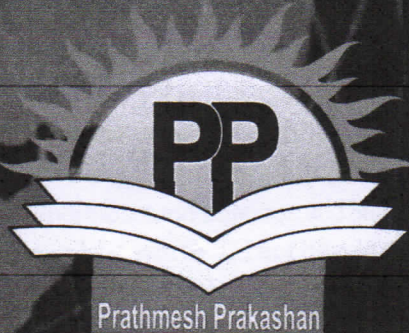


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# **NEW INTERNATIONAL RELIABLE RESEARCH JOURNAL**



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## Emergence of English Language in Media and Bureaucracy: A Journey

**Prof. Karande Manohar Baburao,**

Head & Associate Professor,  
Department of English,  
Radhabai Kale Mahila Mahavidyalaya,  
Ahmednagar:

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### ABSTRACT:

Many years ago, a well known editor and columnist had written that he writes in English, speaks most of the time in English, most of his reading is English, and he even consequently thinks in English, therefore his mother tongue ought to be English. At that time, such statement sounded too arrogant and whimsical. Having being fed in the regional flavour since the school, it's quite easy and 'normal' to be intolerant to such 'heretic' views about adulation of English. However no longer do I hold on to such views, and would be quite charitable with myself in assigning a more dominant slot to English in my mind space and thought space. India is a country where appearance for the policy makers is more important than the reality at the ground. In such situations we find very inane policy and legal situations. One such thing is the language policy in India. English as a language does not find itself in the list of languages in the Schedule of the Constitution. At the same breath, the constitution in one of its articles speaks that English shall continue to be the language of the judiciary.

**KEYWORDS:** vernacular, regional language, TV Channels, local language

In pursuance of the National policy of education in languages, we find that the three language policy is adopted at the state levels in the schools. It makes for a situation where the hapless student has to master the Regional Language, National Language (Hindi), and a third language - depending on the kind of school, medium of studies, and the state in which one is situated. For example, we had English medium (non Government schools), so English was our 'first' language, Hindi the second language, and Sanskrit the third language. This was because we were studying in MP, which did not have a regional language - so the natural choice for the policy makers was to make the students go through the hazards of a 'subject' which everyone was happy to forget about the day when the exams ended. In the vernacular states, which have their own regional language, the government schools, would have the regional language, followed by Hindi and English.

Despite our being in English medium, the language of conversation was the 'patriotic' Hindi. I remember that one of our teachers would even make fun at the kind of Hindi spoken by the then prime minister. In effect, when the student has the most grasping power and high learning curve, instead of mastering the areas of Science and Commerce and Computers

and Mathematics, the creativity of the student is used in mastering the different languages - that at best ends up in a scene where s/he is mugging up the languages and left with little time to think on the more important practical subjects which are going to be useful in real life.

The situation is that large population of students being unable to deal with English language properly, are not good with computers and also with 'English' communications which is the need of the globalised world. So we find situations where college going students and even those in working life join private English coaching centers to improve on their job prospects. And these coaching centers attempt to replace the 12 years of school grooming in a vital area of learning in a three to six month shot.

But more than that, we can often find that language activists (political as well as otherwise) would keep up inflating and arousing the passions of nativity. Communist government in West Bengal till recently did not allow English to be taught in the primary. Now they have realized the loss of skill set for a full generation of students. Similarly in Karnataka, we find the political protesters wanting to reserve employment in the private sectors for the native Kannada speaking people. Often state level political leaders can easily be found exhorting their political base to be more 'patriot' and do away with the 'firangi' system.

We must keep in mind that while India is a land of many languages, and also of the culture of pluralism, it becomes hardly useful for the political set up to foist certain languages on its people in name of imagined pride. If Hindi is a national language, then it is so due to a single casting vote by the chairman of the Constituent Assembly, when the whole assembly was divided equally on the issue. In some ways, the bulwark of English for many years were the states of the South - but now we find that even the South has got influenced by the parochial ideology and would prefer only the local English speakers!

The neglect of English at school level would only add to the incompetency of India in the global world full of competition and trans-border trades. This however does not mean a one way situation - the things should be balanced and left to choice of the user of the language. We find that companies like Microsoft are building up their office software in Indian languages. The 'firangi' cable Television channels now speak Hindi, and even well known American cartoon characters can be found speaking Indian regional languages. And that is how the market forces work. Multinational coke companies may recruit from English speaking 11 Ms, but would prefer to advertise in vernacular language. Financial institution and Private Banks may be English speaking, but their target investor is one who may not know English remotely, and is at home with 'Awaaz' and 'Aaj Tak' channels. Telecom and Insurance companies may be doing all their work in English, but their marketing executives are busy selling the product in the native speakers' language. If one goes to the regional centers, one can easily find people from far away places that have come there to work have picked up the local language - and for which they did not have to attend schools - and that is societal dynamics. Marwaris in Bengal speak as good Bengali, as Bengalis in Tamil Nadu would speak Tamil, and Punjabis in Mumbai would speak Marathi.

One should let language be a part of the dynamics of the society, rather than that of government intervention. In fact, the student should be free to have a single language of his or her choice to study in the schools, and devote their time in more productive learning of sciences, commerce and arts.

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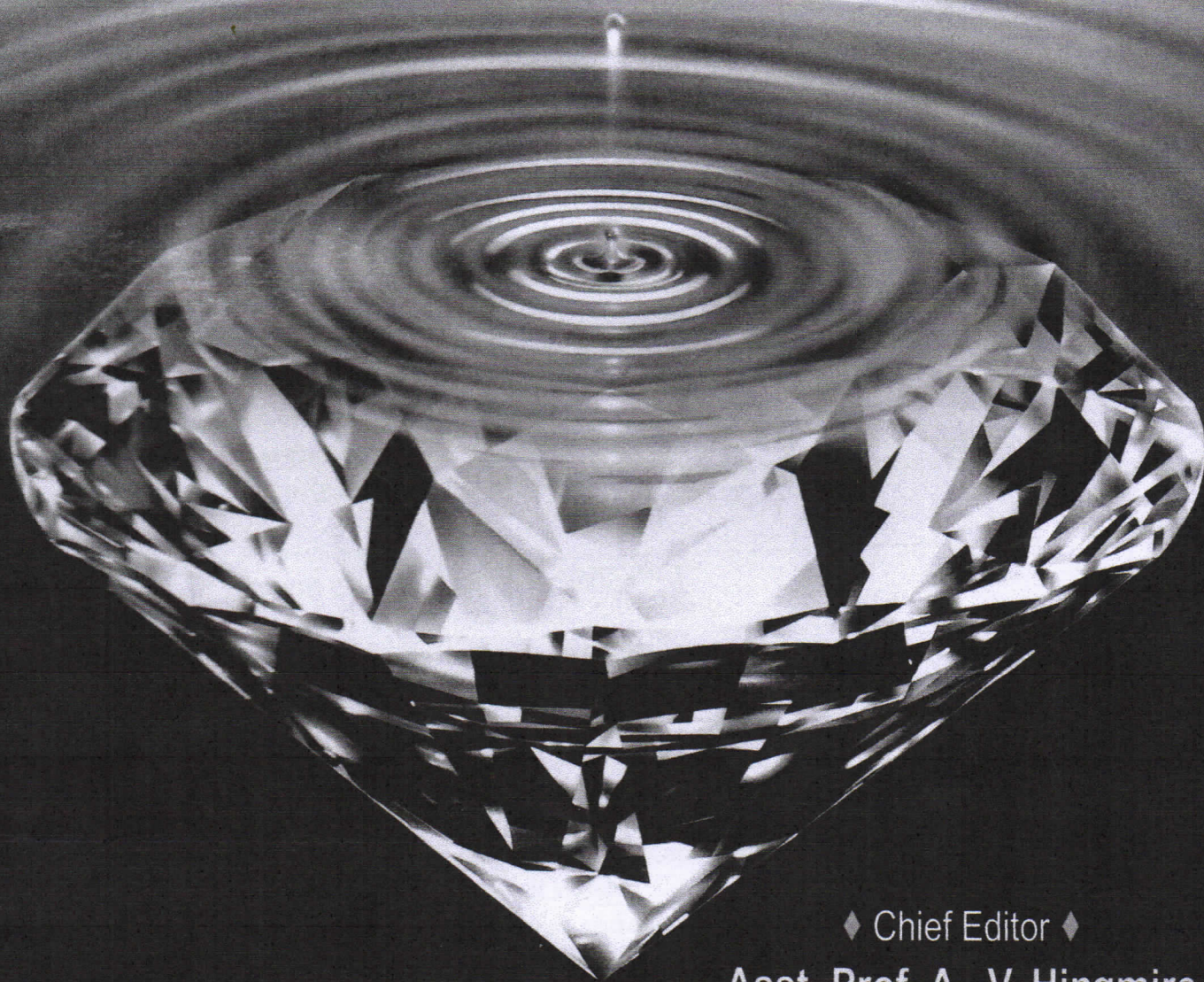
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## Indianization of English : A Sociolinguistic Survey

**Prof. Manohar Baburao Karande,**

Head and Associate Professor,

Department of English,

Radhabai Kale Mahila Mahavidyalaya, Ahmednagar.

### ABSTRACT:

Indian English is spoken primarily in the Indian subcontinent. It has been emerged during and after the colonial rule of Britain in India which is considered one of the official languages of India, with about ninety million speakers. Less than a quarter of a million people speak English as their first language. Speakers of Indian English use it as a second or third language, after their respective language/s. India, widely has been recognized as a country observing "Unity in Diversity". Despite this, there is general homogeneity in syntax and vocabulary among the varieties of Indian English.

**Key Words:** Indianization, Hinglish, code mixing, code switching, bilingualism

'Indianization' of English generally means that the word, phrase, idiom, expression or the syntactical usage of the Standard English (British English or American English) which has become a part of the Indian subcontinent. It involves usage and the meaning which is peculiarly of Indian taste and colour. This creativity of English has enhanced the popularity and the use of English in the Indian context. Gradually English language has become a symbol of political power, legal system, administrative network, business, science and technology. With its prestigious and powerful status English provided a window to the new world of knowledge to the Indians. Thus, English started to take a totally different form of 'Indian English' in multilingual India from its original British and American English. While Indian speakers of English use idioms peculiar to their homeland, often literal translations of words and phrases from their native languages is observed. Only British English is considered grammatically correct. In case of phonology of Indian English, Indian accents vary greatly. Some Indians speak English with an accent very close to a Standard British (Received Pronunciation) accent (though not the same); others lean toward a more 'vernacular', native accent for their English speech.

In present day Indian English is widely accepted and has gained recognition with various different varieties of 'Indian Englishes'. English spoken in India indicates the social behaviour of the people which is reflected in their attitude towards different dialects and accents. This may be because the grammarians followed the standards of the superior variety of English and applied those rules to the English spoken in India. This rule based practice was mostly applied to written English and some formal style of speaking. Therefore, such usage of English which followed the principles of the standard language was accordingly defined as correct form. The notion of correct and incorrect form of English is still a basis of concern for Standard English. It is no longer a language used during colonial times when it was mainly used for the

colonial and official purposes. Today Indian English has become much more interesting, and now it's free from the standard norms and rules of the language. The complex multilingual situation of India makes difficult for the Standard variety of English language to establish in India. Code switching and code mixing are the major processes for the Indianization of English in India.

Due to modernization, liberalization, and globalization and with the advent of TV channels a new kind of language is emerging which is neither Hindi nor English but it can be called Hinglish. In other words TV is serving us a cocktail of Hindi-English. TV has not only affected our eyesight but it has affected our language as well. Grammar which was considered as the back bone of a language is being neglected. A new culture is emerging which speaks Hinglish with great pride. For e.g. The loss of fourth wicket is a Jabardast Jhatka (great shock) for the Pakistan team, Ham kisi bhi secular

government ka samarthan karenge. (We will support any secular government.) Besides Hinglish they are doing code-switching and reduplication which is totally ungrammatical. For example: Maine abhi just khana khaya hai. (I have just taken my meal) Suppose karo Barak Obama India aayen. (Suppose Obama comes to India) These reduplications— 'suppose karo' and 'abhi' just are grammatically incorrect and it appears that someone has put on sari and skirt together. Language has left the Grammar in the same way as the fashion has left the gracefulness. As in the age of new fashion the size of clothes is reducing similarly the size of words is also decreasing. Several English words are so frequent in Hindi that they have become a part of Hindi language. For example school, tuition, platform, station, train, rickshaw, signal, class, coffee, glass, table tennis. If these words are translated in Marathi it will be against the rule. For e.g. Marathi translation of train is "Louhpathgamini, Signal as "awat jawat suchak chinha". Certain English words are there whose Marathi equivalent are not there, for e.g. bus, truck, tempo, cycle, scooter etc. Certain technical words are easy to articulate in English, for e.g. social survey, field work, mass media, office staff, traffic rules. Certain constructions undergo morphological changes. We find Hindi plural markers to English nouns. For example- samosas, gundas, chaiwalas etc. Similarly Hindi suffixes are applied in English words. For e.g. confusijana (to get confused), sirji, computerji, etc. English prefixes also appear in Hindi words. For e.g. ex-mantri, non- Hindi, non- filmi. etc.

A large proportion of the world's population is bilingual. Bilingualism is like a present practically in every country of the world, in all classes of the society. Language alternation has become significant in the Indian context in view of the variety of language throughout the country. Bilingual processes such as diglossia, code-mixing and code-switching are the most commonly noticed instances of code alternation. Globalization is a threat to the regional languages. We live in the country, where the survival of our own language is threatened by success of English. The college students of Marathi origin pronounce English words in their dialectal tone. The Indians accepted the language of British in their typical way, they "articulated" it. They used the language in a native culture. Consequently, cultural features were reflected in it. This phenomenon is unique not to one colony alone but typical of all situations of language contact.



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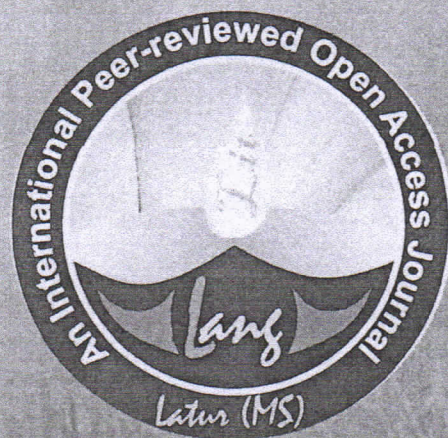


# LangLit

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CODE SWITCHING AND CODE MIXING IN SHOBHA DE'S  
SOCIALITE EVENINGS

MANOHAR KARANDE,

Assistant Professor,  
Radhabai Kale Mahila Mahavidyalaya,  
Ahmednagar.

## ABSTRACT

Code switching and code mixing are the two important sociolinguistic devices which are often used by Indian writers in English especially novelists. All the novelists starting from the first generations of the Indian English have exploited this strategy while writing their novels such as Mulk Raj Anand, Raja Rao, R. K. Narayan, Khushwant Singh Shashi Deshpande, Shobha De and others. Code Mixing is one of the mixtures of varieties like code-switching. Various items are mixed from one language to another as a new communicative strategy. Wide range of use has been made to avoid ambiguities. For the sake of clear meaning of language in certain context, specific words are required. These words are transferred from one language to another according to particular context. This transfer of word is called as code-mixing. The words, phrases, sentences transferred from one language for certain context such as the words and ceremonies have different shades of meaning. The specific words are used to describe sweets and ceremonies. These contexts are different in different regions vis-a-vis countries. Hence there is necessity of transfer of typical words, sweets as representatives of that particular, region or country. These transferred words may be various types, such as collocation, hybridization etc. 'Code-Mixing' means mixing of lexical items and phrases in to the system of native language, whereas, 'Code-switching' refers to a switch from one language system to another, in a unit of discourse. The present article is devoted to the study of code switching and code mixing in Shobha De's *Socialite Evenings*.

## INTRODUCTION

In multilingual and bilingual society, many language items are mixed in one language from another. Mixing of the various language items more than words with their social, functional, attitudinal situation, connotations means, code-switching. All the language features, structures are mixed. The items from words to sentences are mixed into each other. The main motive of mixing is development of language as new strategy for communication. The following are some of the noteworthy definitions of code switching and code mixing.



## Various Definitions

BrajKachru (1979:28) defines *code-switching* as a device used in the functional context in which a multilingual person makes alternate use of two or more languages.

Dell Hymes (1977:103) observes code-switching as, "the alternate use of two or more languages, varieties of a language or even speech styles."

Michael Halliday (1978:65) says, "code-switching is code-shift actualized as a process within the individual: the speaker moves from one code to another and back, more or less rapidly, in course of a single sentence".

Sharma (1977:3) thinks that, "Code-switching and code-mixing of various dimensions have been common occurrence throughout the development of human cultures and civilizations."

Trudgill (1980:82) preferred to use code-switching as "switching from one language variety to another when the situation demands".

Hudson (1983:56) calls code-switching as "use of different varieties at different times by single speaker".

BrajKachru, (1983) tries to define the difference between the code-mixing and code-switching. According to him, code-switching entails the ability to switch from code A to code B. The alteration of codes is determined by the function, the situation and the participants. In other words, it refers to categorization of one's verbal repertoire in term of functions and roles. Code-mixing, on the other hand, entails transferring linguistic units from one code into another. Kacharu thinks of code-switching as the use of one of more language system in different functional context, and code mixing as the use of two or more languages for consistent transfer of linguistic units from one language to another.

## Types of code-switching

There are four types of code-switching. They are as follows:

### 1. Tag switching

In tag switching a tag in one language is inserted into an utterance, which is otherwise entirely in the other language. Tags may be inserted easily at a number of points in a monolingual utterance without violating syntactic rules since they are subject to minimal syntactic restriction. Poplack (1980)

### 2. Intersentential switching:

A code switching takes place at a clause or the sentence boundary, where each clause or a sentence is in one language or another language. In other words it is changing languages between clauses. It may also occur between speakers' turn. Intersentential switching requires greater fluency in both languages than tag switching, since major portion of the languages must be confirmed to the rules of both languages. Poplack, (1980).



### 3. Intrasentential switching

Switching of different types occur within the clause or sentence boundary. It also includes mixing within word boundaries. This type of switching involves greater syntactic risk, and may be avoided by all but the most fluent bilinguals. Poplack (1980).

### 4. Switching within a word

In this particular instance there is switch between a bound morpheme and a phonologically un-integrated lexical form.

### Types of Code-Mixing

BrajKachru (1983:200-201) highlights code-mixed varieties used in India, with special reference to their use of communicative strategies. According to him there are four types of code-mixing. They can be discussed as follows:

1. **Englishization**-It is a modern style of using English. It highlights modernization, socio-economic position and membership in elite group. Englishization focuses the deliberate style used by the speaker.

2. **Sanskritization**: This type of mixing is shared by all Indian languages. In other words, it may mark religion and caste, as we have in the case of Kashmiri. It also has developed registers for philosophy, literary criticism and religious discourse. In other contexts, Sanskrit lexicalization marks 'pedantic style'.

3. **Persianization**:-This type of mixing highlights all the parts, which came under the domain of Muslims during the Muslim period of Indian history. Persianization is associated with the legal register, primary that of the lower courts.

4. **Pidginization**:-This type of mixing tries to simplify the language used in institutions where the participants speak languages which are not mutually intelligible. It results into different typical varieties like Bazar English, Butler English or Chi Chi English.

### The Novel at a Glance

The novel *Socialite Evenings* is one of the most acclaimed novels written by Shobha De. This novel was launched with a publicity stunt. She wanted to bring to the notice of the people in the world that an Indian woman has the capacity to write on the bold theme depicting the lives of the women rising from the middle class to the upper class by adopting unusual, modern and unexpected ways to lead the life at their own will disregarding the customs and the traditions of the patriarchal Indian society. The entire novel focuses on the high society in Mumbai. In fact, this novel is about the house wives of the rich and affluent families who indulge in extra marital relations because their husbands remain extremely busy in their offices or with their industrial work. The attitude of these husbands towards their wives is very casual as they treat their women as a commodity which is known as 'comodification of women'. They do not consider them as their real life partners of intimate friends. The intimacy between the husband and wife is dried up owing to the indifferent attitude towards

There are many festivals celebrated throughout the year in India. Indians celebrate them with much pomp and gaiety. The terms that are used for festivals are religious bound and there are thus no equivalent English terms. In *Socialite Evenings*, the Novelist Shobha De makes very vivid description of Ganesh Festival by making use of code mixed language. The following extract is a fine example of code mixing:

*'The noise, the bustle, the energy eased the sorrow from my mind as I recalled Ganesh Ustaves from the past. From the age of five till my days of trying to be a sophisticate I had participated enthusiastically in them. It was my favorite festival, even more special than Diwali. Though we didn't bring moorti to our house, it didn't really matter since it came to my father's older brother's home. We were expected to be present for aartis, which took place twice a day. I loved the rituals that went with puja. I enjoyed watching my aunt arranging the gleaming silver and brass thalis alongside altar, heaping one with flowers one with fruits, one with Prasad, and one with diyas. The smell of incense, combined with aroma of sandalwood paste and coconut oil. Wonderful. I'd watch with fascination as the pot bellied priest chanted the "sukhakarta ... dukhharta..." and elders joined in the chorus.'* (P.430)

The narrator of the novel *Karuna* makes description of the Ganesh Festival which is celebrated very enthusiastically for ten days in India and particularly in Bombay city and Maharashtra. The novelist borrows many words from native language Hindi to bring authenticity in the situations. The borrowed words such as 'ustave' means celebration, 'moorti' means idol, 'Diwali' means festival of lights, 'puja' means worship, 'diyas' means candles lights and 'sukhkarta ... dukhharta' means the God which makes us happy and saves us from dangers.

There are some more glaring examples of code mixing and code switching as given below:

*'I met a real big memsaab today.'* (P.05).

*'Have some bhang baby,' said Anjali to me. 'Grow up. Enjoy yourself. You are a big girl now.'* (P.62)

*He said to her, 'Beti, tum bahutdookhi ho.'* She nodded her head vigorously. (P.245)

*Abe had given me enough after the talaq—that's been invested too.'* (P. 223).

*'I've tried—but he laughs it off. "You are my Kohinoor," he says. "Nobody else matters."* (P. 225).

*'Cool breeze, cool, cool breeze. Beti—your kundalini is rising.'* (P.246)

*'This Gārhwali unpadh did more to heal my wounds than all pricey psychiatrists and doctors in Bombay.'* (P.367).



## Conclusion

The above discussion reveals that Shoba De has extensively used the strategy of code switching and code mixing in her novel *Socialite Evenings* to bring out the socio-cultural reality in the modern, urban cosmopolitan society in India. Through the code switching and code mixing De has made a sociolinguistic experimentation to depict her characters and social situations.

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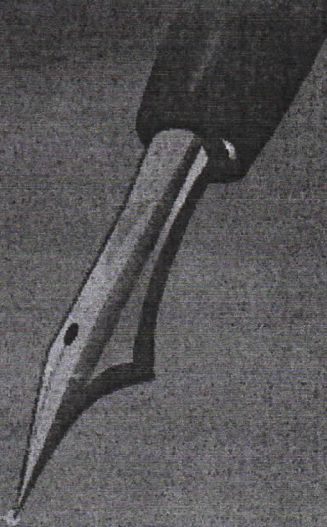
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## Nativization of English in Shobhaa De's 'Sultry Days'

Dr. Geeta M. Patil,  
(Principal Investigator)  
Professor,  
Department of English,  
Dr. Babasaheb Ambedkar Marathwada  
University, Aurangabad.

Prof. Manohar B. Karande,  
(Research Student)  
Associate Professor,  
Department of English,  
Radhabai Kale Mahila Mahavidyalaya,  
Ahmednagar.

**KEY WORDS:** Code- mixing, code- switching, hybridization, borrowing, indianized expressions with repetitions, kinship terms, honorifics, diminutives, unusual collections, reduplications, cuisine and attire words etc.

### ABSTRACT:

The purpose of the present research paper is to study the Indianization of English. It is through the process of nativization of English, the characters and the speech situations are revealed. The novelist has skillfully exploited Indian English, which is full of code-switched, and code mixed words, phrases and sentences to suit her characters. She has made linguistic experiments through the process of Indianization because she would like to give the Indian flavor to the situations and the characters in her novels as they depict modern Indian culture. In addition, they reveal the aristocratic ways of life in the Indian society. De is well acquainted with the kind of English being spoken by her characters that come from the upper middle class of the metropolitan cities in India. In her fictional works, De has made a linguistic experimentation with the English language depicting cultural nuances. The present research is an attempt to analyze the selected extracts from 'Sultry Days' and conversations of the characters in which this experiment is explicit. It is also an attempt to analyze the different ways in which Shobhaa De uses English to express Indian thoughts and feelings. She has resorted to many linguistic devices such as code switching, code mixing, hybridization, borrowing, reduplication, honorifics, diminutives, curses, blessings, abuses, slang expressions, regional dialect, sociolect, idiolect etc to exhibit the Indianness of the characters.

It is understood that there is an inherent relationship between language, society, and culture. Language is primarily a medium of expressing thoughts, feelings and perceptions of the users of that language. Since languages are constantly changing, it gives rise to new varieties of speech and writing. It leads to differences in which the individuals present themselves to others. It is noticed that language is necessarily a vehicle of culture. It is also true that the impact of culture on a language is something intrinsic and unavoidable. Therefore, there has been a close relationship between language, society, and culture. Since Shobhaa De's most of the novels reflect Indian metropolitan culture, her characters are likely to use the existing trends in the language. She has used Indian English as a tool to depict the linguistic behavior of the characters. It is undeniable that language is a social institution that helps us live, grow and communicate with the members of the society. The social factors play an important role in the way in which we use language. This sociolinguistic study directs the meaning in different speech situations and speech events. People come from diverse communities, geographical and different socio-economic backgrounds. These factors determine the use of language in a given situation. The characters of Shobhaa De's novels come from different strata of the society. Most of her characters are from Indian film industry representing the upper middle class. Their family and social life are different from the ordinary people's living styles in India. Her characters often make use of mixed nativized words, phrases and sentences to establish their interpersonal and social relations.

The novelist makes use of code-switching and code-mixing profusely in her novels. An effort is made to examine these strategies and analyzes the conversations of the characters

in the light of social, economic and cultural aspects in order to establish the authenticity of the actions of the characters. The social distance or the intimacy of the interlocutors is revealed via different linguistic strategies.

Nativization is the process in which a language undergoes changes according to the needs of communication. A foreign language gets nativized when it accumulates the native speakers of that language. This happens necessarily when the adults start using a second language which eventually becomes the native language for their children. Nativization has been of a great interest not only to the researchers but also to the language scientists. The sociolinguists and anthropologists are mainly concerned with the process of nativization. According to 'Concise Oxford Companion to the English Language' (1998):

"Nativization is the process by which a transplanted language becomes native to a people or place either in addition to or in place of any language already in use" (www.encyclopedia.com dated 1/6/2015)

The above definition of 'nativization' makes it clear that a language becomes nativized if the local people start using that language in context even if it is in a fragmented form. For instance, when the process of colonization started in India with the establishment of East India Company in 1600, the process of nativization of English started simultaneously.

The nativization of English is due to the transfer of a foreign language to the local language as a new cultural phenomenon. The process of nativization emerged and spread because of the communicative needs of the local people. The fact of the matter is that it was the beginning of bilingualism in the Indian context. There is no detailed work on the early stages of bilingualism in English in India. We come to know about the history of bilingualism mainly from the official reports or the books published by the government agencies. The growth of bilingualism is closely connected with the beginning of the colonialism by the British. There are a large number of surveys which discuss the introduction of bilingualism in English in Indian subcontinent.

This novel is replete with instances of nativization because the novelist deals with the contemporary realities in India. She has focused on the upper middle-class life in this novel. The sociolinguistic strategies such as code-mixing, code-switching, honorification, diminutives, abusive expressions, slang expressions, morphological deviations etc are abundantly used by the novelist to highlight the process of nativization. The language used by the characters reveals their inner world as well as interpersonal relations. The use of Indianized words, phrases and expressions are related to the social world of the characters.

'Sultry Days' is a different type of novel where De has presented the modern life-style of rich people. This novel was published in the year 1994. Nisha, the main character, is the narrator of the novel. She can be grouped among other women characters of Shobhaa De's novels such as Karuna and Mikki because all these are engaged in healthy striving and they guard the core of the 'real self' from the damages caused by the anxieties of life. Only the periphery of their personalities gets affected. They are strong willed, capable of making a choice and directing their lives towards self-actualization. 'Sultry Days' is the story of an upper-middle-class society of Mumbai. Deb is the protagonist of the novel, having mean views about women. He is just interested in women for getting sexual pleasure. Nisha and Deb are in love with each other. But Deb is not serious in their relationship. In some extent this novel is an autobiographical one because the narrator and the protagonist of this novel is Nisha, who is a mouthpiece of the novelist and portrayed the diversity of characters from the cosmopolitan city like Bombay.

**Some glaring examples of code-mixing and code-switching in the novel, 'Sultry Days':**  
'God would grin maliciously and wave me off. ' Jao, jao... kuch ley ke ao ( go on... get something) '(p.07).

'samosas—get four. The big ones. OK ? And don't forget the chutney' (p. 09).  
 'Forget it, yaar. You don't need any chappal- wappal' (p. 20).  
 'Give up grass? You must be pagal, yaar, completely mad. It's like asking me to give up....urinating' (p. 27).

'When the party's over, sab kuch khatam yaar. You will have to travel in bus and train like the rest of us.' (p. 28).

'So what did Mr. Multinational say about me is this beloved daughter, his ladli beti...Hey—that's a nice little pet name for you—I'll call you L.B. short for Ladli Beti.'(p.35).

'Such sheet, yaar. All faltugiri, all nonsense. When will my father learn that they can never lick the system? Your old man is a chaalu chap.' (p. 37).

'Wait? For eternity? Who knows about marriage sharriage, yaar. I am happy as I am.' (p. 45)

'Who cares, yaar? Do you? I love Bijli and she loves me ...bas, matter ends. Why should I bother about what all these chamchas on the road must be thinking? Anyway...' (p. 47).

'Besides, Belu is much too straightforward. No tamashagiri with him. With Iqbal one can be certain there will be lot of Stuntbazi. That's half fun yaar' (p.68).

'At this point Laxman spoke up (he understood English but pretend that he couldn't). He told his 'baby' that he would certainly not stop his car in this randi gali, the street of whores( I hadn't heard the term till then) and that if she insisted he'd tell her mother.'(p. 80).

'Don't ask such questions,' Laxman interrupted again, speaking sharply to Minal. I will tell the Sethani. Such dirty talk! Babylog from good families don't say such things baap re! I will tell your father also.'(p. 82).

'Ladka chahiye ya lakdki (Do you want a boy or a girl)?a dwarf with a red scarf around his thick neck called out from a dark stairway. 'Sub mall milega (You can get anything you want),' he beckoned.'(p. 83). 'The dwarf toddled up and took God's hand.'Chat hatt bhadwa (get lost pimp), 'God snarled and shook him off. (p. 84).

'Are, Comrade ka bachcha.... Kaisa hai tu, saala (how are you)?' (p. 84). Bachchi hai chhod do uski baat (she's just a kid—forget about her).'(p. 85).

'Chameli kidhar hai tu? Tera baccha ro raha hai. ( where are you? your child is crying)'(p.86). 'He'd say that's bloody fairy.... I m not surprised yaar the guys looks like bawarchi. He can't talk... have you cared his voice? Pansy! Sissy hai saala. Hijda! He probably embroiders in his spare time...ask him.'(p. 135).

He waved his hand and shouted, 'Shut up, woman I can't hear you .Want to create hungama on the street? Let me concentrate on getting out of this shit-hole.' (p.139).

'Get off my back. You must be growing cuckoo like your Pagli mother. Hearing things.' (p. 140) 'Shut up, you silly woman. Who said anything about marriage?Lagaging line, that's all, don't take it seriously.'(p. 140).

'Yeah? Maybe for pansy buggers like him. I don't have time to waste discussing this behenchod's cooking. I can't keep Sujata waiting.' (p. 141).

'Kamaal hai...one minute that other phellow comes here on a motorcycle. Now this phellow also comes. And you go...is this office or maidan?'(p. 142).

'He's some sort of a neta or something—isn't he? A leader...Trade unionist...Local dada...whatever.'(p. 146).

He wasn't bitching' (p.353).

### Hybridization

De has skillfully made the hybridization of the following expressions-

'awful beedies'(p.02), 'special chai'(p.02), 'chai boy'(p.03), 'bhari inconsiderate'(p.06), 'maha-accent'(p.11), 'mama's man'(p.21), 'small kholi'(p.30), 'parsee ladies'(p.32), 'bloody rundis'(p.45), 'chai-girl'(p.50), 'crisp dosas'(p.50), 'udipi restaurant'(p.50), 'perfect biryani'(p.60), 'stuntbaazi'(p.68), 'nepali prostitutes'(p.81), 'paan beediwallah'(p.83), 'potential randi'(p.83), 'filmwallah'(p.87), 'five star khana'(p.96), 'twentyish'(p.107), 'Thumri

**b) Words related to Attire**

'Chaddis'(p.12), 'Blouse with bandhani scarves and mirror work pieces' (p. 24), 'Khadi-jholas'(p.25), 'Choli' (p. 29), 'Chiffon sari' (p. 32), 'French sari' (p. 32), 'Indian sari' (p. 32), 'Sleeveless blouse' (p. 32), 'Fiddling with duppatta' (p. 53), 'Magnificent garas (Chinese silk embroidered saris)' (p. 58), 'Only mill saris-khatau, Bombay Dyeing' (p. 91), 'Cotton saris, hand block printed, bandhni, leheriya-prints of that sort' (p. 101), 'Venkatgiri sari-pallu'(p.104), 'Kurtas for casual feature' (p. 113), 'Pin stripes for press conference' (p. 113), 'Open collars track suits' (p. 144), 'Swirling ghagara with backless choli' (p. 116), 'Cut-away sleeved choli blouses' (p. 125), 'Vimal sari' (p. 129), 'Silk sari' (p. 129), 'Temple sari' (p. 208), 'ghagara'(p.240)

**c) Terms related to Religion and festival**

'we will have to your horoscope to shankerao, There must be a mangal in the marriage house'(p.23), 'Krishna reborn'(p.43), 'Diwali' (p.165), 'No baba, our community wives don't behave like that , Anyway, she knew her husband was never going to leave her for Bindiya'(p.207), 'Navratri' (p. 238), 'Dandiya-garba-raas'(p.238), 'haldi-kumkums'(p.262), 'Sarvajanik ganpati festivals'(p.262), ' Krishna's Gopikas'(p.313), 'my numerologist, confessed Lotika- I disturbed a rishi's meditation'(p.348), 'Hanuman'(p.356).

**d) Food Terms (Cuisine)**

'samosas'(p.09), 'chutney'(p.09), 'special chai' (p.02), 'lassi'(p.12), 'perfect biryani' (p.60), 'baida roti'(p.82), 'fag'(p.83), 'squashed pakora'(p.118), 'chicken tikkas'(p.161), 'shami kababs'(p.161), 'pudina chai'(p.168), 'mutton-do-pizza'(p.196), 'chapattis'(p.201), 'chiken, cow meat'(p.209), 'samosas' (p.211), 'seekh kababs'(p.234), 'papdi'(p.238), 'asli ghee'(p.238), 'dall-roti'(p.261), 'puris'(p.261), 'shev puris'(p.348).

**e) Abuses and Slang expressions**

'ball-less eunuch' (p.14), 'pagal' (p.27), 'chootiya driver' (p.28), 'Bloody Bandar monkey' (p.28), 'saalas' (p.37), 'Tight ass (father of Nisha)'(p.37), 'fucking world'(p.45), 'bloody bengali'(p.74), 'gandus (homosexual)'(p.74), 'bhadwa'(p.74), 'saala'(p.84), 'Saala chootiya'(p.121), 'fat cow or a carrot'(p.125), 'pansy buggers' (p.141), 'sissy'(p.135), 'besheram'(p.143), 'bhangi'(p.144), 'bloody dogs'(p.149), 'scum, skunk, worm'(p.149), 'supari-killer'(p.150), 'swine'(p.151), 'gorila'(p.167), 'bhuddhu'(p.194), 'randiyonka mela'(p.309), 'writing bug'(p.340), 'haraami'(p.354), 'pramila kutti'(p.365).

**f) Blessings**

There are no examples of blessings in the novel.

**g) Kinship Terms and Honorifics**

'baby'(p.03), 'yaar'(p.04), 'ma'(p.10), 'papa'(p.23), 'Didi' (p.34), 'ok baba'(p.38), 'grandma'(p.49), 'ba-grandmother of nishas mothers mother'(p.100), 'babe'(p.144), 'grandpa, vikkibaba'(p.279), 'Nasha, jaan-e-man'(p.324), 'Mr, Muttinational, comradsaab'(p.48), 'maharajs & barons'(p.59), 'setani'(p.82), 'seth'(p.82), 'God was ready it wipe the madam's filthy feet with a scented towel by then'(p.87), 'Rajkumari'(p.287), 'Her Highness Kanwal kumari of Dhogragerh'(p.288).

**h) Greetings**

'Hay, Rukhmanibai...namaskar. He greeted her'(p.84)'Salaam prostitutes'(p.310).

**i) Diminutives**

'Specs'—spectacles, (p.14), The word 'C'mon', is used for 'come on' (p. 30), 'Mr.-Multinational-- Nisha's father' (p. 35). 'God' is nickname of 'Deb' which means in Marathi language 'Dev' and translated in English as 'God'. Sujata calls God by using nickname as 'Debu' while 'Nisha' means night in English but God calls her 'Nasa' and not poornima, Neeta, Neha, or Nidhi (p. 54), 'L.B.' means 'Ladli beti' (p.35), 'M.D'—Managing Director (p. 38), 'bijli' is name of God's motorbike (p.46), 'D.O.M.' is the diminutive of-- dirty old

man' (p. 48), 'Nana is nickname' (p.54), College 'mag' means college magazine' (p. 58), 'Lady 'S' is a diminutive of Lady Shirinbai' (p. 60),

#### j) Reduplication

'Change-wange' (p.07), 'Steady-weddy business' (p.14), 'Chappel-wappal' (p.20), 'marriage-sharriage' (p.45), 'altu-Faltu' (p. 52), 'Rift-raft' (p.61), 'hot-shot' (p.96), 'Culture-vultures' (p.163), 'poet-shoet' (p.166), 'parties-sharties' (p.168), 'dare-bare girls' (p.174), 'bindi-shindi, jhumka-wumka, kaajal-waajal' (p.200), 'coffee-shoffee' (p.200), 'party-sharty' (p.203), 'stubby-hubby' (p.207), 'riff-raff' (p.244), 'seedha-saadha' (p.261), 'shaadi-waadi' (p.261), 'hag-bag' (p.289), 'Who's this Ron-shon, yaar' (p.296).

#### k) Words related to Alliteration with unusual collocations

'God's girl' (p.15), 'Sandal store' (p.20), 'Mama's man' (p.21), 'Crazy kid' (p.22), 'Bloody Bandar, (p. 28), 'Chaalul chap' (p.37), 'Free fuck' (p. 45), 'Stale sex' (p.49), 'Granny glasses' (p. 55), 'Golden goose' (p.55), 'Bloody Bengali' (p.74), 'Professional pimp' (p.83), 'Bloody beautiful' (p.87), 'Available Bombay woman' - brazen, bold, brassy, (p.117), 'Creative cabin' (p.145), 'California-Sun-Surface and sex' (p.153), 'Cheap Charlie' (p.168), 'Toothless tiger' (p.169), 'New Newspaper' (p.175), 'Model market' (p.174), 'Minor matter' (p.179), 'Classy Call girl' (p.187), 'Soup Spoon' (p.244), 'Love-Lorn maidan' (p.248), 'Kiki's kamasutra', 'Kiki's Contessa' (p.317), 'Bloody beach' (p.320), 'screechy societies', 'Status Symbol' (p.321), 'prominent people' (p.321), 'popping a prawn pakora' (p.348), 'wash and wear' (p.362), 'shitty stuff' (p.364).

#### l) Odd words/unusual collocations

'Sugar baron' (p. 14), 'Commie beggar' (p. 14), 'Paste up boys, lay out girls' (p. 17), 'Beedy-money' (p. 20), 'Capitalist pig' (p. 22), 'Company wives' (p. 38), 'blousy woman' (p.48), 'Arty circle' (p. 53), 'Sugar mouse' (p. 53), 'Phellow (fellow)-' (p.69), 'phoren (foreign) cigarettes' (p.85), 'phrankly (frankly), phor (for), phirst (first), phiring (firing) - All these words are mispronounced by Kawla, the M.D.' (p.142), 'Bloody weather' (p. 151), 'chaalu fucker' (p.169), 'Communist pimp' (p. 170), 'nouvelle- (novel, new) in French' (p.185), 'I feel like a geisha' (p. 186), 'Stray kittens and street puppies' (p.220).

In the beginning, the highly marked examples of nativization from the novel 'Sultry Days' are illustrated in the light of the process of nativization of English. In this novel, there are more examples of this kind in the world of advertisements. Therefore, an attempt has been made to discuss Indianized words, and phrases in this novel. The sociolinguistic experimentation made by De gives color and flavor to the Indian modern culture where the relations between the individuals are strained. De also brings out the difference between the life of Calcutta and Bombay using various sociolinguistic strategies. The novelist has used many words and phrases borrowed from the regional languages of India such as Hindi, Bengali and Marathi. Thus, the chapter throws light on the aspect of Indianization of English in the true sense of the term.

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## Habitat Dependent Variations in The Rate of Oxygen Consumption, Rate of Ammonia Excretion and O: N Ratio of Freshwater Bivalve, *Lamellidens marginalis* From Lotic and Lentic Water of Godavari River at Paithan, During Summer. .

P. Ramanlal Gugale\*, A.N. Vedpathak and M.S. Salve

\*Molluscan Endocrinology and Physiology Laboratory, Department of Zoology, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad-431004 (M.S.), India.

[\*Corresponding Author's E-mail: pritesh.gugale09@gmail.com, arunn.vedpathak@gmail.com ]

**Abstract:** Considering the site (habitat) specific variations in the metabolic activities in the freshwater bivalves, we reported here the changes in the rate of oxygen consumption, rate of ammonia excretion and O: N ratio in the freshwater bivalve mollusc, *Lamellidens marginalis* (Lamarck) from lotic and lentic water habitats on April-May during summer season. The adult freshwater bivalves, *Lamellidens marginalis* (82-84 mm shell length) from lotic and lentic water near Jayakwadi dam on Godavari river was selected for determination of rate of oxygen consumption, rate of ammonia excretion and O: N ratio. The adult bivalves from lotic water habitat showed high rate of oxygen consumption and low rate of ammonia excretion. The O: N ratio showed higher values in bivalves collected from lotic water than lentic water during summer season.

The results of study are discussed in the light of possible physiological processes in freshwater bivalve molluscs.

**Keywords:** Oxygen consumption, Ammonia excretion, O: N ratio, Habitat specificity, Freshwater, bivalve, *Lamellidens marginalis*

### 1 Introduction

The location and meteorological conditions has profound effect on the metabolic activities in all organisms. Relatively very few habitats affect the animals with constant environmental conditions, especially temperature. In response to this relativity, the animal at all levels of habitats changes its physiology by developing

a mechanism to meets the normal ecological factors. Temperature rise on specific habitat above the optimum requirement can affect the physiology of bivalves (Bayne, 1976). One major reason for changes in the metabolic activities often used is the rate of oxygen consumption, which is affected by food availability and water temperature. The animals from different habitats experiences



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**JOURNAL OF BASIC SCIENCES**



## STUDY OF BIODIVERSITY OF APHIDS IN AND AROUND AHMEDNAGAR

Pawar S. L.\*

\*Department of Zoology, Radhabai Kale Mahila Mahavidyalaya, Ahmednagar-414001 (M.S.), India.  
[\*Corresponding Author's E-mail: pawar.suman3@gmail.com]

**Abstract:** An extensive survey was conducted during July 2014 to June 2015 to study the occurrence and abundance of aphids and their associated host plants in the agricultural fields around Ahmednagar city. The aphids are the sap suckers and are considered as a serious agricultural pest of great importance. About 11 species of aphids belonging to family Aphididae were found during the field investigation. It was observed that, of the 11 species found, 5 species of aphids are more destructive and affects major host plants belonging to family Malvaceae, Fabaceae, Solanaceae, and Asclepiadaceae, which are the most important plant species preferred by aphids in the area of Ahmednagar where the survey was conducted. For this Survey, about 10-15 km area from east, west, south and north of Ahmednagar city was selected. The identification of aphids was done by using standard taxonomic keys. The collected data was summarized in table format.

**Keywords:** *Malvaceae, Fabaceae, Solanaceae, Asclepiadaceae, Aphids, Host plants*

### 1 Introduction

Aphids feed by sucking plant juices, causing distortion of young leaves and stunting new growth. Hence, aphids are considered as serious agricultural and horticultural pests (Hill, 1997). The sap-suckers or belongs to order Hemiptera and family Aphidiae are small, slow-moving, soft-bodied inconspicuous insects with piercing-sucking mouth parts that feed in groups near the tips of new shoots and flower buds. They transmit various plant viruses that are pathogenic to their hosts (Schepers, 1987), Honeydew excreted by the aphids attracts saprophytic fungi which cover the leaves leading to reduction of photosynthetic capacity of the host plant (Schepers, 1987).

About 4702 species of aphids are recorded in the world (Agarwal, B.K., 2007) and about 300 species are known as vectors of 300 different

viruses, infecting large number of plants (Eastop V.F., 1977) and (A.J. Dhembare, *et. al*, 2012). Thus the present investigation reveals some of the aphid species affecting the flora of Ahmednagar and its nearby localities.

### 2 Materials and Methods

The present investigation was related with the study of aphids from four different sites around Ahmednagar city by considering the limit of 10-15 km to east, west, south and north during July 2014 to June 2015. During this investigation, mostly the leafy vegetables, fruits plants, flowering plants, grasses, weeds, herbs and shrubs were taken into consideration for collection of aphids.

The observed aphids with their host plant material were collected using fine forceps and stored in vials containing 70% ethyl alcohol (A.J. Dhembare, *et. al*, 2012). The collected aphids were observed under microscope and identified using aphid identification keys (Blackman, R.L. and Eastop, V.F. 2006) and by using internet source.

### 3 Results and Discussion

There is profusion in insect biodiversity due to specific green zones developed by the M.I.R.C of defense department and Municipal Corporation in and around Ahmednagar city. The city is surrounded by number of

agricultural and floral farms. Survey of these fields in and around Ahmednagar city was conducted for a year i.e. during July 2014 to June 2015.

The aphids were observed causing damage to their host plants in agricultural fields, floral farms, gardens and floral Islands in the city. During this survey, it was observed that the crops like sorghum, bajra, wheat, soyabean, maize, castor and brinjal as well as flowers like rose and chrysanths having high market value were found to be infested by aphids. 11 species of aphids were collected and identified along with their host plants.

**Table 1: List of host plants and the aphids found associated with them.**

Sr.No	Host plants	Common names	Aphids
1.	<i>Gossypium hirsutum</i> (L.)	Cotton	<i>Aphis gossypii</i>
	<i>Ricinus communis</i> (L.)	Castor	
	<i>Abelmaschus esculentus</i> (L.)	Lady's finger	
	<i>Solanum melongea</i> (L.)	Brinjal	
	<i>Cucumis sativus</i> (L.)	Cucumber	
	<i>Hibiscus mutubilis</i> (L.)	Cotton rosemallow	
	<i>Hibiscus rosa-sinensis</i> (L.)	China rose	
	<i>Chrysanthemum sp.</i> (L.)	Chrysanths	
	<i>Urtica dioica.</i> (L.)	Stinging nettle	
	<i>Datura metel</i> (L.)	Angel's trumpet	
2.	<i>Cajanus cajan</i> (L.Millsp.)	Pigeon pea	<i>A. crassivora</i>
	<i>Vigna unguiculata</i> (L.)	Cow pea	
	<i>Ocimum sanctum</i> (L.)	Tulsi	
3.	<i>Zea mays</i> (L.)	Maize	<i>A. nerii</i>
	<i>Triticum aestivum</i> (L.)	Wheat	
	<i>Vinca rosea</i> (L.)	Periwinkle	
	<i>Citrus limonium</i> (L.)	Lemon	
	<i>Gomphocarpus sp.</i> (E.mey.)	Cotton bushes,	
	<i>Asclepias</i> (E.mey.)	Milk weeds	
4.	<i>Lycopersicon esculentum</i> (L.)	Tomato	<i>A. fabae</i>
	<i>Tagete serecta</i> (L.)	Marigold	
	<i>Helianthus annuus</i> (L.)	Sunflower	
	<i>Chenopodium album</i> (L.)	Pigweed	
5.	<i>Gossypium hirsutum</i> (L.)	Cotton	<i>M.persicae</i>
	<i>Solanum melongea</i> (L.)	Brinjal	
	<i>Brassica oleracea</i> ( Linn)	Cabbage	

	<i>Momordica charantia</i>	bitter gourd	
	<i>Carica papaya L</i>	Papaya	
	<i>Spinaciaoleracea (L.)</i>	Spinach	
6.	<i>Pisum sativum</i>	pea aphid	<i>Acyrtosiphon pisum</i>
7.	<i>Helianthus annuus</i>	Sunflower aphid	<i>Aphis helianthi</i>
8.	<i>Rosa indica</i>	Rose aphid	<i>Macrosiphum rosae</i>
9.	<i>Chysanthemum</i>	Chrysanthus	<i>Macrosiphoniella sanborni</i>
10.	<i>Glycine max</i>	Soyabean	<i>Aphis glycines</i>
11.	<i>Citrus limonium (L.)</i>	Lemon	<i>Toxoptera aurantii</i>

It was observed that the occurrence of aphids is more in the month of October to March although there were fluctuations in the raining pattern in this study year. Because of the polyphagus feeding habit, aphids are serious pest of almost all agricultural crops as well as floral farms (Minks and Harrewijn, 1987). As they feeds upon different parts of plant like leaves, stem, fruits, flowers, buds and even roots (Blackman and Eastop, 2000). They cause severe damage to the commercial crops as well as to other host plants.

About 34 host plant species were recorded and it was observed that *Aphis gossypii* became the most common aphid species attacking about 10 plants species in this survey. It was also observed that the winter season is favorable for the growth of aphids as the population of aphids is recorded more in the month of December and January of the investigation period.

Several vegetable farms Around Ahmednagar city producing vegetables like brinjal, lady's finger, tomato, cabbage, green peas, etc are found damaged by different species of aphids. The severe infestation was observed in Chrysanthus farm by *A. gossypii* and *Microsiphoniella sanborni* while the cash crop like soyabean was badly destroyed by *A. glycines*.

#### 4 Conclusions

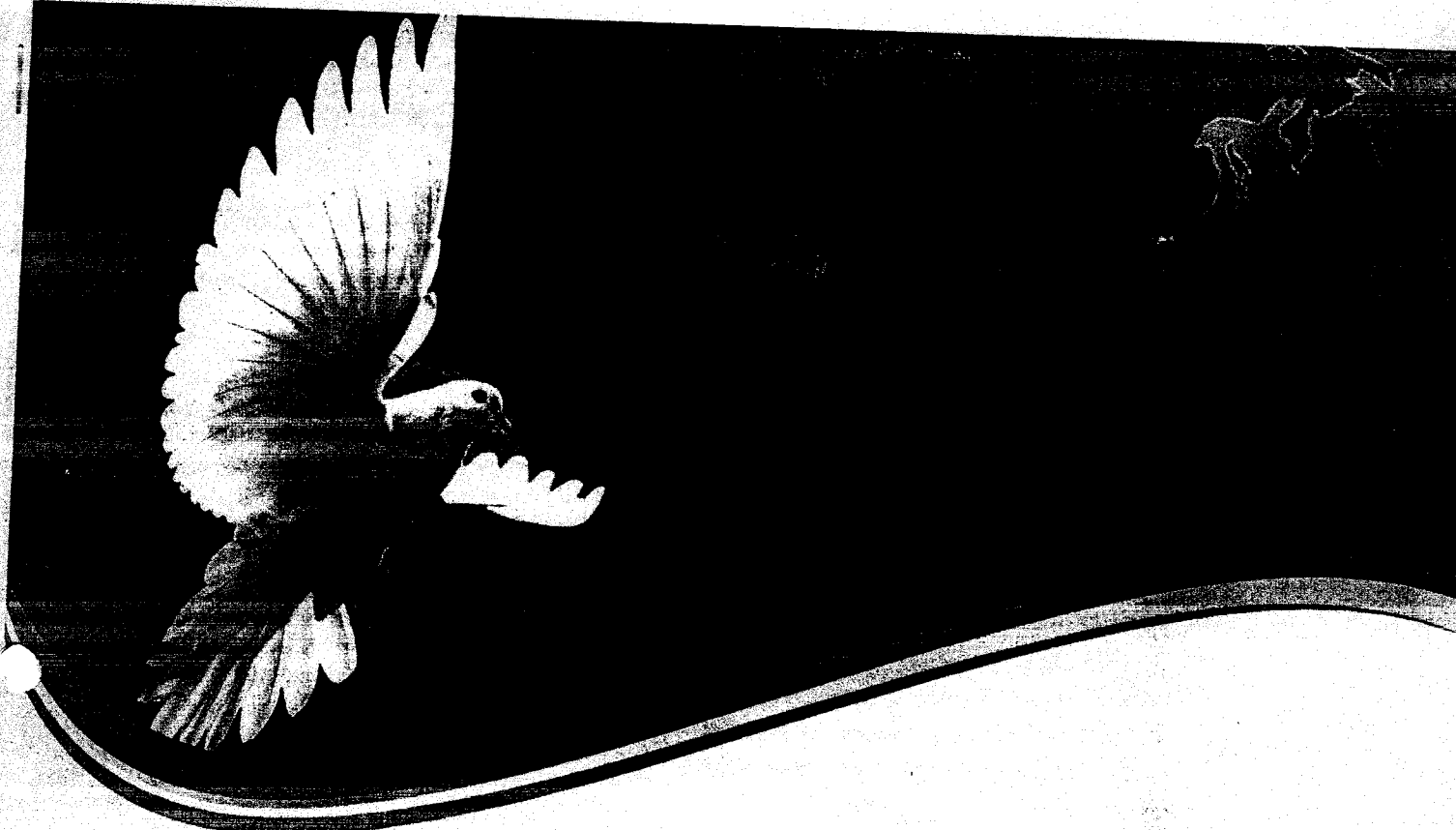
For prevention of such crop pest, farmers were applying different insecticides. Due to the excessive application of such insecticides, the

quality of crop, vegetables or fruits gets badly affected with some other problems like residues in water, soil, destruction of natural enemies of these pests as well as ecosystem disturbance of that location (Palikhe, 2002). Hence the proper management of aphids through biological control is needed. There should be an integrated pest management programme against aphids and other insect pests along with the applications of ecofriendly pesticides so that the production of crop, its quality and ecosystem of the farm can remain in good condition.

Thus the conducted survey provides the information about the polyphagus aphid species and their different host plants. By using this information, the changing crop pattern can control the infestation of aphids at certain level which will result in proper production of crops having good market value and the farmers can yield considerable production of their crop.

#### 5 References

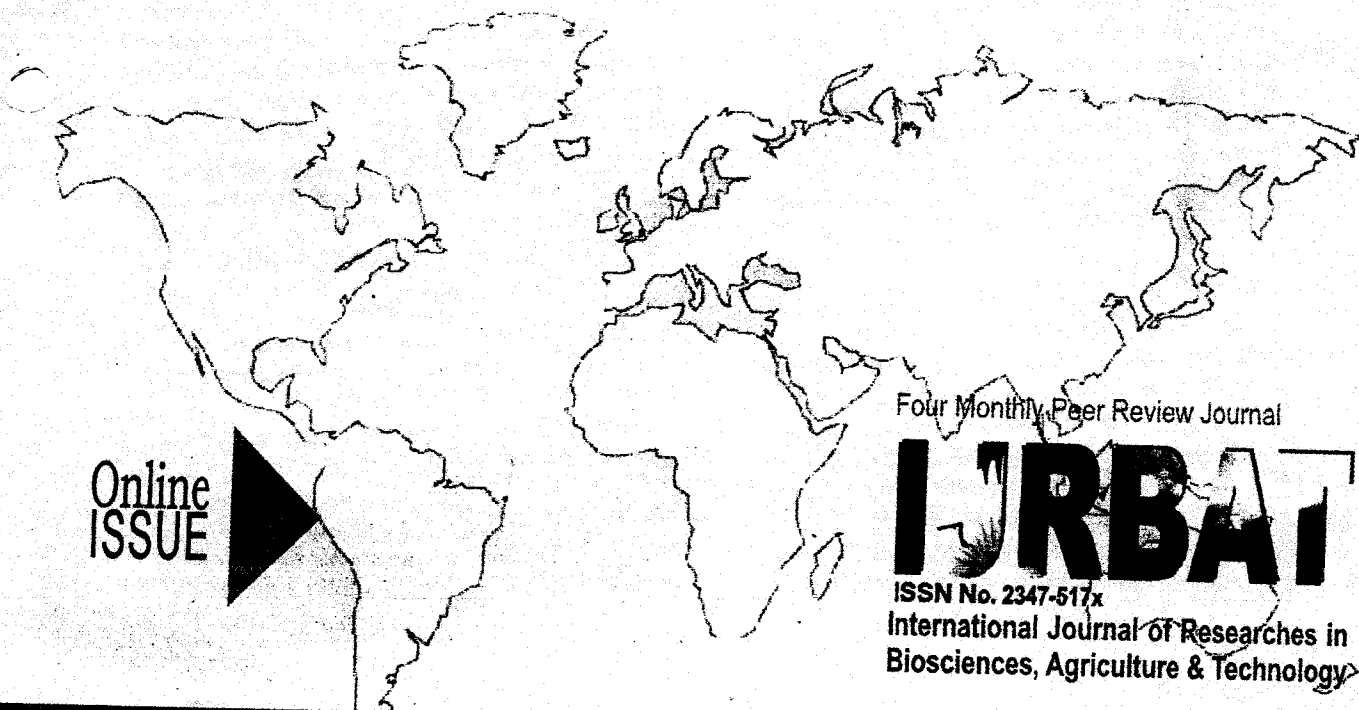
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## APHID INFESTATION AT FLORAL FARMS IN NAGARDEVALE, AHMEDNAGAR

**Pawar S. L.**

Radhabai Kale Mahila Mahavidyalaya Ahmednagar, Ahmednagar- 414 001.  
pawar.suman3@gmail.com

### Abstract:

Sonala dam is an earthen dam, constructed by irrigation department of Maharashtra Govt. The present work is an extensive survey conducted from July to December, 2015 to study the occurrence and abundance of floral aphids and their associated floral plants in the area of Nagardevale, the place with abundance of floral farms just 4 k. m. away from Ahmednagar city. The aphids are the sap suckers and are considered as a serious floral pest of great importance. About 11 species of aphids belonging to family Aphididae were found during investigative studies of the floral farms. It was observed that, 5 species of aphids are more destructive and affects the commercially important flowering plants belonging to family Rosaceae, Asteraceae, Asparagaceae, Malvaceae and Lamiaceae including the most important flowering plants like rose, aster, tuberose, marigold and tulsii in the area of Nagardevale where the survey was conducted. The remaining 6 species were associated with sunflower, soyabean, cabbage, ladies finger, brinjal and castor. The identification of aphids was done by using standard taxonomic keys. The collected data was summarized. This investigative study will help in identification and Control of the aphid population to yield more from the flower production.

**Keywords:** Malvaceae, Rosaceae, Asteraceae, Asparagaceae, Aphids, Host plants.

### Introduction

Aphids are considered as serious agricultural and horticultural pests (Hill, 1997) as they feed by sucking plant juices, causing distortion of young leaves and stunting new growth. The sap-suckers belongs to order Hemiptera and family Aphididae. These are soft-bodied, small, slow-moving inconspicuous insects with piercing and sucking type of mouth parts. They feed in groups near the tips of new shoots and flower buds. They are responsible for transmission of different plant pathogens causing serious plant diseases. (Schepers, 1987). The saprophytic fungi are attracted by the sticky fluid excreted by the aphids. It also forms a coating over the leaves leading to reduction of photosynthetic competence of the host plant (Schepers, 1987).

There are about 4702 species of aphids recorded in the world so far (Agarwal, B. K., 2007). There are about 300 aphid species are known as vectors carrying several plant pathogens, infecting large number of plants (Eastop V.F., 1977) and (A. J. Dhembare, et.al. 2012). Thus the present survey focuses on some of the aphid species affecting the commercial flora of Nagardevale and its nearby localities.

### Materials and Methods

The present investigation is related with the study survey of floral aphids from different floral farms at Nagardevale near Ahmednagar city. It is conducted during July 2015 to December 2015. During this investigative survey, mostly the floral farms were taken into consideration for collection of aphids.

The observed aphids were collected using fine forceps with their host flowering plant materials and stored in vials containing 70% ethyl alcohol (A. J. Dhembare, et.al, 2012). The collected aphids were examined with the help of microscope and identified using aphid identification keys (Blackman, R.L. and Eastop, V.F. 2006) as well as by using internet source.

### Results and Discussion

There is abundance in insect biodiversity due to specific dense vegetation zones maintained by Mechanized Infantry Regimental Centre, Ahmednagar of defense department and Municipal Corporation in and around Ahmednagar city. The city is surrounded by number of agricultural and floral farms. Survey of the floral fields at Nagardevale near Ahmednagar city was conducted during July 2015 to December 2015.

**Table 1:** List of commercial flowering host plants and the aphid species found with them.

Sr.No	Host plants	Common names	Aphids
1	<i>Pollianthes tuberosa (L.)</i>	Tuberose	<i>Aphis gossypii</i>
2	<i>Chrysanthemum sp. (L.)</i>	Chrysanths	<i>Aphis gossypii</i>
3	<i>Ocimum sanctum (L.)</i>	Tulsi	<i>A. crassivora</i>
4	<i>Tagetes erecta (L.)</i>	Marigold	<i>A. fabae</i>
5	<i>Rosa indica</i>	Rose	<i>Macrosiphum rosae</i>
6	<i>Chrysanthemum</i>	Chrysanths	<i>Macrosiphoniellasanborni</i>

The aphids observed were causing damage to their host plants in floral farms, gardens and floral Islands in the survey area. During this survey, it was observed that the flowers like rose, aster marigold, tuberose, chrysanths having high market value were found to be infested by aphids on large scale.

It was observed that the occurrence of aphids increases in early winter season although there were fluctuations in the pattern of climate during this study period. Because of the polyphagous feeding habit, aphids are serious pest of almost all floral farms (Minks and Harrewijn, 1987). They feed upon almost all parts of the plant like leaves, shoot, fruit, flower, bud and even roots (Blackman and Eastop, 2000). Thus they cause severe damage to the commercial flowering plants as well as other host plants.

About 6 different types of flowering plant species were recorded with high infestation of aphids and it was observed that *Aphis gossypii* became the most common aphid species attacking almost all flowering plants species in this survey. It was also observed that the winter season is favorable for the growth of aphids as the population of aphids is recorded maximum in the month of November of the investigation period.

Several vegetable farms producing vegetables like cauliflower, brinjal, lady's finger, tomato, cabbage, green peas, etc are found damaged by different species of aphids. The severe infestation by *A. gossypii* and *Microsiphoniellasanborni* is recorded in Chrysanths farm while the cash crop like soya bean was shoddily destroyed by *A. glycines*.

### Conclusion

For prevention of such crop pest, farmers are applying different insecticides. Due to the excessive application of such insecticides, the quality of flower crop, vegetables or fruits gets deficiently affected with some other problems like insecticidal residues in water, soil, destruction of natural enemies of these pests as well as disturbance in ecosystem of that location (Palikhe, 2002).

Hence the proper management of aphids through biological agent is required. There should be an integrated pest management programme against aphids and other insect pests along with the applications of biodegradable pesticides so that the production of commercially important flowers, their quality and ecosystem of the floral farm can remain in good condition.

Thus the conducted survey provides the information about the polyphagous aphid species, period of their infestation on flowering host plants. By using this information, the changing pattern of cultivation of such plants can control the infestation of aphids at certain level which will result in proper production of flowers having good market value and the farmers can yield considerable production of their flower crops.

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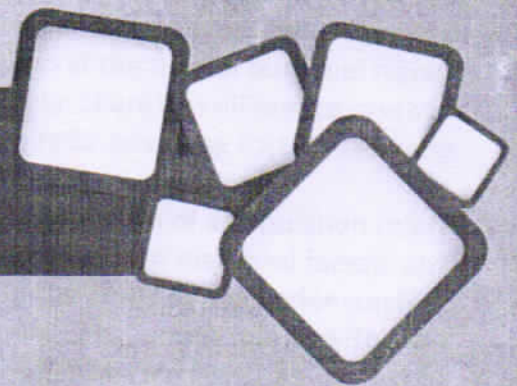
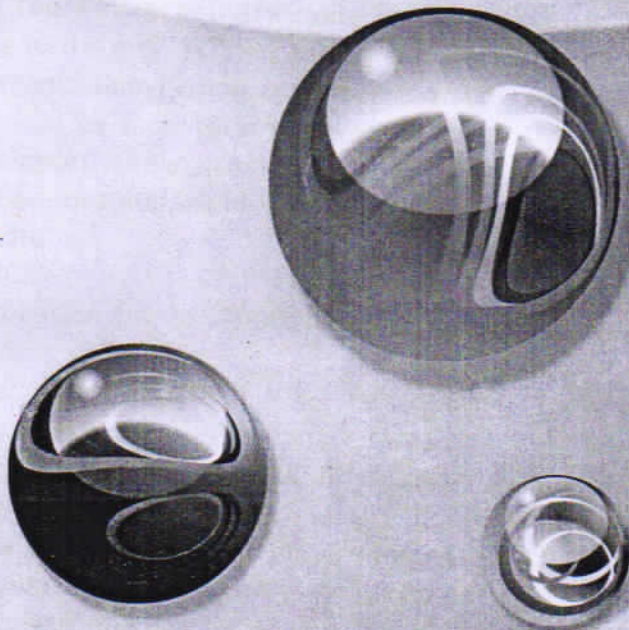


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# rinting Area



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**CONCLUSION**

TQM is managing the concept of quality with the objective to meet and exceed the customer's expectation by developing leadership-driven forces for providing a product or service with built-in quality. The total quality should aim at the needs of the library users of present and future. The main requirements may include availability, delivery reliability, maintainability and cost effectiveness, among many other features. Now-a-days the concept of quality has changed from the provider-oriented into customer oriented. Quality is the driving force of the entire activity cycle from the beginning to the end. TQM in any organization are the organizational vision, customer-focused, management by fact, total involvement and system support. The success of TQM in those organisation- hospital, Railways, education and Libraries etc.

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## A CHANGING PATTERN OF SEX RATIO STRUCTURE OF NASHIK DISTRICT 1951-2011

Dr. A. I. Khan

Asst. Professor of Geography  
Govt. College of Arts, Comm., Science,  
Aurangabad

RaviPrakash Thombre ✓

Research Students  
Govt. College of Arts, Comm., Science,  
Aurangabad

\*\*\*\*\*

**Abstract:**

Sex ratio is the basic tool for the analysis of the composition population. A part from its directly influence married person in a population and birth rate, it also determine the socio economic and political structure of the population.

A several geographer have been made his work on the sex ratio is as fallows Krishnan and Chandana (1973) explained sex ratio at district level in Haryana population observed the deficiency of female which was attribute to low sex ratio at the time of birth and higher rate of mortality. There was difference in urban and rural sex ratio according to state sex ratio is lower the nation.

Sex composition of a population refers to the balance between male and female any population. In the study of population any analysis of the sex ratio is important role play. The sex ratio of the India is calculated as the No of females per 1000 males. The present study is entirely based on secondary data.

favorable & in adverse condition becomes low.

In 1951 total sex ratio 941 per 1000 in rural areas these ratio are 1000 and the urban Area 807 per 1000. In 1961 total sex ratio 936 per 1000 in rural areas these ratio are 995 and the urban Area 801 per 1000. In 1971 total sex ratio 936 per 1000 in rural areas these ratio are 995 and the urban Area 820 per 1000. In 1981 total sex ratio 930 per 1000 in rural areas these ratio are 985. In 1991 total sex ratio 937 per 1000 in rural areas these ratio are 985 and the urban Area 850 per 1000. In 2001 total sex ratio 934 per 1000 in rural areas these ratio are 985 and the urban Area 875 per 1000. In 2011 total sex ratio 925 per 1000 in rural areas these ratio are 948 and the urban Area 899 per 1000.

#### Conclusion:

- 1) The above analysis reveals rapid decrease in general sex ratio from 1981 to 2011 in the study region. As per 1951 low sex ratio in region in 2011 also sex ratio in region
- 2) Agriculturally developed, irrigated industrially developed economically developed, having high per capita income and relatively more availability of health facilities such region rapid declining sex ratio in the study region.

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## Eco-consciousness Through Symbolism in Salman Rushdie's "Haroun & the Sea of Stories"

Vihire Swati Ravindra

Asst. Professor.

S.P.D.M.College Shirpur Dist Dhule

\*\*\*\*\*

"Haroun and Sea of Stories" is basically a child book containing fairytale like structure. Salman Rushdie wrote this book for his son Zafar. The story rotates round a small boy Haroun and his father Rashid, a story teller and their adventures. As usual Rushdie has blended comic, real life and fantasy together.

The Eco criticism was propounded in 1980s as the need of time. The environmental problems have become more serious than nuclear fallout. Salman Rushdie believes that human being does not exist without environment. In the present novel he has tried to attract the attention of the readers towards this serious problem through symbolism.

In the novel 'Sea of Stories' is the supplier of all stories which is located on an imaginary moon 'Kahani'. We find allegorical references in the description of the city Alifbay.

"There was once, in the country of Alifbay, a sad city, the saddest cities, a city so ruinously sad that it had forgotten its name. it stood by a mournful sea full of glum fish which were so miserable to eat that they made people belch with melancholy — It was city full of mighty factories in which sadness was actually manufactured, packaged and sent all over the worlds which never seemed to get enough of

**Key word:** Sex ratio, Sex composition, changes in sex ratio.

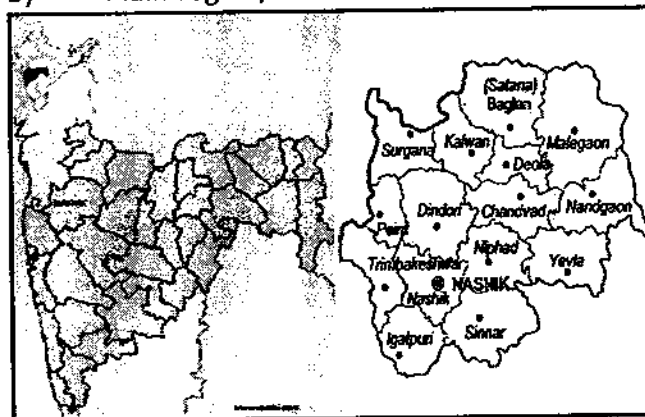
**Introduction:**

Geography deals with wide area of study. Geography had since long been considered as an Earth science where the study of earth received gather attention than it's in habitants. But the Geographers to attention the study of environments to man. Vidal-da-Blash was significance in giving anthropology orientation to geography. This study also includes study of sex ratio changing pattern of the study area.

**The Study Region:**

India is second populous century in the world and has crossed one billion figure. Maharashtra is the second populas state if India, which forms about 10% of India's population. The Topographical the district can be divided in to three parts i. esahyadre ranges the plateau region and one mainbasin. The study region covers an area about 17,417.

- 1) Hilly region
- 2) Plateau region
- 3) Plain region/River basin



**Objectives:**

- 1) To study the distributional pattern fgeneral sex ratio in the study region.
- 2) To find out the changes in general sex ratio the study region

**Hypotheses of the study**

- 1) There is a positive improvement in each of the selected characteristic occurring from 1951-2011.
- 2) There is a negative correlation between population

growth rate & improvement of the above selected population characteristics.

**Methodology:**

- i) Random sampling method
- ii) Census of India, district census & handbook.
- iii) Demographic survey and NFHS2.

**SEX RATIO**

Total Female population

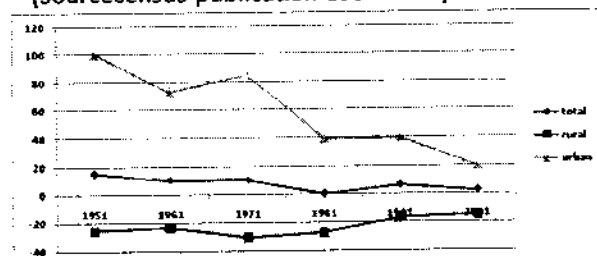
i) Sex Ratio (Total) =  $\frac{\text{Total Female population}}{\text{Total Male population}} \times 100$

ii) Rural sex ratio      iii) Urban sex ratio

Census related sex ratio scale Nasik district  
1951-2011

Years	State			District			Sex ration Difference		
	Total	Rural	Urban	Total	Rural	Urban	Total	Rural	Urban
1951	941	1000	807	956	974	907	15	-26	100
1961	936	995	801	946	971	874	1	-24	073
1971	930	985	820	940	964	905	10	-31	085
1981	937	987	850	937	959	889	00	-28	089
1991	934	972	875	940	955	915	06	-17	040
2001	922	960	873	924	945	893	02	-15	020
2011	925	948	899	931	942	916	06	-06	017

(Source census publication 1951-2011) Chart No 1



**Subject Analysis:**

In Nasik district the population sex ratio is finding in low medium and maximum range population change sex ratio according to geographical & human elements become

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and  
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# *In-vitro* culture of an endemic and endangered medicinal succulent plant species *Caralluma fimbriata* wall

B K Auti<sup>1\*</sup>, K M Nitnaware<sup>2</sup>

<sup>1,2</sup>Department of Botany, Radhabai Kale Mahila Mahavidyalaya, Ahmednagar, Maharashtra, INDIA.  
Email: autibhausah@yahoo.com

## Abstract

*Caralluma fimbriata* Wall (family Asclepiadaceae) is an endangered and medicinal small erect fleshy herb endemic to India. It is devoid of leaves and the stems are edible and forms a part of the traditional medicine system. The plant is commonly used in treatment of rheumatism, diabetes, leprosy, antipyretic and anthelmintic, tumor, fungal diseases, snake-scorpion bite, appetite and also antinociceptive activity. It is source of many pregnane glycosides which used as appetite suppressant. Therefore, the species are of great interest and are under risk due to excessive and indiscriminate collection and due to loss of its habitat. Therefore, extensive in-situ as well as ex-situ conservation is needed for restoration and exploitation. In the present investigation, attempts were made for induction of callus in *Caralluma fimbriata* Wall.

**Keywords:** In-vitro culture, medicinal plant, *Caralluma fimbriata* Wall.

## \*Address for Correspondence:

Dr. B K Auti, Department of Botany, Radhabai Kale Mahila Mahavidyalaya, Ahmednagar, Maharashtra, INDIA.  
Received Date: 10/01/2016 Revised Date: 07/02/2016 Accepted Date: 14/03/2016  
Email: autibhausah@yahoo.com

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## INTRODUCTION

*Caralluma fimbriata* Wall (Asclepiadaceae) is a small erect fleshy plant endemic to India (Jagtap and Singh, 1999). The four grooved round shaped stems devoid of leaves are edible and forms a part of the traditional medicine system of the country (Al-Yaha *et al.*, 2000). The plant is commonly used in treatment of rheumatism, diabetes, leprosy, antipyretic and anthelmintic, tumor, fungal diseases, snake-scorpion bite, appetite and also antinociceptive activity (Tatiya, *et al.*, 2010; Saivasanthi, *et al.*, 2011). It is source of many pregnane glycosides which used as appetite suppressant. Therefore, the species are of great interest and are under risk due to excessive and indiscriminate collection and due to loss of its habitat. Seed setting and development of new plants is

poor may be due to reciprocal pollination and availability of limited number of plants. Now it is endangered medicinal plant of India (Ugraiyah *et al.*, 2011). Therefore, extensive *in situ* as well as *ex situ* conservation is needed for restoration and exploitation. In the present investigation, in preliminary experiments attempts were made for induction of callus in *Caralluma fimbriata*: an endemic and endangered species.

## MATERIALS AND METHODS

Plant material of *Caralluma fimbriata* Wall. were collected from Narayangaon, Punewadi, Jangaon and Goregaon sites belonging to district Ahmednagar (M. S. ) and planted in earthen pots and maintained in botanic garden of the college. The stem explants were excised from maintained plants. The explants were surface sterilized by using 0.1 % HgCl<sub>2</sub> (W/V) for 5 minutes and then washed with SDW for 5 times. The explants were maintained on MS medium with auxins (2, 4-D, IAA and NAA) and cytokinins (BA, Kin., and BA) alone and in combination. The cultures were maintained at temperature: 25±0.5°C with photoperiod: 8 hrs light (30 μmole m<sup>-2</sup> s<sup>-1</sup>). For present investigation experimental design followed was CRD with replications-minimum 15 and experiments were repeated at least thrice. It was supported by statistical analysis. The data obtained were analyzed by analysis of variance (ANOVA) and DMRT.

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Original Article

# In-vitro culture of an endemic and endangered medicinal succulent plant species *Caralluma fimbriata* wall

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Email: [autibhausahb@yahoo.com](mailto:autibhausahb@yahoo.com)

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**Keywords:** In-vitro culture, medicinal plant, *Caralluma fimbriata* Wall.

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poor may be due to reciprocal pollination and availability of limited number of plants. Now it is endangered medicinal plant of India (Ugraiyah *et al.*, 2011). Therefore, extensive *in situ* as well as *ex situ* conservation is needed for restoration and exploitation. In the present investigation, in preliminary experiments attempts were made for induction of callus in *Caralluma fimbriata*: an endemic and endangered species.

### MATERIALS AND METHODS

Plant material of *Caralluma fimbriata* Wall. were collected from Narayangaon, Punewadi, Jamgaon and Goregaon sites belonging to district Ahmednagar (M. S. ) and planted in earthen pots and maintained in botanic garden of the college. The stem explants were excised from maintained plants. The explants were surface sterilized by using 0.1 % HgCl<sub>2</sub> (W/V) for 5 minutes and then washed with SDW for 5 times. The explants were maintained on MS medium with auxins (2, 4-D, IAA and NAA) and cytokinins (BA, Kin., and BA) alone and in combination. The cultures were maintained at temperature: 25±0.5°C with photoperiod: 8 hrs light (30 µmolem<sup>-2</sup>S<sup>-1</sup>). For present investigation experimental design followed was CRD with replications-minimum 15 and experiments were repeated at least thrice. It was supported by statistical analysis. The data obtained were analyzed by analysis of variance (ANOVA) and DMRT

### INTRODUCTION

*Caralluma fimbriata* Wall (Asclepiadaceae) is a small erect fleshy plant endemic to India (Jagtap and Singh, 1999). The four grooved round shaped stems devoid of leaves are edible and forms a part of the traditional medicine system of the country (Al-Yaha *et al.*, 2000). The plant is commonly used in treatment of rheumatism, diabetes, leprosy, antipyretic and anthelmintic, tumor, fungal diseases, snake-scorpion bite, appetite and also antinociceptive activity (Tatiya, *et al.*, 2010; Saivasanthi, *et al.*, 2011). It is source of many pregnane glycosides which used as appetite suppressant. Therefore, the species are of great interest and are under risk due to excessive and indiscriminate collection and due to loss of its habitat. Seed setting and development of new plants is



## HISTOCHEMICAL STUDIES ON ONTOGENY OF ANther WITH SPECIAL REFERENCE TO TOTAL PROTEINS IN *CLITORIA TERNATEA* LINN.

**B. K. AUTI**

Department of Botany,  
Radhabai Kale Mahila Mahavidyalaya,  
AHMEDNAGAR. (M. S.)  
Email: autibhausheb@yahoo.com

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### ABSTRACT

The present histochemical studies were carried out to know the ontogeny of anther with special reference to total proteins, in *Clitoria ternatea* Linn. The anthers were bicelled and tetrasporangiate following dicotyledonous type of development. The wall layers comprised an epidermis, an endothecium, middle layers and a secretary tapetum. The microspore tetrads were tetrahedral and pollen grains were triporate. Realizing the importance, the species was undertaken for histochemical studies with reference to total proteins during ontogeny of the anther and anthesis in *C. ternatea* Linn.

Figures : 08

References : 11

Table : 00

KEY WORDS : Anthers, *Clitoria ternatea* Linn., Histochemistry, Total proteins.

### Introduction

*Clitoria ternatea* Linn. belongs to family Fabaceae (Leguminosae). It is one of the ornamental climber plants, cultivated in India and Northern Australia due to having forage and some medicinal values. It could replace *Medicago sativa*<sup>2</sup>. Realizing importance, the study was undertaken for histochemical studies with special reference to total proteins during ontogeny of the anther and anthesis in *Clitoria ternate*. The growth and differentiation are vital processes in the development of plant organism. It starts from the embryonic apices. It involves both vegetative and reproductive growth phases in the plant organization. The flower, an organ of reproduction, shows many functions during its development, ultimately to produce renewed individuals with good heredity changes for survival. Each organism has its own characteristic in sexual reproduction being marked by variations within a series of different co-ordinated steps, such as, differentiation of sporogenous cells, meiosis, cell isolation and insulation by a callose wall, attraction and

recognition, cell fusion and the resting period. The origin of the anther and ovules from the reproductive shoot is basically comparable and similar, especially in their functions. Both micro- and megagametophytes determine very specific individuality of the sexual reproduction of each distinct species.

The entire plant organism is diploid and heterogeneous. Plant organs made up of tissues which are histologically different, showing cytological diversities. Anatomical and cytological diversities reflect biochemical and physiological variations. Morphological differentiations of plant organs are equally dependent on growth, differentiation, regeneration and biochemical correlation. Histochemical techniques locate the site of a particular reaction, thereby indicating change in the metabolism at a cellular level. It helps to understand the histochemical composition of the tissues concerned, their origin and differentiation<sup>4</sup>.

Histochemical methods enable identification and localization of biochemical metabolites specific for the nature of cell wall,

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cytoplasm and nucleus, within the cells and tissues.

Biochemical constitution of a tissue in any heterogeneous structure can be assessed by standard histochemical methods. Histochemical methods applied on the tissue sections of fixed as well as fresh material alone reveal not only the biochemical content of each tissue, but also the physiological basis of their differentiation too.

Microsporogenesis is a serial but complex, ontogenetic process involves differentiation of archesporium and successive delimitation of different tissues from its specific to their functional areas, culminating in formation of the pollens, from pollen mother cells, after meiosis. The anther tissues are epidermis, endothecium, middle wall layers, tapetum and sporogenous tissue are quite different in their composition during growth and differentiation.

The main aim behind the present study on *Clitoria tematea*, was to know the developmental organization of an anther and the functional role of their different tissues; and to explain the changes in the concentration of some metabolic macromolecular substances particularly total proteins during the successive growth and differentiation of anther using standard histochemical techniques under the light microscope.

### Materials and Methods

The different developmental stages of flower buds and opened flowers of *Clitoria tematea*, were collected and were fixed in Carnoy's fluid for 12 hrs. These collected floral buds were dehydrated, infiltrated and embedded in paraffin wax (52 to 54°C temp.). Then 8µm thick sections of floral buds and anthers from processed opened flowers were cut with rotary microtome and processed for the staining. The localization of total proteins was done by using mercuric bromophenol blue dye<sup>4,6</sup>. The results were recorded for development of anthers and localization of total proteins in the form of microphotographs. The total proteins stain blue or deep blue with stain and are expressed as rich or feeble or low to denote visual intensities of stain in the observations.

### Observations

**Epidermis:** In the young anther, epidermis is rich in total proteins, both cytoplasm and nucleoli

react strongly (Fig. 1). But as it matures the protein content declines (Figs. 4-6) and remains low until the layer degenerates (Figs. 7-8).

**Endothecium:** During early stages of anther development, endothecium is rich in total proteins similar to epidermis. During further growth as it loses RNA content it shows low quantity of proteins (Fig. 6). The fibrous thickenings are not uniform but it develops more fibrous thickenings towards connective. The endothelial thickenings at pollen stage show feeble response to protein test (Fig. 8).

**Middle wall layers:** It shows positive protein test when young, while during its growth proteins are much reduced in cytoplasm from sporogenous tissue to microspore stage but the nuclear proteins remain rich in them (Fig. 3, 5). At maturity the nuclear proteins reduce to low level (Fig. 6).

**Tapetum:** At the beginning the tapetum shows low protein content than the central sporogenous tissue (Fig. 1). The tissue when it is young not much vacuolated, but subsequently an increase in vacuolation is observed in it (Figs. 3,5,6). The tapetal cells towards the connective are more vacuolated than the cells present at parietal side and their size is also large. The quantity of protein increases as the sporogenous tissue prepares itself for meiosis and persists during the entire period of meiosis, but a pollen mother cell stage it declines. The cells at maturity become disorganized and appear separated, show decline in protein content (Fig. 6). Parallel increase in vacuolation is also noticed. At microspore stage tapetum starts degenerating and its content falls and finally lost completely (Fig. 7).

**Sporogenous tissue:** It shows insignificant rich protein stainability. The nuclear proteins are always higher than that of the cytoplasm (Figs. 3, 5). During formation of pollen mother cells, however the concentration of proteins lowers down (Fig. 6).

**Pollen grains:** The cytoplasm of the released microspores shows gradual increase in the protein contents, indicated by dark stainability. Additionally deposited layer around the tetrad shows fair staining with protein test. Protein content in tetrad also declines (lowers) but it increases in the mature pollen grain (Fig. 7). The anthesis i. e. pollen grain dehisces at 2-celled stage. The exine shows a protein reaction while intine gives rich deep blue colour, indicating accumulation of rich protein (Fig. 8).

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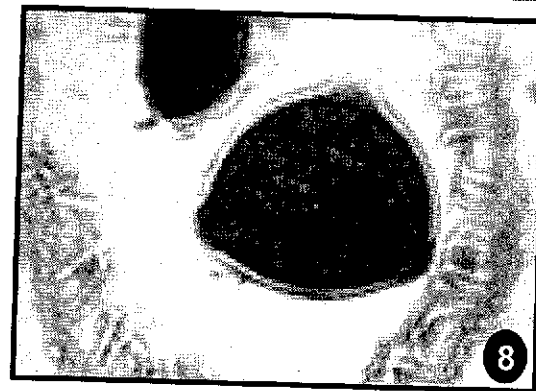
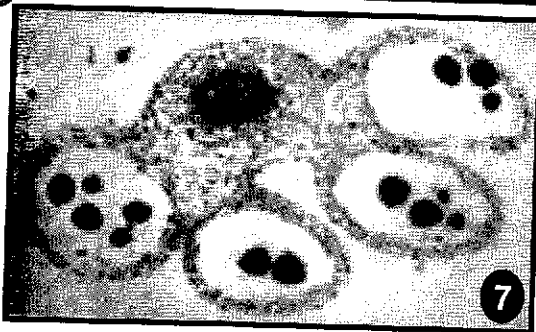
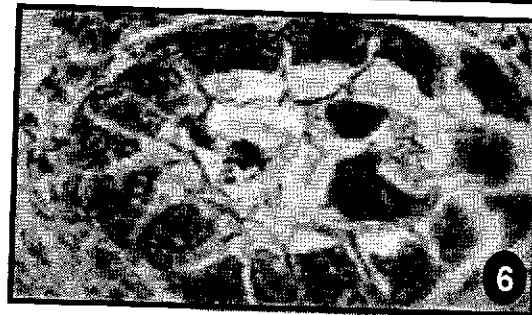
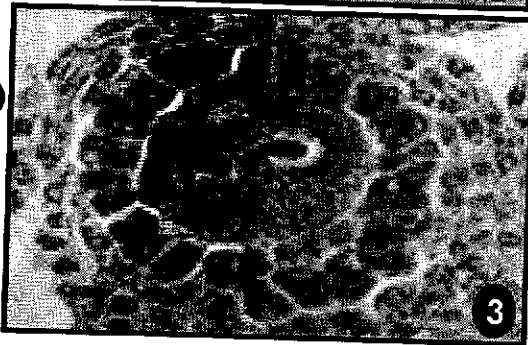
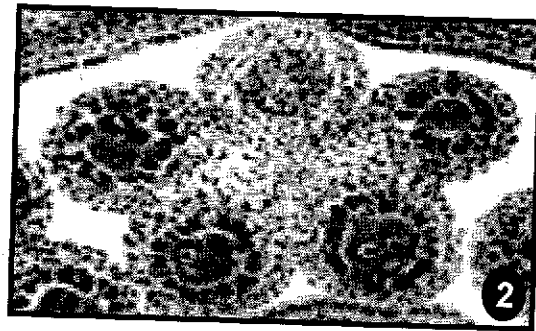
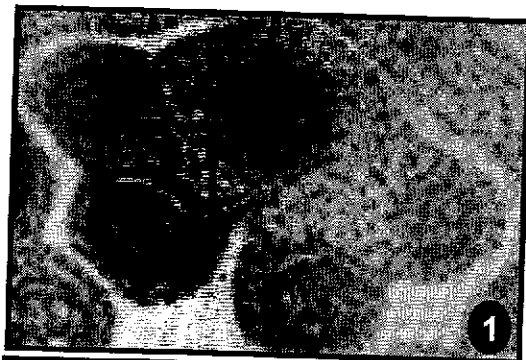


Plate I. Transverse sections to know anther development in *Clitoria ternatea* Linn. for localization of total proteins showing epidermis, endothecium, middle layers, tapetum, sporogenous tissue and pollen grains having variations in blue colour as deep or feeble. (Original figures: 1, 4, 7 x84; 2, 5 x87 & 3, 6, 8 x300).

## Results and Discussion

Histochemical assessment using light microscope is of specific advantage, in getting large quantity of data regarding biochemical basis of tissue and organ differentiation such as anther. The cell or the tissue differentiation in them depends on the synthesis and concentration of various biochemical metabolites. Histochemical studies have revealed that major biochemical substances like carbohydrates, proteins, lipids, enzymes, nucleic acids *etc.* play an important role in the development and differentiation of various structures in the anther<sup>1,3-5,7-11</sup>. Protein content is high in young anther epidermis but as it matures the protein content declines, which coincides with relative rise in protein content in endothelial layer. The two middle wall layers show identity with endothecium in its content in early stages. Degeneration of wall layers relate with rise in metabolic content in tapetum. The tapetum is single

layered, secretory and nutritive in nature. The tapetum, until meiosis is completed, stores very high protein content, both in the cytoplasm and nuclei. The tapetum being highly vesiculated and in all probability it functions as a storage tissue in the anther. During meiosis and separation of microspores, increase in proteins is very unique. The mature pollen grain exhibit rich protein content. In the sporogenous tissue, pollen mother cells and microspore tetrads, the total protein content is high. This might be the prerequisite for pollen tube growth. The interaction and probable role of the protein content in the anther tissues is discussed by making use of relevant previous data.

The present study dealt with growth differentiation and role of total proteins during ontogeny of anther in *C. tematea* L. An increase and decrease in concentrations of the total proteins depend on the activity of the tissues involved during pollen grain formation.

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## STUDIES ON ANTAGONISTIC ACTINOMYCETES FROM CASUARINA EQUISELIFOLIA L.

**Sangita Kulkarni\* & Abhijit Kulkarni**

\*Radhabai Kale Mahila Mahavidyalaya, Ahmednagar (MS)  
 sangitakulkarni69@gmail.com

Department of Botany, Ahmednagar College, Ahmednagar (MS)  
 abhjitkulkar@gmail.com

### Abstract:

The Rhizosphere soils are rich in microflora. A number of Actinomycetes were found associated with rhizosphere soils of *Casuarina* plants. A total of 20 different actinomycetes were isolated from the rhizosphere soil of *Casuarina equisetifolia* L. from different localities of Maharashtra. These included 14 species of *Streptomyces*, four species of *Streptovorticillium* and two unidentified Actinomycetes species. The Actinomycetes are rich source of antibiotics. The isolates were tested for their antagonistic properties against phyto-pathogenic and human pathogenic bacteria and fungi.

*Streptomyces chattaohogensis* & *Streptomyces violaceochromogenes* inhibited the growth of *Bacillus subtilis* while *Streptomyces violaceochromogenes*, *Streptovorticillium fervens* and Actinomycete (1) were antagonistic to all phyto-pathogenic fungi. These experiments clearly indicated that actinomycetes isolated from rhizosphere of *Casuarina equisetifolia* L. show antagonism against the soil pathogens

**Keywords:** Actinomycetes, *Streptomyces*, Antagonism.

### Introduction

The Rhizosphere soils are near to the plant roots and is rich in microflora. The Actinomycetes are one of group of microorganisms that are beneficial in nature and source of many antibiotics which are active against pathogenic organisms (Abhijit kulkarni, 2010). The antibiotic compounds are useful as human & veterinary medicine, in agriculture & biochemistry. It is a transitional group between simple bacteria & Fungi. They are gram positive & are classified under the order Actinomycetales (Bergy's Manual, 1989). Most of Microbial equilibrium is always maintained by the activity of these organisms.

The main economical role of Actinomycetes is as a decomposer of organic matter, help in carrying out many biochemical reactions in soil & increase the soil fertility. Numerically though they are less dominant than fungi but are potentially more active. They provide a granular & viable structure to soil for crop production. The various antibiotics produced by Actinomycetes selectively antagonise other soil microorganisms and help in maintaining microbial equilibrium (Williams, 1978). Genus *Frankia* grow in nodules of non leguminous trees and fix atmospheric nitrogen (Halbe & Nair, 2002).

Vegetative hyphae produce an extensively branched mycelium that rarely fragments. The aerial mycelium at maturity forms 3 to many spores. Initially colonies are relatively smooth surfaced but later they develop a web of aerial mycelium that may appear

granular, powdery or velvety. They produce wide range of pigments responsible for colour of vegetative & aerial mycelium. They may form colour diffusible pigments in the medium also (Kutzner 1981). Many actinomycetes use wide range of organic compound as a sole source of carbon for energy and growth at optimum temp 25-35°C, optimum pH range for growth at 6.5 - 8.0 (Pridham, 1974). The cell wall of Actinomycetes contain LL-diaminopimelic acid and DL-DAP (Lechevalier & Lechevalier; 1967).

### Materials and Methods

For selective isolation of Actinomycetes, treatment of soil was essential. Therefore, 1 gm of soil was thoroughly dried at room temperature and mixed with 0.1 gm of calcium carbonate. It was incubated for 7 days at 26°C in water saturated environment. This treated soil was used for dilutions in phenol water solution (phenol: water 1:40). 0.1 ml of each dilution was used for each plate. The plates were incubated for 4-5 days.

Different media like starch-casein Agar, Inorganic salt starch Agar, MGA - SE Agar medium were used for isolation of actinomycetes and the Starch - Casein Agar and MGA-SE agar gave good results. After three days of incubation, actinomycete colonies started appearing on the medium. They were counted from the 5<sup>th</sup> day till 10 days. The colour and number of colonies were recorded.

Actinomycetes were identified upto the generic level with the help of slide & coverslip cultures ( Walksman, 1961 ; Buchnar & Gibson,

# SYNTHESIS AND ANTIMICROBIAL EVALUATION OF NOVEL PYRIDINE ANCHORED THIAZOLYL 1,3,4-THIADIAZOLES AND 1,2,4-TRIAZOLES

H.N. Akolkar, N.R. Darekar, S.G. Kundlikar and B.K. Karale\*

P.G. Department of Chemistry, Radhabai Kale Mahilā Mahavidyalaya, Ahmednagar-414001  
E-mail : bkkarale@yahoo.com

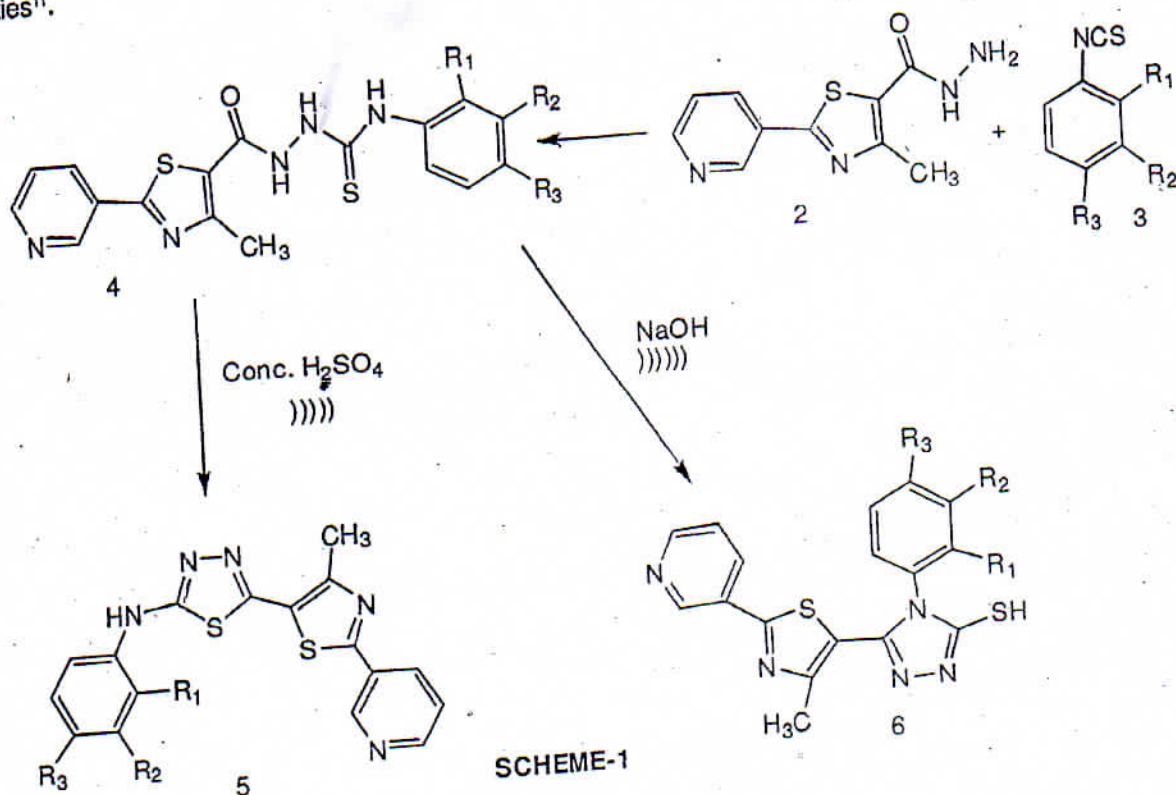
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A new series of novel pyridine anchored thiazolyl 1,3,4-thiadiazoles and 1,2,4-triazoles have been synthesized by conventional and ultrasonication method. The synthesized compounds were characterized with the help of spectral techniques and screened for antimicrobial activities.

Pyridine is six membered nitrogen containing heterocyclic compound, attracted strong interest among the researchers in the field of medicinal research due to important pharmacological activities. Pyridine and their derivatives are associated with phosphodiesterase-3 inhibitors<sup>1</sup>, COX-2 inhibitors<sup>2</sup>, antiosteoporotic<sup>3</sup>, anticonvulsant<sup>4</sup>, antifungal<sup>5</sup>, non peptidic angiotensin II receptor antagonists activities<sup>6</sup>. Thiazole containing compounds are associated with MRSA PK inhibitor<sup>7</sup>, antitumor<sup>8</sup>, antiinflammatory<sup>9</sup>, herbicidal<sup>10</sup>, antifungal<sup>11</sup> and plant growth regularoty activities<sup>11</sup>.

Thiosemicarbazide and their derivatives attract researchers due to their various biological activities. Thiosemicarbazide derivatives are associated with IDO inhibition properties<sup>12</sup>, antifungal<sup>13</sup>, antioxidant<sup>13</sup>, antimalarial<sup>14</sup>, antitrypanosomal<sup>15</sup> activities. 1,3,4-Thiadiazole scaffold possess various pharmacological activities such as antiinflammatory<sup>16</sup>, anticonvulsant<sup>17</sup>, insecticidal<sup>18</sup>, anticancer<sup>19</sup>, antimicrobial<sup>20</sup>. 1,2,4-Triazole nucleus exhibits antimicrobial<sup>20</sup>, antitubercular<sup>21</sup> and antiinflammatory<sup>21</sup>, activities.

Bearing this in mind, some novel 1,3,4-thiadiazole and 1,2,4-triazole compounds containing thiazole and



SCHEME-1

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H.N. Akolkar, N.R. Darekar, S.G. Kundlikar and **B.K. Karale\***

P.G. Department of Chemistry, Radhabai Kale Mahilā Mahavidyalaya, Ahmednagar-414001  
E-mail : bkkarale@yahoo.com

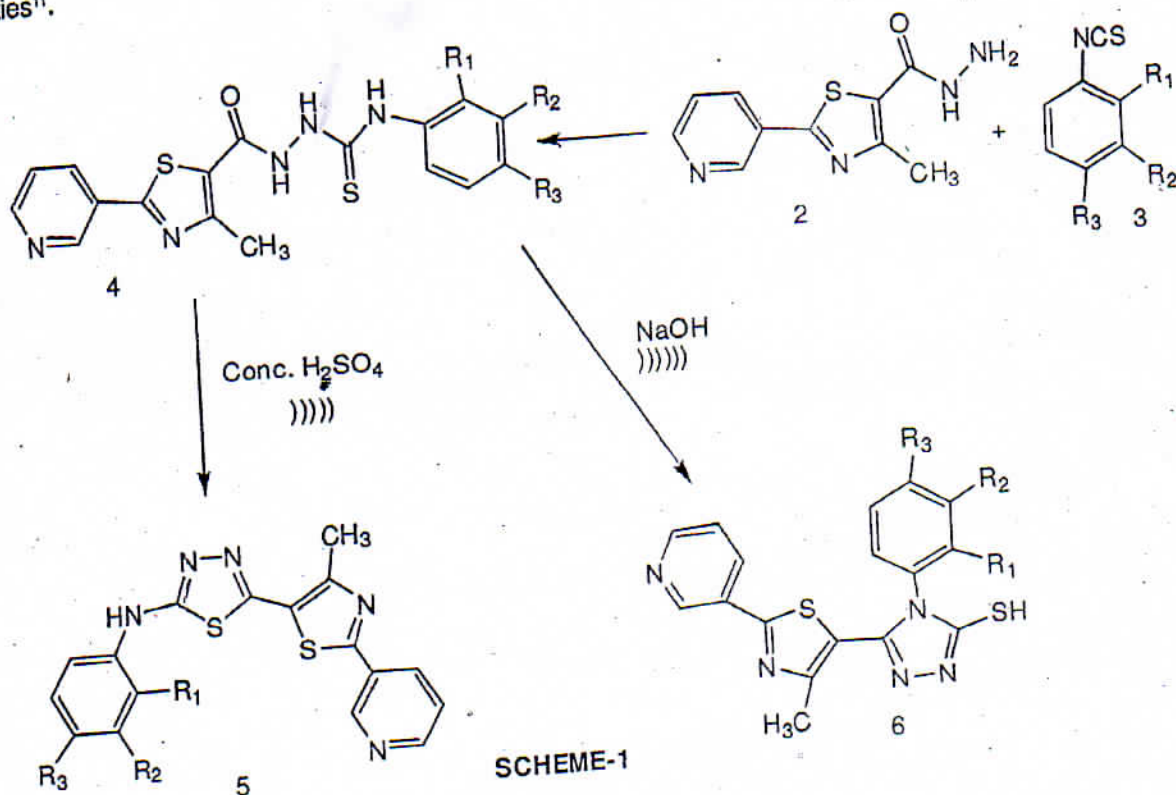
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H.N. Akolkar, N.R. Darekar, S.G. Kundlikar and B.K. Karale\*

P.G. Department of Chemistry, Radhabai Kale Mahilā Mahavidyalaya, Ahmednagar-414001  
E-mail: bkkarale@yahoo.com

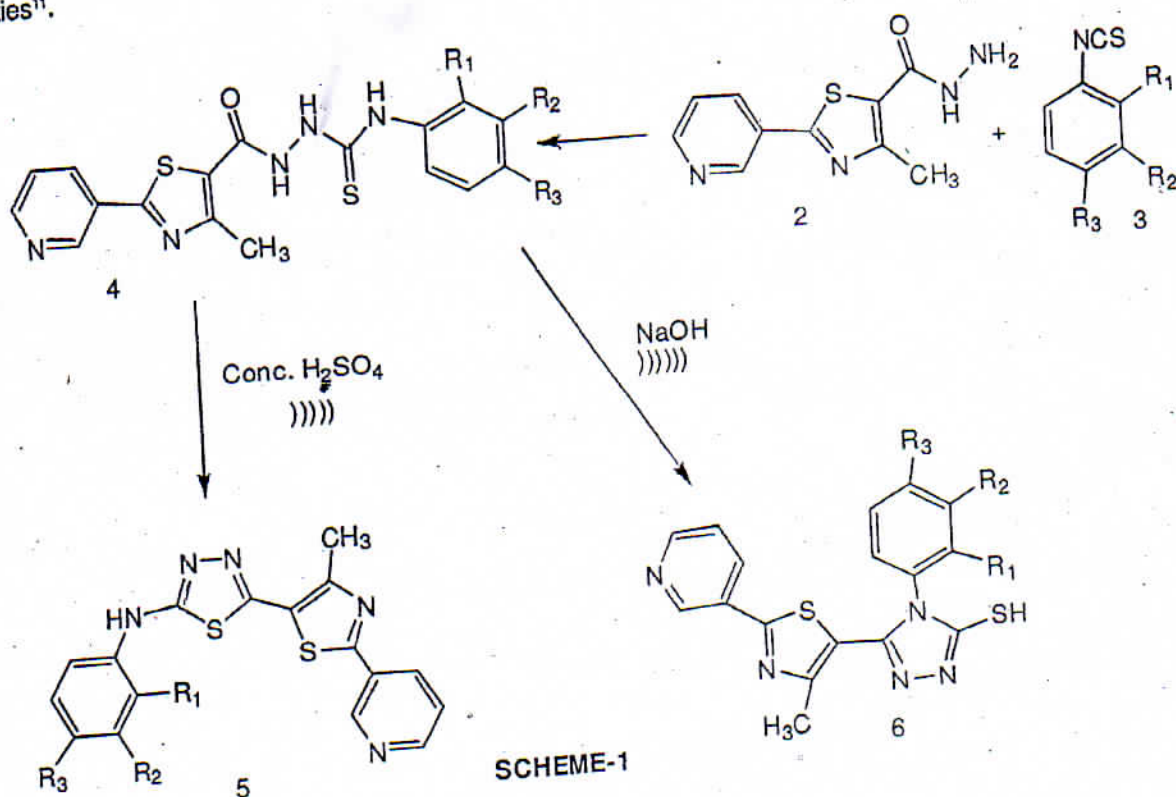
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## SYNTHESIS OF NOVEL FLUORINE AND PYRIDINE CONTAINING THIAZOLYL 1,3,4-OXADIAZOLE DERIVATIVES

H.N. Akolkar, K.K. Deshmukh, S.D. Mhaske and B.K. Karale\*

P.G. Department of Chemistry, Radhabai Kale Mahila Mahavidyalaya, Ahmednagar-414001  
E-mail: bkkarale@yahoo.com

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2-(4-Fluorophenyl)-4-methylthiazole-5-carbohydrazide and 4-methyl-2-(pyridine-3-yl) thiazole-5-carbohydrazide **1** on reaction with different aldehydes **2** gave hydrazones **3**. Hydrazones **3** on reaction with propionic anhydride gave fluorine and pyridine containing thiazolyl 1,3,4-oxadiazole derivatives **4**. The structures of synthesized compounds were confirmed by spectral analysis.

Oxadiazole, thiazole and pyridine are the most important heterocyclic compounds having diverse pharmacological activities. 1,3,4-Oxadiazole containing compounds possess various biological activities such as tyrosinase inhibitors<sup>1</sup>, antiinflammatory<sup>2</sup>, analgesic<sup>2</sup>, anticonvulsant<sup>3</sup>, antiproliferative<sup>4</sup> and antitubercular<sup>5</sup> activities.

Thiazole and their derivatives possess antiprotozoal<sup>6</sup>, antioxidant<sup>7</sup>, antiinflammatory<sup>8</sup>, antimicrobial<sup>9</sup>, cyclooxygenase-2 inhibitor<sup>9</sup> and antitumor<sup>10</sup> activities. Pyridine containing compounds were found to be associated with various pharmacological activities such as anticancer<sup>11</sup>, antichagasic<sup>12</sup>, antidiabetic<sup>13</sup> and COX-2 inhibitors<sup>14</sup> activities.

Substituted acyl hydrazones show a variety of biological activity, such as antimalarial<sup>15</sup>, vasodilatory<sup>16</sup>, anticonvulsant<sup>17</sup>, antitubercular<sup>18</sup>, antiinflammatory and analgesic<sup>19</sup> activities.

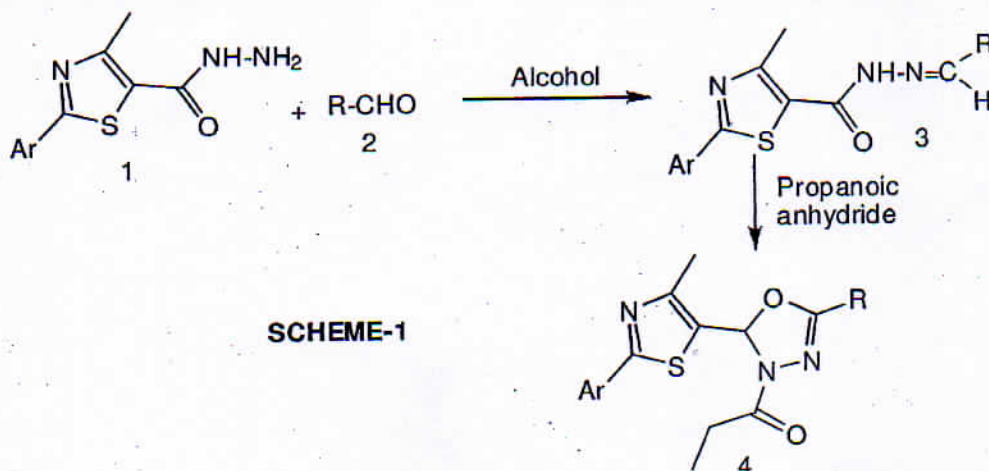
The activities associated with these various heterocycles prompted us to synthesize some novel fluorine and pyridine anchored thiazolyl 1,3,4-oxadiazole derivatives.

### Experimental

All the melting points were recorded in DBK prog. Melting point apparatus and are uncorrected. IR spectra were recorded on Shimadzu FTIR spectrophotometer in KBr disc. <sup>1</sup>H NMR spectra were recorded on Bruker Avance II 400 MHz spectrometer in DMSO-*d*<sub>6</sub> as a solvent. Mass spectra were obtained by Finnigan mass spectrometer.

### Synthesis of acyl hydrazone **3** : General procedure

Acid hydrazide (0.001 mol) **1** and different aldehydes (0.001 mol) **2** were dissolved in alcohol and refluxed for 2 hr. After completion of the reaction, contents were concentrated and allow to cool at RT,





## SYNTHESIS OF NOVEL FLUORINE AND PYRIDINE CONTAINING THIAZOLYL 1,3,4-OXADIAZOLE DERIVATIVES

H.N. Akolkar, K.K. Deshmukh, S.D. Mhaske and **B.K. Karale\***

P.G. Department of Chemistry, Radhabai Kale Mahila Mahavidyalaya, Ahmednagar-414001  
E-mail: bkkarale@yahoo.com

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2-(4-Fluorophenyl)-4-methylthiazole-5-carbohydrazide and 4-methyl-2-(pyridine-3-yl) thiazole-5-carbohydrazide **1** on reaction with different aldehydes **2** gave hydrazones **3**. Hydrazones **3** on reaction with propionic anhydride gave fluorine and pyridine containing thiazolyl 1,3,4-oxadiazole derivatives **4**. The structures of synthesized compounds were confirmed by spectral analysis.

Oxadiazole, thiazole and pyridine are the most important heterocyclic compounds having diverse pharmacological activities. 1,3,4-Oxadiazole containing compounds possess various biological activities such as tyrosinase inhibitors<sup>1</sup>, antiinflammatory<sup>2</sup>, analgesic<sup>2</sup>, anticonvulsant<sup>3</sup>, antiproliferative<sup>4</sup> and antitubercular<sup>5</sup> activities.

Thiazole and their derivatives possess antiprotozoal<sup>6</sup>, antioxidant<sup>7</sup>, antiinflammatory<sup>8</sup>, antimicrobial<sup>8</sup>, cyclooxygenase-2 inhibitor<sup>9</sup> and antitumor<sup>10</sup> activities. Pyridine containing compounds were found to be associated with various pharmacological activities such as anticancer<sup>11</sup>, antichagasic<sup>12</sup>, antidiabetic<sup>13</sup> and COX-2 inhibitors<sup>14</sup> activities.

Substituted acyl hydrazones show a variety of biological activity, such as antimalarial<sup>15</sup>, vasodilatory<sup>16</sup>, anticonvulsant<sup>17</sup>, antitubercular<sup>18</sup>, antiinflammatory and analgesic<sup>19</sup> activities.

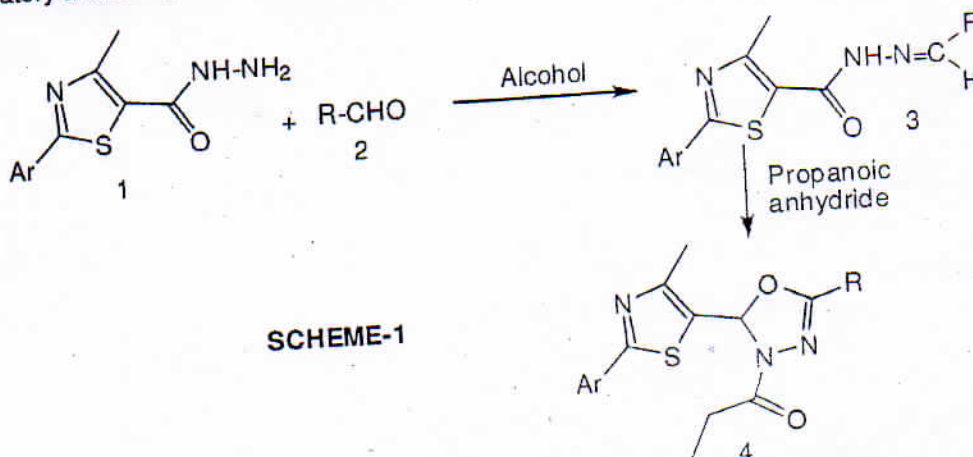
The activities associated with these various heterocycles prompted us to synthesize some novel fluorine and pyridine anchored thiazolyl 1,3,4-oxadiazole derivatives.

### Experimental

All the melting points were recorded in DBK prog. Melting point apparatus and are uncorrected. IR spectra were recorded on Shimadzu FTIR spectrophotometer in KBr disc. <sup>1</sup>H NMR spectra were recorded on Bruker Avance II 400 MHz spectrometer in DMSO-*d*<sub>6</sub> as a solvent. Mass spectra were obtained by Finnigan mass spectrometer.

### Synthesis of acyl hydrazone **3** : General procedure

Acid hydrazide (0.001 mol) **1** and different aldehydes (0.001 mol) **2** were dissolved in alcohol and refluxed for 2 hr. After completion of the reaction, contents were concentrated and allow to cool at RT,



## Synthesis and biological screening of some novel thiazolyl chromones and pyrazoles

B K Karale<sup>a\*</sup>, S J Takate<sup>b</sup>, S P Salve<sup>b</sup>, B H Zaware<sup>b</sup> & S S Jadhav<sup>b</sup>

<sup>a</sup>Department of Chemistry, Radhabai Kale Mahila Mahavidyalya (University of Pune), Ahmednagar 414 001, India

<sup>b</sup>Department of Chemistry, New Arts, Commerce and Science College (University of Pune), Ahmednagar 414 001, India  
E-mail: bkkarale@yahoo.com

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Esterification of acid **2** with 2-hydroxyacetophenones **1** yielded compounds **3** which have been converted to  $\beta$ -diketones **4** by Baker-Venkatraman transformation. A series of 2-substituted chromones **5** have been obtained by acid catalysed intramolecular cyclization of  $\beta$ -diketones. Substituted pyrazoles **6** have been obtained from chromones **5**. All the synthesized compounds have been confirmed by the spectroscopic techniques. Chromones and pyrazoles have been evaluated for their antibacterial and antifungal efficacy.

**Keywords:** Baker-Venkatraman transformation,  $\beta$ -diketones, chromones, pyrazoles

As a result of increased microbial infections, great attention has been directed in recent years towards the discovery and development of new antimicrobial drugs. The main problem in the treatment of microbial infections is the increasing prevalence of drug resistance. Therefore, the development of new and efficacious antimicrobial drugs is a very important goal and most of research efforts in this field are directed towards the design of new agents<sup>1,2</sup>.

Chromones constitute one of the major classes of naturally occurring compounds (Figure 1) and interest in their chemistry continues unabated because of their usefulness as biologically active agents. Some of the biological activities attributed to chromone derivatives include antibacterial<sup>3</sup>, anticholesterinic<sup>4</sup>, antidiabetic<sup>4</sup>, antifungal<sup>4,5</sup>, antiallergic<sup>6</sup>, anti-HIV<sup>7</sup> and anti-inflammatory<sup>8</sup>. Chromones possessing heterocyclic substituents at 2 and 3 positions possess coronary dialatory<sup>9</sup>, muscle relaxant property<sup>10</sup> and antimicrobial activities<sup>11</sup>.

Recently pyrazole containing compounds have attracted researchers because of their wide applications in the field of medicines. Pyrazoles exhibit anti-inflammatory<sup>12</sup>, bactericidal<sup>13</sup>, antitumor<sup>14</sup>, antiviral<sup>15</sup>, antitubercular<sup>16</sup> and antioxidant properties<sup>17</sup>. Celecoxib (Figure 2) is the first-to-market drug of a number of selective cyclo-oxygenase 2 (COX-2) inhibitors which are potent anti-inflammatory and analgesic agents without the undesirable side effects associated with other non-steroidal anti-inflammatory drugs<sup>18</sup>.

Molecules containing a thiazole moiety exhibit interesting biological activities. Many natural and

synthetic biologically active molecules containing thiazole moiety show anti-inflammatory<sup>19,20</sup>, anti-HIV<sup>21</sup>, antibacterial<sup>22</sup> and anticancer<sup>23</sup> properties.

Thiophene derivatives are reported to exhibit a broad range of biological activities including anticancer<sup>24</sup>, antituberculosis<sup>25</sup>, anticonvulsant<sup>26</sup>, antifungal<sup>27</sup>, anti-inflammatory<sup>28</sup> and analgesic<sup>29</sup> activities.

It was of value to combine chromone, pyrazole, thiazole and thiophene moieties in a series of derivatives with the objective of investigating their biological activities.

### Results and Discussion

For the synthesis of target molecules, a series of substituted 2-hydroxyacetophenones **1** and 4-methyl-2-(3-methylthiophene-2-yl)-1,3-thiazole-5-carboxylic acid **2** were used. Compounds **1a-f** and **2** were prepared by well known literature method as shown in Scheme I and II. Esterification of acid **2** with 2-hydroxyacetophenones **1a-f** yielded compounds **3a-f**.

$\beta$ -Diketones **4a-f** were obtained from **3a-f** by stirring in pyridine and KOH. 2-Heteryl chromones **5b-f** were synthesized by intramolecular cyclization of **4b-f** in presence of HCl. Compounds **5b-f** on refluxing with hydrazine hydrate resulted in pyrazoles **6b-f** (Scheme III). The physical characterization data of the synthesized compounds is given in Table I. The IR spectrum of **3f** showed 1724 and 1691 cm<sup>-1</sup> bands for conjugated ester and ketone carbonyl stretching frequencies. The <sup>1</sup>H NMR spectrum of **3f**

## MICROWAVE ASSISTED SYNTHESIS OF AZOLE DERIVATIVES

S. D. Mhaske<sup>1</sup>, S. B. Dare<sup>2</sup>, B. H. Zaware<sup>2</sup>, S. S. Jadhav<sup>2</sup>, B. K. Karale<sup>3</sup> and S. J. Takate<sup>1,2</sup>

<sup>1</sup>Department of Chemistry, Dada Patil Rajale Arts and Science College, Adinathnagar, 414506

<sup>2</sup>Department of Chemistry, New Arts, Commerce and Science College, Ahmednagar, 414001

<sup>3</sup>Department of Chemistry, Radhabai Kale Mahila Mahavidyalaya, Ahmednagar, 414001

E-mail: sjtakate26@gmail.com

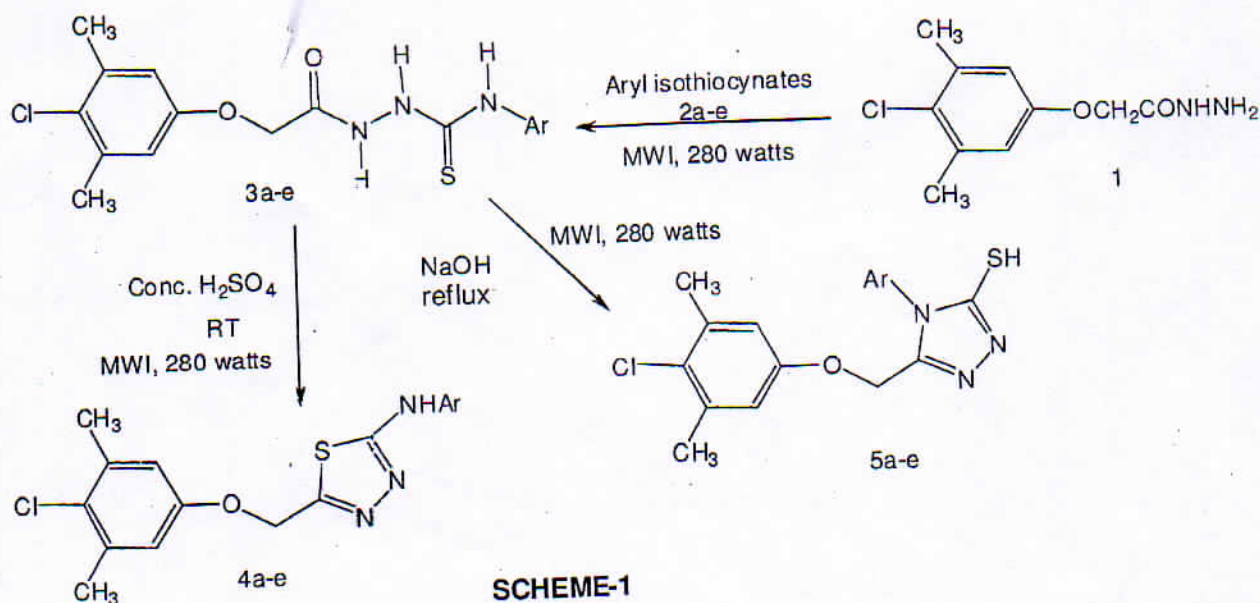
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An ecofriendly synthesis of thiadiazoles and triazoles by intramolecular cyclization of 2-[(4-chloro-3,5-dimethylphenoxy)acetyl]-*N*-arylhydrazinecarbothioamides have been carried out by microwave irradiation.

Among the various heterocycles, azole based compounds are known to exhibit potential bioactivities. 1,3,4-Thiadiazoles and 1,2,4-triazoles<sup>1-4</sup> are well known for their efficacy as biologically active heterocycles. Substituted thiosemicarbazides can be transformed into triazoles and thiadiazoles in basic and acidic conditions respectively. Recent literature data shows that synthesis of these heterocycles proceeds with increased yields while considerable

decrease in reaction time by non-conventional<sup>5, 6</sup> methods.

Keeping in focus potential bioactivities of thiadiazoles and triazoles, 2-[(4-chloro-3,5-dimethylphenoxy) acetyl]-*N*-arylhydrazinecarbothioamides were cyclized to thiadiazoles and triazoles as a part of our previous work<sup>7</sup> by conventional method. In continuation to that, in present study we have synthesized azoles by using microwave



## Microwave assisted synthesis of 1-(6,8-dimethyl coumarin-4-yl)-2-(chroman-3-yl) ethenes under solvent free conditions

 M.T.Bachute<sup>1\*</sup>, C.H.Gill<sup>2</sup>, **B.K.Karale<sup>3</sup>**, R.T.Bachute<sup>4</sup>
<sup>1</sup>P.G.Dept of Chem, KBPMahavidyalaya, Pandharpur (MS), (INDIA)

<sup>2</sup>School of Chemical Sciences, Dr. BAMU, Aurangabad (MS), (INDIA)

<sup>3</sup>P.G.Dept. of Chemistry, Radhabai Kale Mahila Mahavidyalaya, Ahmednagar, (INDIA)

<sup>4</sup>IPCA, Laboratories, Ratlam (MP), (INDIA)

E-mail: mbachute@gmail.com; chgill50@yahoo.com; bkkarale@gmail.co

### ABSTRACT

1-(6, 8-dimethylcoumarin-4-yl)-2-(chroman-3-yl)ethenes (**3**) were prepared by MW assisted Knoevangel condensation of 3-formyl chromones (**1**) with 1-(6,8-dimethylcoumarin-3-yl)-4-acetic acid (**2**) under solvent free conditions. New compounds were scanned for antimicrobial activities.

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### KEYWORDS

Chromones;  
Coumarins;  
Microwave assisted;  
Solvent free;  
Knoevangel condensation.

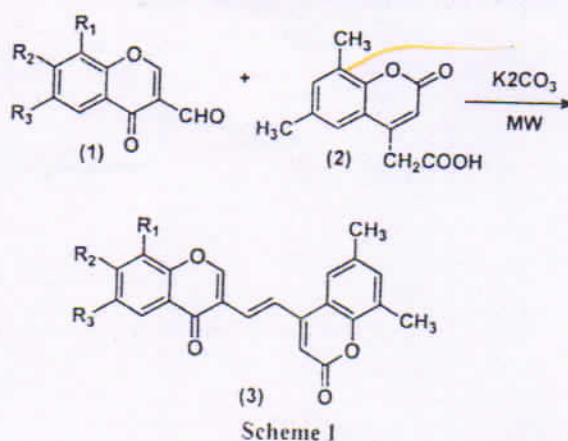
### INTRODUCTION

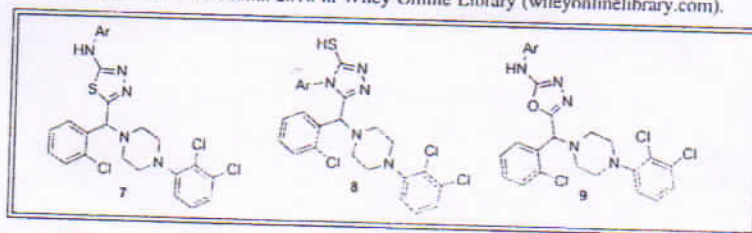
Owing to the widespread applications of chromones<sup>[1-13]</sup> and coumarins<sup>[14-23]</sup>, it was thought worthwhile to synthesise heterocyclic compounds containing combination of chromone and coumarin moieties, which would result in added potential.

Among the important tools, the use of microwave radiations<sup>[24]</sup>, as the source of energy for chemical reactions, is an eco-friendly alternative to traditional heating. This results in reduction in time, increase in yield and thus eco-friendly.

A reaction under solvent free conditions is an added factor to minimize the pollution. Literature survey revealed that up till now 1-[(6,8-dimethylcoumarin-4-yl)-2-(chroman-3-yl)]ethenes (**3**) have not been synthesised using MW assistance and solvent free conditions. Condensation reactions of active methylene compounds with 3-formyl chromones are well known<sup>[25]</sup>. Karale<sup>[26]</sup> synthesised such compounds by conventional method.

In the present investigation 1-[(6,8-dimethylcoumarin-4-yl)-2-(chroman-3-yl)]ethenes (**3**) have been synthesised by MW assisted Knoevangel condensation of variously substituted 3-formyl chromones (**1**) with 1-(6,8-dimethyl coumarin-3-yl)-4-acetic acid (**2**) in the presence of potassium carbonate under solvent free conditions as shown in the Scheme 1. The yields of the products obtained are better than





A series of novel 1,3,4-thiadiazoles, 1,2,4-triazoles, and 1,3,4-oxadiazoles were synthesized by cyclization of substituted 1-(2-(2-chlorophenyl)-2-(4-(2,3-dichlorophenyl)piperazin-1-yl)acetyl)thiosemicarbazide. The structures of all newly synthesized compounds were elucidated on the basis of spectral studies. Some of them were screened for their antibacterial activity. The compounds 6b, 6c, 8e, 9a, and 9b have shown moderate activity towards *Bacillus Subtilis* and *Escherichiu Coli*.

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## INTRODUCTION

Piperazines are the saturated analogues of pyrazines having nitrogen atoms at opposite positions. Piperazines are an important class of compounds with biological activities like anthelmintic [1],  $\alpha_1$ -adrenergic receptor blockers [2], and antibacterial [3]. Aryl piperazine derivatives show remarkable activity in neuropathic pain without sedative side effect [4]. Some important marketed drugs that contain piperazine nucleus are Cetirizine (antihistamine), Perphenazine (antipsychotic), Trazodone (antidepressant), and Ranolazine (antianginal).

Thiosemicarbazides are the valuable starting compounds used for the synthesis of azoles. Thiosemicarbazides are important compounds having a variety of applications [5]. They have shown activities like anticancer [6], anti-HIV [7], antimalarial [8], antifungal [9], and antibacterial [10].

Thiadiazoles are five-membered heterocyclic compounds containing two nitrogen atoms and one sulfur atom as part of the aromatic ring. Recently, intense investigation has been carried out on thiadiazoles having different substituents. They show various biological activities like antibacterial [11], antioxidant [12], antimicrobial [13] cyclooxygenase-2 inhibitors [14], antifungal [15], and antidepressant [16].

1,2,4-Triazoles are important group of heterocyclic compounds characterized by a five-membered ring having three nitrogen atoms. The biological activities of 1,2,4-triazoles have been investigated by various studies. They possess biological activities like antitubercular [17], antitumor [18], analgesic [19], diuretic [19], anti-inflammatory [20], anti-convulsant [20], and antimicrobial [21].

1,3,4-Oxadiazoles are five-membered heterocyclic compounds containing two nitrogen atoms and one oxygen atom. The heterocyclic compounds anchored with 1,3,4-oxadiazoles exhibit the pharmacological activities like antimicrobial [22], anthelmintic [23], anti-inflammatory [24], analgesic [24], antimitotic [25], and anti-HIV [26].

Literature survey showed that incorporation of halogen in heterocyclic compounds increases their activities. Several synthetic organic chemists have synthesized halogenated heterocycles and evaluated them for biological screening. Kumar and coworkers have synthesized series of 3-[4'(*p*-chlorophenyl)thiazol-2'-yl]-2-[(substituted azetidinone/thiazolidinone)-aminomethyl]-6-bromoquinazolin-4-ones and reported their anti-inflammatory and analgesic activities [27]. Several commercially available drugs also contain chlorinated heterocyclic compounds such as clotrimazole, econazole, miconazole, and ketoconazole (Scheme 1).

Present research article describes the synthesis and antibacterial screening of thiadiazoles, triazoles, and oxadiazoles containing piperazine nucleus.

## RESULTS AND DISCUSSION

Substituted 1-(2-(2-chlorophenyl)-2-(4-(2,3-dichlorophenyl)piperazin-1-yl)acetyl)-4-phenyl thiosemicarbazide **6** was synthesized in five steps starting from 2-(2-chlorophenyl)acetic acid **1**. 2-(2-Chlorophenyl)acetic acid **1** was converted into 2-bromo-2-(2-chlorophenyl)acetic acid **2** by using *N*-bromosuccinimide [28]. Methyl ester **3** of compound **2** was treated with 1-(2,3-dichlorophenyl)piperazine hydrochloride in



## Synthesis and Screening of Fluoro Substituted Pyrazolyl Benzoxazoles

R. K. JADHAV<sup>1</sup>, A. B. NIKUMBH<sup>1</sup> and **B. K. KARALE<sup>2\*</sup>**

<sup>1</sup>Department of Chemistry, S.S.G.M. College, Kopergaon, Dist. Ahmednagar- 423601, India.  
<sup>2</sup>Department of Chemistry, Radhabai Kale Mahila Mahavidyalaya, Ahmednagar - 414001, India.

\*Corresponding author Email: bkkarale@yahoo.com

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### ABSTRACT

A series of 3-Formylchromone **1** was reacted with 1-(4-(4-fluorophenyl)thiazol-2-yl)hydrazine **2** to get 1-(4-(4-fluorophenyl)thiazol-2-yl)-1H-pyrazol-4-yl(2-hydroxyphenyl) methanone **3** which on reaction with hydroxylamine hydrochloride given methanone oxime **4** and **4** on treatment with POCl<sub>3</sub> formed 2-(1-(4-(4-fluorophenyl)thiazol-2-yl)-1H-pyrazol-4-yl)benzo[d]oxazole **5**. The structures of synthesized compounds were confirmed by spectral analysis further they were screened for their biological activity.

**Key words:** 3-Formylchromones, Methanone, Oxime, Benzoxazole, Spectral analysis, Biological activity.

### INTRODUCTION

3-Formylchromones give several versatile condensation reactions as they contain 3-electrophilic centers in the molecule<sup>1</sup> which can be converted into various biological active compounds. 3-Formylchromones achieved by the most stable method through the application of Vilsmeier Haack reaction<sup>1,2</sup> from 2-hydroxyacetophenone. It has an instantaneous aldehyde group and undergoes Knoevenagel condensation reaction and gives several important synthetic compounds. Different researchers were studying the condensation reactions of various nucleophiles with 3-formylchromones. 2-Hydroxyacetophenones are

good precursors for several applications, which were synthesized by Fries rearrangement by known procedure<sup>3</sup>.

Pyrazole nucleus based compounds exhibits focus on medicinal and agriculture chemistry because they found vast scope for biological activities like antitumor and anti-HCV agents<sup>4</sup>, hepatoprotective<sup>5</sup>, antidiabetic<sup>6</sup>, anticancer<sup>5</sup>, cytotoxic<sup>7</sup>, herbicidal<sup>8</sup> and fungicidal<sup>9</sup> activities.

Fluorinated moieties have been found unique properties in synthesizing the compounds in the drug world.

## Accepted Manuscript

The first naphthosemiquinone complex of  $K^+$  with vitamin K3 analog: Experiment and Density Functional Theory

Laxmi Kathawate, Shridhar P. Gejji, Sachin D. Yeole, Prakash L. Verma, Vedavati G. Puranik, Sunita Salunke-Gawali

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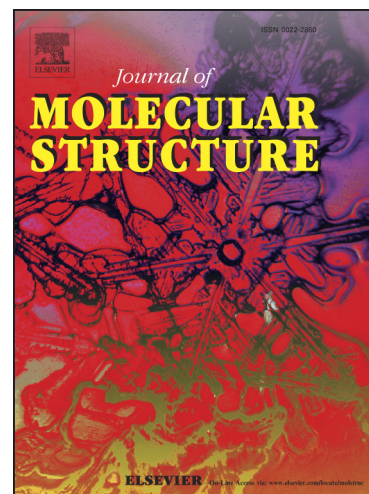
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# The first naphthosemiquinone complex of $K^+$ with vitamin K3 analog: Experiment and Density Functional Theory

Laxmi Kathawate<sup>a</sup>, Shridhar P. Gejji<sup>a\*</sup>, Sachin D. Yeole<sup>a</sup>, Prakash L. Verma<sup>a</sup>, Vedavati G. Puranik<sup>b</sup>, Sunita Salunke-Gawali<sup>a\*</sup>

<sup>a</sup>Department of Chemistry, Savitribai Phule Pune University, Pune 411007, India

<sup>b</sup>Center for Material Characterization, CSIR-National Chemical Laboratory, Pune 411008, India

## Abstract

Synthesis and characterization of potassium complex of 2-hydroxy-3-methyl-1,4-naphthoquinone (phthiocol), the vitamin K3 analog, has been carried out with FT-IR, UV-visible, <sup>1</sup>H and <sup>13</sup>C NMR, EPR, cyclic voltammetry and single crystal X-ray diffraction experiments combined with the density functional theory. It has been observed that naphthosemiquinone binds to two  $K^+$  ions extending the polymeric chain through bridging oxygens O(2) and O(3). The crystal network possesses hydrogen bonding interactions from coordinated water molecules showing water channels along the c-axis. <sup>13</sup>C NMR spectra revealed that complexation of phthiocol with the potassium ion engenders deshielding of C(2) signals, which appear at  $\delta \sim 14.6$  ppm unlike those of C(3) exhibiting up-field signals near  $\delta \sim 6.9$  ppm. These inferences are supported by the M05-2x based density functional theory. Electrochemical experiments further have shown that the reduction of naphthosemiquinone results in only a cathodic peak from catechol. A triplet state arising from interactions between neighboring phthiocol anion lead to half field signal at  $g = 4.1$  in polycrystalline X-band EPR spectra at 133 K.

**Key Words:** Vitamin K3, phthiocol, naphthosemiquinone, hydrogen bonding, <sup>13</sup>C NMR, DFT

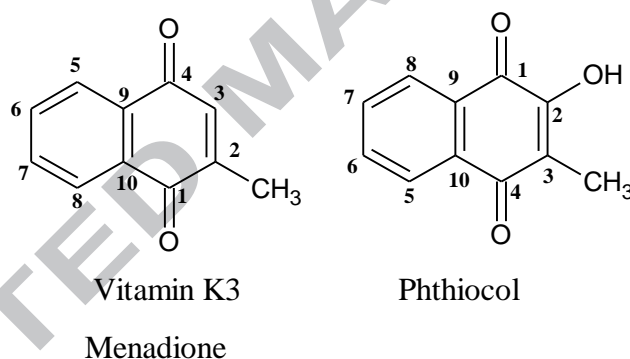
\*Corresponding author

E-mail: [sunitas@chem.unipune.ac.in](mailto:sunitas@chem.unipune.ac.in), [spgejji@chem.unipune.ac.in](mailto:spgejji@chem.unipune.ac.in)

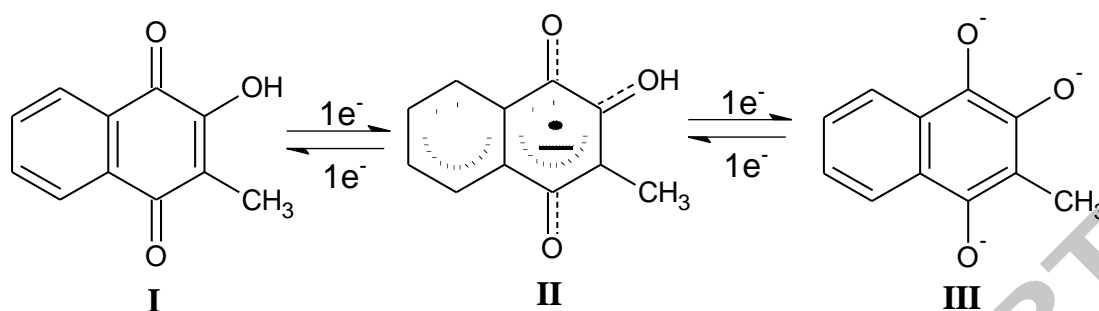
Tel. No. : +912025601397 -Ext-531, fax: +912025693981

## Introduction

Synthesis and isolation of 2-hydroxy-3-methyl-1,4-naphthoquinone was carried out in ether soluble constituents by saponification of acetone soluble fat of tubercule bacillus. The compound [1] crystallizes as yellow prisms with molecular formula  $C_{11}H_8O_3$  that melts near  $174\text{ }^\circ\text{C}$  forming deep red water soluble salts with alkali and other bases. The oxidation of [1] with hydrogen peroxide in alkaline solution yield phthalic acid hence, the pigment was named 'phthiocol' [1]. This yellow pigment possesses vitamin K like activity [2]. The phthiocol can be obtained in the laboratory on epoxidation by hydrogen peroxide followed by hydrolysis of vitamin K3 (2-methyl-1,4-naphthoquinone)[3,4] that belongs to the K group vitamin and finds applications in medicine as antitumor, anticancer drug possessing anti-oncogenic [5-7] and antihemorrhagic properties [8-9]. The antihemorrhagic activity of vitamin K group depends on molecular structure [10] and reduction potential [11]. Besides this K group vitamins act as cofactor in blood clotting.



Phthiocol binds metal ion with bidentate/tridentate coordination yielding different oxidation states as in: completely oxidized (form I), one electron reduced naphthosemiquinone (form II) and two electron reduced catechol forms (form III), which are shown in Scheme 1. Molecular structures of coordination complexes of phthiocol ligand with the transition metal ions *viz.*,  $Zn^{2+}$  [4],  $Cu^{2+}$  [13] and  $Mn^{2+}$  [15] have been reported. Phthiocol engender coordination polymers with  $Sm^{3+}$  and  $Cd^{2+}$  ions [16-17]. To the best of our knowledge the hitherto investigation is the first report on characterization of  $K^+$  complex of naphthosemiquinone ligand.



**Scheme 1** Redox forms of 2-hydroxy-3-methyl-1,4-naphthoquinone. I, oxidized naphthoquinone form (NQ); II, naphthosemiquinone form ( $\text{NSQ}^{2\cdot-}$ ) and III, catechol form (CAT)

## Experimental

Analytical grade chemicals are used. Menadione (2-methyl-1,4-naphthoquinone) obtained from Sigma Aldrich was recrystallized in methanol prior to synthesis. Milli-Q water was used in flame photometry experiments. Anhydrous methanol was purified using standard procedure [18].

### *Synthesis of Phthiocol*

The preparation followed a slight modification of the published procedure [3]. Menadione (1.0 g; 5.8 mM) was dissolved in 10 ml methanol and chilled on an ice bath. A solution of 0.2 g of anhydrous  $\text{Na}_2\text{CO}_3$  and 1 ml of 30%  $\text{H}_2\text{O}_2$  in 5 ml of water was then added with the reaction mixture maintained at 0 °C. Addition of 100 ml of chilled water precipitates 2-methyl-1,4-naphthoquinoneoxide as colorless crystals which were collected by filtration and dried. The solid was treated with 5 ml concentrated  $\text{H}_2\text{SO}_4$  and allowed to stand for 10 minutes. Subsequent addition of 20 ml water gave a yellow precipitate which was recrystallized with methanol containing a few drops of concentrated  $\text{H}_2\text{SO}_4$ . The crude product was column chromatographed using 5% methanol in toluene.

### *Characterization of Phthiocol*

Yellow solid, Yield: 0.84 g, 84%. FT-IR; (KBr,  $\text{cm}^{-1}$ ): 3371, 1660, 1591, 1456, 1392, 1344, 1301, 1276, 1211, 1178, 1074, 1228, 985, 900, 833, 788, 727, 684, 634, 534, 439, 412, 381.  $^1\text{H}$  NMR; ( $\text{DMSO}-d_6$ , 300 MHz)  $\delta$ /ppm: 1.956 (s, 3H), 7.969 (d,  $J = 6.3$ , 2H), 7.821 (t,  $J = 6.15$ , 2H), 7.778 (t,  $J = 6.3$ , 2H), 7.989 (d,  $J = 5.4$ , 2H), 10.900 (s, Ar-OH).  $^{13}\text{C}$  NMR

(DMSO- $d_6$ , 500 MHz)  $\delta$ /ppm: 8.97, 120.31, 126.03, 126.04, 130.38, 132.41, 133.7, 134.78, 155.83, 181.02, 185.05. UV-Vis; (Methanol,  $\lambda_{\max}$ , nm): 295, 324, 479. UV-Vis; (Methanol,  $\lambda_{\max}$ , nm): 287, 330, 388, 479. Anal. data calc. for [C<sub>11</sub>H<sub>8</sub>O<sub>3</sub>] (188.17 g): C, 70.21; H, 4.29 %. Found: C, 70; H, 20 %, LC-MS ( $m/z$ ): 188.

#### *Synthesis of Phth-K<sub>2</sub>*

1mM of phthiocol (0.188 g) was dissolved in 15 ml anhydrous methanol. 1 mM of KOH (0.560 g) was dissolved in 10 ml of anhydrous methanol. The two solutions were mixed with constant stirring for 20 minutes at 26°C. The pH of the solution was found to be close to 7. The products precipitated products were filtered and washed with diethyl ether and dried under vacuum. The synthesis of Phth-K<sub>2</sub> was carried out at the room temperature (26°C). The mole ratio of naphthoquinone and KOH was retained to 1:1. The concentration of K<sup>+</sup> ions was determined by flame photometry. Thermogravimetric (TG) analysis confirmed the presence of adsorbed as well as coordinated water molecules in the title complex. The residue following complete decomposition of organic entity was found to be K<sub>2</sub>O.

#### *Characterization of Phth-K<sub>2</sub>*

Red orange solid, Yield: 0.22 g, 73 %. FT-IR (KBr; cm<sup>-1</sup>): 3381, 3215, 1670, 1589, 1521, 1392, 1350, 1280, 1230, 1124, 952, 844, 734, 682, 621, 553, 422. <sup>1</sup>H NMR (DMSO- $d_6$ , 500 MHz)  $\delta$ /ppm: 1.748 (s, 3H), 7.799 (d,  $J = 7.5$ , 2H), 7.680 (d,  $J = 7.0$ , 2H), 7.560 (t,  $J = 7.5$ , 2H), 7.742 (t,  $J = 7.5$ , 2H). <sup>13</sup>C NMR (DMSO- $d_6$ , 500 MHz)  $\delta$ /ppm: 9.54, 113.41, 124.43, 124.59, 129.43, 131.52, 132.07, 136.12, 170.44, 178.57, 185.97. UV-Vis; (Methanol,  $\lambda_{\max}$ , nm): 295, 324, 479. Anal. data calc. for [K<sub>2</sub>C<sub>11</sub>H<sub>7</sub>O<sub>3</sub>] 2.5 H<sub>2</sub>O, (310.41 g): C, 42.56; H, 03.89 %., Found: C, 42.82; H, 03.86 %.

#### *Physical Measurements*

Elemental analysis was carried out on Thermo Finnigan EA 1112 Flash series elemental analyzer. The concentration of K<sup>+</sup> in Phth-K<sub>2</sub> was determined on SYSTRONICS flame photometer 128. AR grade KCl was standard for flame photometry analysis. UV-Visible spectra of phthiocol ligand and the K<sup>+</sup> complex were recorded on SHIMADZU UV 1650 in methanol between 200 to 800 nm. <sup>1</sup>H and <sup>13</sup>C NMR spectra of compounds were recorded in DMSO- $d_6$ , on Varian 500 MHz NMR spectrophotometer with the tetramethylsilane (TMS) as a reference. Liquid chromatograph mass spectrum of phthiocol

was recorded on Shimadzu, liquid chromatograph mass spectrophotometer, LC-MS-2010EV with ESI as the source was used for ionization

#### *Cyclic voltammetry studies*

Electrochemical measurements were performed with CHI 6054E electrochemical analyser equipped with a commercial platinum disc electrode (CHI Instruments, USA, 2 mm diameter), AgNO<sub>3</sub> wire and platinum wire loop which serve as working, reference and counter electrodes, respectively. After fixing the electrodes to the cell 0.513 g of tetra butyl ammonium perchlorate (100 mM in 15 mL solution) was transferred to cell through high purity argon gas. The blank or controlled voltammograms were acquired in tetra butyl ammonium perchlorate–DMSO mixture prior to measurements. Sample dispersed in small amount of solvent injected in cell for further measurement (analytic concentration 5 mg/15 mL). At the end of each set of experiments the potentials were calibrated with respect to the normal hydrogen electrode (NHE) using the ferrocene as internal standard.

#### *Single Crystal X-ray Crystallography*

Single crystal of Phth-K<sub>2</sub> was grown by slow evaporation of the solution in methanol. Red coloured needle type crystal of approximate size 0.12 x 0.10 x 0.01 mm<sup>3</sup>, was mounted for data collection on Bruker SMART APEX CCD diffractometer employing Mo K<sub>α</sub> radiation with fine focus tube of 50 kV and 30 mA. Crystal to detector distance 6.05 cm, 512 x 512 pixels/frame, multirun data acquisition, four data sets. Total frames = 1829, Oscillation / frame -0.3°, exposure / frame = 25.0 sec / frame, maximum detector swing angle = -30.0°, beam centre = (260.2, 252.5), in plane spot width = 1.24, SAINT integration,  $\theta$  range = 1.10 to 24.75°, completeness to  $\theta$  of 24.75° is 99.7%. SADABS correction applied.

All the data were corrected for Lorentzian, polarisation and absorption effects. SHELX-97 (ShelxTL) [19] was used for structure solution and full matrix least squares refinement on F<sup>2</sup>. Carbon atom C(2) was thermally not stable and refined isotropically. Hydrogen atoms were included in the refinement as per the riding model, the hydrogens of the water molecule and those of O(2)H were thus determined by difference fourier and refined subsequently. Data collection and refinement parameters are listed in Table 1.

#### *Computational Method*

The anion and Phth-K<sub>2</sub> were optimized using the analytical gradient method relaxing all the geometric parameters simultaneously. The density functional theory based on

dispersion corrected exchange correlation functional M06-2x [20] from the Minnesota group, with the internally stored 6-31+G(d,p) basis set was employed. The Gaussian-09 program [21] was used. Optimizations were performed with the SCF= 'ultrafine' grid option. The vibrational frequencies were computed analytically using the second derivatives of energy from the hessian matrix. The harmonic frequencies thus obtained were scaled by a factor of 0.9541 as recommended for the M06-2x functional [22]. All the normal vibration frequencies turned out to be real (no frequency was imaginary) hence, the optimized structures were confirmed to be local minima on the potential energy surfaces. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shifts were computed by subtracting respective shielding constants from those of the tetramethylsilane (TMS) which was used as the reference within the framework of the gauge-independent atomic orbital (GIAO) method. The influence of solvent on  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shifts was modeled through self-consistent reaction field (SCRF) theory employing the polarized continuum model (PCM) in the presence of DMSO (solvent).

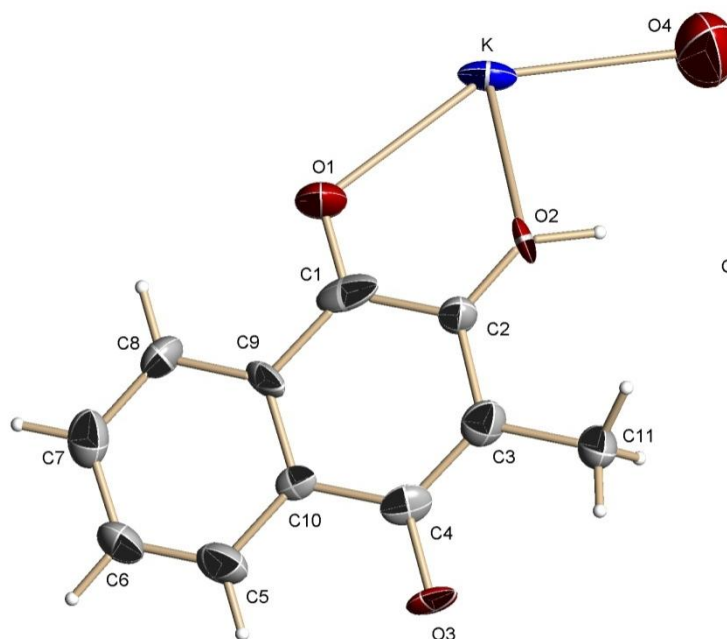
## Results and Discussion

### *Single Crystal X-ray Crystallography*

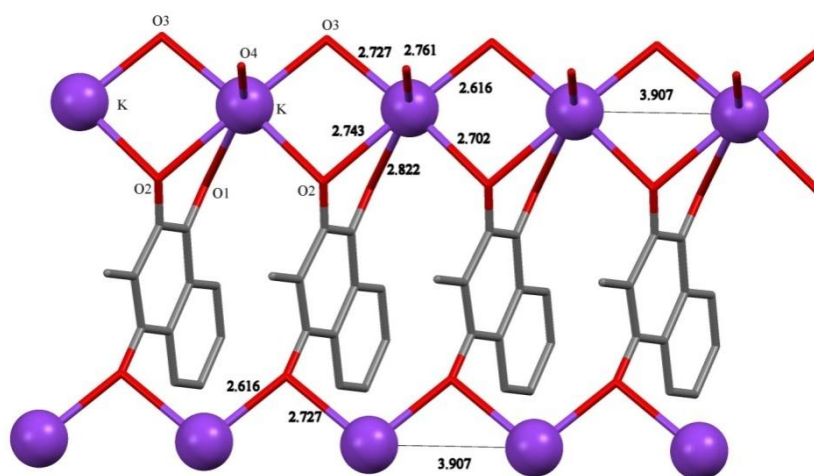
Single crystal X-ray data for Phth- $\text{K}_2$  was collected at room temperature. The molecular structure, ORTEP diagram has been depicted in Fig.1. Crystallographic data is summarized in Table 1. Selected bond distances are reported in Table 2. An extensive data has further been given in the Table S1 of the ESI† of supporting information. As shown in Fig. 1 the potassium ion shows distorted octahedral geometry and coordinates to *four* phthiocols and a  $\text{H}_2\text{O}$  molecule. The extending polymeric chain resulted through binding of phthiocol to metal ion *via* O(1), O(2) and O(3) as depicted in Fig.2. The potassium oxygen contact distances in distorted octahedron around  $\text{K}^+$  vary from  $\sim 2.6$  to  $2.8 \text{ \AA}$  [23-33]. The phthiocol facilitating hydrogen bonding interactions [(i)  $\text{O}(2)\text{-H}=0.96(7)\text{\AA}$ ,  $\text{H}\cdots\text{O}(5)=1.75\text{\AA}$ ,  $\text{O}(2)\cdots\text{O}(5)=2.71(1)\text{\AA}$ ,  $\angle\text{O}(2)\text{-H}\cdots\text{O}(5) = 179(7)^\circ$ ,  $(-1+x,y,z)$ , (ii)  $\text{O}(4)\cdots\text{O}(5)=2.82(2)\text{\AA}$ ] (Fig.3) engender water channels along the 'c' axis as depicted in Figure.

The C=O bond distances in the phthiocol complex are displayed in Table 2 are relatively large compared to those observed in the complexes of phthiocol [4]. The C-C and C=O bond distances of quinones are sensitive to oxidation state of ligands in their complexes [34-41]. The bond distances in redox susceptible quinonoid ligands, have proven useful to identifying the oxidation number of phthiocol in the complexes. The C=O distances in catecholate complexes have been observed to be  $1.32\text{-}1.39\text{\AA}$ , whereas the C-C bond distances in hexatomic carbon ring closer to those of aromatic systems with the average of these being

in the range 1.39-1.41 Å. The respective C=O and C-C bond distances in semiquinone complexes usually are found to be 1.28Å-1.31 Å and 1.42Å -1.45 Å.



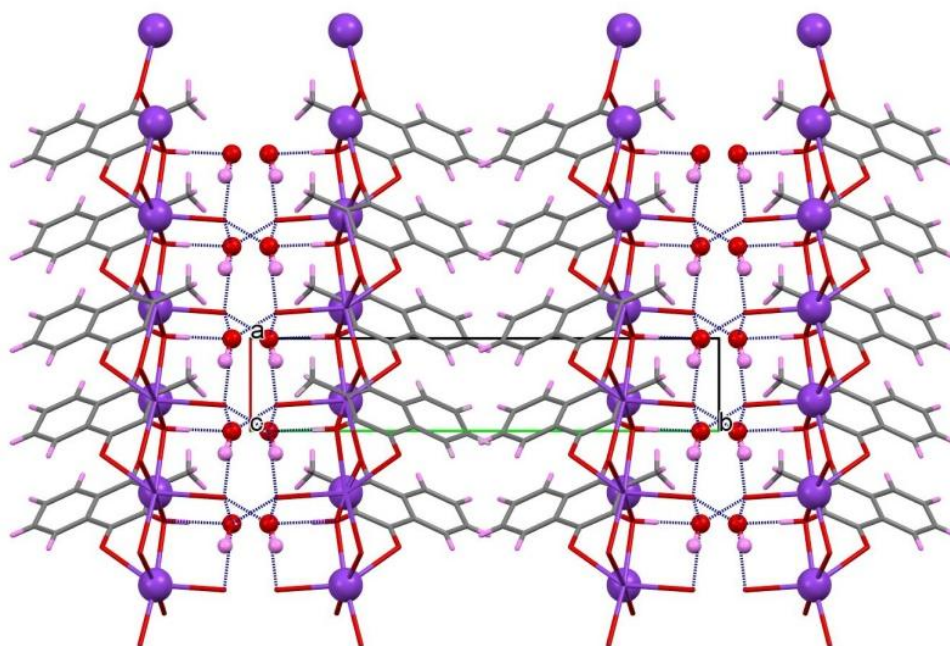
**Fig.1** ORTEP diagram of Phth-K<sub>2</sub>. Ellipsoids are drawn at 50 % probability



**Fig.2** Polymeric chain of 'K<sup>+</sup>' formed due to bridged ligands in Phth-K<sub>2</sub>

Compared to these data, the neutral quinones complexes possess the carbonyl and C-C bond distances to be ~1.23 Å and ~1.53 Å in [34-41]. Nonetheless, the bond distances do not distinguish metal-quinone antiferromagnetic interactions and the quinonoid C=O distances in 2-oxido-1,4-naphthoquinone anion are observed to be longer[42]. Furthermore charge delocalization engenders relatively long C(2)-O(2) and C(4)-O(3) bonds. Besides the

C(1)-O(1) bond distance in the oxidized form of phthiocol anion are nearly unchanged and turn out to be 1.23 Å [43]. Thus it may be conjectured that variation in oxidation state of naphthoquinone emerge with its signature in C(1)-O(1) bond distances.



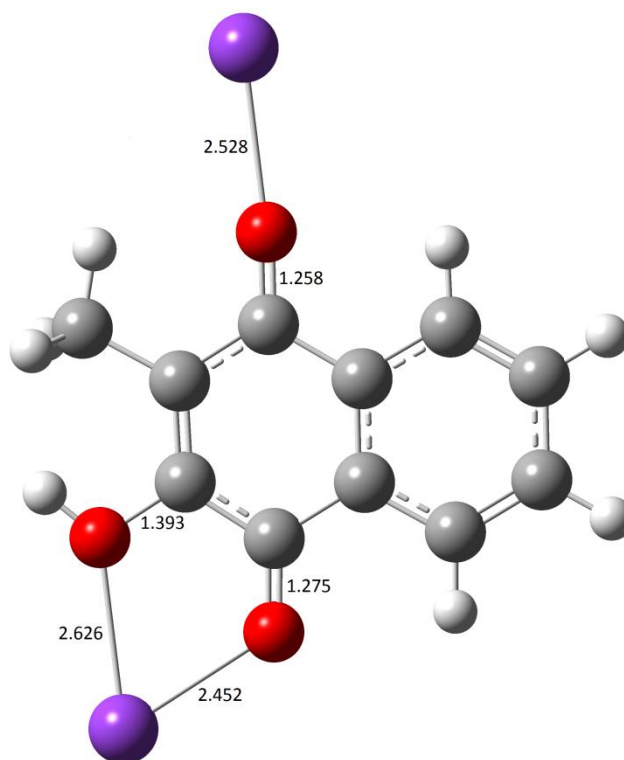
**Fig.3** Packing viewed down ‘c’ axis. The ligand forms channels with water molecule hydrogen bonded to the ligands in Phth-K<sub>2</sub>

Selected bond distances in phthiocol complex [4] and free phthiocol [43] are compared in Table 3. The C=O bond distances in Phth-K<sub>2</sub> are longer than the corresponding ones in the oxidized form of phthiocol. A comparison of catecholate and quinone has shown that the carbonyl bond distances in the latter are relatively short. Observed C(2)-C(3) distances (1.44 Å) thus show intermediate C-C and C=C character. Thus, the presence of dianion phthiocol radical as form II (*cf.* Scheme 1) in the titled K<sup>+</sup> naphthoquinone complex is evident. These inferences have further been supported by the EPR and electrochemical experiments.

#### *Electronic structure*

Optimized structure along with selected bond distances (in Å) of Phth-K<sub>2</sub> complex from the M06-2x/6-31+G(d,p) theory has been displayed in Fig.4





**Fig. 4** Optimized geometry of the Phth-K<sub>2</sub> complex

Phth-K<sub>2</sub> structure obtained from the M06-2x based density functional theory is in consonant with that observed in the single crystal X-ray experiments. The separation between K<sup>+</sup> and carbonyl oxygens O(1) and O(2) was predicted to be ~ 2.54 Å in the complex.

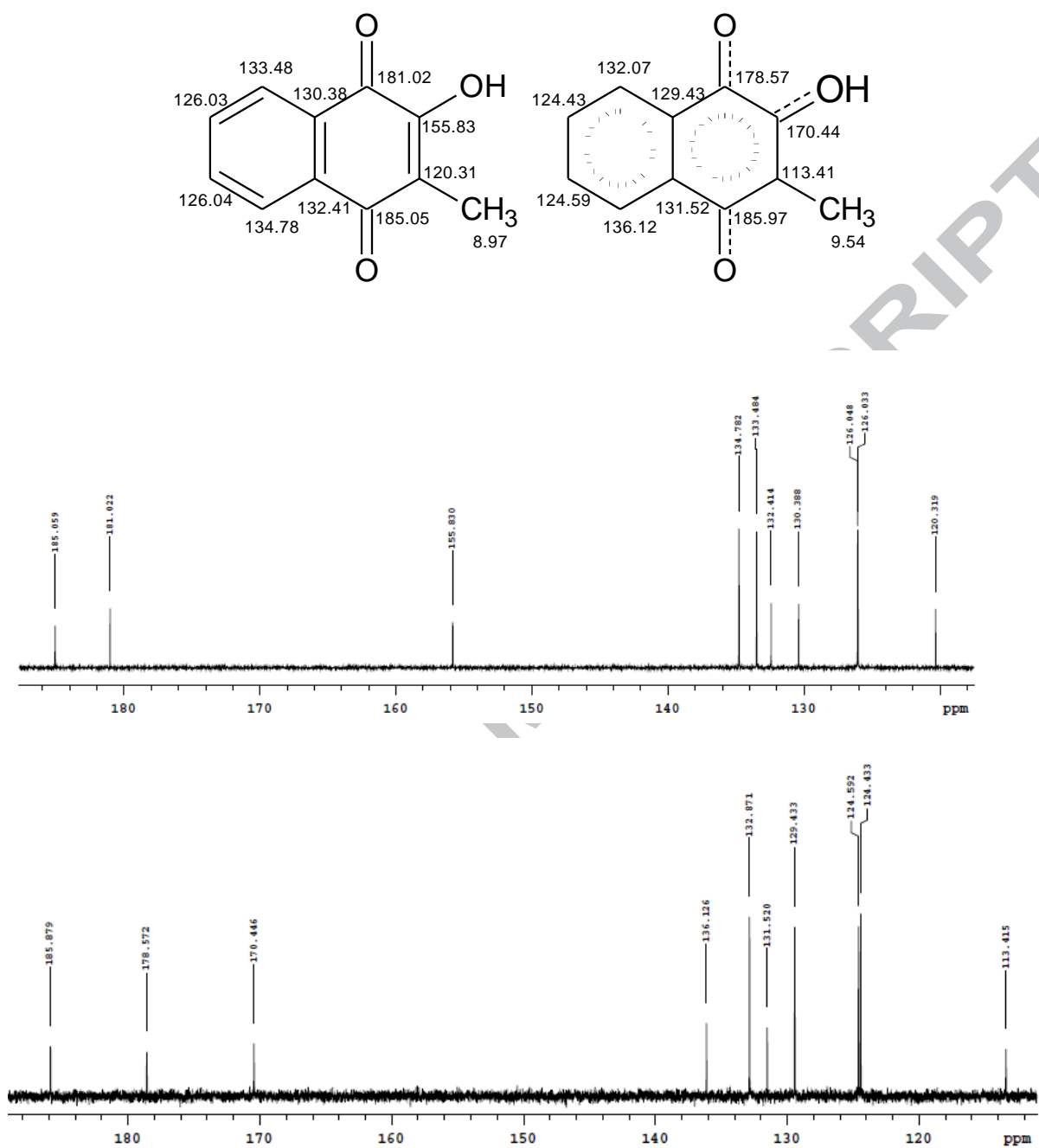
#### *<sup>1</sup>H and <sup>13</sup>C NMR, FT-IR and Electronic Spectra*

<sup>1</sup>H NMR spectra revealed *six* peaks for isolated phthiocol compared to *five* for the Phth-K<sub>2</sub> as displayed in Fig.S1 in ESI†. A singlet due to -OH, and -CH<sub>3</sub>, doublet from C(5)H and C(8)H and triplet of C(6)H and C(7)H can also be noticed. Further the Phth-K<sub>2</sub> protons on C(5) to C(8) and those from the methyl group exhibit upfield signals compared to the phthiocol anion. It may further be remarked here that the complexation of phthiocol anion with the metal can be monitored by measurements of the <sup>13</sup>C NMR chemical shifts. The corresponding NMR signals in Phth-K<sub>2</sub> complex (Fig.5) engender upfield signals for C(1), C(3), C(5), C(6), C(7), C(8), C(9) and C(10)). As opposed to this the signals due to (CH<sub>3</sub>, C(2), C(4)) deshielding in the <sup>13</sup>C NMR spectra in the Phth-K<sub>2</sub> complex. It is therefore, evident that the complexation with the metal ion influences C(2) and C(3) signals significantly. A large shielding of C(3) signals ( $\delta_C$  6.9 ppm) in the spectra further suggests paramagnetic interaction.

As far as the methyl protons are concerned, the  $\delta_{\text{H}}$  values from the M06-2x/6-31+G(d,p) theory given in Table 4 refer to mean of those of individual protons in the group. Theoretically calculated chemical shifts by and large, agree well with those observed in the experiment. Experimental  $^{13}\text{C}$  NMR chemical shifts further led to following inferences. The C(4), C(1) and C(2) signals from 184 ppm to 170 ppm, are largely deshielded. A large up-field signal of the methyl carbon ( $\delta_{\text{c}}$  9.5 ppm) has also been observed. As shown in Table 4, the calculated chemical shifts are in accordance with the experiment. The largest shielding of C(3) predicted from the present density functional theory concurs with the experimental data.

The infrared spectra in  $3400\text{cm}^{-1}$  -  $2800\text{cm}^{-1}$  region of phthiocol (Fig.S2 in ESI†) shows a band at  $3371\text{cm}^{-1}$  arising from coupling of -OH and -CH stretchings, which becomes broader on complexation. Two sharp peaks near  $1591\text{cm}^{-1}$  and  $1660\text{cm}^{-1}$  of the anion were assigned to carbonyl stretching [44]. The complexation of phthiocol has further been accompanied by emergence of bands near  $1521\text{cm}^{-1}$ ,  $1589\text{cm}^{-1}$  and  $1670\text{cm}^{-1}$  instead. A sharp peak  $\sim 1521\text{cm}^{-1}$  assigned to those of carbonyl group of naphthosemiquinone phthiocol [45].

Table S7 in ESI† reports vibrational frequencies of the isolated  $\text{K}_2\text{C}_{11}\text{H}_{12}\text{O}_5$  complex and those in  $\text{Phth}^{2-}$  from the M06-2x based density functional theory. A band near  $1536\text{cm}^{-1}$  in the calculated spectra assigned to C=O stretching vibration comprising of strong coupling from different internal coordinates corresponds to a broad band near the  $1521\text{cm}^{-1}$  and thus suggests the presence of Phthiocol in semiquinone form in the complex [45]. Moreover, computational studies revealed that C=O stretching vibration is diffused in different normal vibrations from  $1621\text{cm}^{-1}$  -  $1508\text{cm}^{-1}$  (cf. Table S7 of ESI†). It has further been predicted that the OH stretching near  $3718\text{cm}^{-1}$  of the anion shifts to the lower wave number ( $3688\text{cm}^{-1}$ ) with a concomitant increase in its intensity on complexation.



**Fig.5**  $^{13}\text{C}$  NMR spectra of free phthicol (top) and Phth- $\text{K}_2$  (bottom)

UV-Visible spectra of phthicol and Phth- $\text{K}_2$  in methanol are displayed Fig.S3 in ESI†. Two bands centered  $\sim 327$  nm were assigned to  $\pi \rightarrow \pi^*$  transition of quinonoid and benzenoid rings, respectively [4, 46-47] are observed. The  $\sim 329$  nm peak in Phth- $\text{K}_2$  show hypsochromic shift. A single broad band in the visible region arises from  $n \rightarrow \pi^*$  transition.

**Table 1** Crystal data for Phth-K<sub>2</sub>.

Empirical formula	K <sub>2</sub> C <sub>11</sub> H <sub>12</sub> O <sub>5</sub>
Formula weight	263.31
Temperature	273(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	<i>Pc</i>
Unit cell dimensions	a = 3.9070(4) Å, α = 90°. b = 18.510(2) Å, β = 111.347(2) °. c = 8.6690(8) Å, γ = 90°.
Volume	583.92(10) Å <sup>3</sup>
Z	2
Density (calculated)	1.498 g/cc
Absorption coefficient	0.461 mm <sup>-1</sup>
F(000)	274
Crystal size	0.12 x 0.10 x 0.01 mm <sup>3</sup>
Theta range for data collection	1.10 to 24.75°.
Index ranges	-4 ≤ h ≤ 4, -21 ≤ k ≤ 21, -9 ≤ l ≤ 9
Reflections collected	4579
Independent reflections	1950 [R(int) = 0.0790]
Completeness to theta = 24.75°	99.7 %
Max. and min. transmission	0.9949 and 0.9480
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	1950 / 5 / 169
Goodness-of-fit on F <sup>2</sup>	1.274
Final R indices [I > 2σ(I)]	R1 = 0.1046, wR2 = 0.1728
R indices (all data)	R1 = 0.1252, wR2 = 0.1800
Absolute structure parameter	0.12(14)
Largest diff. peak and hole	0.391 and -0.481 e.Å <sup>-3</sup>

**Table 2** Selected structural parameters (bond- lengths in Å] and -angles in °in Phth-K<sub>2</sub>.

Bonds	Bond lengths [Å]	Bonds	angles [°]
K-O(3)#1	2.616(7)	O(3)#1-K-O(2)#2	88.4(2)
K-O(2)#2	2.702(7)	O(3)#1-K-O(3)#3	93.94(19)
K-O(3)#3	2.727(7)	O(2)#2-K-O(3)#3	173.2(2)
K-O(2)	2.743(7)	O(3)#1-K-O(4)	96.5(3)
K-O(4)	2.761(9)	O(2)#2-K-O(4)	89.1(3)
K-O(1)	2.821(7)	O(3)#3-K-O(4)	96.9(3)
K-C(4)#3	3.412(8)	O(2)-K-O(4)	89.8(3)
K-C(2)#2	3.474(9)	O(3)#1-K-O(1)	116.4(2)
O(1)-C(1)	1.230(10)	O(2)#2-K-O(1)	87.5(2)
O(2)-C(2)	1.248(10)	O(3)#3-K-O(1)	85.8(2)
O(2)-K#4	2.702(7)	O(2)-K-O(1)	57.3(2)
O(2)-H	0.96(7)	O(4)-K-O(1)	146.8(3)
O(3)-C(4)	1.268(10)	O(1)-C(1)-C(2)	118.9(10)
C(1)-C(2)	1.462(13)	O(1)-C(1)-C(9)	119.4(10)
C(1)-C(9)	1.482(12)	C(2)-C(1)-C(9)	121.7(8)
C(2)-C(3)	1.441(13)	O(2)-C(2)-C(3)	123.4(8)
C(3)-C(4)	1.407(14)	O(2)-C(2)-C(1)	119.4(8)
C(5)-C(6)	1.351(13)	C(3)-C(2)-C(1)	117.2(8)
C(5)-C(10)	1.370(12)	C(7)-C(8)-H(8)	120.1
C(6)-C(7)	1.386(13)	C(9)-C(8)-H(8)	120.1
C(7)-C(8)	1.375(13)	C(10)-C(9)-C(8)	120.7(8)
C(8)-C(9)	1.383(12)		
C(9)-C(10)	1.375(12)		

Symmetry transformations used to generate equivalent atoms:

#1 x-2,y,z-1 #2 x-1,y,z #3 x-1,y,z-1 #4 x+1,y,z #5 x+2,y,z+1 #6 x+1,y,z+1

**Table 3** Bond distances (in Å) of Phth-K<sub>2</sub> and [Zn(Phthiocol)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] from the experiment and M06-2x/6-31+G(d,p) theory.

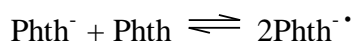
Bond	Phth-K <sub>2</sub>		Phthiocol		[Zn(Phthiocol) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	
	Expt.	DFT	Expt.	DFT	Expt.	DFT
C(1)-O(1)	1.230(10)	1.275	1.228(2)	1.212	1.227(5)	1.241
C(2)-O(2)	1.248(11)	1.393	1.346(2)	1.341	1.292(4)	1.303
C(4)-O(3)	1.268(10)	1.258	1.224(2)	1.220	1.245(5)	1.222
C(1)-C(2)	1.462(13)	1.431	1.486(2)	1.501	1.509(5)	1.501
C(2)-C(3)	1.441(14)	1.379	1.352(2)	1.352	1.363(5)	1.368
C(3)-C(4)	1.407(14)	1.442	1.477(2)	1.481	1.449(5)	1.469
C(1)-C(9)	1.482(12)	1.456	1.477(2)	1.489	1.472(5)	1.470
C(4)-C(10)	1.461(12)	1.470	1.493(2)	1.497	1.494(6)	1.505

**Table 4** Comparison of  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shifts of Phthiocol anion and Phth $\text{K}_2$  complex from the experiment and M06-2x/6-31+G(d,p) theory. The numbers in parenthesis refer to those obtained from theory.

Types of carbons/protons	Phth-K <sub>2</sub> $\delta_{\text{H}}$	Phth-K <sub>2</sub> $\delta_{\text{C}}$	Phth $\delta_{\text{C}}$
C(1)		178.57 (170.12)	181.02 (152.68)
C(2)-OH	(3.7)	170.44 (154.65)	155.83 (154.94)
C(3)-CH <sub>3</sub>	1.748 (2.1)	113.41 (121.24)	120.31 (107.54)
C(4)		185.97 (180.73)	185.05 (166.04)
C(5)H	7.680 (9.2)	136.12 (141.65)	134.78 (139.61)
C(6)H	7.560 (8.5)	124.59 (139.42)	126.04 (113.61)
C(7)H	7.742 (8.3)	124.43 (140.06)	126.03 (120.40)
C(8)H	7.799 (8.7)	132.07 (139.64)	133.48 (138.11)
C(9)		129.43 (143.87)	130.38 (145.51)
C(10)		131.52 (142.56)	132.41 (137.61)
CH <sub>3</sub>		9.54 (15.54)	8.97 (9.13)

#### *Electron Paramagnetic Resonance and Electrochemical Studies*

EPR spectra of polycrystalline Phth-K<sub>2</sub> were recorded at the room temperature (298 K) and at 133 K (Fig.S4 and Fig.S5 in ESI<sup>†</sup>). A broad signal near  $g = 2.00$  and a weak triplet near  $g \sim 4$  was observed. The Phth-K<sub>2</sub> being polymeric a triplet state possibly generated from ferromagnetic interactions between neighboring radical spins in the complex [48]. With 1:1 mole ratio of KOH to phthiocol used in synthesis the hydroxyl group of Phth-K<sub>2</sub> gets deprotonated:

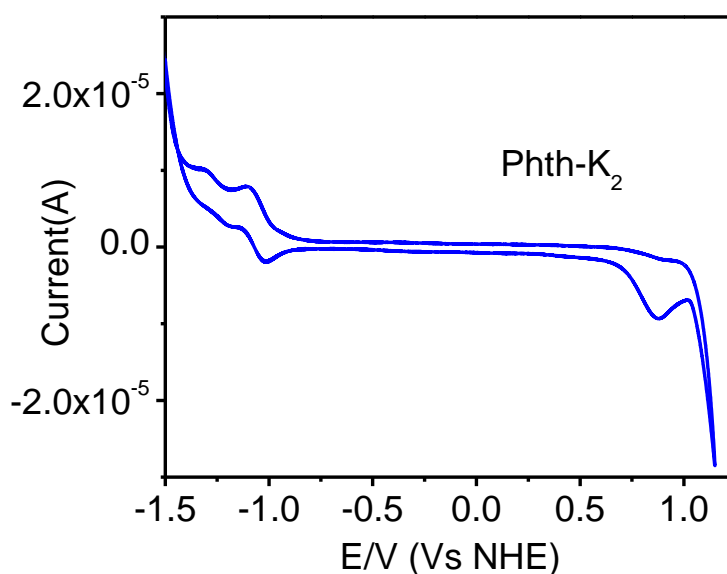


Disproportionate reaction between anionic phthiocol and protonated phthiocol generates naphthoquinone dianion in Phth-K<sub>2</sub>. A similar mechanism was suggested in case of the 2-hydroxy-1,4-naphthoquinone [42]. It should be pointed out here that the generation of the anion radical from menadione in the presence of alkali through disproportionate reaction was conjectured earlier in the literature [48-57]. Alkali metal NaOH, KOH, KF are used in solvent

(0.1 NaOH, methanol/water, ethanol/water, ethanol (abs), methanol, DMSO, THF) generate the anionic radical of menadione ( $\text{MNQ}^{\cdot-}$ ). The observed 'g' value in the presence of salt in different solvents was found to be  $2.00045 \pm 0.00002$ . The hydroquinone reacts with potassium fluoride (KF) in methanolic solution producing the dipotassium salt. A disproportionation reaction yields radical through:



Cyclic voltammogram of Phth- $\text{K}_2$  in DMSO (Fig.6 and Fig.S6 in ESI†) reveals Cathodic quasi-reversible peak  $\sim 0.52$  V vs NHE in free phthiocol [58]. No such a peak observed in Phth- $\text{K}_2$ . The observed cathodic peak at  $\sim 1.10$  V assigned to naphthosemiquinone (form II in Scheme 1) stem from catechol (form III in Scheme 1) reduction. Anodic irreversible peak at  $+0.88$  V assigned to the reoxidation of coordinated phthiocol in Phth- $\text{K}_2$  [58, 62]. Electrochemical studies hence, ascertain coordination of phthiocol in one electron reduced naphthosemiquinone form.



**Fig.6** Cyclic voltammogram of Phth- $\text{K}_2$  at 0.1 V/s scan rate.

## Conclusions

A room temperature stable Phth- $\text{K}_2$  complex was synthesized with phthiocol binds to  $\text{K}^+$  ions in naphthosemiquinone form. The complex was characterized by FTIR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR, EPR, electrochemical, single crystal X-ray diffraction experiments. Polymeric Phth- $\text{K}_2$  shows metal ion located in the vicinity of four phthiocol neighbours. Naphthosemiquinone generated

in disproportion reaction of catechol and oxidised form of phthiocol ligand. Half field signal observed  $\sim g=4$  at 133 K in the X-band EPR spectra of polycrystalline Phth-K<sub>2</sub>, attributed to 'triplet state' consequent to ferromagnetic interactions of neighbouring spins of phthiocol.

### Supporting information available

Fig. S1 to S7, crystallographic Tables S1 to S7. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre and may be obtained on request quoting the deposition number 1034515 from the CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: +44 1223 336 033; E-mail address: deposit@ccdc.cam.ac.uk).

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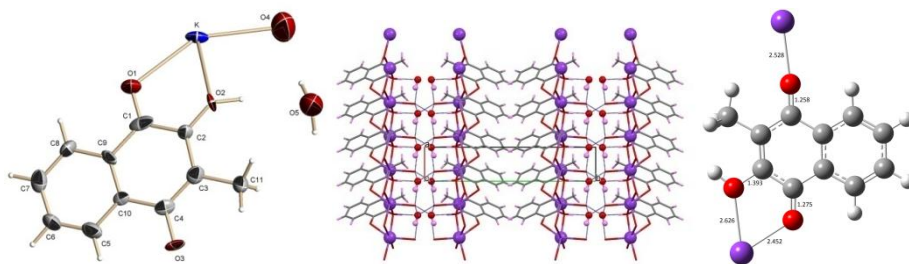
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ACCEPTED MANUSCRIPT

## Graphical Abstract

**Highlights**

- The first naphthosemiquinone coordination complex of vitamin K3 analog is reported.
- Hydrogen bonded water channels to the phthalocyanine are observed.
- Redox couple naphthosemiquinone to catechol is evident in electrochemical studies.
- $^{13}\text{C}$  NMR chemical shifts are in consonant with experiments.

## RESEARCH ARTICLE

BENTHAM  
SCIENCE

## Nanosized ZnO Under Solvent Free Condition: A Smart and Ecofriendly Catalyst to Microwave Assisted Synthesis of 3, 4-dihydropyrimidin-2(1H)-ones/Thiones



Santosh T. Shinde<sup>1</sup>, Kaluram G. Kanade<sup>1,2\*</sup>, Bhausahab K. Karale<sup>1</sup>, Dinesh P. Amalnerkar<sup>3</sup>, Nitin M. Thorat<sup>4</sup>, Sudhir S. Arbuj<sup>5</sup> and Sachin P. Kunde<sup>1</sup>

<sup>1</sup>Post Graduate Department of Chemistry, Radhabai Kale Mahila Mahavidyalaya, Ahmednagar-414001, India; <sup>2</sup>Post graduate Department of Chemistry, Yashwantrao Chavan Institute of Science, Satara-415001, India; <sup>3</sup>School of Mechanical Engineering, Sungkyunkwan University (SKKU)300, Cheoncheon-dong, Jangan-gu, Suwon, Gyeonggi, 440-746, South Korea; <sup>4</sup>Post Graduate Department of Chemistry, Maharaja Jivajirao Shinde Mahavidyalaya, Shrigonda, Ahmednagar-413701, India; <sup>5</sup>Centre for Materials for Electronic Technology (C-MET), Off Pashan Road, Panchwati, Pune-411008, India

**Abstract: Background:** Heterogeneous synthesis of nitrogen containing heterocyclic compounds such as dihydropyrimidin-2(1H)-one/thione derivatives is an important research. Use of nanocrystalline ZnO has demonstrated for heterocyclic compounds which are routinely used in medicinal chemistry due to their therapeutic and pharmacological properties. In this context the solvent free synthesis of pyrimidine derivatives are reported.

**Methods:** Synthesis of ZnO nanomaterials is carried out by precipitation method, which is further used for synthesis of dihydropyrimidin-2(1H)-ones/thiones derivatives. Stoichiometric amount of aromatic aldehydes (1), urea (2) and ethyl acetoacetate (3) were taken in beaker. Then, 10 mmol percent nanocrystalline ZnO powder was added as a catalyst in the reaction mixture which was subjected to heated at 55°C in microwave oven.

**Results:** Microwave assisted synthesis of 3,4-Dihydropyrimidin-2(1H)-ones/thiones has been successfully carried out using eco-friendly ZnO nanoparticles as catalysts. Nanocrystalline ZnO of particle size in the range 60-80nm was prepared by decomposing the Zinc Oxalate intermediate at 500°C XRD analysis indicates the formation of highly crystalline hexagonal phase of ZnO. Solvent free synthesis using reported method have confer 95% yield which is greater than organic solvents such as DMF, Dioxane, THF, Toluene for heterogeneous synthesis.

**Conclusion:** Successfully accomplished 'green' synthesis of dihydropyrimidone/thiones derivatives was demonstrated. Use of nanocrystalline ZnO is found to be an efficient catalyst for heterogeneous Biginelli reaction. Solvent free reactions gave the better yield compared to the use of organic solvents.



K.G. Kanade

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**Keywords:** Biginelli reaction, green synthesis, heterogeneous catalysis, nanocrystalline ZnO.

## 1. INTRODUCTION

Dihydropyrimidin-2(1H)-ones/thiones derivatives form an important class of heterocyclic compounds due to their therapeutic and pharmacological properties [1]. Dihydropyrimidinones (DHPMs Fig. 1A) moiety occurs in many drugs and synthetic products. DHPMs and their derivatives

are very important; since, they behave as a calcium channel blocker, such as antihypertensive agents (R-SQ 32 926) [2],  $\alpha_1$ -adrenrgic antagonists, inhibitors of fatty acid transporters, and in mitotic kinesin inhibition [3-6] (Monastrol, Fig. 1B). Batzelladine (Fig. 1C 1D 1E) alkaloids contain a dihydropyrimidine core, which has been found to possess anti-HIV activity [7, 8]. DHPMs moiety exhibits antiviral [9], antibacterial and antifungal [10], anticancer [11, 12] (S-Monastrol) activity. They are also used as starting material for the synthesis of Rosuvastatin (Fig. 2), selective and competitive inhibitor of HMG-CoA reductase [13], the enzyme responsi-

\*Address correspondence to this author at the Post Graduate Department of Chemistry, Radhabai Kale Mahila Mahavidyalaya, Ahmednagar-414001, India; Tel: +91-2162-234392; Fax: +91-2162-234392; E-mail: kgkanade@yahoo.co.in

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## Targeting a chemorefractory COLO205 (BRAF V600E) cell line using substituted benzo[ $\alpha$ ]phenoxazines†

Sanjima Pal,<sup>a</sup> V. Badireenath Konkimalla,<sup>\*a</sup> Laxmi Kathawate,<sup>b</sup> Soniya S. Rao,<sup>b</sup> Shridhar P. Gejji,<sup>b</sup> Vedavati G. Puranik,<sup>c</sup> Thomas Weyhermüller<sup>d</sup> and Sunita Salunke-Gawali<sup>\*b</sup>

Mutational activations of the oncogene BRAF (especially BRAF V600E) result in a poor prognosis for colon cancer patients and are associated with chemoresistance rendering them refractory to treatment. The development of novel bioactive compounds with specific targeting abilities under such conditions is an urgent need in drug discovery. In this report we synthesize and characterize three fluorescent benzo[ $\alpha$ ]phenoxazine compounds (10R-benzo[ $\alpha$ ]phenoxazine-5-one, **1B**; R = Cl, **2B**; R = CH<sub>3</sub>, **3B**; R = H) and their anticancer activities are evaluated in a COLO205 cell line. All three compounds with a log *P* value around 2 were cell permeable. However, **2B** and **3B** showed specific cytotoxicity in a malignant COLO205 cell line with a BRAF mutation (V600E) in comparison to a non-malignant wild-type BRAF HEK293T cell line. From further cell-based assays (cell cycle analysis, DNA fragmentation and caspase activation), we conclude that **2B** and **3B** treatment-induced selective cell death by inducing cell cycle arrest at the G0/G1 phase and caspase-mediated apoptosis (activation of the intrinsic and extrinsic pathways) are present only in BRAF V600E COLO205 cells. Further studies in the drug discovery pipeline might help develop these benzo[ $\alpha$ ]phenoxazines as promising chemotherapeutics for such refractory mutated cancers.

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### Introduction

RAS and RAF kinases are integral parts of the RAS–RAF–MAP2K (MEK)–MAPK signalling pathway that responds to several growth factors and cytokines.<sup>1–3</sup> There are several reports available indicating the importance of aberrantly functional KRAS and BRAF protein kinases in tumor maintenance.<sup>2,4–6</sup> Despite having a common activator (Ras) and substrate (MEK), the BRAF isoform has the highest activity among its three isoforms (A-,B- and C-RAF).<sup>7–10</sup> A specific point mutation BRAF

V600E (c.1799T→A) within the kinase activation domain of the BRAF protein is the most common BRAF mutation that constitutively activates substrate MEK eventually leading to development of several types of malignant and drug resistant cancers.<sup>11–14</sup>

Epidemiological studies have demonstrated that almost 8% of all solid tumors including 50% of melanomas, 30–70% of papillary thyroid carcinomas and 5–8% of colorectal adenocarcinomas are associated with this particular V600E mutation.<sup>15</sup> A dramatic response rate was observed when malignant melanoma cells with BRAF V600E mutation were treated with vemurafenib (a BRAF V600E selective inhibitor), however, a low clinical response was reported in colon cancer patients bearing the same mutation.<sup>16–18</sup> Most colon cancer cells harboring such a point mutation are highly metastatic and non-responsive to established treatment regimes *e.g.*, an anti-EGFR mAb (cetuximab, panitumumab) and/or chemotherapeutic inhibitors (vemurafenib, sorafenib, or MEK inhibitors).<sup>19–22</sup> Colon cancer cells acquire such characteristics by adopting different mechanisms *e.g.* amplification or altered splicing of BRAF genes, and an altered status of EGFR.<sup>13,23–25</sup> With no suitable biomarkers available to date, a proper prognosis for BRAF V600E mutation in cancers is still elusive for treatment of colorectal cancer with standard chemotherapeutic agents or anti-EGFR monoclonal antibodies.<sup>20,26–29</sup> Therefore understanding the importance and

<sup>a</sup>School of Biological Sciences, National Institute of Science Education and Research (NISER), Bhubaneswar 751005, Orissa, India. E-mail: badireenath@niser.ac.in

<sup>b</sup>Department of Chemistry, Savitribai Phule Pune University, Pune 411007, India. E-mail: sunitas@chem.unipune.ac.in; Fax: +91 2025693981; Tel: +91 2025601397 ext. 531

<sup>c</sup>Center for Material Characterization, National Chemical Laboratory, Pune 411008, India

<sup>d</sup>MPI für Chemische Energiekonversion, Stiftstr. 34-36, 45470 Mülheim an der Ruhr, Germany

† Electronic supplementary information (ESI) available: Characterization of **1B–3B**, HR-MS figures (Fig. S1, S5 and S9), FT-IR figures (Fig. S2, S6 and S10), <sup>1</sup>H and <sup>13</sup>C NMR (Fig. S3, S7 and S11), 2D gHSQCAD (Fig. S4, S8 and S12), and cyclic voltammetry (Fig. S13). Crystallography figures (Fig. S14–S17) and crystallographic tables (Tables S1–S8). CCDC 1412950 and 1413927. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5ra14949e



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**शोध पत्र - अर्थशास्त्र**

**अहमदनगर तालुक्यातील सेंद्रिय शेतीचा शेतकऱ्यांच्या उत्पन्नातील बदलाचा चिकित्सक अभ्यास (सन २००७ ते २०१२)**



\* प्रा. डॉ. श्रीमती व्ही. डी. पाटील

\*\* कु. शायिन यासिन शेख

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\* अर्थशास्त्र विभागप्रमुख, राधाबाई काळे महिला महाविद्यालय, अहमदनगर

\* सहायक विद्यार्थिनी

सेंद्रिय शेती :- भारत व चीन या देशात सर्वप्रथम शेतीची सुरुवात झालेली आहे. सेंद्रिय शेती करण्याकडे शेतकऱ्यांचा कल वाढत गेलेला दृष्टीस येतो कारण निसर्ग स्वतःच सेंद्रिय शेती करण्यासाठी एक आदर्श गरू असल्यामुळे संपूर्ण सेंद्रिय शेती पद्धतीच निसर्गाशी जवळीक साधणारी आहे. ह्या पद्धतीत जमिनीतील अन्नद्रव्यांचा ऱ्हास होत नाही. अथवा आजच्या गरजा भागविण्यासाठी मातीत निकृष्ट होऊ देत नाही. म्हणजेच मातीची सुपिकता कायम ठेवण्यास मदत करते. तसेच शेतजमीन एक जिवंत घटक मानला जातो व मातीतील सूक्ष्म जीवाणूंचे संरक्षण होते.

आय. फार्स :- सेंद्रिय शेती म्हणजे अशी वैविध्यपूर्ण शेती पद्धती की ज्यामध्ये शेती नियोजन सर्व प्रकारच्या रसायनांचा वापर टाळून

केलेली एकात्मिक शेती पद्धती, ज्यात पशुधन व्यवस्थापन पद्धतीचा अवलंब करून शेतीवरील व स्थानिकरित्या उपलब्ध स्त्रोतांचा वापर केला जातो.

नमुना निवड :- संशोधनासाठी अहमदनगर तालुक्यातील सेंद्रिय शेती पद्धतीचा ५ गावातील ९ शेतकरी कुटुंबांचा अवलंब करण्याचा एकूण १२७ एकर जमिनीचा अभ्यास केला आहे. त्यातील १०२ एकर जमीन प्रागायत आहे तर १८ एकर जमीन कोरडवाहू आहे. उद्दिष्टे :- १. सेंद्रिय शेती पद्धतीचा उत्पन्न साधनांत झालेल्या प्रादलांचा अभ्यास करणे.

२. सेंद्रिय शेती पद्धतीमुळे एकूण वार्षिक उत्पन्न सरासरी वार्षिक उत्पन्नातील झालेला प्रादलाचा अभ्यास करणे.

तक्ता क्र. १

शेतकरी कुटुंबांचा एकूण उत्पन्न स्त्रोतात झालेला बदल दर्शक तक्ता (आकडे रुपयामध्ये)

अ.क्र.	नियंत्रक गावाचे नांव	कुटुंब संख्या	शेती	उत्पन्न स्त्रोत (२००७-२००८)					एकूण वार्षिक उत्पन्न
				शेतीपुरक व्यवसाय	नोकरी	व्यापार	शेतमजुरी	स्वतःचा व्यवसाय	
१	गुंडेगांव	०५	६४.५२.००	२,८०,०००	३,००,०००	-	३,००,०००	१,००,०००	१०५,३२,०००
२	वाळकी	०१	१८,२८,०००	४०,०००	१,००,०००	-	६०,०००	३,००,०००	२३,४८,०००
३	हातवळण	०१	२,९०,०००	२५,०००	-	-	२०,०००	३,००,०००	१३,४५,०००
४	बहिरवाडी	०१	१०,००,०००	४०,०००	-	-	२०,०००	-	१०,८०,०००
५	ससेवाडी	०१	३,७७,०००	३०,०००	-	-	१०,०००	३,०००	४,२२,०००
एकूण			८३,६६	०३,२६	०३,९४	००	०३,२२	०५,५०	०१,२२

उत्पन्न स्त्रोत (२०११-२०१२)

अ.क्र.	नियंत्रक गावाचे नांव	शेती	शेतीपुरक व्यवसाय	नोकरी	व्यापार	शेतमजुरी	स्वतःचा व्यवसाय	इतर	एकूण वार्षिक उत्पन्न
२	वाळकी		७०,०००	१,५०,०००	-	५,००,०००	५,००,०००	५०,०००	७,७०,०००
३	हातवळण		५०,०००	-	-	५,००,०००	५,००,०००	३०,०००	५,००,०००
४	बहिरवाडी		४०,००,०००	७०,०००	-	-	-	५०,०००	४१,६०,०००
५	ससेवाडी		५,००,०००	६०,०००	-	-	-	१०,०००	५,९०,०००
एकूण			६१,३१	०९,४०	०८,६५	००	०८,२	१५,६३	०३,८१

संदर्भ:- प्राथमिक सर्वेक्षण नियंत्रित गट पाहणी अभ्यास

३. वरील तक्त्यावरून पुढील अनुमान काढता येईल.

१) सन २००७-०८ मध्ये शेती व्यवसायापासून मिळणारे एकूण उत्पन्न रु. १,०६,४७,०००/- इतके असून एकूण उत्पन्नाशी हे प्रमाण ८३.६६ आहे सन २०११-१२ मध्ये शेती व्यवसायापासून मिळणारे उत्पन्न रु. ४५,००,०००/- इतके घटलेले असून एकूण उत्पन्नाशी हे प्रमाण ६१.३१ इतके कमी झालेले आहे. गुंडेगाव, वाळकी व हातवळण या गावात दुष्काळाची स्थिती असल्यान शेतीपासून मिळणाऱ्या उत्पन्नात घट झालेली आढळून येते.

२) सन २००७-०८ मध्ये गुंडेगावातील सेंद्रिय शेतकरी कुटुंबांचे शेती व्यवसायापासूनचे उत्पन्न रु. ६,४५,२०००/- असून ते सर्वाधिक आहे. ससेवाडीत सेंद्रिय शेतकरी कुटुंबांना सर्वात कमी रु. ३,७७,०००/- इतके उत्पन्न मिळालेले आहे. सन २०११-१२ मध्ये बहिरवाडीतील शेतकरी कुटुंबांना शेती व्यवसायापासून सर्वात अधिक रु. ४०,००,०००/- इतके उत्पन्न मिळालेले आहे; तर सर्वात कमी उत्पन्न ससेवाडीत रु. ५,००,०००/- इतके आहे.

३) शेतीपुरक व्यवसाय, नोकरी स्वतःचा व्यवसाय व इतरापासून मिळणारे एकूण उत्पन्न सन २००७-०८ व सन २०११-१२ कालावधीत