CHAPTER I

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CHEMICAL MARKERS IN PLANT SYSTEMATICS

Chemotaxonomy is a branch of taxonomy in which the distribution of chemical compounds in the plant body is used for a better understanding of the taxonomic and phylogenetic interrelationships of the taxa. Such an application of chemical evidences is of relatively recent origin and is increasingly being used in solving many taxonomic puzzles. Phytochemical characters are frequently considered as more basic, fundamental or privileged than other classes of characters because these characteristics are genetically controlled and have an advantage over morphological characters in that. These can be exactly explained in terms of structural and configurational formulae. This view, however, is not very much acceptable. Presently the chemical characters are given equal importance at par with other taxonomic characters.

Identical compounds are often found in quite unrelated plants. Chemical characters are also found to vary from one organ to another. But while considering the chemical characters two biologically homologous plants or organs must be compared. Only those compounds are taken into consideration which are accumulated in a plant organ to an
appreciable extent. It is always directly dependent on its concentration in a particular plant tissue or an organ.

Chemotaxonomy as a branch of taxonomy came into limelight with the publication of "Chemical Plant Taxonomy" by T. Swain (1963). Other publications like "Chemotaxonomie der Pflanzen" by Hegnauer (1962-64) and "Chemotaxonomy of Flowering Plants" of R. D. Gibbs (1974) gave detailed account of the chemistry of various compounds and their distribution in plant groups and provided necessary impetus to further development of the subject.

The idea to correlate plant classification with distribution of certain chemical plant constituents is very ancient and could be traced as far back as 1886 (Gibbs, 1963). Microscopically visible compounds were used earlier in many taxonomic treatments however, the recent techniques of isolation and identification of compounds developed during the fifties and the sixties have made the study less time-consuming and easier to handle by a biologist with limited chemical knowledge. Of late many new compounds have been studied as chemical markers. Because of the unlimited number of chemical characters, their selection is guided by a number of factors such as stability, ease of determination and non-susceptability of the compound to environmental conditions.
Phenolics meet all these requirements satisfactorily and thus are abundantly used as viable chemical markers. The fact that they are not actively concerned in cellular metabolism supports their selection.

Phenolic substances tend to be watersoluble since they frequently occur combined with sugars as glycosides and are located in cell vacuoles. Phenolics possess aromatic rings bearing a hydroxyl substituent, including their functional derivatives. They can be divided into 2 arbitrary groups, simple benzene derivatives (hydroxy benzoic acids, cinnamic acids, coumarins etc.) and flavonoids which have a C15 skeleton. From these two large groups of compounds, phenolic acids from first group and flavones, flavonols and leucoanthocyanins from the second group have been taken up for the detailed studies incorporated in the present work.

Acid hydrolysis of plant tissue releases a number of ether soluble phenolic acids. These acids possess acidic and phenolic properties. They may be derivatives of benzoic, cinnamic or phenyl aliphatic acids. Benzoin and cinnamic derivatives of the acids are found to be more frequent in plants.
Chemically flavonoids are polyphenols consisting of two aromatic rings joined by a 3-C unit. This skeleton could be regarded as being composed of two distinct units, (1) the C\textsubscript{6}-C\textsubscript{3} fragment (a phenyl propane unit) containing the 'B' ring and (2) a C\textsubscript{6} fragment, "A" ring. Flavonoids are subdivided based on oxidation level of phenyl propane unit into flavones, flavonols, chalcones, aurones, iso-flavones etc. Flavonoids show chemical evolution too. The presence of flavonols, leucoanthocyanins, C-substitution are said to be primitive characters while flavones, elimination of leucoanthocyanins, O-glycosylation and O-methylation are said to be advanced characters.

In the present investigation, along with the phenolics; tannins, sugars, alkaloids and different terpenoids have been used as chemical characters wherever it was felt that the data regarding their distribution would be relevant to the understanding of interrelationships of the taxa screened.

Tannins form another group of phenolic constituents, possessing an astringent taste and ability to tan hide to leather. They are of two types - condensed tannins (catechins) and hydrolysable tannins. The former is related to flavonoids.
Sugars, another group of chemical characters, occupy a central position in plant metabolism. Sugars are the first complex organic compounds formed in the plant as a result of photosynthesis. They provide major source of stored energy (as starch), transport energy (as sucrose) and the building blocks of the cell wall (cellulose). Sugars occur free or combined as - monosaccharides (glucose, fructose, traces of xylose, rhamnose and galactose), oligosaccharides - formed by condensation of two or more monosaccharides (sucrose) and polysaccharides - a large polymer of monosaccharides. Pentose sugars - ribose and deoxyribose - components of RNA and DNA respectively, are rarely encountered in plants in any other association. A number of oligosaccharides are not present in free state but occur combined with other organic molecules as plant glycosides (flavonoids, steroidal alkaloids and saponins). Only storage sugars are accepted as chemical markers.

Alkaloids are secondary plant substances, which contain nitrogen in a heterocyclic ring. Alkaloids are widely distributed throughout the plant kingdom but the distribution is very uneven and many families lack them. Because of the heterogenous chemical nature they cannot be identified in plant extracts using single method;
and a combination of techniques are to be used for their identification. These compounds have been found to be susceptible to ecological conditions and the age of plant. Alkaloids were used as chemical markers by many (Manske, 1944; Price, 1963; Gibbs, 1974). Terpenoids are based on the isoprene molecules - CH₂ - C (CH₃) - CH = CH₂ and their carbon skeletons are built up from the union of two or more of these C₅ units. Chemically terpenoids are lipid soluble and located in the cytoplasm of the plant cell. Essential oils sometimes occur in special glandular cells on leaf surface, in leaves and petals. Simple monoterpenoids are widespread and tend to occur as components of the majority of essential oils. The majority of these compounds occur widely and are not characteristic of particular plants or plant groups. It is a general observation that lower terpenoids are rather restricted to phylogenetically young plant groups (Robinson, 1975).

Iridoids are monoterpenoid lactones, widely distributed in plants combined with sugar as glycosides. The data on their distribution is very less and many plant groups are believed to contain these substances in free or combined form (Jenssen et al., 1975).
Many terpenoids and steroid alcohols exist in nature as free alcohols and as glycosides (sterolins, saponins and cardiac glycosides). The name saponin is given to some of these glycosides because of their soaplike nature. They are powerful surface active agents, which cause foaming when shaken with water. Saponins are soluble in water but insoluble in nonpolar solvents. These compounds are having a very limited distribution, but has a strong relation to the taxonomy of groups in which they contain (Harborne, 1971).

The present thesis is an attempt at critical assessment of two controversial taxa - Zingiberales and Cyperales - on the basis of the distribution of various chemical compounds. In the former group the markers used are flavonoids, phenolic acids, tannins, alkaloids, saponins, volatile oils and sugars, while in the latter taxa only flavonoids and phenolic acids are employed.