$x^T Aw \leq (x^T Ax)^{\frac{1}{2}}$$

If the functions $l_i$, $g_i$ and $m_i$ in problem (FP) are continuously differentiable with respect to $x \in R^n$, then Lai et al [52] derived the following necessary conditions for optimality of (FP).

**Theorem 1 (Necessary Conditions):**

If $x^*$ is a solution of (FP) satisfying $x^{*T}Dx^* > 0,\ x^{*T}Ex^* > 0$ and $\nabla g_h(x^*),\ h \in H(x^*)$ are linearly independent, then there exist $(s, t^*, \bar{y}) \in k(x^*),\ k_0 \in R_+,\ w, v \in R^n$ and $\mu^* \in R_+^p$ such that

$$\sum_{i=1}^{s} t_i^* \left\{\nabla l_i(x^*, \bar{y}_i)\right\} + Dw - k_0\left\{\nabla m_i(x^*, \bar{y}_i) - EV\right\} + \nabla \sum_{h=1}^{p} t_i^*\ \mu_h^* g_h(x^*) = 0 \tag{2}$$

$$l_i(x^*, \bar{y}_i) + \left(x^{*T}\ Dx^*\right)^{\frac{1}{2}} - k_0\left(m\left(x^*, \bar{y}_i\right) - \left(x^{*T}\ Ex^*\right)^{\frac{1}{2}}\right) = 0, i = 1, 2, \ldots, s \tag{3}$$

$$\sum_{h=1}^{p} \mu_h^*\ g_h(x^*) = 0 \tag{4}$$

$$t_i^* \geq 0\ \ (i = 1, 2, \ldots, s),\ \sum_{i=1}^{s} t_i^* = 1, \tag{5}$$

$$\left.\begin{aligned} &w^T Dw \leq 1,\ v^T EV \leq 1, \\ &\left(x^{*T}\ Dx^*\right)^{\frac{1}{2}} = x^{*T}\ Dw, \\ &\left(x^{*T}\ Ex^*\right)^{\frac{1}{2}} = x^{*T}\ EV \end{aligned}\right\} \tag{6}$$

## Sufficient Conditions:

Under smooth conditions say, convexity and generalized convexity as well as differentiability, optimality conditions for these problems have been studied in the past few years. The intrinsic presence of nonsmoothness (the necessity to deal with nondifferentiable functions, sets with nonsmooth boundaries, and set-valued mappings) is one of the most characteristic features of modern variational analysis. The optimality conditions for nondifferentiable multiobjective case by Kim et al [49]. Now, we prove the sufficient condition for optimality of (Fp) under the assumptions B-(p, r)-invexity.

## Theorem 2 (Sufficient condition):

Let $x^*$ be a feasible of (FP) and there exist a positive integer $s, 1 \le s \le n+1$, $t^* \in R_+^s$, $\bar{y}_i \in Y(x^*)\,(i = 1, 2, ...., s)$, $k_0 \in R_+$, $w, v \in R^n$ *and* $\mu^* \in R_+^p$, Assume that

(i) $\sum_{i=1}^{s} t_i^* \left( l_i(\cdot, \bar{y}_i) + (\cdot)^T Dw - k_0 \left( m_i(\cdot, \bar{y}_i) \right) - (\cdot)^T EV \right)$ *is* $B-(p,r)$-invex at $x^*$ on s with respect to $\eta$ and b satisfying $b(x, x^*) > 0$ for all $x \in s$.

(ii) $\sum_{h=1}^{p} \mu_h^* g_h(\cdot)$ is $B_g-(p,r)$-invex at $x^*$ on s with respect to the same function $\eta$, and with respect to the function $b_g$, not necessarily, equal to b.

Then $x^*$ is an optimal solution of (FP).

**Proof:** Suppose to the contrary that $x^*$ is not an optimal solution of (FP). Then there exists an $\bar{x} \in s$ such that

$$\underset{y\in Y}{Sup}\frac{l_i(\bar{x},y)+(\bar{x}^T\ D\bar{x})^{\frac{1}{2}}}{m_i(\bar{x},y)-(\bar{x}^T\ E\bar{x})^{\frac{1}{2}}}<\underset{y\in Y}{Sup}\ \frac{l_i(x^*,y)+(x^{*T}\ Dx^*)^{\frac{1}{2}}}{m_i(x^*,y)-(x^{*^T}\ Ex^*)^{\frac{1}{2}}}$$

We note that

$$\underset{y\in Y}{Sup}\ =\frac{l_i(x^*,y)+(x^{*T}\ Dx^*)^{\frac{1}{2}}}{m_i(x^*,y)-(x^{*T}\ Ex^*)^{\frac{1}{2}}}\ \frac{l_i(x^*,\bar{y}_i)+(x^{*T}\ Dx^*)^{\frac{1}{2}}}{m_i(x^*,\bar{y}_i)-(x^{*T}\ Ex^*)^{\frac{1}{2}}}=k_0,$$

for $\bar{y}_i\in Y(x^*),\ i=1,2,.....s$ and

$$\frac{l_i(\bar{x},\bar{y}_i)+(\bar{x}^T\ D\bar{x})^{\frac{1}{2}}}{m_i(\bar{x},\bar{y}_i)-(\bar{x}^T\ E\bar{x})^{\frac{1}{2}}}\le\underset{y\in Y}{Sup}\ \frac{l_i(\bar{x},y)+(\bar{x}^T\ D\bar{x})^{\frac{1}{2}}}{m_i(\bar{x},y)-(\bar{x}^T\ E\bar{x})^{\frac{1}{2}}}$$

Thus, we have

$$\frac{l_i(\bar{x},\bar{y}_i)+(\bar{x}^T\ D\bar{x})^{\frac{1}{2}}}{m_i(\bar{x},\bar{y}_i)-(\bar{x}^T\ E\bar{x})^{\frac{1}{2}}}<k_0,\ \ for\ \ i=1,2,.....s$$

it follows that

$$l_i(\bar{x},\bar{y}_i)+(\bar{x}^T\ D\bar{x})^{\frac{1}{2}}-k_0\left(m_i(\bar{x},\bar{y}_i)-(\bar{x}^T\ E\bar{x})^{\frac{1}{2}}\right)<0,\ \ for\ i=1,2,.....s$$

(7)

From (1), (3), (5), (6) and (7), we obtain

$$\sum_{i=1}^{s}t_i^*\left\{l_i(\bar{x},\bar{y}_i)+\bar{x}^T\ Dw-k_0\left(m_i(\bar{x},\bar{y}_i)-\bar{x}^T\ EV\right)\right\}$$

$$\leq \sum_{i=1}^{s} t_i^* \left\{ l_i \left( \bar{x}, \bar{y}_i \right) + \left( \bar{x}^T D\bar{x} \right)^{\frac{1}{2}} - k_0 \left( m_i \left( \bar{x}, \bar{y}_i \right) - \left( \bar{x}^T E\bar{x} \right)^{\frac{1}{2}} \right) \right\}$$

$$< 0 = \sum_{i=1}^{s} t_i^* \left\{ l_i \left( x^*, \bar{y}_i \right) + \left( x^{*T} Dx^* \right)^{\frac{1}{2}} - k_0 \left( m_i \left( x^*, \bar{y}_i \right) - \left( x^{*T} Ex^* \right)^{\frac{1}{2}} \right) \right\}$$

$$= \sum_{i=1}^{s} t_i^* \left\{ l_i \left( x^*, \bar{y}_i \right) + x^{*T} Dw - k_0 \left( m_i \left( x^*, \bar{y}_i \right) - \left( x^{*T} EV \right) \right) \right\}$$

It follows that

$$\sum_{i=1}^{s} t_i^* \left\{ l_i \left( \bar{x}, \bar{y}_i \right) + \bar{x}^T Dw - k_0 \left( m_i \left( \bar{x}, \bar{y}_i \right) - \bar{x}^T EV \right) \right\}$$

$$< \sum_{i=1}^{s} t_i^* \left\{ l_i \left( x^*, \bar{y}_i \right) + x^{*T} Dw - k_0 \left( m_i \left( x^*, \bar{y}_i \right) - x^{*T} EV \right) \right\} \qquad (8)$$

As $\sum_{i=1}^{s} t_i^* \left( l_i \left( \cdot, \bar{y}_i \right) + (\cdot)^T Dw - k_0 m_i \left( \cdot, \bar{y}_i \right) - (\cdot)^T EV \right)$ is B-(p, r)-invex at $x^*$ on s with respect to $\eta$ and b, we have

$$\frac{1}{r} b(x, x^*) \left\{ e^r \left[ \sum_{i=1}^{s} t_i^* \left( l_i \left( x, \bar{y}_i \right) + x^T Dw - k_0 \left( m_i \left( x, \bar{y}_i \right) - x^T EV \right) \right) \right] \right.$$

$$\left. - \sum_{i=1}^{s} t_i^* \left( l_i \left( x^*, \bar{y}_i \right) + x^{*T} Dw - k_0 \left( m \left( x^*, \bar{y}_i \right) - x^{*T} EV \right) - 1 \right) \right\}$$

$$\geq \frac{1}{p} \left\{ \sum_{i=1}^{s} t_i^* \left( \nabla l_i \left( x^*, \bar{y}_i \right) \right) + Dw - k_0 \left( \nabla m_i \left( x^*, \bar{y}_i \right) - EV \right) \right\} \left\{ e^{p\eta(x, x^*)} - 1 \right\}$$

holds for all $x \in s$, and so for $x = \bar{x}$. Using (10.8) and $b(\bar{x}, x^*) > 0$ together with the inequality above, we get

$$\frac{1}{p}\left\{\sum_{i=1}^{s} t_i^*\left(\nabla l_i(x^*, \bar{y}_i)\right) + Dw - k_0\left(\nabla m_i(x^*, \bar{y}_i) - EV\right)\right\}\left\{e^{p\eta(\bar{x}, x^*)} - 1\right\} < 0$$

(9)

From the feasibility of $\bar{x}$ together with $\mu_h^* \geq 0,\ h \in H$, we have

$$\sum_{h=1}^{s} \mu_h^* g_h(\bar{x}) \leq 0 \qquad (10)$$

By $Bg-(p,r)$-invexity of $\sum_{h=1}^{s} \mu_h^* g_h(\cdot)$ at $x^*$ on s with respect to the same function $\eta$, and with respect to the function $b_g$, we have

$$\frac{1}{r} b_g(\bar{x}, x^*)\left\{e^{r\left[\sum_{h=1}^{p} \mu_h^* g_h(\bar{x}) - \sum_{h=1}^{p} \mu_h^* g_h(x^*)\right]} - 1\right\} \geq \frac{1}{p}\sum_{h=1}^{p} \nabla \mu_h^* g_h(x^*)\left\{e^{p\eta(\bar{x}, x^*)} - 1\right\}$$

Since $(x, x^*) \geq 0$ for all $x \in s$ then by (4) and (10), we obtain

$$\frac{1}{p}\sum_{h=1}^{p} \nabla \mu_h^* g_h(x^*)\left\{e^{p\eta(\bar{x}, x^*)} - 1\right\} \leq 0 \qquad (11)$$

By adding the inequalities (9) and (11) we have

$$\frac{1}{p}\left\{\sum_{i=1}^{s} t_i^*\left(\nabla l_i(x^*, \bar{y}_i)\right) + Dw - k_0\left(\nabla m_i(x^*, \bar{y}_i) - EV\right) + \sum_{h=1}^{p} \nabla \mu_h^* g_h(x^*)\right\}$$

$$\left\{e^{p\eta(\bar{x}, x^*)} - 1\right\} < 0,$$

Which contradicts (2). Hence the result.

## 4. Duality Result:

In this section, we consider the following dual to (Fp).

$$(FD) \quad \max_{(s,t,\bar{y})\in k(a)} \quad \sup_{(a,\mu,k,v,w)\in H_1(s,t,\bar{y})} k$$

where $H_1(s,t,\bar{y})$ denotes the set of all

$$(a,\mu,k,v,w)\in R^n\times R_+^p R_+\times R^n R^n$$

Satisfying

$$\sum_{i=1}^{s} t_i\left\{\nabla l_i(a,\bar{y}_i)+Dw-k\left(\nabla m_i(a,\bar{y}_i)-EV\right)+\nabla\sum_{h=1}^{p}\mu_h g_h(a)\right\}=0 \tag{12}$$

$$\sum_{i=1}^{s} t_i\left\{l_i(a,\bar{y}_i)+a^T Dw-k\left(m_i(a,\bar{y}_i)-a^T EV\right)\right\}\geq 0 \tag{13}$$

$$\sum_{h=1}^{p}\mu_h g_h(a)\geq 0 \tag{14}$$

$$(s,t,\bar{y})\in k(a) \tag{15}$$

$$w^T Dw\leq 1,\quad V^T EV\leq 1 \tag{16}$$

If, for a triplet $(s,t,\bar{y})\in k(a)$, the set $H_1(s,t,\bar{y})=\phi$, then we define the supremum over it to be $-\infty$. For convenience,

we let,

$$\Psi_1(\cdot)=\sum_{i=1}^{s} t_i \left(l_i(\cdot,\bar{y}_i)+(\cdot)^T Dw-k\left(m_i(\cdot,\bar{y}_i)-(\cdot)^T EV\right)\right)$$

Let $S_{FD}$ denote a set of all feasible solutions of problem (FD). Moreover, let $S_1$ denote

$$S_1=\left\{a\in R^n:\left(a,\mu,k,v,w,s,t,\bar{y}\right)\in S_{FD}\right\}$$

Now we derive the following weak, strong and strict converse duality theorems.

**Theorem 3 (Weak Duality):**

Let x be a feasible solution of (p) and $\left(a,\mu,k,v,w,s,t,\bar{y}\right)$ be a feasible of (FD). Let

(1) $\sum_{i=1}^{s} t_i^* \left(l_i(\cdot,\bar{y}_i)+(\cdot)^T Dw-k_1\left(m_i(\cdot,\bar{y}_i)-(\cdot)^T EV\right)\right)$ is B-(p, r)-invex at a on $SUS_1$ with respect to $\eta$ and b satisfying $b(x,a)>0$, $\sum_{h=1}^{p}\mu_h g_h(\cdot)$ is $B_g-(p,r)$-invex at a on $SUS_1$ with respect to the same function $\eta$ and with respect to the function $b_g$ not necessarily, equal to b.

Then

$$\sup_{y\in Y}\frac{l_i(x,y)+(x^T Dx)^{\frac{1}{2}}}{m_i(x,y)-(x^T Ex)^{\frac{1}{2}}}\geq k \qquad (17)$$

**Proof:** Suppose to the contrary that

$$\sup_{y\in Y}\frac{l_i(x,y)+(x^T Dx)^{\frac{1}{2}}}{m_i(x,y)-(x^T Ex)^{\frac{1}{2}}}<k$$

Then, we have

$$l_i(x, \bar{y}_i) + (x^T Dx)^{\frac{1}{2}} - k\left( m_i(x, \bar{y}_i) - (x^T Ex)^{\frac{1}{2}} \right) \leq 0, \text{ for all } \bar{y}_i \in Y.$$

It follows from (10.5) that

$$t_i \left\{ l_i(x, \bar{y}_i) + (x^T Dx)^{\frac{1}{2}} - k\left( m_i(x, \bar{y}_i) - (x^T Ex)^{\frac{1}{2}} \right) \right\} \leq 0 \qquad (18)$$

with at least one strict inequality, since

$$t = (t_1, t_2, \ldots\ldots, t_s) \neq 0$$

From (1), (13), (16) and (18), we have

$$\Psi_1(x) = \sum_{i=1}^{s} t_i \left\{ l_i(x, \bar{y}_i) + x^T Dw - k\left( m_i(x, \bar{y}_i) - x^T EV \right) \right\}$$

$$\leq \sum_{i=1}^{s} t_i \left\{ l_i(x, \bar{y}_i) + (x^T Dx)^{\frac{1}{2}} - k\left( m_i(x, \bar{y}_i) - (x^T Ex)^{\frac{1}{2}} \right) \right\}$$

$$< 0 \leq \sum_{i=1}^{s} t_i \left\{ l_i(a, \bar{y}_i) + a^T Dw - k\left( m_i(a, \bar{y}_i) - a^T EV \right) \right\}$$

$$= \Psi_1(a)$$

Hence

$$\Psi_1(x) < \Psi_1(a) \qquad (19)$$

Since $\sum_{i=1}^{s} t_i \left( l_i(\cdot, \bar{y}_i) + (\cdot)^T Dw - k \left( m_i(\cdot, \bar{y}_i) - (\cdot)^T EV \right) \right)$ is B-(p, r)-invex at a on $SUS_1$ with respect to $\eta$ and b, we have

$$\frac{1}{r} b(x,a) \left\{ e^r \left[ \sum_{i=1}^{s} t_i \; l_i(x, \bar{y}_i) + x^T Dw - k\left( m_i(x, \bar{y}_i) - x^T EV \right) - \sum_{i=1}^{s} t_i \left( l_i(a, \bar{y}_i) \right) \right. \right.$$

$$\left. \left. + a^T Dw - k\left( m_i(a, \bar{y}_i) - a^T EV \right) \right] - 1 \right\}$$

From (19) and b(x, a)>0 together with the inequality above,

We get

$$\frac{1}{p} \left[ \sum_{i=1}^{s} t_i \left\{ \nabla l_i(a, \bar{y}_i) + Dw - k\left( \nabla m_i(a, \bar{y}_i) - EV \right) \right\} \right] \left( e^{p\eta(x,a)} - 1 \right) < 0 \tag{20}$$

Using the feasibility of x-together with $\mu_h \geq 0, \quad h \in H,$ we obtain

$$\sum_{h=1}^{p} \mu_h g_h(x) \leq 0 \tag{21}$$

From hypothesis (ii) we have

$$\frac{1}{r} b_g(x,a) \left\{ e^r \left[ \sum_{h=1}^{p} \mu_h g_h(x) - \sum_{h=1}^{p} \mu_h g_h(a) \right] \right\}_{-1} \geq \frac{1}{p} \sum_{h=1}^{p} \nabla \mu_h g_h(a) \left\{ e^{p\eta(x,a)} - 1 \right\}$$

$b_g(x,a) \geq 0$ then by (10.14) and (10.21), we obtain

$$\frac{1}{p} \sum_{h=1}^{p} \nabla \mu_h g_h(a) \left\{ e^{p\eta(x,a)} - 1 \right\} \leq 0 \tag{22}$$

Thus, by (20) and (22), we obtain the inequality

$$\frac{1}{p}\left\{\sum_{i=1}^{s} t_i \left(\nabla l_i(a, \bar{y}_i) + Dw - k\left(\nabla m_i(a, \bar{y}_i) - EV\right)\right) + \sum_{h=1}^{p} \nabla \mu_h g_h(a)\right\} \quad \left\{e^{p\eta(x,a)} - 1\right\} < 0$$

which contradicts (12). Hence (17) holds.

**Theorem 4 (Strong Duality):**

Let $x^*$ be an optimal solution of (FP) and $\nabla g_h(x^*),\ h \in H(x^*)$ are linearly independent. Then there exist $(s, t^*, \bar{y}) \in k(x^*)$, and $(x^*, \bar{\mu}, \bar{k}, \bar{v}, \bar{w}) \in H_1(\bar{s}, \bar{t}, \bar{y}^*)$ such that $(x^*, \bar{\mu}, \bar{k}, \bar{v}, \bar{w}, \bar{s}, \bar{t}, \bar{y}^*)$ is a feasible solution of (FD) .Further the hypotheses of weak duality theorem are satisfied for all feasible solutions $(a, \mu, k, v, w, s, t, \bar{y})$ of (FD), then $(x^*, \bar{\mu}, \bar{k}, \bar{v}, \bar{w}, \bar{s}, \bar{t}, \bar{y}^*)$ is an optimal of (FD), and the two objectives have the same optimal values.

**Proof:** If $x^*$ be an optimal solution of (FP) and $\nabla g_h(x^*),\ h \in H(x^*)$ is linearly independent, then by Theorem 1, there exist $(s, t^*, \bar{y}) \in k(x^*)$ and $(x^*, \bar{\mu}, \bar{k}, \bar{v}, \bar{w}) \in H_1(\bar{s}, \bar{t}, \bar{y}^*)$ such that $(x^*, \bar{\mu}, \bar{k}, \bar{v}, \bar{w}, \bar{s}, \bar{t}, \bar{y}^*)$ is feasible for (FD) and problems (FP) and (FD) have the same objective values and

$$\bar{K} = \frac{l_i(x^*, \bar{y}^*) + (x^{*T} Dx^*)^{\frac{1}{2}}}{m_i(x^*, \bar{y}^*) - (x^{*T} Ex^*)^{\frac{1}{2}}}$$

The optimality of this feasible solution for (FD) thus follows from Theorem 3.

**Theorem 5 (Strict Converse Duality):**

Let x* and $\left(\bar{a}, \bar{\mu}, \bar{k}, \bar{v}, \bar{w}, \bar{s}, \bar{t}, \bar{y}^*\right)$ be the optimal solutions of (FP) and (FD), respectively, and $\nabla g_h(x^*),\ h \in H(x^*)$ is linearly independent. Suppose that $\sum_{i=1}^{s} t_i^* \left(l_i(\cdot, \bar{y}_i) + (\cdot)^T Dw - \bar{k}\left(m_i(\cdot, \bar{y}_i) - (\cdot)^T EV\right)\right)$ is strictly B-(p, r)-invex at a on $SUS_1$ with respect to $\eta$ and b satisfying $b(x, a) > 0$ for all $x \in s$. Furthermore, assume that $\sum_{h=1}^{p} \mu_h g_h(\cdot)$ is $B_g$-(p, r)-invex at a on $SUS_1$ with respect to the same function $\eta$ and with respect to the function $b_g$, but not necessarily, equal to the function b. Then $x^* = \bar{a}$, that is, $\bar{a}$ is an optimal point in (FP) and

$$\sup_{y \in Y} \frac{l_i(\bar{a}, \bar{y}^*) + (\bar{a}^T D\bar{a})^{\frac{1}{2}}}{m_i(\bar{a}, \bar{y}^*) - (\bar{a}^T E\bar{a})^{\frac{1}{2}}} = \bar{K}$$

**Proof:** We shall assume that $x^* \neq \bar{a}$, and reach a contradiction fom the strong duality theorm (theorm 4) it follws that that is, $\bar{a}$ is an optimal point in (FP) and

$$\sup_{y \in Y} \frac{l_i(x^*, \bar{y}^*) + (x^{*T} Dx^*)^{\frac{1}{2}}}{m_i(x^*, \bar{y}^*) - (x^{*T} Ex^*)^{\frac{1}{2}}} = \bar{K} \qquad (23)$$

By feasibility of $x^*$ together with $\mu_h \geq 0,\ h \in H$, we obtain

$$\sum_{h=1}^{p} \mu_h g_h(x^*) \leq 0 \qquad (24)$$

By assumption, $\sum_{h=1}^{p}\mu_h g_h(\cdot)$ is $B_g$-(p, r)-invex at a on $SUS_1$ with respect to $\eta$ and with respect to the $b_g$. Then, by Definition (12), there exists a function by such that $b_g(x,a)\geq 0$ for all $x\in s \;\; and \;\; a\in s_1$. Hence by (14) and (24).

$$\frac{1}{r}b_g(x^*,\bar{a})\;\left\{e^r\left[\sum_{h=1}^{p}\mu_h g_h(x^*)-\sum_{h=1}^{p}\mu_h g_h(\bar{a})\right]\right\}_{-1}\leq 0$$

Then, from Definition (10.2), we get

$$\frac{1}{p}\sum_{h=1}^{p}\nabla\mu_h g_h(\bar{a})\left\{e^{p\eta}(x^*,a)-1\right\}\leq 0 \qquad (25)$$

Therefore, by (10.25), we obtain the inequality

$$\frac{1}{p}\left\{\sum_{i=1}^{s}t_i\left(\nabla l_i(\bar{a},\bar{y}_i)+Dw-\bar{k}\left(\nabla m_i(\bar{a},\bar{y}_i)-EV\right)\right)\right\}\left\{e^{p\eta}(x^*,\bar{a})-1\right\}\geq 0$$

As $\sum_{i=1}^{s}t_i^*\left(l_i(\cdot,\bar{y}_i)+(\cdot)^T Dw-\bar{k}\left(m_i(\cdot,\bar{y}_i)-(\cdot)^T EV\right)\right)$ is strictly B-(p, r)-invex with respect to $\eta$ b at $\bar{a}$ on $SUS_1$. Then, by definition of strictly B-(p, r)-invexity and from above inequality, it follows that

$$\left\{\frac{1}{r}b(x^*,\bar{a})\times\sum_{i=1}^{s}t_i\left(l_i(x^*,\bar{y}_i)+x^{*T}Dw-\bar{k}\left(m_i(x^*,\bar{y}_i)-x^*EV\right)\right)\right.$$

$$\left.-\sum_{i=1}^{s}t_i\left(l(\bar{a},\bar{y}_i)+\bar{a}^T Dw-\bar{k}\left(m_i(\bar{a},\bar{y}_i)-\bar{a}^T EV\right)\right)-1\;\;>0\right\}$$

From the hypothesis $b(x^*,\bar{a})>0$, and the above inequality,

We get

$$\sum_{i=1}^{s} t_i \left( l_i (x^*, \bar{y}_i) + x^{*T} Dw - \bar{k} \left( m_i (x^*, \bar{y}_i) - x^{*T} EV \right) \right)$$

$$- \sum_{i=1}^{s} t_i \left( l_i (\bar{a}, \bar{y}_i) + \bar{a}^T Dw - \bar{k} \left( m_i (\bar{a}, \bar{y}_i) - \bar{a}^T EV \right) \right) > 0$$

Therefore, by (13),

$$\sum_{i=1}^{s} t_i \left( l_i (x^*, \bar{y}_i) + x^{*T} Dw - \bar{k} \left( m_i (x^*, \bar{y}_i) - x^{*T} EV \right) \right) > 0$$

Since $t_i \geq 0, \quad i = 1, 2, ..... s,$ therefore there exists $i^*$ such that

$$l_i (x^*, \bar{y}_i^*) + x^{*T} Dw - \bar{k} \left( m_i (x^*, \bar{y}_i^*) - x^{*T} EV \right) > 0$$

Hence, we obtain the following inequality

$$\frac{l_i (x^*, \bar{y}^*) + (x^{*T} Dx^*)^{\frac{1}{2}}}{m_i (x^*, \bar{y}^*) - (x^{*T} Ex^*)^{\frac{1}{2}}} > \bar{K},$$

which contradicts (23). Hence the result.

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# Second Order Dual Minimax Fractional Programming Under Binvexity

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**Abstract:** In this paper, we derive some theorems and duality theorems on Second Order DualMinimax Fractional Programming under binvexity

**Keywords:** Binvex functions and second order Duality.

## . Introduction

In this Chapter, we consider the following minimax fractional programming problem.

(p) minimize $\Psi(x) = \underset{y \in Y}{\text{Sup}} \dfrac{f_i(x, y)}{g_i(x, y)}$

s.t $h(x) \le 0$ , $x \in R^n$

where Y is a compact subset of $R^l$, $f(\cdot,\cdot): R^n \times R^l \to R$, $g(\cdot,\cdot): R^n \times R^l \to R$ are twice continuously differentiable on $R^n \times R^l$ and $h(\cdot,\cdot): R^n \to R^m$ is twice continuously differentiable on $R^n$. It is assumed that for each (x, y) in $R^n \times R^l$, $f_i(x, y) \ge 0$ and $g_i(x, y) \ge 0$.

Since minimax fractional programming has wide applications, much attention has been paid optimality conditions and duality theorems for minimax fractional programming problems. For the case of convex differentiable minimax fractional programming, Yadav and Mukherjee [10] formulated two dual models for (p) and derived duality theorems. Chandra and Kumar [3] pointed out certain omissions in the dual formulation of Yadav and Mukherjee [9], they constructed two modified dual problems for minimiax fractional programming problem and proved duality results. Liu and Wu [5,6], and Yang and Hou [10] discussed optimality conditions and duality results for (p) involving generalized convexity assumptions.

Mangasarian [7] introduced the notation of second order duality for nonlinear programs by introducing an additional vector $p \in R^n$. He has indicated a possible computational advantage of the second order dual over the first order dual. Instead of imposing explicit condition on p, Mond [8] included p in a second order type convexity. Bector et al [2] discussed second order duality results for minimax programming problems under generalized B-Convexity. Later on, Liu [4] extended these results involving second order generalized B-Convexity. Recently, Husain et al [3] have formulated two types of second order dual models for minimax fractional programming problems, and derived weak, strong and strict coverse duality theorems under binvex assumptions.

In this paper, two types of second order duality in minimax fractional programming are formulated by introducing an additional vector r. The weak, strong and converse duality theorems are proved for these programes under binvexity assumptions. Our result generalizes these existing dual formulations which were discussed by the authors in but they not consider this in binvexity. Hence in this Paper an attempt to made to full this gap in the aim of research by developing some theorems and duality theorems in second order duality for minimax fractional programming.

## 2. Preliminaries

Let $S = \{x \in R^n : h(x) \le 0\}$ denote the set of all feasible solutions of (p). For each $(x, y) \in R^n \times R^l$, we define

$$J(x) = \{j \in M = \{1, 2, \} : h_j(x) \le 0\}$$

$$Y(x) = \left\{ y \in Y : \frac{f_i(x, y)}{g_i(x, y)} = \sup_{Z \in Y} \frac{f_i(x, z)}{g_i(x, z)} \right\},$$

and $k(x) = \{(s, t, \tilde{y}) \in N \times R_s^+ X R^{ls} : l \le s \le n+1, t = (t_1, t_2, ....., t_s) \in R_+^s,$

$$\sum_{t=1}^{s} t_i = 1, \tilde{y} = (\tilde{y}_1, \tilde{y}_2, ....., \tilde{y}_s);\ \tilde{y}_i \in Y(x), i = 1, 2, ..... s\}$$

let $f : R^n \to R$ be a twice differentiable function.

**Definition (1):**

Function f is said to be binvex at $\bar{x} \in R^n$, such that for all $x, p \in R^n$, we have

$$\frac{f_i(x)}{g_i(x)} - \frac{f_i(\bar{x})}{g_i(\bar{x})} + \frac{1}{2} p^T \nabla^2 \frac{f_i(\bar{x})}{g_i(\bar{x})} p \ge (x - \bar{x})^t \left[ \nabla f(\bar{x}) + \nabla^2 f(\bar{x}) p \right]$$

**Definition (2) :** Function f is said to be strictly binvex at $\bar{x} \in R^n$ such that for all $x, p \in R^n$, we have

$$\frac{f_i(x)}{g_i(x)} - \frac{f_i(\bar{x})}{g_i(\bar{x})} + \frac{1}{2} p^T \nabla^2 \frac{f_i(\bar{x})}{g_i(\bar{x})} p > (x - \bar{x})^t \left[ \nabla \frac{f_i(\bar{x})}{g_i(\bar{x})} + \nabla^2 \frac{f_i(\bar{x})}{g_i(\bar{x})} p \right]$$

The following theorem will be needed in the proofs of strong duality theorems.

**Theorem (1) (Necessary Conditions).** Let $x^*$ be a solution of $(p)$ and let $\nabla g_j(x^*),\ j \in J(x^*)$ be linearly independent. There exist $\left(s^*, t^*, \bar{y}^*\right) \in k(x^*),\ \lambda^* \in R_+$ and $\mu^* \in R_+^m$ such that

$$\nabla \sum_{i=1}^{s^*} t_i^* \left(f_i(x^*, \bar{y}_i^*)\right) - \lambda^* g_i(x^*, \bar{y}_i^*) + \nabla \sum_{j=1}^{m} \mu_j^* h_j(x^*) = 0$$

$$\left(f_i(x^*, \bar{y}_i^*)\right) - \lambda^* g_i(x^*, \bar{y}_i^*) = 0,\ i = 1, 2, \ldots\ldots, s^*$$

$$\sum_{j=1}^{m} \mu_j^* h_j(x^*) = 0,$$

$$t_i^* \geq 0,\ \sum_{i=1}^{s^*} t_i^* = 1,\ \ \bar{y}_i^* \in y(x^*),\ i = 1, 2, \ldots\ldots, s^*$$

### 3. First Duality Model

By utilizing the necessary optimality conditions of the previous section, we formulate the following second order dual to (p) as follows.

$$(MD) \qquad \max_{(s,t,\bar{y}) \in k(z)} \ \sup_{(z,\mu,\lambda,r,p) \in H_1(s,t,\bar{y})} \lambda$$

where $H_1(s, t, \bar{y})$ denotes the set of all $(z, \mu, \lambda, \gamma, p) \in R^n \times R_+^m \times R_+ \times R^n \times R^n$

Satisfying $\nabla \sum_{i=1}^{s} t_i \left(f_i(z, \bar{y}_i)\right) - \lambda gi(z, \bar{y}_i) + \nabla^2 \sum_{i=1}^{s} t_i \left(f_i(z, \bar{y}_i) - \lambda gi(z, \bar{y}_i)\right) p$

$$+ \nabla \sum_{j=1}^{m} \mu_j g_j(z) + \nabla^2 \sum_{j=1}^{m} \mu_j g_j(z) p = 0 \qquad (1)$$

$$\sum_{i=1}^{s} t_i \left( f_i (z, \bar{y}_i) \right) - \lambda g_i (z, \bar{y}_i) + \left( \nabla \sum_{i=1}^{s} t_i \left( f_i (z, \bar{y}_i) - \lambda g_i (z, \bar{y}_i) \right) r \right)$$

$$- \frac{1}{2} p^T \nabla^2 \sum_{i=1}^{s} t_i \left( f_i (z, \bar{y}_i) - \lambda g_i (z, \bar{y}_i) \right) p \geq 0 \qquad (2)$$

$$\sum_{j=1}^{m} \mu_j g_j (z) + \left( \nabla \sum_{j=1}^{m} \mu_j g_j (z) \right) r - \frac{1}{2} p^T \nabla^2 \sum_{j=1}^{m} \mu_j g_j (z) p \geq 0 \qquad (3)$$

$$\left( \nabla \sum_{i=1}^{s} t_i \left( f_i (z, \bar{y}_i) - \lambda g_i (z, \bar{y}_i) \right) \right) r + \left( \nabla \sum_{j=1}^{m} \mu_j g_j (z) \right) r \leq 0 \qquad (4)$$

if, for a triplet $(s, t, \bar{y}) \in k(z)$, the set $H_1 (s, t, \bar{y}) = \phi$, then we define the supremum over it to be $-\infty$.

**Theorem1 (Weak Duality):** Let x and $(z, \mu, \lambda, s, t, \bar{y}, r, p)$ be feasible solutions of (p) and (MD), respectively. Assume that

(i) $\sum_{i=1}^{s} t_i \left( f_i , \bar{y}_i \right) - \lambda g_i (\cdot , \bar{y}_i)$ is $\eta$-bonvex at z;

(ii) $\sum_{j=1}^{m} \mu_j g_j (\cdot)$ is $\eta$-bonvex at z.

Then $\sup_{y \in Y} \frac{f_i (x, y)}{g_i (x, y)} \geq \lambda$

**Proof:** by the feasibility of x for (p), $\mu \geq 0$ and (3), we get

$$\sum_{j=1}^{m} \mu_j g_j (x) \leq 0 \leq \sum_{j=1}^{m} \mu_j g_j (z) + \left( \nabla \sum_{j=1}^{m} \mu_j g_j (z) \right) r - \frac{1}{2} p^T \nabla^2 \sum_{j=1}^{m} \mu_j g_j (z) p$$

The above inequality together with hypothesis (ii) implies

$$\left(\nabla\sum_{j=1}^{m}\mu_j g_j(x)+\nabla^2\sum_{j=1}^{m}\mu_j g_j(z)\,p\right)(x-z)^t\le\left(\nabla\sum_{j=1}^{m}\mu_j g_j(z)\right)r$$

From (9.3.1), (9.3.4) and (9.3.5), we have

$$\left(\nabla\sum_{i=1}^{s}t_i\left(f_i(z,\bar{y}_i)-\lambda gi(z,\bar{y}_i)\right)\right)+\left(\nabla^2\sum_{i=1}^{s}t_i\left(f_i(z,\bar{y}_i)-\lambda gi(z,\bar{y}_i)\right)p\right)(x-z)^t\ge-\left(\nabla\sum_{j=1}^{m}\mu_j g_j(z)\right)r$$

$$\ge\left(\nabla\sum_{i=1}^{s}t_i\left(f_i(z,\bar{y}_i)-\lambda gi(z,\bar{y}_i)\right)\right)r$$

which in view of hypothesis (i) and (2) fields

$$\nabla\sum_{i=1}^{s}t_i\left(f_i(x,\bar{y}_i)\right)-\lambda gi(x,\bar{y}_i)\ge\sum_{i=1}^{s}t_i\left(f_i(z,\bar{y}_i)-\lambda gi(z,\bar{y}_i)\right)+$$

$$\left(\nabla\sum_{i=1}^{s}t_i\left(f_i(z,\bar{y}_i)-\lambda gi(z,\bar{y}_i)\right)r\right)$$

$$-\frac{1}{2}p^T\nabla^2\left(\sum_{i=1}^{s}t_i\left(f(z,\bar{y}_i)-\lambda h(z,\bar{y}_i)\right)\right)p\ge0$$

Therefore, there exists a certain $i_o$ such that

$$f_i(x,\bar{y}_{io})-\lambda gi(x,\bar{y}_{io})\ge0$$

Hence $\sup_{y\in Y}\dfrac{f_i(x,y)}{g_i(x,y)}\ge\dfrac{f_i(x,\bar{y}_{io})}{g_i(x,\bar{y}_{io})}\ge\lambda$

**Theorem 2 (Strong Duality)**

Assume that $x^*$ is an optimal solution of (p) and $\nabla g_i(x^*),\ j \in J(x^*)$ are linearly independent. Then there exist $(s^*, t^*, y^*) \in k(x^*)$ and $(x^*, \mu^*, \lambda^*, r^* = 0, p^* = 0) \in H_1(s^*, t^*, y^*)$ such that $\left(x^*, \mu^*, \lambda^*, s^*, t^*, \bar{y}^*, r^* = 0, p^* = 0\right)$ is a feasible solution of (MD) and the two objectives have the same values. If, in addition, the assumptions of weak duality hold for all feasible solutions $\left(x, \mu, \lambda, s, t, \bar{y}, r, p\right)$ of (MD), then $\left(x^*, \mu^*, \lambda^*, s^*, t^*, \bar{y}^*, r^* = 0, p^* = 0\right)$ is an optimal solution of (MD).

**Proof:** Since $x^*$ is an optimal solution of (p) and $\nabla g_i(x^*),\ j \in J(x^*)$ are linearly independent, then by Theorem (1), thee exist $(s^*, t^*, y^*) \in k(x^*)$ and $(x^*, \mu^*, \lambda^*, r^* = 0, p^* = 0) \in H_1(s^*, t^*, \bar{y}^*)$ such that

$(x^*, \mu^*, \lambda^*, s^*, t^*, \bar{y}^*, r^* = 0, p^* = 0)$ is a feasible solution of (MD) and the two objectives have the same values. Optimality of $(x^*, \mu^*, \lambda^*, s^*, t^*, \bar{y}^*, r^*, p^* = 0)$ for (MD), thus follows weak duality (Theorem 9.3.1).

**Theorem 3 (Strict Converse Duality)**

Let $x^*$ and $(z^*, \mu^*, \lambda^*, s^*, t^*, \bar{y}^*, r^*, p^*)$ be optimal solutions of (p) and (MD), respectively, suppose that

(i) $\nabla g_j(x^*),\ j \in J(x^*)$ are linearly independent,

(ii) $\sum_{i=1}^{s} t_i^* \left(f_i(\cdot, \bar{y}_i^*) - \lambda^* gi(\cdot, \bar{y}_i^*)\right)$ is strictly binvex at z*,

(iii) $\sum_{j=1}^{m} \mu_j^* g_j(\cdot)$ is binvex at z*. Then $z^* = x^*$.

**Proof:** Suppose to the contrary that $z^* \neq x^*$, and we will derive a contradiction. Since $x^*$ and $(z^*, \mu^*, \lambda^*, s^*, t^*, \bar{y}^*, r^*, p^*)$ be optimal solutions of (p) and (MD), respectively, and $\nabla g_j(x^*),\ j \in J(x^*)$ are linearly independent, therefore, by theorem (2), we have

$$\sup_{y^* \in Y} \frac{f_i(x^*, y^*)}{g_i(x^*, y^*)} = \lambda^* \qquad (6)$$

The feasibility of $x^*$ for (p), $\mu^* \geq 0$ and (3) imply

$$\sum_{j=1}^{m} \mu_j^* g_j(x^*) \leq 0 \leq \sum_{j=1}^{m} \mu_j^* g_j(z^*) + \left( \sum_{j=1}^{m} \mu_j^* g_j(z^*) \right) r^* -$$

$$-\frac{1}{2} p^{*T} \nabla^2 \sum_{j=1}^{m} \mu_j^* g_j(z^*)\, p^*,$$

Which along with hypothesis (iii) gives

$$\left( \nabla \sum_{i=1}^{m} \mu_j^* g_j(z^*) + \nabla^2 \sum_{j=1}^{m} \mu_j^* g_j(z^*) p \right)(x^* - z^*)^t \leq \left( \nabla \sum_{i=1}^{m} \mu_j^* g_j(z^*) \right)$$

Therefore, inequality (9.3.1) along with (9.3.7) yields

$$\nabla \sum_{i=1}^{s} t_i^* \left( f(z^*, \bar{y}_i^*) \right) - \lambda^* h(z^*, \bar{y}_i^*) + \left( \nabla^2 \sum_{i=1}^{s} t_i^* \left( f_i(z^*, \bar{y}_i^*) - \lambda g_i(z^*, \bar{y}_i^*) \right) p \right)(x^* - z^*)^t$$

$$\geq \left( \nabla \sum_{i=1}^{s} t_i^* \left( f_i(z^*, \bar{y}_i^*) - \lambda^* g_i(z^*, \bar{y}_i^*) \right) \right) r^*,$$

which by hypothesis (ii) and inequality (9. 3.2) gives

$$\sum_{i=1}^{s} t_i^* \left( f(x^*, \bar{y}_i^*) - \lambda^* h(x^*, \bar{y}_i^*) \right) > 0$$

For a certain $i_o$, this implies

$$\sup_{y^* \in Y} \frac{f_i(x^*, y^*)}{g_i(x^*, y^*)} \geq \frac{f_i(x^*, \bar{y}_{io}^*)}{g_i(x^*, \bar{y}_{io}^*)} > \lambda^*,$$

which is a contradiction to (6). Hence $z^* = x^*$.

**4. Second duality model**

In this section, we formulate the following second order dual to (p) as follows.

$$(GMD) \qquad \max_{(s,t,\bar{y}) \in k(z)} \quad \sup_{(z,\mu,\lambda,r,p) \in H_2(s,t,\bar{y})} \lambda$$

where $H_2(s, t, \bar{y})$ denotes the set of all $(z, \mu, \lambda, r, p) \in R^n \times R_+^m \times R_+ \times R^n \times R^n$

Satisfying

$$\nabla \sum_{i=1}^{s} t_i \left( f_i(z, \bar{y}_i) \right) - \lambda g_i(z, \bar{y}_i) + \nabla^2 \sum_{i=1}^{s} t_i \left( f_i(z, \bar{y}_i) - \lambda h(z, \bar{y}_i) \right) p$$

$$+ \nabla \sum_{j=1}^{m} \mu_j g_j(z) + \nabla^2 \sum_{j=1}^{m} \mu_j g_j(z) p = 0 \qquad (4.1)$$

$$\sum_{i=1}^{s} t_i f_i(z, \bar{y}_i) - \lambda g_i(z, \bar{y}_i) + \sum_{j \in J_0} \mu_j g_j(z) + \left( \nabla \sum_{i=1}^{s} t_i f_i(z, \bar{y}_i) - \lambda g_i(z, \bar{y}_i) + \sum_{j \in J_0} \mu_j g_j(z) \right) r$$

$$-\frac{1}{2} p^T \nabla^2 \sum_{i=1}^{s} t_i \left( f_i(z, \bar{y}_i) - \lambda g_i(z, \bar{y}_i) + \sum_{j \in J_0} \mu_j g_j(z) \right) p \geq 0 \qquad (4.2)$$

$$\sum_{j\in J_\alpha}\mu_j g_j(z)+\left(\sum_{j\in J_\alpha}\mu_j g_j(z)\right)r-\frac{1}{2}p^T\nabla^2\sum_{j\in J_\alpha}\mu_j g_j(z)p\geq 0,\quad \alpha=1,2,....r$$

(4.3)

$$\left(\nabla\sum_{j\in J_\alpha}t_i\left(f_i(z,\bar{y}_i)-\lambda g_i(z,\bar{y}_i)\right)+\left(\nabla\sum_{j=1}^{m}\mu_j g_j(z)\right)\right)r\leq 0 \qquad (4.4)$$

where $J_\alpha\subseteq M,\ \alpha=0,1,2,....,k$ with $\bigcup_{\alpha=0}^{k}J_\alpha=M$ and $J_\alpha\cap J_\beta=\phi,$ if $\alpha\neq\beta.$ If, for a triplet $(s,t,\bar{y})\in k(z),$ the set $H_1(s,t,\bar{y})=\phi,$ then we define the supremum over it to be $-\infty$.

**Theorem 4.1 (Weak Duality):** let x and $(z,\mu,\lambda,s,t,\bar{y},r,p)$ be feasible solutions of (p) and (GMD), respectively. Assume that

(i) $\sum_{i=1}^{s}t_i\left(f_i(\cdot,\bar{y}_i)-\lambda gi(\cdot,\bar{y}_i)\right)+\sum_{j\in J_0}\mu_i g_j(\cdot)$ is binvex at z;

(ii) $\sum_{j\in J_\alpha}\mu_i g_j(\cdot),\quad \alpha=1,2,.....r$ binvex at z.

Then $\sup_{y\in Y}\dfrac{f_i(x,y)}{g_i(x,y)}\geq\lambda$

**Proof:** By the feasibility of x for (p), $\mu\geq 0$ and (9.4.3), we get

$$\sum_{j\in J_\alpha}\mu_i g_j(x)\leq 0\leq\sum_{j\in J_\alpha}\mu_i g_j(z)+\left(\nabla\sum_{j\in J_\alpha}\mu_i g_j(z)\right)r-\frac{1}{2}p^T\nabla^2\sum_{j\in J_\alpha}\mu_i g_j(z)p,\ \alpha=1,2,....r$$

(4.5)

The above inequality (4.5) with hypothesis (ii) implies

$$\left(\nabla\sum_{j\in J_\alpha}\mu_j g_j(z)+\nabla^2\sum_{j\in J_\alpha}\mu_j g_j(z)p\right)(x-z)^t\le\left(\nabla\sum_{j\in J_\alpha}\mu_j g_j(z)\right)r,\ \alpha=1,2,....r$$

which together with (4.1), (4.4) yields

$$\nabla\sum_{i=1}^{s}t_i\left(f_i(z,\bar{y}_i)\right)-\lambda gi(z,\bar{y}_i)+\nabla^2\sum_{i=1}^{s}t_i\left(f_i(z,\bar{y}_i)-\lambda g_i(z,\bar{y}_i)\right)p$$

$$+\ \nabla\sum_{j\in J_0}\mu_j g_j(z)+\left(\nabla^2\sum_{j\in J_0}\mu_j g_j(z)p\right)(x-z)^t$$

$$\ge\nabla\sum_{i=1}^{s}t_i\left(f_i(z,\bar{y}_i)\right)-\lambda gi(z,\bar{y}_i)+\left(\sum_{j\in J_0}\mu_j g_i(z)p\right)r$$

In view of hypothesis (i) and the above inequality implies

$$\sum_{i=1}^{s}t_i\left(f_i(x,\bar{y}_i)\right)-\lambda gi(x,\bar{y}_i)+\sum_{j\in J_0}\mu_j g_i(x)$$

$$\ge\sum_{i=1}^{s}t_i\left(f_i(z,\bar{y}_i)\right)-\lambda g_i(z,\bar{y}_i)+\sum_{j\in J_0}\mu_j g_j(z)+\left(\nabla\sum_{i=1}^{s}t_i\left(f_i(z,\bar{y}_i)\right)-\lambda g_i(z,\bar{y}_i)+\sum_{j\in J_0}\mu_j g_j(z)\right)r$$

$$-\frac{1}{2}p^T\left(\nabla^2\sum_{i=1}^{s}t_i\left(f_i(z,\bar{y}_i)-\lambda g_i(z,\bar{y}_i)\right)+\sum_{j\in J_0}\mu_j g_j(z)\right)p$$

By $\mu\ge 0,\ g(x)\le 0$ and (4.2) it follows that

$$\sum_{i=1}^{s}t_i\left(f_i(x,\bar{y}_i)-\lambda g_i(x,\bar{y}_i)\right)\ge 0$$

Therefore, there exists a certain $i_o$ such that

$$f_i(x, \bar{y}_{io}) - \lambda g_i(x, \bar{y}_{io}) \geq 0$$

$$\sup_{y \in Y} \frac{f_i(x, y)}{g_i(x, y)} \geq \frac{f_i(x, \bar{y}_{io})}{g_i(x, \bar{y}_{io})} > \lambda$$

The proof of the following theorem is similar to that of Theorem (9.3.2) and hence, is omitted.

**Theorem 4.2 Strong Duality:** Assume that $x^*$ is an optimal solution of (p) and $\nabla g_j(x^*),\ j \in J(x^*)$ are linearly independent. Then there exist $(s^*, t^*, \bar{y}^*) \in k(x^*)$ and $(x^*, \mu^*, \lambda^*, r^* = 0, p^* = 0) \in H_1(s^*, t^*, \bar{y}^*)$ such that

$(x^*, \mu^*, \lambda^*, s^*, t^*, \bar{y}^*, r^* = 0, p^* = 0)$ is a feasible solution of (GMD) and the two objectives have the same values. If, in addition, the assumptions of weak duality hold for all feasible solutions $(x, \mu, \lambda, s, t, \bar{y}, r, p)$ of (GMD), then $(x^*, \mu^*, \lambda^*, s^*, t^*, \bar{y}^*, r^* = 0, p^* = 0)$ is an optimal solution of (GMD).

**Theorem 4.3 (Strict Converse Duality)**

Let $x^*$ and $(z^*, s^*, t^*, \bar{y}^*, r^*, p^*)$ be optimal solutions of (p) and (GMD), respectively, suppose that

(i) $\nabla g_j(x^*),\ j \in J(x^*)$ are linearly independent.

(ii) $\sum_{i=1}^{s} t_i^* \left( f_i(\cdot, \bar{y}_i^*) - \lambda^* g_i(\cdot, \bar{y}_i^*) \right) + \sum_{j \in J_0} \mu_j^* g_j(\cdot)$ is strictly binvex at $z^*$.

(iii) $\sum_{j \in J_\alpha} \mu_j^* g_j(\cdot),\quad \alpha = 1, 2, \ldots . k$ binvex at $z^*$.

Then $z^* = x^*$.

**Proof:** It can be proved similarly to Theorem (3.3.).

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