Importance of Terpenoids and Essential Oils in Chemotaxonomic Approach

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Chemotaxonomy of plants involves the study of chemical variation in different types of plants and use of this information in classification of plants. Chemotaxonomy consists of the investigation of the distribution of chemical compounds or groups of biosynthetically related compounds in series of related or supposedly related plants. Since ancient times, the essential oil and terpenoids of many aromatic plants have been used as bioactive ingredients in drug, food, perfumery and cosmetic formulations all over the world and so it is worthwhile to study their role in chemotaxonomy. They are distributed in families like Myrtaceae, Lauraceae, Rutaceae, Lamiaceae, Asteraceae, Umbelliferae, Verbenaceae and Piperaceae. To detect even traces of chemical compounds during chemical analysis sophisticated techniques have also been introduced in chemotaxonomy of medicinal plants.

Keyword: Chemotaxonomy, Essential Oils, Terpenoids, Chemical Analysis.

1. Introduction

The application of chemistry to systematics is chemotaxonomy or chemical taxonomy. Natural systems of classification should be based on the analysis and harmonization of evidence from all organs, tissues and parts. The external morphological study alone is not adequate and other branches of study are of considerable value in proper assessment of the systematic status of a taxon and its phylogeny. The taxonomic contributions of chemotaxonomy have made an equally great help to support the ideas of classification and phylogeny. The rise of chemotaxonomy has been the development of sophisticated techniques in chemical analysis which can detect even trace of chemical compounds[1]. Why we go for chemotaxonomic classification?

- Disagreement among botanist for insufficiencies of the origin and progression of plant life and also they are less complex.
- Invariable composition and structure of given determined chemical constituents.
- The percentage or composition of any given compound in a plant would give the progression of a plant, species, genus.
- Variation in chemical constituents can be exactly described in terms of definite structural configuration.
- Provide way to understand their biosynthesis.
- These biosynthetic pathways are helpful in chemical classification[2].

An enormous range of plant substances are covered by the word ‘terpenoid’, a term which is used to indicate that all such substances have a common origin. They have units of isoprene. They range from the
essential oil components the volatile monoterpenes and sesquiterpenes (C\textsubscript{10} and C\textsubscript{15}) through less volatile diterpenes (C\textsubscript{20}) to involatile triterpenoids and sterols (C\textsubscript{30}) and carotenoid pigments (C\textsubscript{40}).

<table>
<thead>
<tr>
<th>No. of isoprene units</th>
<th>Carbon No.</th>
<th>Name/Class</th>
<th>Main Types and Occurrence</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C\textsubscript{5}</td>
<td>Isoprene</td>
<td>Detected in Hamamelis japonica leaf</td>
</tr>
<tr>
<td>2</td>
<td>C\textsubscript{10}</td>
<td>Monoterpene</td>
<td>Menthol from mint</td>
</tr>
<tr>
<td>3</td>
<td>C\textsubscript{15}</td>
<td>Sesquiterpene</td>
<td>In essential oils</td>
</tr>
<tr>
<td>4</td>
<td>C\textsubscript{20}</td>
<td>Diterpene</td>
<td>In plant resins</td>
</tr>
<tr>
<td>6</td>
<td>C\textsubscript{30}</td>
<td>Triterpene</td>
<td>Sterols (Sitosterol)</td>
</tr>
<tr>
<td>8</td>
<td>C\textsubscript{40}</td>
<td>Tetraterpene</td>
<td>Carotenoids (Beta-carotene)</td>
</tr>
<tr>
<td>N</td>
<td>C\textsubscript{n}</td>
<td>Polyisoprene</td>
<td>Rubber, ex.: in Hevea brasiliensis</td>
</tr>
</tbody>
</table>

Table 1: Classification of volatile oils on the basis of number of isoprene units:

They are present in all volatile oils and they are colourless liquids or solids. They have a characteristic smell and most of them are optically active. They easily get oxidised. They are soluble in alcohol, chloroform, ether, acetone and carbon disulphide and insoluble in water. Therapeutically exhibits activities like analgesic, carminatives, anthelmintics, antiseptic, counter irritant. They are also used in soaps, cosmetics, incense sticks, perfumery and food articles. They also play a major part in pesticides and insecticides industries\textsuperscript{[5]}. Terpenoids contributed major part of the worldwide trade of plant derived refined compounds, valued about US$ 7.7 billion. The present export volume of crude drugs from India stands at about 42,600 tonnes valued around US$ 30 million. In India, the production of turpentine oil from pine is well established industry; having annual production about 35000-40000 tonnes annually. India’s share in world export of essential oil and perfumery materials is merely 0.4%. Often the terpenoids are thought of in narrow sense as the components of plant essential oils. Volatile oils are odorous and volatile constituents of plant and animal species. Chemically they are derived from oxygenated derivatives and hydrocarbons. They are present in entire plant or any other part such as bark, leaf, fruit, root, wood and seed. They are secreted in lysogenous and schizogenous gland, ducts and glandular trichomes. In few cases the volatile oil does not prexist, but is formed by the decomposition of a glycoside. \textsuperscript{[5]} When terpenes are removed from volatile oils we call them terpeneless volatile oil. The world trade in essential oils and its products is vast and the oils of major importance are anise, citronella, clove, geranium, lemon grass, sandalwood and vetiver which occupy a prominent position in the world market of medicinal and aromatic plants serving as raw material to pharmaceutical and other plant industry. Essential oils are used in aromatherapy, as antiseptic, in cough and cold, soothing agent, skin irritation, skin care, burns, anthelmintic, potent sedative, respiratory and sinus problems, cooling effect on muscles and tissues and in digestion of food. The total consumption of perfumery and flavouring materials in India is about 4800 metric tonnes per annum. The food technology, oral hygiene and pharmaceutical flavours share around 900 metric tonnes and rest represent perfumery.
Presence or absence of essential oils regardless of their compositions provides a very valuable taxonomic character. In fact, the volatile oil constituents of aromatic plants are at present regarded not only as important bioactive ingredients, but also as target metabolites emitted by plants to balance their status in their natural habitat or in agronomic conditions of fixed protocol. Some of the important essential oils of chemotaxonomic importance are:

1.1 Terpenoids in Chemotaxonomy:
Terpenoids occur mostly in higher plants. According to Lawrence they are mostly found in Myrtaceae, Lauraceae, Rutaceae, Lamiaceae, Asteraceae, Apiaceae, Poaceae, and Cupressaceae.

1.1.1 Monoterpenes: They are the hydrocarbons which are most abundantly present. They have their boiling point range between 140°-180°C. They may be acyclic (example: Myrcene), monocyclic (example: p-cymene), or bicyclic (example: pinenes). Sometimes they constitute 90% of essential oil (example: Citrus oils or in turpentines. Further these may be optically active. The predominance of monoterpene (-) enantiomers in the emission of some European Pinus and Abies species was explained by Pearson (1990, 1993). A monoterpene lactone is nepetalactone, the principle odour constituent of Catmint Nepetacataria, Labiatae, a plant which has a peculiar attraction for the domestic cat because of its odour.

1.1.2 Sesquiterpenes: A very large number of Sesquiterpenes are common constituents of the essential oils of higher plants and therefore, may contribute to the pharmacological properties attributed to these volatile fractions.
variations in this series are of the same nature as in monoterpenes with hydrocarbon alcohols and ketones being the most important ones. Examples are β-bisabolene, longifoline, farnesol, santalol, sinesals, cedryl acetate. Recently by GC broad chemodenes were distinguished by the presence of carvone and presence of absence of dill apiole[9].

1.1.3 Diterpenes: The structure of diterpenes is highly variable and strictly dependent on their biogenesis. Diterpene containing drugs have different applications such as anti hypertensive, co–carcinogenic, anti-oxidant, hallucinogenic properties etc. Diterpenoids occur in the Garryaceae, a family difficult to classify on the base of morphological grounds. The chemotaxonomy of Sideritis species was evaluated and its acetone extract was shown to possess insecticidal and ascaricidal activity. The extract was found to contain linearol, linearal, isolinearol and siderol[10].

1.1.4 Triterpenes: These show a lot of taxonomic value when combined with other constituents such as phenols and flavanoids. Triterpenes have therapeutic potential in many fields such as cytostatics, insecticides, antinflammatory agent etc. They play role in confirming the relation of Pittosporaceae. This family has more affinity with Araliaceae than Saxifragaceae. The triterpenes of 5 lithocarpus species were examined and they were of friedo unrearranged oleanene group viz, friedelin, friedelan, 3-β-taraxerol and β-amyrin. Glutinol was also present except in L.-harlandi where frielan 2-α, 3-β diol was found. In addition , 3 new cycloarantane triterpene, lithocarpolone, lithocarpdial and 24- methylene cycloartane 3-β, 21 diol were found in L. polystachya[11].

1.1.5 Tetraterpenes: Carotenoids interfere with photoxidation processes such as treatment of photosensitization linked to porphyria, also ingredient of tanning pills and food technology industry. A qualitative and quantitative examination of carotenoids of pure cultures of four marine micro algae including chroomonas salina, vaucheria sassilis, cacolithus and Huxleyi is reported. The latex contains a new natural carotenoid and fucoxanthin[12].

1.1.6 Polyisoprenes: Erigeron bonariensis (L.) is a common weed which is traditionally used in urine problems (Asteraceae). Erigeron genus has about 390 species of flowering plants. Intercontinental plant inventions resulted in a number of taxonomic problems especially in distinguishing it from Conyza. From the investigation on the basis of chemotaxonomy it was concluded that the phenolic content and caffeol derivatives present in it has a closer relationship to Erigeron than species of conyza[13].

1.2 Essential Oils in Chemotaxonomy: The following taxonomic discussions intend to illustrate the impact of “Essential Oils” on scientific plant classification. Rutaceae: Rutaceae family plants are chemically characterised by the synthesis and accumulation of essential oils, furanocoumarins, antranilic acid derived alkaloids and limonoids. Cneoraceae have represented a taxon in certaesedis for a long time. Their oil cells and the chemical nature of their bitter principles and of their 2-methylchromones leave absolutely no doubts about their intimate rutaceous-meliaceous- simaroubaceous affinity. Prenylation of aromatic compounds is common in this family; examples of this tendency are furano and dimethyl pyran coumarins and a number of essential oil constituents evodionol.
1.2.1 Umbelliflorae: Umbelliferae family constitute the plants with furano and dimethyl pyrano coumarins and essential oils which tend to contain phthalides; for example Ligustilide ferulol type monoterpenoids and acetylinic compounds like falcarinone. Essential oils in schizogenous ducts are highly characteristics of Araliaceae and umbelliferae together with other chemical characters they accentuate the overall similarities of these two families and the need for reclassification of other 5 families often included in umbelliflorae, cornaceae and allied families are iridoid producing taxa which seem to have affinities with Dipsacales rather than with Araliaceae and Umbelliferae. Prenylation of aromatic compounds is also common in this family such as Umbelliferone (coumarin).

1.2.2 Verbenaceae and Labiatae: Many members of these two families are highly aromatic and yield essential oil. In Labiatae there is a clear cut vicarism. The group of aromatic plants does not produce iridoid glycosides; at the most some non glycosylated compounds like myodesertal and myodesertin may be present in essential oils; the non- aromatic group of Labiataes is characterised by iridoid glycosides like ajugol, galiridoside, harpagide, lamiol and others. The main taxonomic importance is two chemical groups of Labiatae which coincide with classification proposed by Wundulich (1967) for this family. Iridoids are insecticidal and insect deterrent and well described for steam volatile iridoids.

1.2.3 Piperales: Overall presence of oil cells and isolation of aporphine type alkaloids from roots of Piper auritum and stems of Piper sanctum (Hansel neuschke 1975, 1976) accentuate affinities between Magnoliales and Piperales.

1.2.4 Malvales: In this family mucilage cells and cavities are widespread but oleoresin cavities are much more restricted.

1.2.5 Myrtaceae: Myrtaceae family consists of tannin-rich essential oil plants. Methylated, prenylated and acetylated phloroglucinol derivatives occurs frequently in their essential oils; production of this very characteristic of acetogenins (Torquatone, a phloroglucinol derivative; present in some species of Eucalyptus) represent a chemical trend of this family.

1.2.6 Dipsacales: With one exception all members of Dipsacaceae produce iridoid or secoiridoid glucosides and lack essential oils. The exception is the genus morina whose species does not produce iridoids but have essential oil in oil cells.
1.3. Role of Terpenoids and Essential Oils in Medicine and in Industries:

- Medical application proposed by those who sell medicinal oil range from skin treatment to remedies for cancer and are often based on historical use of these oils for this purpose. Interest in essential oils has revived in recent decades with the popularity of aromatherapy, a branch of alternative medicine which claims that the specific aromas carried by essential oils have curative effects. It is a purely natural therapy and it can reduce tension and stress as well as promote peace of mind of human being. This is because of psychodynamic action of fragrance or hedonic (influence the effect of pleasure and displeasure linked to odour) mechanism and a semantic mechanism (memory linked with an odour and exceptionally emotional situation) For example, the use of saffrole is to synthesize heliotropin, used in perfumery.

- Essential oils are more or less powerful external or internal antiseptics, others possess an analgesic, hemolytic or anti-enzymatic action, still others act as sedatives, stimulants and stomachic. They are also useful for treating stress linked problems, digestive problems, tension, headache, allergy, insomnia and eruptions. It also affects the body’s hormone producing glands.

- Antibacterial, antifungal properties of essential oils play important roles in their topical applications on cuts, burns and wounds. For example, eucalyptus oil has antibacterial effect on pathogenic bacteria in the respiratory tract.

- Since, cleanliness is associated with the removal of bacteria, antiseptic properties are usually sought often in dental preparations and mouthwashes. The essential oils generally used in oral hygiene preparations are peppermint, cassia, anise, thyme, clove, caraway, spearmint etc.

- The essential oil obtained from thyme, cinnamon, clove, lavender, eucalyptus have antiseptic activity against various pathogenic bacteria. The plant components like citral, geranial, linalool and thymol have antiseptic activities many times more than phenol. There are reports that thymol is 20 times stronger than phenol.

- With the advancement in analytical methods like GC, GLC, GC-MS it is possible to know most of the constituents of essential oils and their substitutes developed for many of the essential oils but natural products still occupy a formidable position in industry. Infact, there has been an increasing demand for aromatic raw material for industrial formulations. Natural products obtained as plant isolate may be useful directly or may serve as starting material for the synthesis of active agent. For example, limonene content of the orange peel is used for the production of synthetic carvone.

- Essential oils have industrial importance for the scenting and flavouring, in perfumes, cosmetics and the scenting of soaps. They are also used as masking agent made from raw materials that were formerly having disagreeable odours by covering it with the use of volatile oils. Oils of ginger from rhizomes of *Ginziber officinalis*, oil of vetiver...
from roots of *Vetiver zizanoides* are widely used in soaps, perfumes as an excellent fixative and diluents in sanitary supplies and polishes and for masking odour.

1.4 Industrial Importance of Volatile Oil in India:
Herbal medicine industry is one the fast growing industries in the world. Global market in herbal medicines was estimated US$ 12.4 billion in 1994 increasing up to US$ 19.6 billion in 1999. Terpenoids contributed major part of the worldwide trade of plant derived refined compounds.

1.5 Industries Dealing with Essential Oil Production:
- Amsar Private Limited, Indore.
- Central Institute of Medicinal and Aromatic Plants, Lucknow
- Chemiloids, Vijayawada.
- Regional Research Laboratory, Jammu Tawi.
- Standard Essential Oil Distillers, Kanpur.
- Jos Eucalyptus Oil Distillery
- Highland Eucalyptus Oil Refinery, Ooty
- Reliance Eucalyptus Oil Company, Coonor.
- Nilgiris Green Land Eucalyptus Oil Company, Coimbatore.
- Bluehill Eucalyptus Oil Distillery, Kodaikanal

2. Conclusion
Today so many groups of plants are there in which phytochemical data has contributed to substantial taxonomic improvements. But this is not true for all the plants. Even when these data have been successfully used such information is very rarely incorporated into keys or standard description in floraes, because it is not used in identification without special facilities. Sometimes, chemical characters can be observed by swift and simple operation, and the use in such cases of spot-test is valuable routine procedure. Thus, modern chemotaxonomy has infact served to define precisely and to strengthen the long practice use of chemical character rather than to uncover new ones. The use of order to separate taxa in to genera such as Mentha, Stachys, Allium, Thapsi and many others is of great fame. The last decade has been of great importance because of happy outcome of physicochemical data and also because some of the basic concepts have been generated during this period which was influenced by scientific techniques such as paper chromatography thin layer chromatography, gas chromatography, gel electrophoresis, uv spectrometry etc. The factors responsible for such favourable outcomes are perfection and simplification of biochemical techniques and contribution of phytochemistry in solving some of specific problems faced by systematics.[14] The essential oils and terpenoids obtained by the above mentioned techniques show that in India, about 30% of the fine chemicals used annually in perfumes and flavours are obtained from essential oils. Hence, essential oils are natural products of economic importance. It is for sure that future studies of chemical polymorphism and chemical polytypism in essential oil bearing species will contribute much to our understanding of microevolution. At the same time such studies will enable man better to breed for odour and flavour or for any economically interesting oil constituents within many thousands of aromatic plants.

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