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Review

The evolution of chemosystematics

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Abstract

Chemosystematics has been used to distinguish plants and other organisms that are useful for food and those best avoided. Originally unwritten, this knowledge has been progressively formalized with useful, harmful and inactive chemical constituents from relevant taxa now identified and recorded. This knowledge has led to insights into taxonomy of these plants, animals and micro-organisms. Advances in analytical instrumentation, in particular chromatography, followed by electronic detection methods, have speeded these studies, culminating in metabolic profiling, (“metabolomics”). The huge array of chemical constituents isolated from plants combined with morphological and cytological data take their place as part of the overall Natural History of the organism in its environment. The study of, DNA (genomics) and to a certain extent m-RNA (transcriptomics) and proteins (proteomics), has led to the immense subject of molecular biology which relates the phenotype of a taxon to its genome. This type of chemosystematics on its own does not of course describe the small molecules in plants, often called, perhaps misguidedly, “secondary compounds”, or how they relate to each other, to the plant containing them or to the environment. Economic uses flow from this knowledge, such as the topic of non-protein amino acids and amines, which from 1958 to the present has produced information from the chemotaxonomic to the severely practical. Literature on the subject from 1909 to the present charts developments in the discovery of new compounds and their use in systematics. Often a mere catalogue, a list of plant constituents is nevertheless part of the overall description of a plant.

Keywords: Chemical constituents; Phylogenetics; Symposia; Chromatography; Mass spectrometry; Non-protein amino acids

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1. Introduction

One of the outstanding features of plants in addition to their form is their chemistry. The initial chemical observation is also visual, their colour. Then other senses observe their scent and taste. More intimate observation reveals their nutritional value or their poisonous nature (Fig. 1). Instinctive chemosystematics has always been a feature of living things. All of these lead the inquisitive person to a study of the chemical components and this in turn leads

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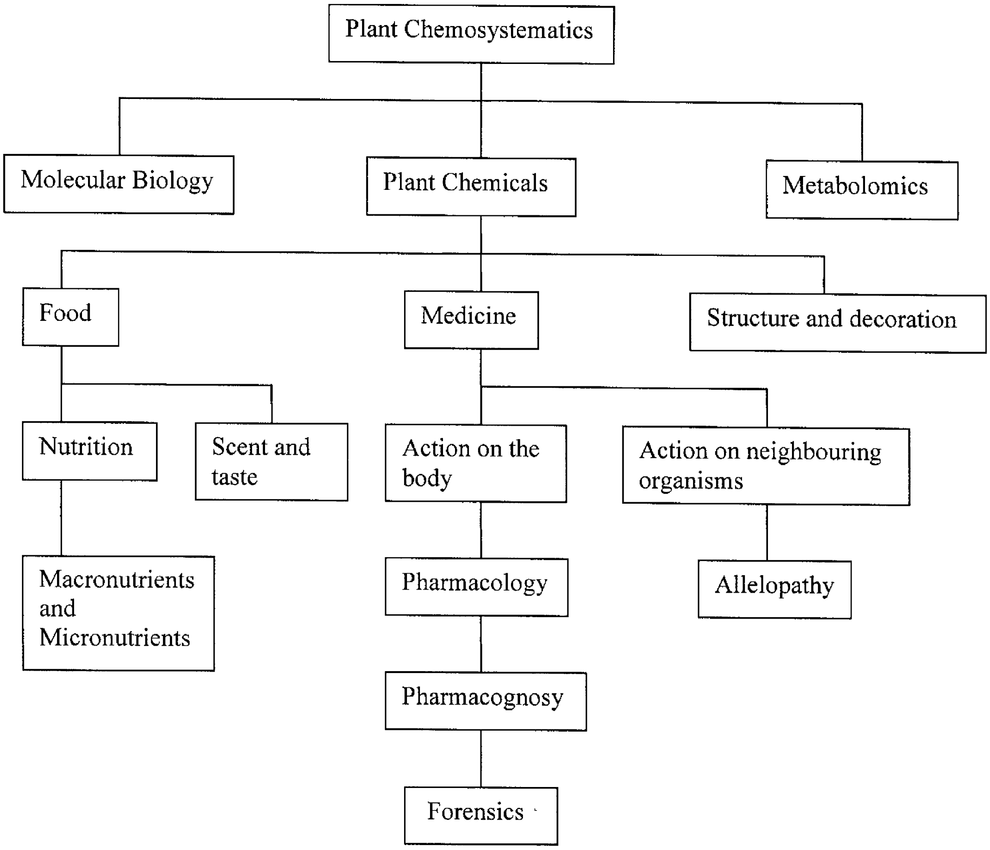

Fig. 1. Subjects arising from the systematic study of plant chemical constituents.

to uses of these chemicals for practical economic purposes. The scientist who is studying a plant for intellectual or practical reasons or perhaps both, will look at everything that can be seen by eye or aided by instruments and then will delve deeper to consider the very materials contained in the plant. These will differ from plant to plant and so a chemical aspect of systematics and taxonomy emerges. As D.M. Smith wrote in the introduction to "Phytochemistry and Angiosperm Phylogeny" (Smith, 1981), "Taxonomic botany in particular, having been born of the shaman's art and the herbalist's practice of medicine should be most benefited by a renewed occupation with the chemical properties of plants".

The early history of chemosystematics has been described fully by Professor Darnley Gibbs (1963, 1974), a member of the original Board of Phytochemistry, in a paper entitled "History of Chemical Taxonomy" in which he summarized "comparative phytochemistry as applied to plant systematics", thereby including the words "taxonomy" and "systematics" in the same treatment. I shall take chemosystematics to include chemistry as part of the general Natural History of the plant with reference to its relationship to similar plants and its interaction with its environment, both living and non-living. Perhaps this merges into Phytochemistry. I shall regard Chemotaxonomy as the use of chemistry in naming and classifying a plant. Some say that taxonomy is part of systematics. Others stress systematics as the study of the diversity and differentiation of organisms and their inter-relationships (Heywood, 1973). A thoughtful commentary on these terms was made at a symposium in Bhagalpur University (Puri, 1990), where it was stressed that in a multidisciplinary area such as this, both chemical and botanical expertise were required. Caution should be exercised when only one characteristic was being studied and in particular phylogenetic data should also be sought. These ideas were reiterated in the Introduction to a survey of the systematics of plant Orders by Bhattacharyya and Johri (1998), who spelled out the purposes of plant identification, nomenclature and classification for the plant breeder, the natural products chemist, the ecologist the forester and the agriculturist.

Among the many early workers in this field Gibbs mentioned Greshoff (1909), who carried out chemical investigations on a number of plants at Kew. He was one of the earliest to urge the chemical study of plants. He said in his remarks on "comparative phytochemistry"; "Since plants are no longer classified according to a single character … the systematic botanist desires to know that relationship in *all* its manifestations. Some investigators have attempted to elaborate this investigation by applying microchemical tests … chemistry has already come to the assistance of the botanist … It appears clear that chemistry and botany should co-operate in the study of the plant world…, one might demand that every accurate description of a new genus or of a new species should be accompanied by a short "chemical description of the plant". These remarks made a 100 years ago seem just as pertinent today and his paper deserves reading in full. Between 1916 and 1945 McNair published a series of 26 papers on plant chemistry, many with a systematic/taxonomic content, which he collected into one volume (McNair, 1965). During this period he investigated most groups of plant chemicals recognized at the time; fats, waxes, tannins, alkaloids, carbohydrates, saponins, cyanogenetic glucosides and sulphur compounds. He studied them in relation to each other and to the plants that produced them, in relation to other plants and to the environment. He endeavoured to link all this to phylogeny.

In 1963, Alston and Turner wrote a book called "Biochemical Systematics" (Alston and Turner, 1963), which summarised basic ideas of chemosystematics. They discussed plant constituents under the headings, amino acids, fatty acids, carbohydrates, alkaloids, cyanogenetic substance, phenolic substances, quinones and terpenoids. Significantly, they included a chapter on macromolecules under the heading of serology. They posed four questions which phytochemists today might well ponder:-

1. Will chemical investigations yield data making possible a better phylogenetic scheme?
2. Will they give answers to taxonomic problems that previous methods did not permit?
3. Will chemotaxonomy become as significant in the next half-century as cytotaxonomy was in the last?
4. Is the time at hand for this molecular approach?

Long after the early paper by Greshoff (1909), Darnley Gibbs himself wrote a paper on what he called "comparative chemistry" (Gibbs, 1945), 30 years before producing his massive compendium (Gibbs, 1974). The experimental work of E.C. Bate-Smith, "Phenolic constituents of plants and their taxonomic significance" (Bate-Smith, 1962, 1968) opened an era of more intense laboratory-based research, particularly on phenolic compounds and using the newly-introduced technique of paper chromatography. Natural products research continued apace before and after this time. A notable series of books produced from 1962 onwards by Professor R Hegnauer, the latest of which, vol. 11 was published in 2001, recorded and discussed virtually all compounds from plants recorded in the literature according to family listed alphabetically but with many systematic comments (Hegnauer, 1962–2001). This was followed with a more structured systematic approach by many workers, notably Jeffrey Harborne and his co-workers particularly, C. Williams and by T. Swain who edited many of the significant Conference Proceedings and was the catalyst of many research projects.

The state of research up until 1975 has been discussed in detail in a wide-ranging paper (Fairbrothers et al., 1975). Two topics in plant natural products research, "micromolecules", embracing pigments, glucosinolates, phenolics, cyanogenic glucosides, sesquiterpene lactones and alkaloids and "macromolecules", embracing serology, amino acid sequences and nucleic acid hybridization, were compared in relation to a number of taxonomic groupings.

2. Literature of plant chemosystematics

This upsurge of interest in natural products chemistry resulted in a number of text books. An early one "The Organic Constituents of Higher Plants" by T. Robinson (Robinson, 1963) described a surprising, for its time, range of plant constituents in a biosynthetic context and provided a useful introduction to the subject. This was followed later by "The Chemotaxonomy of Plants" (Smith, 1976) in which the systematic aspect was emphasised. Again a chapter in this book, "Macromolecules and Phylogeny", was perhaps prophetic. Eight years later the heavyweights entered the arena with "Plant Chemosystematics" (Harborne and Turner, 1984) and more text books around the subject emerged in ensuing years.

The research literature and scientific meetings burgeoned in the 1960s, with natural products papers of chemosystematic interest. The first of the major symposium proceedings was Chemical Plant Taxonomy (ed. Swain, 1963) which reported on a 1962 meeting in Paris supported by NATO. As well as papers on general chemotaxonomy, there were papers on specific groups of compounds; alkanes, acetylenes, fatty acids, polyol and cyclitol glycosides, anthocyanins, alkaloids and sulphur compounds. Three years later, another conference proceedings, this time reporting a Cambridge meeting of the Phytochemical Group, precursor of the Phytochemical Society, again supported by NATO, was edited by T. Swain as "Comparative Phytochemistry" (ed. Swain, 1966). It is interesting that now there were three papers on flavonoids. Other groups reviewed included alkanes, acetylenes, terpenoids, carotenoids, polysaccharides, asperulosides and aucubins, cyanogenetic compounds, amino acids, alkaloids, betacyanins and betaxanthins, hydroxyquinones and sulphur compounds. In 1973, the Nobel Foundation sponsored a symposium in Sweden on "Chemistry in Botanical Classification" (Bendz and Santesson, 1973), which contained many thoughtful papers, taxonomic and chemical, speculating on the links between the two subjects. More recently, a very comprehensive review of the chemistry and biochemistry of natural products was that of Barton and Nakanishi (1999).

The Systematics Association had long fostered an interest in chemosystematics, holding a symposium "Chemotaxonomy and Serotaxonomy" at Birmingham in 1967, published in 1968 and edited by T.G. Hawkes (1968). This had been preceded and perhaps inspired by a review edited by Leone (1964) entitled "Taxonomic Biochemistry and Serology". Here, work on both proteins and nucleic acids was described with, invited papers on botanical aspects by J. Harborne, E.C. Bate-Smith and H. Erdtman. The Association brought the work up to date in 1980 by a further symposium, "Chemosystematics Principles and Practice" held at Southampton in 1979 edited as a volume by Bisby et al. (1980). The Preface by Frank Bisby is well worth reading still but too long to be detailed here. The presented papers dealt with methods of using the chemical data rather than describing individual compounds. Chemosystematic and taxonomic studies on a range of plant groups were discussed at a symposium "Phytochemistry in relation to botanical classification" held in 1985 at Bhagalpur University (ed. Bilgrami and Dogra, 1990) and displayed some of the potential of the discipline.

The boundary between chemosystematics and phytochemistry, if there is one, was crossed in the first volume of the series "Progress in Phytochemistry" edited by Reinhold and Liwschitz (1968) which dealt largely with the chemistry and biosynthesis of plant compounds. The editors stated that both the "static and dynamic sides" of phytochemistry would be dealt with in their book. The study of biosynthesis led to phylogeny, another aspect of relations between plants,. A Phytochemical Society symposium at Bristol in 1969 brought together disparate but inter-related strands of work seeking to explain how the biosynthetic relationships in time between plant taxa illuminate their systematic position. The symposium volume "Phytochemical Phylogeny (ed. Harborne, 1970) contained chapters on biochemical markers from several chemical groups and disciplines. Phytochemists and plant systematists were brought together at a symposium "Phytochemistry and Angiosperm Phytogeny" in Oklahoma in 1981. This resulted in a review volume (ed. Young and Seigler, 1981) containing papers on glucosinolates, cyanogenic compounds, terpenes, flavonoids and significantly, amino acid sequences and DNA hybridization. These studies were finally focussed away from systematics as such, towards the evolution of biosynthetic systems in another symposium "Evolution of Metabolic Pathways" in Montreal in 1999 organised by the Phytochemical Society of North America and edited as a volume in the "Recent Advances in Phytochemistry" series (eds Romeo et al., 2000). Perhaps the two subjects will be reunited.

This spate of research reviews and conference proceedings was accompanied by new research journals. The first of these was Phytochemistry (1961), followed by Biochemical Systematics (1973), soon to become Biochemical Systematics and Ecology (1974), both products of Pergamon Press. There were of course plenty of journals that reported natural products research, sometimes with reference to chemosystematics: Progress in the Chemistry of Organic Natural Products had been founded in Germany in 1938 and at the same time in America Lloydia, "Quarterly Journal of Biological Science", started, to be transmogrified in 1979 into Journal of Natural Products. Other notable sources of plant chemistry are Planta Medica (1953), Natural Products Reports (1984) and Zeischrift für Naturforschung; Section B (1946, 1973); Section C (1973).

Other data compilations have taken two forms, a listing of many groups of flowering plants or a taxonomic description of the flora in a geographical region. The first approach is exemplified by "Flowering Plants, taxonomy and phylogeny" (Bhattacharyya and Johri, 1998) which gives a brief description of the main diagnostic features of Angiosperm Orders, including rather brief chemical data where available. A good example of the second approach is "Phytochemistry of the flora of Qatar" (Rizk, 1986) which describes chemical features of endemic plants of that region. Both approaches are capable of expansion. A wealth of chemical data is given in many entries of the vast and continuing "Biological Flora of the British Isles", published as parts in the Journal of Ecology from No. 1, 1941, *Juncus* (Richards and Clapham, 1941), to No. 245, *Pteridium aquilinum* (Marrs and Watt, 2006).. This could well form the basis of a "Phytochemistry of the British Flora".

3. Laboratory techniques

In the years, since the 1960s a huge number of plant constituents have been extracted and characterised and also readily identified in analytical systems. This has been brought about by the advent and development of chromatography in its many forms. To start with, paper chromatography in both one or two dimensions allowed the recognition of the number of compounds of a particular class which might be present in a plant. These were to some extent identified by their absorption of ultraviolet light or their reaction with various colorimetric indicators. This demanded comparison with known standards and was of only limited value in determining novel, chemical structures. The use of thin silica powder layers instead of paper allowed more rapid, precise separations (thin layer chromatography, TLC). Furthermore, compounds which acquired a charge at a suitable pH could be separated in an electric field (electrophoresis). However, within these limitations a vast assessment of chemical content could be made and taxonomic relationships postulated merely on the basis of the appearance of the separated zones ("spots"). A useful advance was made by cutting out and washing these zones in the hope, often fulfilled, of isolating the compounds in a more or less, pure state. An extension of this was to put the solid material (the stationary phase), in powder form, in a glass column and elute with the appropriate solvent (the mobile phase) under gravity. Later the eluting process was speeded by applying pressure in steel tubes and using carefully tailored particles. This led to the technique of high pressure ("high performance") liquid chromatography (HPLC). All this was expanded by the development of new partition or absorption supports. In another development an unreactive gas was used as the mobile phase and a liquid absorbed on to the surface of an inert solid, or the column wall, as the stationary phase (gas–liquid chromatography, GC). A review of the more advanced techniques was presented at a symposium of the Phytochemical Society of North America in 1981 and subsequently published as a Proceedings (ed. Fischer et al., 1991), More sophisticated separations required more accurate detection methods. Following observation of the zones under UV-light came measurements of the absorption of UV-light at various wavelengths and eventually many, observations which could be made continuously on the eluting solvent flow. Other detection methods were introduced to detect specific physical properties and these culminated in the attachment of a mass spectrometer to the separation system (GC/MS; HPLC/MS) and even in very advanced systems to a link with a nuclear magnetic resonance spectrometer (HPLC/NMR). These sophisticated techniques have led to the possibility of scanning all the constituents of a plant, metabolic processing or metabolomics, which has been used to good effect to compare normal and diseased organisms (Lindon et al., 2007). The analysis has been achieved by the use of hyphenated techniques mentioned above and in particular a more sophisticated line-up, Fourier transform-cyclotron resonance-mass spectrometry (FT-ICR-MS) (Aharoni et al., 2002). More recently still, the analytical method has been extended by a development of ion trap technology, the Kingdom trap (Orbitrap™, Makarov, 2000). Plant analysis was well served by a series of volumes, "Modern Methods of Plant Analysis", published in the 1950s and 1960s by Springer (Paech and Tracey, 1955–56; Linskens and Tracey, 1962–63; Linskens et al., 1964). Later, a very comprehensive review of analytical methods in 9 volumes, "Methods in Plant Biochemistry" was produced by Dey and Harborne (1989–1993).

4. Phytochemical phylogeny

Relationships between plant taxa indicated by their chemical constituents can be considered from two angles. The chemicals in a group of plants can lead to a postulated phylogenetic and therefore natural grouping, or the postulated phylogeny from other sources leads to comments on the chemical makeup (e.g. Hegnauer, 1986). If on the other hand the chemistry is just an adjunct to other plant characters to construct a useful, if artificial, classification, then the phylogeny may be less relevant. These two approaches were discussed by Heywood (1966) and Mentzer (1966) and the discussion is reiterated in much of the literature since that time, especially in thoughtful detail in "Plant Chemosystematics" (Harborne and Turner, 1984).

The compilation of all these data on chemical composition of plants is interesting in itself. However, the mere recording of a compound or type of compound in apparently unrelated taxa is no indication of their systematic affinity, because often the biosynthesis of the structures takes different routes (e.g. Wink and Waterman, 1999). Frequently the same compounds are produced by quite different biosynthetic pathways in unrelated plants. The incorporation of phylogenetic into chemosystematic studies is thus essential. A recent review (Wink and Waterman, 1999) described this methodology in detail and other papers in the volume, a title in the series "Annual Plant Reviews", edited by M. Wink (1999), described many examples. The Leguminosae are a very large family whose members contain between them a huge array of chemicals, many of which are of economic importance. It is thus not surprising that chemosystematics has been used extensively in order to sort out taxonomic problems (Harborne et al., 1971; Hegnauer and Hegnauer, 1994–2001.) and continues to be used, sometimes with only partial success, for example where absence of certain compounds was more significant than presence of others (e.g. Reynolds et al., 2007). In these cases, it is only in comparison with other features that a contribution to systematics is successful. An example of seemingly similar chemical structures that are not biologically related is the piperidine alkaloids. Those based around the structure of coniine (2-propylpiperidine) are synthesized from acetate units, at least in the genus *Conium* (Leete, 1963). Most other piperidine compounds, including pipecolic acid, are derived from lysine. The coniine alkaloids were reported originally only from *Conium* and surprisingly, *Sarracenia* but they were then found to occur in several species of *Aloe*, not normally regarded as a poisonous plant (reviewed by Reynolds, 2005). There is no information as yet as to the biosynthetic route in *Aloe*.

Another large and diverse range of plant constituents, the terpenes, have been widely used in taxonomic studies and to a certain extent in phylogeny, although the specific biosynthesis of all its members has not always been known (e.g. Seigler, 1981). Recently this has been clarified showing that four coupling reactions of the simple five-carbon precursors have been recognized and many of the enzymes characterized (Thalasiram et al., 2007). The four coupling enzymes seem to relate to a fundamental ancestor which underwent relatively small changes in structure. This particular chemical library of a plant has even been given a name, the terpenome (e.g. Christianson, 2007).

This information relates especially to the taxonomic aspects of chemosystematics and it has been said that most of the major insights into the distribution of low molecular weight compounds have been made (Wink and Waterman, 1999). However in the broader aspect of the Natural History of the plant in its environment there is still much to be said. An aspect of this, biological activity, has been studied at a somewhat slower pace within the subject of phytochemical ecology, which was reviewed at a symposium of that name by the Phytochemical Society in 1971, of which the proceedings were subsequently published (ed. Harborne, 1972). This was followed by a text book, "Introduction to Ecological Biochemistry", (Harborne, 1971–1993), which has run to four editions. Systematics did not loom large in these reviews, although they were rich in chemical structures from plant species. For instance, a recent summary concentrated on plant–insect interactions and plant defence (Harborne, 2001). This latter aspect has given rise to the subject of allelopathy, again with little chemosystematic content at present but has produced enough chemical data to give rise to two symposia of the American Chemical Society (ed. Thompson, 1985, ed. Waller, 1987) and one at the Institute of Botany, Taipei (ed. Chou and Waller, 1989). Long before these studies, a rationale for the diversity of plant chemicals was presented as being the result of co-evolution between plants and animals predating them (e.g. Ehrlich and Raven, 1964). This sought to explain the presence of such compounds that have an ecological function and the argument can be extended to other factors contributing to survival and propagation in an environment (e.g. Waterman, 1992).

5. Molecular systematics

The structures of biological polymers, in particular proteins and nucleic acids, have been used as a chemosystematic test since the 1960s but this interest has blossomed in the 1990s with the introduction of new methodologies, both chemical and statistical. DNA sequencing has proved especially precise and has been used widely for phylogenetic reconstruction and elucidation of biological diversity. (reviewed by Soltis et al., 1992, 1998). Under the name of molecular systematics, this method probes the very heart of the genetic systems that govern the phenotype. Although fundamental in this sense, this approach does not describe the chemical make-up of the plant, although it may comment on the inter-relationship of the chemicals and their biosynthetic systems. Very recent developments in the molecular biology approach have led to the elucidation of fascinating insights into the phylogeny of several chemical systems such as betalain and glucosinolate production, nitrogen-fixing symbioses and C_4 photosynthesis (Soltis et al., 2005).

Molecular systematics looks towards a complete genetic profiling of the plant (genomics). This leads logically to a description of mRNA produced by transcription from the DNA (transcriptomics). From here arises a study of the protein structures coded by the mRNAs (proteomics). Study of the diverse polysaccharide structures occurring naturally has led to the title “glycomics”. The study of protein diversity was stimulated by the recognition of multiple forms of individual proteins, aided by the separation technique of gel electrophoresis. Often the protein in question had enzymic activity and the multiple forms were called isoenzymes or isozymes (e.g. Soltis and Soltis, 1990). Recently there have been attempts to determine the whole spectrum of chemical constituents in a plant (metabolic profiling) and this has been dubbed “metabolomics” and its potential summarized in the Foreword to a new journal of that name (Goodacre, 2005; reviewed Rochfort, 2005; Hall, 2006). This illustrates how constantly advancing instrumentation leads to the obtaining of more data that can be fed into chemosytematics but not necessarily accompanied by theoretical backup. This molecular biology (perhaps it should be termed “macromolecular systematics”), encompasses a comparison of the structures of biological polymers (macromolecules), the nucleic acids, proteins and perhaps polysaccharides occurring in the various taxa whose relationship is being studied. Another aspect coming to the fore is the interaction of small molecules with the macromolecules, acting thus as information carriers (Jarvis, 2000). These thoughts in turn lead to investigations into the relationships and development of metabolic pathways leading to the compounds, reviewed in a recent symposium of the Phytochemical Society of North America and published as a Proceedings (Romeo et al., 2000).

6. Developments

All the above comprise just a catalogue of constituents of a particular extract of a plant and if systematics is said to be part of a whole Natural History of the taxon, then biological activities of the chemical entities still need to be established.

An illustration of the progress of a chemosystematic study involving both taxonomy and biological activity over a 40 year span is that of the non-protein amino acids and polyhydroxy alkaloids. In the late 1950’s, Professor Leslie Fowden (now Sir Leslie) (1958, 1962) and collaborators investigated a number of amino acids not found in protein hydrolysates, from a number of plants. In a review with a main collaborator, Arthur Bell, he recorded the presence, among others, of γ-methyleneglutamic acid in most *Tulipa* species and also sporadically in a few unrelated plants and azetidine-2-carboxylic acid in some Liliaceae but especially *Convallaria* (Bell and Fowden, 1964). Another example, canavanine, was confined to seeds of Papilionideae in the Leguminosae, although it did not occur in certain tribes. Because of its high concentration, up to 5% in some seeds, a storage function was ascribed to the compound, although later its activity as a metabolic inhibitor was reported widely (reviewed Rosenthal, 1977). Canavanine mimicked arginine in many biochemical pathways although in some organisms there was a resistance to its reaction with tRNA synthetase. In other species, ingested canavanine was destroyed by high levels of urease. Previously the toxicity of a number of amino acids analogous to those in proteins had been reviewed extensively (Fowden et al., 1967). Later, another review covered subsequent work and dealt with the biosynthesis of some of the compounds and their metabolic action (Fowden et al., 1979).

Studies by Steve Evans et al. (1985) resulted in the identification of several amino acids and amines as markers for a number of Leguminous species. The supposed toxic properties of these compounds as a protection against rodent predation in the seeds of at least one genus, *Lonchocarpus*, have been questioned however, flavonoids seeming to be the active agents (Janzen et al., 1990).

Around this time, Merv Hegarty in Australia was investigating the neurotoxic effects of the seeds of *Castanospermum australe*, the Moreton Bay Chestnut, when ingested by cattle. Collaborating with Bell, the polyhydroxy alkaloid castanospermine was identified as the active component. More work by Linda Fellows and Robert Nash disclosed a number of similar compounds, including DMDP (2,5-dihydroxymethyl-3,4-dihydroxypyrrolidine), reported as having chemotaxonomic significance in the previous study (Evans et al., 1985). It was noted that the structures of these compounds were analogous to sugars in their cyclic conformation, but with a nitrogen atom in the ring instead of oxygen (Evans et al., 1985). Glycosidase activity was correlated with this structure. Inhibition of this enzyme by these compounds led to the discovery of several useful biological activities (Fellows and Nash, 1990). Particularly noteworthy was inhibition of the formation of the carbohydrate coating during proliferation of the HIV virus. More recently the nematocidal activity of DMDP has been patented and the product is available commercially in Costa Rica.

The subject has thus advanced from a mere catalogue of chemicals and the plants that contain them to a structure relating these chemicals to taxonomic groupings and also to each other in a biosynthetic framework and eventually to an economic outcome. Slowly the biological activity of the compounds is being examined, leading to speculation as to their function outside the plant, an ecological perspective and their function within the plant, a physiological perspective. Perhaps this will require complicated statistical methods creating correlations between ethnobotanical and chemical databases (Gottlieb et al., 2002) or between historic ethnopharmacology and ethnobotany (Heinrich et al., 2006). If and when the chemical structure can be related to the biological activity then the whole subject of quantitative structure–activity relationships (QSAR) can be invoked. These all start to have economic implications for human welfare, bringing chemosystematics back to its original mission, the use of chemical plant products (Fig. 1).

Whether it has evolved or developed, chemosystematics has moved on in the last 50 years, in that a vast number of chemical compounds have been discovered and associated with taxa. Often the phylogenetic origin of these compounds has been revealed by their biosynthesis. The admonition made by Smith (1976) still stands; "Often the aspiring taxonomist may have little time and perhaps less taste for chemistry ... the chemist who realizes his results have a taxonomic relevance is seldom trained to appreciate the demands and approaches of the biological subject". Perhaps this is the distinction between chemotaxonomy and chemosystematics. The presence or absence of a particular constituent in a plant without our knowing anything of its chemistry or biochemistry, can be used to assign its taxonomic position. The systematics of the plant requires knowledge of the biosynthesis of its constituents, their functions and the part that they play in the plant's physiology and ecology.

Finally it would be interesting to discuss the questions posed by Alston (1966):

1. How does a chemical plant constituent come into existence?
2. How did the compound come to be present in the species?
3. How is production of the compound regulated?
4. The reason (function), if any, for the compound to be present in the plant.

Giving thought to:

5. Botanical (species) incompleteness of the survey.
6. Inadequate population sampling.
7. Inadequate intra-individual sampling.
8. Failure to detect a minimal concentration of constituent.

The ramifications of plant chemosystematics shown in Fig. 1 include topics of interest from those of early times to those which are still developing. They involve attention from several disciplines, biology, chemistry, medicine and technology, in the wider sense, the whole Natural History of the plant.

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