Chemical evolution within the Asteridae

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Chemical evolutionary pathways operating in the subclass Asteridae have been critically assessed. The different groups of plants are found to experiment with the various plant products such as alkaloids, cardiac glycosides, tannins, volatile oils, quinones and iridoids. Compounds which help plants to combat pathogens, discourage herbivores and act as allelochemics are found to provide a selective advantage to those individuals that possess them. Compounds providing little or no selective advantage are discarded. Trends in the chemical evolution of Asteridae are (i) reduction/elimination of alkaloids, flavonols and proanthocyanidins/tannins, (ii) introduction and further methoxylation of 6-deoxy- and 6-oxyflavones, (iii) introduction of iridoids, especially aucubins, (iv) development of volatile oils rich in sesquiterpenes, and (v) increased reliability on quinones as antimicrobials and allelochemics. The advanced groups of Asteridae possess a specific assortment of antimicrobials, bitter substances and allelochemics. The classification within the Asteridae is examined in the light of these trends.

Key-words—Asteridae, Flavonoids, Iridoids, Quinones, Chemical evolution.

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साराँश

एस्टेरिडी में रासायनिक विकास

एम० डेनियल एवं एस० डी० सेबनिस

एस्टेरिडी नामक उपवर्ग में हुए रासायनिक विकास का मूल्यॉंकन किया गया है। पौधों के विभिन्न समूहों में विभिन्न पादप-उत्पाद—एल्केलॉयड, कार्डियक, ग्लाइकोसाइड, टेनिन, वाष्पशील तेल, क्वीनॉन्स एवं इरिडॉयड पाये जाते हैं। वे यौगिक जो पौधों की शाकभक्षीयों एवं रोगजनकों से रक्षा करते हैं तथा विकल्पी-रसायनों की भाँति कार्य करते हैं उन पौधों के लिए आत्मरक्षा हेतु अत्यन्त महत्वपूर्ण हैं। एस्टेरिडी नामक उपवर्ग में रासायनिक विकास की प्रवृत्ति इस प्रकार है: (i) एल्केलॉयड, फ़्लेवोनोल एवं प्रोएन्थोसियनिडिन/टेनिन का ह्रास, (ii) 6-डीऑक्सी व 6-ऑक्सीफ़्लेवॉन्स का और मीथॉक्सीकरण तथा उत्पन्न होना, (iii) इरिडॉयड्स विशेषतया एक्यूबिनों की उत्पत्ति, (iv) सेस्क्वीटर्पीन्स से भरपूर वाष्पशील तेलों का विकास, तथा (v) क्वीनॉन्स पर विकल्पी-रसायनों एवं प्रतिसूक्ष्मजैविकों की भाँति निर्भरता। ऐस्टेरिडी उपवर्ग के समुन्नत समूहों में प्रतिजैविक, कड़वे पदार्थ एवं विकल्पी-रसायन पाये जाते हैं। इन्हीं प्रवृत्तियों के आधार पर एस्टेरिडी उपवर्ग का वर्गीकरण किया गया है।

THE chemical compounds elaborated by plants play a significant role in their struggle for survival. Optimal defence mechanisms would help the plant to withstand the onslaught of pathogens and herbivores while the offence mechanisms increase fitness. Bitter principles and tannins fall in the first group and the allelochemics in the second group. Different groups of plants have experimented with almost every class of natural products either as part of their chemical arsenal for defence or offence. Those compounds which are not toxic to the parent plant at high concentrations and which exhibit high antimicrobial properties and bitter taste, conferred a survival advantage to the plant or lineage. Those compounds which do not provide these advantages keep the plants containing them of limited progress incapacitating the taxa for further evolution. The latter group of plants may be considered endlines in evolution. In the present work, chemical adaptations of the Asteridae, the most evolved subclass of Angiosperms, are assessed.

The subclass Asteridae (Cronquist, 1981), which contains most of the Sympetalae of the Englerian system, consists of 11 orders, 49 families and nearly 60,000 species. This group is considered the most diverse, elaborating a wide variety of mechanisms for propagation, pollination, defence and survival.

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The orders included in this subclass are Asterales, Rubiales, Dipsacales, Calycerales, Callitrichales, Plantaginales, Campanulales, Gentianales, Solanales, Scrophulariales and Lamiales.

The chemical characters which bind the Asteridae together are the frequent occurrence of iridoid compounds, absence of ellagic acid and proanthocyanidins and apparently complete absence of betalains and benzylisoquinolines. These characters are not absolute, on the contrary there are many exceptions. It appears that each group of Asteridae has experimented with one class of compounds for its survival and further evolution.

Gentianales, the order considered the most primitive among the Asteridae, generally includes the Apocynaceae, Asclepiadaceae, Loganiaceae and Gentianaceae as the principal families. The first two families are distinct from the rest, in specialising in a great variety of cardiac glycosides and complex indole alkaloids (Gibbs, 1973). They have very few iridoid-containing plants and are rich in flavonols and proanthocyanidins. The independent nature of this group was recognised by Hutchinson (1969) who separated these two families into a new order Apocynales. On the strength of other chemical evidences the authors supported this concept. The Apocynales as circumscribed by Daniel and Sabnis (1990) differs from that of Hutchinson in the content of the families. The family Periplocaceae of these authors include the subfamilies Periplocoideae (Asclepiadaceae) and the Echitoideae (Apocynaceae) merged together. The Apocynaceae *Sensu stricto* contains only the subfamily Plumerioideae, whereas the Asclepiadaceae *sensu stricto* consists of the Cynanchoideae only. Among these families, the Periplocaceae constitutes the basal stock from which two divergent lines evolved. The first one leading to the Apocynaceae gave rise to the Rubiales. The second line of evolution specialised in pollination mechanisms and from a climax group, the Asclepiadaceae. The Rubiales eliminated most of the alkaloids and cardiac glycosides which are the defence mechanisms of the Apocynales and introduced iridoids such as asperulosides and aucubins and anthraquinones. Iridoids are bitter principles with marked antimicrobial activity and thus offer better protection, from the herbivores and pathogens. An added advantage of these compounds is that unlike alkaloids which are toxic at higher concentrations (and tilt the ionic balance of the plant), they do not interfere with the plant metabolism. Production of quinones as the principal phenolic pigments in the wood and to some extent in leaves is another advanced feature of Rubiales. These compounds protect the plants in a highly oxidising environment. Many quinones are potent allelochemics and phytoalexins. Both iridoids and quinones increased the probability of survival for the Rubiaceous members. However, woody taxa retained flavonols and proanthocyanidins (Thomas, 1990). The specialisation achieved by the Rubiales was not continued further and this taxon became a climax group.

Among the other families of the Gentianales, the Loganiaceae, Gentianaceae and Exacaceae are very similar in their chemistry in not synthesising the characteristic compounds of the Apocynales *sensu lato* and Rubiales (i.e., the cardiac glycosides and quinones). The Loganiaceae, the woody family, which may be considered as the basal gentianalean stock, is almost at the same level of evolution as the Periplocaceae. This family contains alkaloids and flavonols but shows evolutionary trends in eliminating tannins and proanthocyanidins. From this group, the Gentianaceae evolved by developing xanthones, a very characteristic group of yellow polyphenols, and glycoflavones. In addition, Gentianaceae produce mono- and diterpenoid bitter principles in great variety. The Exacaceae, a splinter group of the Gentianaceae, on the other hand, resorted to flavones (Daniel & Sabnis, 1978). This line of evolution led to the Scrophulariales.

The Oleaceae, with their characteristic assortment of primitive flavonols and advanced flavones, especially of 5-deoxy and 6-oxy derivatives (Daniel & Sabnis, 1979), form another line of evolution from the Loganiaceae. Even though this family retained the primitive iridoids it failed to synthesise aucubins, the advanced iridoids. Glycoflavones also are produced by an appreciable number of plants in this family. These peculiarities of the Oleaceae warrant its elevation to a distinct order Oleales as practised by Hutchinson (1969) on morphological grounds. The Menyanthaceae, once included in the Gentianaceae, with their herbaceous aquatic habit and predominance of flavonols and absence of flavones/glycoflavones, are more at home with the Solanales.

The order Solanales contains the Solanaceae and Convolvulaceae as the core families. Both these families are rich in alkaloids. The Solanaceae are characterised by the tropane alkaloids which may be considered unique to these plants. In addition, the solanums produce steroidal alkaloids and saponins. Pyridine alkaloids also are seen in a few members of this family. Though heterogeneous in terms of their compliment of alkaloids, members of this family are very similar in that they produce flavonols and coumarins as the dominant phenolics and eliminate proanthocyanidins and syringic acid. The failure to synthesise flavones/glycoflavones (Joseph, 1990) mark this family as chemically primitive. Aucubins are the other group of compounds absent among the Solanaceae. It is quite possible that the Solanaceae specialised in alkaloids (in great variety) and saponins as their defence mechanisms, and remained at a low level of evolution with regard to their flavonoids. The Polemoniaceae developed flavones but discarded the alkaloids and saponins of the Solanaceae and developed further.

The Convolvulaceae form another line of specialisation. These plants produce unique ergot alkaloids which are otherwise seen only in some fungi. This family developed more flavones and glycoflavones (Nair, Daniel & Sabnis, 1988). Proanthocyanidins are retained in a few genera. The biosynthesis of glyco-lipids is another unique feature found in some members of this family, the adaptive significance of which is not yet understood. The presence of tropane alkaloids in a few Convolvulaceous members evidently points to a common ancestry with the Solanaceae.

The Boraginaceae with flavonols and absence of iridoids, glycoflavones and proanthocyanidins does not fit into the order Lamiales where they were grouped by Cronquist (1981) alongwith the Verbenaceae and Lamiaceae. Both the latter families are rich in flavones, that the highly advanced 6-oxy derivatives (Gornall & Bohm, 1978) and iridoids. The presence of quinones may show some relationships with the Verbenaceae. The alkaloids reported from the Boraginaceae are pyrrolizidines (Raffauf, 1970) which are biosynthetically close to tropanes of the Solanaceae. Therefore, chemically, the Boraginaceae are at home with the Solanales.

The Scrophulariales include the Scrophulariaceae, Acanthaceae and Bignoniaceae as the major families. The iridoids (especially the aucubins), which are considered to be the most characteristic feature of this order, are predominant in the Scrophulariaceae only. This family is characterised by flavones, most of which are 6-oxygenated. Flavonols, glycoflavones and proanthocyanidins are almost completely eliminated from this family. The production of volatile oils by some plants of this family, (*Lindenbergia, Stemodia* and *Scrophularia*) may make it easier to derive the Lamiaceae from the Scrophulariaceae. The proposed derivation of the Scrophulariaceae from the Solanaceae through the subfamily Salpiglossideae of the latter family (Robertson, 1891) is chemically unsound. The Salpiglossideae, though exhibit an evolution to the zygomorphy of flower, do not produce iridoids or flavones, compounds characteristic of the Scrophulariaceae (Joseph, Daniel & Sabnis, 1990).

The Orobanchaceae, with their parasitic habit, have their own characteristic assortment of flavonoids. 6-oxyflavones are absent and the plants possess flavonols, flavones, tannins and quinones. Iridoids also are absent here. This family might have arisen from the parasitic members of the Scrophulariaceae such as *Pedicularis* of the tribe Euphrasieae (Cronquist, 1981) which incidently do not possess iridoids and 6-oxy flavones (Joseph, 1990). The Orobanchaceae resorted to tannins and quinones. The Lentibulariaceae show typical adaptations of the submerged aquatic plants. They are similar to the members of the Gratioleae (aquatic—*Limnophila*) of the Scrophulariaceae in eliminating the flavonoids. These plants retain iridoids as their antimicrobial defences and also acquired quinones (Joseph, 1990). The Gesneriaceae are another family close to the Scrophulariaceae. Iridoids and 6-oxyflavones are abundant in this family. The levels of chemical evolution of these two families are almost equal. Similarly the Pedaliaceae with flavones (both 6-oxy and 6-deoxy) and iridoids are another close taxon. However, this family specialises in mucilages. The Martyniaceae remain at a lower level of advancement because of their glycoflavones and 6-deoxyflavones.

The Acanthaceae, another large family, is similar to the Scrophulariaceae in flavonoid chemistry including the production of many 6-oxygenated flavones. However, Acanthaceae differ from the latter in lacking iridoids in most of its members (Daniel & Sabnis, 1987). Proanthocyanidins are retained by the woody genera. Presence of glycoflavones and absence of 6-oxyflavones unite the Thunbergiaceae a distinct taxon.

The Bignoniaceae with their woody habit resorted to quinones. About half the genera in this family, especially those of the Tecomeae elaborate quinones while the remaining genera elaborate advanced flavones (Padhye, 1983). Iridoids are seen rarely.

The order Lamiales containing the Verbenaceae and Lamiaceae continued the trends set by the members of the Scrophulariales. The Verbenaceae have aucubins in the tribe Verbeneae and quinones in the remnant of the family. The reliability on quinones may possibly be due to the predominantly woody nature of the family. The flavones are all methoxylated and a number of them are 6-oxygenated also (Padhye, Daniel & Sabnis, 1990). Glycoflavones and Proanthocyanidins are almost eliminated. The Verbenaceae can be derived directly from the Bignoniaceae. The option of producing volatile oils instead of iridoids, which started with

Table 1—Modified scheme of classification of the Asteridae

Gentianales
- Loganiaceae
- Gentianaceae
- Exacaceae.

Apocynales
- Periplocaceae
- Apocyanaceae
- Asclepiadaceae

Oleales
- Oleaceae

Solanales
- Solanaceae
- Nolanaceae
- Menyanthaceae
- Polemoniaceae
- Convolvulaceae
- Boraginaceae

Scrophulariales
- Scrophulariaceae
- Lentibulariaceae
- Orobanchaceae
- Gesneriaceae
- Pedaliaceae
- Martyniaceae
- Acanthaceae
- Thunbergiaceae
- Bignoniaceae
- Buddleiaceae

Lamiales
- Verbenaceae
- Lamiaceae

Campanulales
- Pentaphragmataceae
- Campanulaceae (incl. *Sphenoclea*)
- Lobeliaceae
- Stylidiaceae
- Brunoniaceae
- Goodeniaceae

Rubiales
- Rubiaceae

Asterales
- Asteraceae

Dipsacales
- Caprifoliaceae
- Adoxaceae
- Valerianaceae
- Dipsacaceae

Plantaginales
- Plantaginaceae

Callitrichales
- Hippuridaceae
- Callitrichaceae
- Hydrostachyaceae

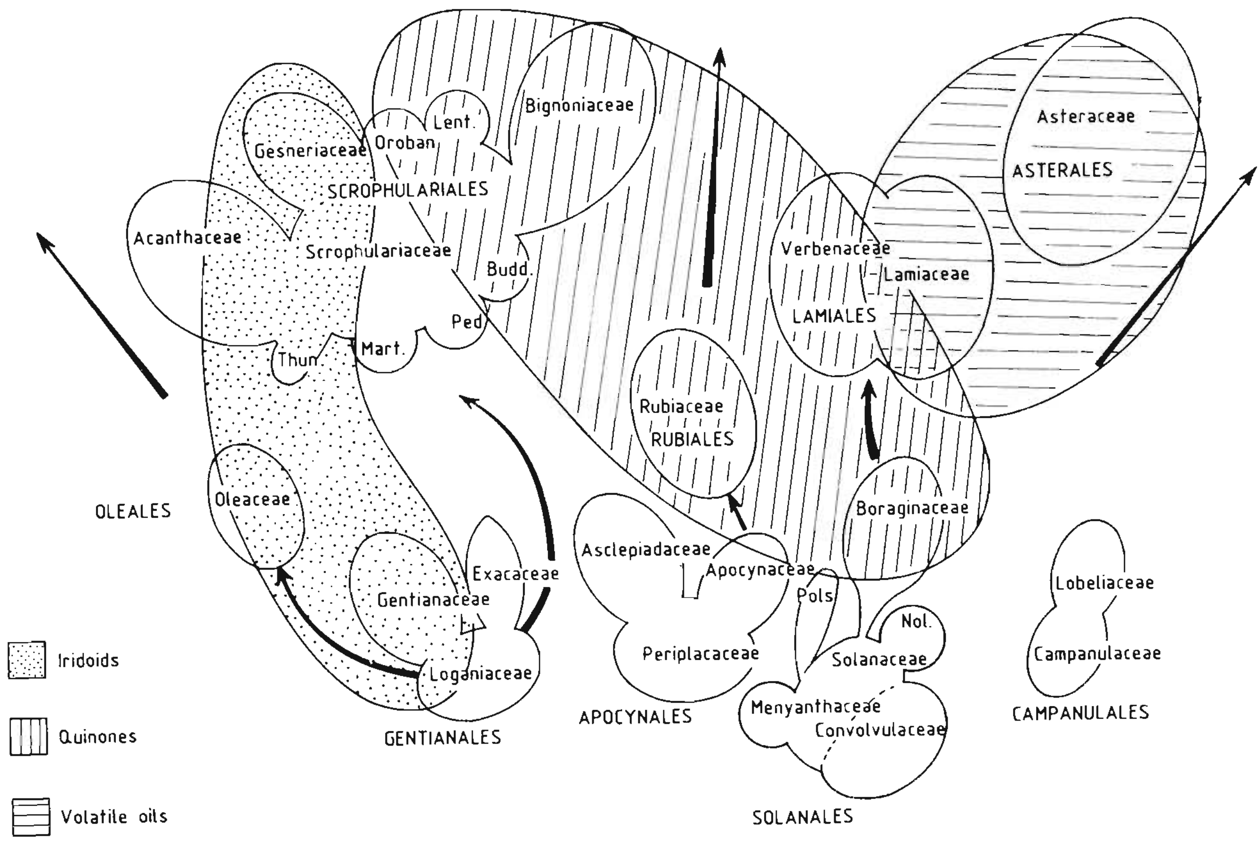
Calycerales
- Calycerales

some of the Scrophulariaceae, is continued in the Lamiaceae. The flavones, both 6-deoxy and 6-oxygenated, are highly methoxylated. Even the flavonols present in some plants are fully methoxylated (unpublished data of authors). The high methoxylation make these flavonoids lipidic in nature and therefore they occur in superficial layers of the leaves such as cutins and waxes where they act as effective UV screens and potential antimicrobial agents. The methoxyflavonoids may serve as sources of hydroxyflavonoids (by demethylation) which act as phytoalexins (Bailey & Mansfield, 1982).

The Asterales are the most successful plants in the Asteridae and therefore highly advanced. They produce a variety of chemical compounds which are used in defense or in offense. Members of the Asteraceae rely heavily on volatile oils rich in sesquiterpene lactones. These terpenoids are antimicrobial in nature and are highly potent allelochemicals. Polyacetylenes with thiophene-ring systems form another group of unique compounds in this family. The replacement of starch by inulin in many tubers and root stocks is another feature, the adaptive significance of which is not yet clear.

The Campanulales evolved parallel to the Asterales but could not achieve the high level of evolution attained by the latter. This order resorted to inulin and polyacetylenes, some members also produce iridoids. Tannins and proanthocyanins are eliminated. Campanulales are less specialised relative to Asterales in terms of the flavonoid chemistry of Campanulaceae and pyridine alkaloid chemistry of Lobeliaceae. Between these two, the latter family is advanced due to their flavones (Daniel & Sabnis, 1987a).

The order Dipsacales is considered derived from the Rubiaceae (Cronquist, 1981). The presence of flavones in many members of the Caprifoliaceae (Thomas, Daniel & Sabnis, 1988) may support such contention. However the successful development of anthraquinones by the Rubiaceae is not traceable in Dipsacales. The alkaloids of the Valerianaceae are of the piperidine type while those of Rubiaceae are of the quinoline and isoquinoline groups. It is quite possible that the Dipsacales might have originated from the basal stock of the Rubiaceae.



Text-figure 1—The chemical evolution within the Asteridae.

The modified scheme of classification of the Asteridae is as follows (Table 1). The chemical evolution in this group is graphically represented in Text-figure 1.

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