INTRODUCTION

Human survival has always depended on plants. As soon as man had reached the stage of reasoning, he discovered plants that might be used as foods, as medicines, as narcotics in religious rituals or as poisons. Standing on the threshold of the third sahastrabdi, mankind has to confront many problems of which the problem of health is the most glaring one and has challenged his very existence of life.

This problem is not new and is rather originated since man existed as a species of *Homo sapiens* and claimed a separate identify for himself amongst the other species of the universe. It is an irony of fate that this problem is existing even today. But the basic difference between the ancient and the present circumstances is, that in the past diseases used to occur due to natural causes, whereas in the present, they occur not only due to natural causes but also due to increasing impact of materialism. The advancement of science and technology has not spared any pains in adversely affecting the normal health of mankind and had posed numerous health hazards. As a matter of fact situation is, that the outcome of modern civilisation and its creations are creating a tremendous havoc in the field of human health.
The history of medicine in India can be traced to the remote past. The earliest mention of the medicinal use of plants is found in the Rig Veda, having been written between 4500 and 1600 BC. In the works which followed, particularly Ayurveda (700 BC), the properties of various drugs have been given in detail. “Susruta Samhita” which was written not later than 1000 BC contains a comprehensive chapter on therapeutics and “Charaka Samhita”, written about the same period, gives a remarkable description of the material medica as it was known to ancient Hindus.

During the Hellenistic age in the Mediterranean area and near east, great many advances were made in medicine, which are exemplified by the great name of Hippocrates, Aristotle and Theophrastus. Hippocrates (460-377 BC), was Greek physician of antiquity and it traditionally regarded as the father of medicine. In his book, the described 400 plants are medical substances. Theophrastus (372-287 BC) was Greek peripatetic philosopher and pupil of Aristotle of his few surviving works, the major and nine books Periphyton historia (“Inquiry into plants”) in which he mentioned 500 drugs, and six books Periphyton action (Growth of plants”).

The prophet (peace be upon him) urged the people to turn away from magic practice priesthood, and idolatory, and to seek treatment based on medical science, as in one occasion he (peace be upon him) said:
“O servant of God, seek for medical treatment, God has put a remedy for every malady, clear to whoever knows it and unclear to whoever does not known it”.

The question arises as to how to face these health hazards and how and where the solution have to be found out. Man is oblivious by nature. It is his very nature that be wanders in the state of oblivion. At the same time be visualises the golden age and wants to enact of golden era. He has always been trying hard to overcome the hazards and holocausts and was always, herefor, inspired by near ideas hopes and aspiration. Man’s integrity is required to harness nature. The creator of the cosmos is indirectly controlling and directing the entire universe through nature.

“Little we see in nature that is ours, so said words – worth. “We have given away our hearts to a “Sordid Boon”. Words-worth, has commented.

Every plant has its herbal value and therefore, capable of providing medicinal effect. In Northern India, even today there is a custom of cooking and eating food under the ‘Amla’ (*Phyllanthus emblica*) tree on Somvati Amavasya or there is a very popular custom of offering water to “Pipal” (*Ficus religosa*) tree. But these customs have religious background and therefore, fast disappearing in the age of science. If sufficient attention has been paid on the scientific values, then something substantial would have
been found out. Systematic and fundamental approach in the chemical analysis of plants would have revealed the magic power hidden in them.

Thus with the rebirth or revival of learning, modern age of medical knowledge begins in 15\textsuperscript{th} century, and the 16\textsuperscript{th} and 17\textsuperscript{th} centuries saw an improvement of the practice of pharmacists and the influx of many new drugs of botanical and mineral origin from the new world.

Chemicals derived from plants have played a central role in the history of human kind. The age of discovery was fostered by explorations to find more economic trade routes to the East to bring back plant derived spices and other products. In deed the discovery of the new word, was a direct consequence of that effort. Plants continue to retain their historical significance as important sources of novel compounds useful directly as medicinal agents, as agrochemicals as model compounds for synthetic or semi synthetic structure modifications and optimization, as biochemical and / or pharmacological probes, and as sources of inspiration for generation of synthetic organic medicinal chemist. However, the discovery and development of fermentation based natural products began in the early 1940’s and the increasing sophistication of synthetic organic chemistry, interest in plant derived natural products a prototype for pharmaceuticals and agrochemicals wanes greatly during the decades of 1960’s through 1980’s.
Today a renewed interest in the potential of substances found in plants to provide prototypes for new pharmaceuticals and agrochemical is being evidenced. Plant derived compounds drugs which have recently undergone development include the anti cancer agents taxol and camptothecin, the Chinese anti malarial drug, artemisinin, the East Indian Ayurvedic drug, forskolin leaves extract of *Ginkgo biloba*, extract of rhizome and root of *Echinacea Pallida*, and extracts of flower head of *Matricaria recutita* (Chamomile). Moreover, etoposide is a reactively new semi synthetic anti neoplastic agent based on podophyllotoxin, a constituent of the mayapple (*Podophyllum peltatum*). *Atracurium besylate* is new synthetic skeletal muscle relaxant which 15 structurally and pharmacologically related to the curare alkaloids. Two important medicines, cromoglycate and aminodarone are based on khellin, a new molecular weight furanochromone, which is the principal active constituent of *Ammi Visnaga*. Indeed, over half the world’s 25 best selling pharmaceuticals for 1991 owe their origin to one a range of natural source materials.

In spite of numerous past successes in the development of plant derived drug products, it has been estimated that only 5 to 15% of the 6,000,00 existing species of plants have been systemically surveyed for the presence of biologically active compounds. It is important to mention that
over the last decade, high throughout screening against mechanistically pure physiologically targets has come to the fore front in the search for new chemical entities, and it totally revolutionized the drug discovery process and development. However, specific curative agents for a number of important diseases for example, malaria, leprosy, heart diseases, cancer, viral diseases and antibiotics resistant infections are still lacking.

The work undertaken for the present doctoral dissertation related to the isolation and structural studies on the chemical constituents of *Moringa pterygosperma* whose pharmacological significances properties were known since ancient times, however, only two flavonoid glycoside and steroidal saponins possessing antimicrobial activity has been isolated prior to these studies from this species. Phytochemical studies presented in this thesis involve the bioassay directed isolation of *Moringa pterygosperma* flower part and stem bark, which led to the isolation of novel drug potentials of the plant and numerous other new compounds present investigation also includes the preparation of several new flavonoids derivatives and evaluation of their anti bacterial, anti fungal and analgesic properties.

**PAST CHEMICAL WORKS**

Different workers had gone through its phytochemistry and the compound isolated from the various parts of the plant are mention in table.
<table>
<thead>
<tr>
<th>Part of the plant</th>
<th>Name of the Compound</th>
<th>Molecular Formula</th>
<th>Structure</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flower</td>
<td>Kaempferol</td>
<td>C_{15}H_{10}O_{6}</td>
<td><img src="image1" alt="Structure" /></td>
<td>1</td>
</tr>
<tr>
<td>Flower</td>
<td>Quercetin</td>
<td>C_{15}H_{10}O_{7}</td>
<td><img src="image2" alt="Structure" /></td>
<td>2</td>
</tr>
<tr>
<td>Flower</td>
<td>Quercetin 3-glyoside</td>
<td>C_{21}H_{20}O_{12}</td>
<td><img src="image3" alt="Structure" /></td>
<td>3</td>
</tr>
<tr>
<td>Flower</td>
<td>Rhamnetin</td>
<td>C_{16}H_{12}O_{7}</td>
<td><img src="image4" alt="Structure" /></td>
<td>1</td>
</tr>
<tr>
<td>Flower</td>
<td>Rhamnetin 3-glycoside</td>
<td>C_{22}H_{22}O_{11}</td>
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<td>2</td>
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<tr>
<td>Bark</td>
<td>β-Sitosterol</td>
<td>C_{29}H_{50}O</td>
<td><img src="image6" alt="Structure" /></td>
<td>3, 4</td>
</tr>
<tr>
<td>Part</td>
<td>Compound</td>
<td>Molecular Formula</td>
<td>Structure</td>
<td>References</td>
</tr>
<tr>
<td>------------</td>
<td>----------------</td>
<td>-------------------</td>
<td>-----------</td>
<td>------------</td>
</tr>
<tr>
<td>Stem</td>
<td>Sitosterone</td>
<td>C_{29}H_{48}O</td>
<td><img src="image1" alt="Structure" /></td>
<td>4</td>
</tr>
<tr>
<td>Leaf</td>
<td>Quercetagenin</td>
<td>C_{15}H_{10}O_{6}</td>
<td><img src="image2" alt="Structure" /></td>
<td>5</td>
</tr>
<tr>
<td>Leaf</td>
<td>3-methory Quercetin</td>
<td>C_{16}H_{12}O_{7}</td>
<td><img src="image3" alt="Structure" /></td>
<td>5</td>
</tr>
<tr>
<td>Leaf</td>
<td>Naiziminin 'A'</td>
<td>C_{18}H_{25}NO_{5}S</td>
<td><img src="image4" alt="Structure" /></td>
<td>6,7</td>
</tr>
<tr>
<td>Leaf</td>
<td>Naiziminin 'B'</td>
<td>C_{18}H_{25}NO_{5}S</td>
<td><img src="image5" alt="Structure" /></td>
<td>6,7</td>
</tr>
<tr>
<td>Leaf</td>
<td>Niazinin 'A'</td>
<td>C_{15}H_{21}NO_{6}S</td>
<td><img src="image6" alt="Structure" /></td>
<td>6,7</td>
</tr>
<tr>
<td>Tissue</td>
<td>Compound</td>
<td>Molecular Formula</td>
<td>Structure</td>
<td>References</td>
</tr>
<tr>
<td>----------</td>
<td>--------------</td>
<td>-------------------</td>
<td>-----------</td>
<td>------------</td>
</tr>
<tr>
<td>Leaf</td>
<td>Niazinin ‘B’</td>
<td>C_{15}H_{21}NO_6S</td>
<td><img src="image" alt="Structure" /></td>
<td>6,7</td>
</tr>
<tr>
<td>Seed</td>
<td>Linoleic acid</td>
<td>C_{18}H_{32}O_2</td>
<td>CH₃-(CH₂)₄ CH=CH-CH₂ -CH=CH(CH₂)₇ -COOH</td>
<td>8,9</td>
</tr>
<tr>
<td>Seed</td>
<td>Phenylalanine</td>
<td>C₉H₁₁O₂N</td>
<td><img src="image" alt="Structure" /></td>
<td>8,9</td>
</tr>
<tr>
<td>Seed</td>
<td>Oleic acid</td>
<td>C_{18}H₄₂O₂</td>
<td>CH₃(CH₂)₇ CH=CH(CH₂)₇ COOH</td>
<td>8,9</td>
</tr>
<tr>
<td>Seed</td>
<td>Stigmsterol</td>
<td>C_{29}H₄₈O</td>
<td><img src="image" alt="Structure" /></td>
<td>10</td>
</tr>
<tr>
<td>Root</td>
<td>Benzyl isothiocyanate</td>
<td>C₈H₇NS</td>
<td><img src="image" alt="Structure" /></td>
<td>11,12</td>
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</tbody>
</table>
Problem Undertaken

The work included in this thesis involves the chemical study of *Moringa pterygosperma* plant.

*Moringa pterygosperma (Gaertn.)*:

*Moringa pterygosperma* is a small, fast growing evergreen or deciduous tree that usually grows up to 10 or 12 m in height. It has a spreading, open crown of drooping fragile branches, feathery foliage of tripinnate leaves, and thick, corky, whitish bark.

The leaves are bipinnate or more commonly tripinnate, up to 45 cm long, and are alternate and spirally arranged on the twigs. Pianate and pinnules are opposite; leaflets are 1.2 to 2.0 cm long and 0.6 to 1.0 cm wide, the lateral leaflets elliptic, the terminal ones obovate; petioles of lateral leaflets are 1.5 to 2.5 mm long, those of terminal ones 3 to 6 mm long. The leaflets are finally hairy, green and allmost hair less on the upper surface, paler and hair less beneath, with red tinged midveins, with entire morgines, and are rounded or blunt – pointed at the apex and short pointed at the base.

The fragrent, bisexual, yellowish white flowers are borne on slender, hairy stalks in spreading are drooping axillary clusters 10 to 25 cm long.
Individual flowers, set in a basal cup 3 mm long, are approximately 0.7 to 1.0 cm long and 2.0 cm broad, with five unequal yellowish-white thinly veined, spathulate petals five stamens with five smaller sterile stamens, and a pistil composed of a one celled ovary and slender style.\textsuperscript{13-15}

The fruits are pendulous, linear, three sided pods with nine longitudinal ridges, usually 20 to 50 cm long, but occasionally up to 1 m or longer, and 2.0 to 2.5 cm broad. The pods, each usually containing up to 26 seeds, are dark green during their development and take approximately 3 months to nature after flowering.\textsuperscript{16} They turn brown on maturity, and split open longitudinally along the three angles, releasing the dark brown, trigonous seeds. Seeds measure about 1.0 cm in diameter, with three whitish papery wing on the angles.\textsuperscript{17}

The bark is whitish gray, thick, soft, fissured and warty or corky, becoming rough. When wounded, the bark exudes a gum which is initially white in colour but changes to reddish brown or brownish black on exposure.
Distribution and Ecology:

Drumstick tree is indigenous to the Himalayan foothills of South Asia from North eastern Pakistan (33°N, 73°E) to Northern West Bengal state in Indian and Northeastern Bangladesh where it is commonly found from sea level to 1,400 m on recent alluvial land or near riverbeds and streams. It grow at elevation from sea level to 1400m.\textsuperscript{15} it is cultivated and has become naturalized in other parts of India, Pakistan, and Nepal, as well as in Afghanistan, Bangladesh, Shri Lanka, Southeast Asia, West Asia, the Arabian Peninsula, East and West Africa, throughout the west Indies and Southern Florida, in central and South America from Mexico to Peru, as well in Brazil and Paraguay.

In the South Asian native range of drumstick tree, annual temperature fluctuations tend to be large, with minimum and maximum shade temperatures ranging from -1 to 3\textdegree C and 38 to 48\textdegree C during the coldest and warmest months respectively. In this region, annual rainfall range from 750 to 2200mm. Within is native and introduced ranges, mean annual temperatures range from 12.6\textdegree C to 40\textdegree C, with annual rainfall of at least 500mm.\textsuperscript{18-22}
Propagation:

*Moringa pterygosperma* is easily propagated by cuttings, but is difficult to propagate by air layering. Propagation by cuttings is often preferred to plants raised from seed, which are reportedly slower to flower and fruit and produce fruit of inferior quality. Large branch or stem cutting 1.0-1.5 m long and 4-5 cm in diameter are typically planted during the summer rainy season in Southern India. Large branch or stem cutting, planted in moist soil to a depth of about 50 cm, root readily and grow to sizeable trees within a few months. Some studies suggest that trees grown from cutting and may be preferable for planting in semiarid and arid regions where water table depth is a potential growth-limiting success of branch cutting was better during the spring months than either the summer rainy season or the cooler or winter months. Higher rooting percentages have been obtained by treating cutting with the plant growth regulator Indolbutyric acid (IBA) at concentration of 50 ppm for 24 hours prior to planting.  

Ethanomedical uses:

*Moringa pterygosperma* has been used in the traditional medicine passed down for centuries in many cultures around the world, for skin infection, anemia, anxiety, asthma, black head, blood impurities, bronchitis chest congestion, cholera, conductivities, cough, diarrhea, eye and ear infections, fever, swelling, headaches, abnormal blood pressure pain in
joints, respiratory disorders, scurvy, semen deficiently, sprain, tuberculosis, for intestinal worms, lactation, diabetes and pregnancy.\textsuperscript{24-72}

**The medicinal application of *Moringa pterygosperma***

<table>
<thead>
<tr>
<th>S. N.</th>
<th>Part of the tree</th>
<th>Medical Purposes</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Flower</td>
<td>anti microbial, ulcer, throat infection, anti tumor, abortifcent, catarrh, hysteria, headaches, anti cancer, diuretic, rheumatism</td>
<td>24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37</td>
</tr>
<tr>
<td>2</td>
<td>Bark</td>
<td>anti microbial, anti ulcer, anti cancer, anti tumor, snakes bite, scorpion bite, epilepsy, headaches, birth control</td>
<td>38, 39, 40, 25, 41, 42, 43, 44, 26, 27, 45, 46</td>
</tr>
<tr>
<td>3</td>
<td>Leaves</td>
<td>Urinary tract infection, anti bacterial, alzheimer's, anit virus, scury, HIV-AIDS hepatic, fever, anti anemic, anti hypertensive, diabetes, diuretic, diarrhea, anti oxidant</td>
<td>47, 48, 49, 50, 51, 52, 53, 43, 54, 55, 56, 35, 26, 57, 58, 59, 60, 61, 62, 63, 64, 27, 36, 37, 42, 46, 65</td>
</tr>
<tr>
<td>4</td>
<td>Seed</td>
<td>Gastritis anti inflammatory, anti cyano bacterial activity, rheumatism, arthritis antispasmodic.</td>
<td>66, 65, 67, 68, 69, 32, 26, 47, 70,</td>
</tr>
<tr>
<td>5</td>
<td>Root</td>
<td>Aphrodisiac, kidney pain, dental caries, fever, ulcer, asthma, endocrine disorders, diarrhea, epilepsy, scurvy.</td>
<td>26, 25, 71, 72, 37, 42,</td>
</tr>
</tbody>
</table>
Present works:

During the present work, following five compound have been isolated and studied from the flower and bark part of the *Moringa pterygosperma*.

MF-1: Kaempferol 7- O- β - D- alloside

MF-2: Quercetin 3-O- α - L rhamosyl (1 \(\rightarrow\) 6) - β - D- glucoside

MF-3: Rhamnetin 3-O- (2\(^\prime\)-galloyl)- β -D-galactopyranosyl

\(-4\'\) - β - D- xylopyranoside

MB-4: β - Sitosterol 3-O- β -D- galactopyranoside

MB-5: 4-Hydroxy 3-methoxy cinnamic acid

During these investigation, the basic concept about the general trends on plant chemistry chromatography\(^ {73-79}\) and spectroscopy\(^ {80-85}\) was made clear by the available literatures.
REVIEW ABOUT OTHER CONSTITUENTS OF MORINGA PLANTS:

During the present work a number of compounds have been isolated from the flower and bark of *Moringa pterygosperma*. The major entities studied have been found to belong to two main group of naturally occurring plant pigments, viz.

1. Flavonoids
2. Terpenoids

1. FLOVONOIDS:

The terms flavonoid was first applied by Geissman and Hinreiner to embrace all those compounds their structure is based on that of flavones (2-phenyl chromone). They are widely distributed yellow plant pigments and occur either in free state or as glycosides or associated with tannins.

![Flavone (I)](image1)

![Flavonol (II)](image2)

When the hydrogen atom at C-3 in the pyrone ring is replaced by a hydroxyl group, 3- hydroxyl flavones or flavonol is produced which is
the first member of the class of flavonols. The various flavones and flavonols are hydroxyl derivatives of the flavones (I) and flavonol (II) respectively. Also included in the flavonoids are the flavanones, flavonols or dihydro flavonol and the flavon – 3,4 – diols. It should be noted that there are also five classes of compounds, the dihydrochalones, the isoflavones, and the aurones, which do not actually possess the basic 2 phenyl –chromane skelton (I) but are closely related both chemically and biosynthetically to the other flavonoid types that they are always included in the flavonoid group.

![Chalcone (III)](image1.png)

![Isoflavone (IV)](image2.png)

![Aurones (2-benzyl coumarone) (V)](image3.png)
BIOSYNTHESIS OF FLAVONOIDS:

Interest in how plants synthesize their flavonoids developed even before the structures of these pigments were fully established. Owing to the curiosity of the chemists and bio-chemists, several attempts have been made in the field since 1910. In the subsequent years, considerable progress has been made in the elucidation of the biosynthesis of flavonoids, mainly by studies of with labelled precursors in vivo. The review by Grisebach (1965) covers the work to the end of 1963. One major conclusion from these earlier studies is that flavonoids are formed in a “grid system” as illustrated in figure (a).

![Flavonoid Synthesis Diagram](image-url)

**Fig- a**
In recent years, bio synthetic studies have been based on feeding experiments using labelled precursors. These have been successful in establishing how the C-15 skeleton is build up but have not yet revealed unequivocally the nature of subsequent steps in synthesis. The feeding experiments using radioactive tracers revealed that flavonoids are formed by a combination of shikimic acid pathway and the acetate (poly ketide) pathway as indicated in the figure “b”. Pathways concerning general phenyl propanoid metabolism and individual pathways of flavonoids bio synthesis have been further reviewed by Ebel. (1974)\(^9\).
The enzymology of flavonoids biosynthesis has made particularly rapid progress. It became firmly established that all classes of flavonoids derive their carbon skeleton from compound of intermediary cell metabolism through the action of two consecutive (general phenyl propanoids, and flavonoid glycoside) pathways.

(a) General phenyl propanoid metabolism:

Phenyl propanoids units derived from the shikimate pathway are common structural elements of all flavonoids compounds and of various other classes of phenyl propanoids such as lignin, stilbenes and cinnamate ester. The sequence of reactions converting phenylalanine into the Co~A ester derivatives of substituted cinnamic acid was therefore termed general phenyl propanoids metabolism (Ebel 1974). The
enzyme catalysing the individual steps are phenylalanine ammonia-lyase, cinnamate 4-hydroxylase and 4-coumarate CoA ligase.
(b) **Individual pathways of flavonoids bio-synthesis:**

All classes of flavonoids are bio-synthetically closely related; with a chalcone being the first common intermediate. Earlier feeding experiments with radioactively labelled precursors have established that the carbon skeleton is derived from acetate and phenylalanine; ring “A” is formed by a “head to tail” condensation of three acetate units and ring “B” as well as carbon atoms 2, 3 and 4 of the heterocyclic ring “C” arise from phenylalanine. Most of the results of this work have been reviewed previously by Hehlbrock and Grisebach (1975).[^90]
phenylalanine

\[ \text{COOH} \]

\[ \text{COOH} \]

4-Coumaroyl-CoA

\[ \text{S-CoA} \]

Acetyl-CoA

\[ \text{COOH} \]

Malonyl-CoA

Flavanone
Scheme illustrating the position of the chalcone as the first common intermediate in the biosynthesis of all classes of flavonoids.

Recent investigations at the enzymatic level have largely confirmed the hypothetic steps which had been deduced from incorporation experiments. In particular, detailed knowledge of the central reaction of flavonoid biosynthesis the condensation acyl residues form molecule of 4- coumaroyl – Co~A and three molecule of malonyl – Co~A was obtained previously.
UDP Glu → UDP

UDP Glu A → UDP Aplose

CO₂ + UDP → Aplose

malonyl-CoA → CoA~ SH

SAM → SAH

UDP Glu → UDP Glu

UDP Glu → UDP

UDP Glu → UDP

UDP Glu → UDP
The reason why plants accumulate flavonoid constituents in them is not altogether clear even today. However, because flavonoids are not closely involved in primary metabolism, it is probably that their major role is a biological one in relation to insects and animals which pollinate or feed on plants. Some flavonoids certainly provide the plant with one of a number of means (colour) of attracting insects such as butter flies and bees to them for purpose of pollination and others may well provide a means (bitter taste) of repelling caterpillars from feeding on their leaves.

The other major function of these class of compounds are as follows:

**FUNCTION OF FLAVONOIDS:**

- Flavone (Chrysoeriol)
  - 7-O-malonyl-apisyl glucoside

- Flavonol (Isorhamnetin)
  - 3,7-Di malonyl glucoside
(1) Antimicrobial activity of flavonoids:

Extracts of various medicinal plants containing flavonoids have been reported to possess antimicrobial activity.\textsuperscript{91-92} The antibacterial activities of isoflavonoids flavonoid\textsuperscript{93} and glycosides of luteolin and apeggenin have been reported. Quercetin has also been reported to inhibit several viruses.\textsuperscript{94-95} Flavonoids from the leaves of various species of grindelia\textsuperscript{96} and a new flavonoid glycoside from \textit{Vicia angustifolia}\textsuperscript{97} have also been reported to exhibit antibacterial activity. A detailed study of 120 species of the pteridophytes has shown that about 70\% of them are antibiotic activity.\textsuperscript{98} Antimicrobial, antiamoebic and antiviral activity of 20 species of tabernoemontana have been recently investigated.\textsuperscript{99} In a recent investigation, the flavonoid rich extract of ten plants were shown to possess both anti fungal and anti bacterial activity against several test organism\textsuperscript{100}.

(2) Flavonoids as antioxidants:

Several flavonoids serve as antioxidants for ascorbic acid, apparently by chelating metals from reaction mixture. This depends primarily on the 3-hydroxy -4- carbonyl and the 3',4' dihydroxy grouping (Clements & Anderson 1961; Samoroclove-Bianka 1965).\textsuperscript{101-102}
(3) **Flavonoids as enzyme inhibitors:**

Flavones and Flavonols with 3'-4' and 7- hydroxyl group are potent inhibitors of bovine pancreatic ribonuclease.\(^{103}\) Methoxylation at the 6 or 8 position decreases inhibitory activity. The aglycones are much more effective inhibitors than their glycosides.

(4) **Flavones and visible colour :**

Flavonoids are capable of giving almost every colour in rainbow except green, (Bloom and Vickery, 1973)\(^{104}\) found that pattern partitioning in yellow flowered *mimulusluteus* was due to mixture of carotenoids and flavonoids.

(5) **Photo sensitizing and energy transferring compounds:**

Ivie and Casida (1971)\(^{105}\) reported that quercetin and related substituted 4 chromones accelerate the photo alteration of chlorinated cyclodiene insecticides under field condition. It is analogous to predict that they may play a role in the photo decomposition of either natural or synthetic toxins falling on these surfaces.

(6) **Flavonoids in Malignancy:**

Several flavonoids are moderately effective against laboratory cultures of malignant cells. Eupatin and Eupatoretin (Kupchan et.al
1969)\(^{106}\) are all moderately effective against a carcinoma from nasopharynx.

**CHEMOSYSTEMATICS**

Flavonoid are common in higher plants but for some reasons they appear to be absent in bacteria, fungi and algae. For a long time, it was through that only vascular plants were able to produce flavonoids but it has recently been shown that certain mosses such as Bryum (Bendz et.al, 1962, Bendz and Martensson, 1963)\(^{107-108}\), are able to synthesise anthocyanins, while another moss genus mnium (Melchert and Alston 1965)\(^{109}\), produces flavones, even flavones C-glycosides. Micro organism although experts in polyketide synthesis, seen rarely to combine the shikimic acid and polyketide pathway.

In several families like Podocarpaceae, Iridaceae, Moraceae, Amaranthaceae, Rosaceae and particularly Leguminosae rearranged flavonoids, isoflavonoids, occur but not to the exclusion of compound of the more generally encountered flavine type. In almost every taxonomically oriented flavonoid. Studies of recent years, new compounds have been found\(^{110}\) some correlations with biological features have emerged and data have been produced to throw new light on plant relationship. Further work in
this field is bound to be rewarding from both the chemical and biological point of view.

2. TERPENOIDS:

The terpenoids from a group of compounds the majority of which occur in the plant kingdom; a few terpenoids have been obtained from other sources. The simple mono and sesauiterpenoids are the chief constituents of the essential oils, these are the volatile oil obtained from the sap and tissue of certain plants and trees.

The di terpenoids and triterpenoids which are not steam volatile are obtained from plant and tree gums and resins.

Triterpenoids:

The term “triterpenoids” refers to a group of natural products containing thirty carbon (C\text{30}) atoms based on six isoprene units. This definition through generally applicable is by no means rigid, since several substances which contain more are less than thirty (C\text{30}) carbon atoms and also those which do not strictly follow the isoprene rule have been isolated and characterised as triterpenoids during the recent years.

Triterpenoids are the most umbiquitous non steroidal secondary metabolites in terrestrial and marine flora and fauna. Their presence, even in
non photosynthetic bacteria, has created interest from both evolutionary and functional aspects. Although medicinal uses of this class of compounds are rather limited considerable recent work in this regard strongly indicates their great potential drug. Moreover, despite the remarkable diversity that is already known to exist among the carbon skeletons of triterpenes, new variants continue to energy.

The invention of highly sophisticated physiochemical techniques and the contemporary development in the biogenetic theories have been mainly responsible for the isolation and identification of new unconventional type of triterpenoids.

Earlier surveys in this field have been made by Holtzen et.al\textsuperscript{111} White\textsuperscript{112} and Halsall et.al\textsuperscript{113}. Recently the triterpenoids saponins and their sapogenins have been reviewed by Basu et.al\textsuperscript{114} and Daloze\textsuperscript{115} has dealt with, current research in triterpenoids chemistry. The triterpenoid field for the period 1963-71 excluding the triterpenoids saponins, their genins and their biogenesis which have already been covered\textsuperscript{116}.
BIOGENESIS:

Another term used in connection with the study of the synthesis of natural products in the living organism in biogenesis.

Biogenesis appears to have several meaning. One is that biogenesis and biosynthesis are synonymous. Biogenesis is a collection of hypothesis which have been proposed to describe the synthesis of natural products in the living organism, whereas bio-synthesis in the living organism. Reaction which are commonly postulated in biosynthesis are oxidation, hydrogenation, dehydrogenation, dehydration, esterification, hydrolysis, carboxylation, decarboxylation, amination, deamination, isomerisation, condensation and polymerization other reaction which are known to occur in biological syntheses are O-,N- and C- methylation but C-methylation is much rarer than those mentioned above.

Isotopic labeled product is isolated after a period of incubation, we have seen according to special isoprene rule, terpenoids are built up of isoprene unit jointed head to tail. The isoprene unit is the basic unit, fundamental units used in the cell in synthesis are water, CO$_2$, formic acid (as active formate) and acetic acid (as active acetate). These active compounds are acyl derivatives of Co-enzymes A. This Co-enzyme is a complex thiol derivatives and it usually written as Co~A-SH, but Co~A is
also in common usage. Thus acetyl co-enzyme A may be represented as $\text{CH}_3\text{Co}^{-}\text{S} \text{CoA}$ or $\text{CH}_3\text{Co} \text{Co}^{-}\text{A}$. Thus compound is energy rich.

The biosynthesis of terpenoids can be subdivided into three definite steps.

1. The formation of a biological isopentane unit from acetate.
2. The condensation of this unit to form acyclic terpenoids.
3. The conversion of acyclic into cyclic terpenoids.

Anisotropic of the functional group also affects the chemical shift of the protons other than methyl group. In the $\beta$-amyrin series a lactone bridge from C-28 to C-21 results in the up field shift of the olefinic protons$^{117}$. A method for the identification of protons on a carbon bearing a hydroxyl group through methylation which result in the up field shift by 0.6 ppm$^{118}$ has been reported as an alternative to acetylation the fact that the protons lying in the region of high electron density tend to be deshielded in benzene solution, has been exploited in structure determination$^{119}$. The configuration of the aldehyde groups located at 4- position in triterpenoids has also been deduced from their chemical shift.
BIOSYNTHESIS OF TERPENOIDS

The diverse metabolic pathway of plant terpenoids are all rooted in the formation of only two isomeric five carbon (C_{5}) precursors, dimethylallyl pyrophosphate (DMAPP) and isopentenyl pyrophosphate (IPP). DMAPP and IPP are formed in the mevalonate (MEV) pathway and in the 2C-methyl-D-erythritol-4-phosphate (MEP) pathway. The smallest plant triterpenoids, the hemiterpenoids (C_{5}), can be formed directly from DMAPP by terpenoid synthase (TPS) activity. Alternatively, assembly of two, three or four C_{5} unit by prenyl transferases (PT) yield geranyl pyrophosphate (GPP; C_{10}). Farnesyl pyrophosphate (FPP C_{15}) and geranyl geranyl pyrophosphate (GGPP, C_{20}) are the substrates for families of TPS enzymes and serve as the immediate precursors for the diverse groups of all monoterpenoids (C_{10}), sesquiterpenoids (C_{15}) and diterpenoids (C_{20}), respectively. In addition, pairwise condensation of FPP and GGPP gives rise to the class of triterpenoids (C_{30}) and tetraterpenoids (C_{40}), respectively and assembly of an undefined number of C_{5} precursors yield polyterpenoids. In addition to the regular terpenoids (C_{n}X_{5}), a large number of irregular terpenoids and terpenoids derivatives as well as terpenoids conjugates are formed in plants.
Glycolysis

Me \( \text{CHO} \)
\[
\begin{align*}
C &= O + \text{CHOH} \\
\text{COOH} &\quad \text{CH}_2\text{O}-\text{PO}_3 \\
\text{Pyruvic acid} &\quad \text{D-Gluceraldehyde} \\
\text{3-Phosphate} &\quad \text{3-Phosphate}
\end{align*}
\]

TPP \rightarrow \text{CO}_2

Me \( \text{C} = \text{O} \)
\[
\begin{align*}
\text{CHOH} &\quad \text{CHOH} \\
\text{CH}_2\text{O}-\text{PO}_3 &\quad \text{CH}_2\text{O}-\text{PO}_3 \\
1\text{-Deoxy-D-xylose} &\quad -5\text{-phosphate} \\
\text{(DOXP)} &\quad \text{(DOXP)}
\end{align*}
\]

Reduction 2x with NADPH

Me \( \text{C} = \text{O} \)
\[
\begin{align*}
\text{CHOH} &\quad \text{CHOH} \\
\text{CH}_2\text{O}-\text{PO}_3 &\quad \text{CH}_2\text{O}-\text{PO}_3 \\
\text{2-C- methyl-D-erythritol} &\quad \text{2-C- methyl-D-erythritol} \\
\text{4-phosphate (MEP)} &\quad \text{4-phosphate (MEP)}
\end{align*}
\]
Mevalonate Pathway:

Mevalonate $\xrightarrow{ATP \rightarrow ADP} 5$-Phosphomevalonate

$\xrightarrow{ATP \rightarrow ADP}$ 5-dihosphomevalonate

Isopentenyl pyrophosphate (IPP)

Dimethylallyl pyrophosphate (DMAPP)
MEP/DOXP/non mevalonate pathway:

2-C-methyl D-erythritol
4-Phosphate

2-C-methyl D-erythritol
2,4-cyclodiphosphate
After the formation of IPP and DMAPP, there exists in all organisms a central route to the universal building blocks needed for mono, sesqui-, di-, tri and tetra-terpene bio synthesis.
DMAPP + IPP \rightarrow \text{Geranyl pyrophosphate (GPP)}

GPP + IPP \rightarrow \text{Farnesyl pyrophosphate (FPP)}

FPP + IPP \rightarrow \text{Geranylgeranyl pyrophosphate (GGPP)}

FPP + FPP \rightarrow \text{Diterpenes}

2 molecules \rightarrow \text{Triterpenes (steroids)}

\text{C-10 building block} \rightarrow \text{C-15 building block} \rightarrow \text{C-20 building block} \rightarrow \text{C-30} \rightarrow \text{C-40 building block} \rightarrow \text{Tetraterpenes}
REFERENCES


47. Shaw, B.P., and Jana, P.; Clinical assessment of Sigru (Moringa oleifera Lam.) on Mutrakrichra Nagarjun, 231-235, (1982).


83. Wehrii, F.W., Wirthlin; "Interpretation of C$^{13}$NMR Spectra", 7,18,19,22,40 (1981).


