PHYTOCHEMICAL ASPECTS OF ANGIOSPERM ORIGIN AND EVOLUTION

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SUMMARY

It is hypothesized that the successful original evolution and subsequent radiation of the angiosperms was facilitated, among other factors, by their extraordinary chemical versatility as compared with previously existing plant groups. This broad chemical spectrum was brought about by two factors, (1) the climax in the expansion of the shikimate pathway, already reached at the level of the gymnosperms; (2) a reduction-oxidation potential much higher that that of pteridophytes and gymnosperms. Together, these traits provided the angiosperms with a much broader capacity for micromolecular variation then was present in earlier plant groups. Co-evolution with herbivores and pathogens (apart from pollinators and seed dispersers), and consequently the pressure to produce novel and less easily detoxified substances, are commonly adduced as the causative factors in the phytochemical diversification of the angiosperms at the level of populations, species and genera. Here we apply this hypothesis to the higher levels of the taxonomic hierarchy. The sequence of primary precursors of the shikimate pathway for the synthesis of secondary metabolites which follows a retrograde biosynthetic sequence, and the gradual replacement of shikimate derived metabolites by mevalonate-acetate derived compounds is interpreted as resulting from natural selection; it exemplifies a case of canalized evolution. Possible relationships between oxidation level and ease of detoxification of secondary metabolites with the aid of the animals' mixed function oxidases are discussed in an evolutionary context. It is concluded that the chemical potential of the angiosperms paved the way for intense evolutionary interactions between plants and animals, interactions which must have been conducive in augmenting the diversity of angiosperm and animal species since Cretaceous times.

1. INTRODUCTION

Ever since the time of Darwin the quest for the origin and early differentiation of the angiosperms has attracted the interest of botanists. Comparative studies of contemporaneous seed plants, as well as the growing knowledge of early angiosperms in the fossil state, have brought us continually nearer to the solution of the "abominable mystery". At present it appears that early angiosperms were more successful than their putative gymnospermous forebears by virtue of a number of structural and functional innovations. Vegetative structures such as the improved conductive tissues of the xylem and phloem, reproductive structures and systems (STEBBINS 1974), mainly the elaboration of bisexual, animal pollinated functional reproductive units (MEEUSE 1978, 1979), their abbreviated

life cycles (TAKHTAJAN 1976), their occupation of specialized habitats (RETAL-LACK & DILCHER 1981), and the elaboration of a luxurious secondary metabolism (EHRLICH & RAVEN (1965) have been adduced to this end.

Although there is little doubt that the initial upswing of the angiosperms was not due to a single characteristic but rather to the advantageous combination of different traits, it is instructive to analyse the different components of the adaptive syndrome of early angiosperms. In a previous publication (KUBITZKI & GOTTLIEB 1984) we hypothesized that the successful original radiation of angiosperms was facilitated, among other factors, through the climax in the expansion of the shikimate pathway, that had been attained by their gymnospermous forebears. This, and a wider oxidation/reduction potential, provided angiosperms with a broader capacity for micromolecular variation than was present in the gymnosperms. The present paper is an attempt to analyse the evolutionary mechanism underlying this particular mode of micromolecular variation.

2. EXTENSION AND ABBREVIATION OF THE SHIKIMATE PATHWAY IN GREEN LAND PLANTS

The shikimate pathway for the synthesis of aromatic amino acids is ubiquitous in microorganisms, fungi and plants. Here we deal with the shikimate pathway leading to primary precursors of secondary metabolites. It is only in green land plants that a post-tyrosine chemistry, based on cinnamic acid, appears really important (LUCKNER 1972). Deamination of aromatic amino acids takes place in fungi (TURNER & ALDRIDGE 1983) and may occur sporadically in other groups of lower plants. However, in bryophytes the special relevance that cinnamoyl units acquired is due to their activation by coenzyme A. Polyketides, compounds formed by the condensation of acetyl-CoA for chain initiation and (via malonyl-CoA) extension, dominate the secondary chemistry of bacteria, fungi and algae (LUCKNER 1972). In this process the substitution of the starter unit by cinnamoyl-CoA in bryophytes led to flavonols and flavones. Flavonoids absorb UV-light and seem to act as photoscreens (MACCLURE 1975), forming an essential prerequisite for the conquest of the terrestrial part of the biosphere by plants.

In addition to condensations, reductions are also activated by the thiol ester function of cinnamoyl-CoA. The resulting cinnamyl alcohols polymerize oxidatively into lignins which stabilize the cellulose cell wall of pteridophytes and seed plants, another condition for the existence of land plants. In gymnosperms, further elaboration of cinnamyl alcohols led to their oxidative dimerization to lignans and reduction to allyl- and propenylphenols (GOTTLIEB et al. 1978). Thus the sequence cinnamic acids → cinnamyl alcohols → allyl- and propenylphenols accompanies the evolution of land plants until reaching its climax[1] at the interface gymnosperms/angiosperms. In angiosperms, where there appear comparatively many more highly oxidized substances (see following section), a reverse

[1] Theoretically the reductive sequence could continue to n-propylphenols. That such compounds have rarely, if ever, been found may be due to their possible lack of reactivity and hence relevance to plant life.

trend starts which implies a gradual abbreviation of steps of the shikimate pathway in the synthesis of precursors of biosynthetic groups of secondary metabolites (see *fig. 1*). The oxidative dimers of propenyl- and/or allylphenols (neolignans, see GOTTLIEB 1978) from present-day Myristicaceae and Lauraceae, and perhaps the highly reduced flavonoids of the virolan type from the Myristicaceae (BRAZ FILHO et al. 1973) may be reminscent of the micromolecular constitution of the earliest angiosperms.

Further utilization of shikimate-derived precursors for the synthesis of secondary compounds is characterized by a gradual reduction of biosynthetic steps of this pathway. Within the Magnoliidae, phenylalanine and/or tyrosine are still utilized for the production of benzylisoquinoline alkaloids which are only rarely found outside this subclass. Biogenetically related compounds, such as phenylethylisoquinoline and benzylphenylethylamine alkaloids, and betalains (chromoalkaloids), are based on the same amino acids. They occur in the Magnoliidae, the monocotyledons and the centrosperms, which form the *magnolialean block* (KUBITZKI & GOTTLIEB 1984). The somewhat advanced state of benzylisoquinoline synthesis explains why some families of the woody Magnoliidae, as the Winteraceae, Myristicaceae and Canellaceae are devoid of these alkaloids, a problem that has puzzled phytochemists time and again. Further steps in the abbreviation of the shikimate pathway include the utilization of chorismic acid for the synthesis of anthranilate-derived alkaloids and finally that of shikimic acid for the synthesis of gallo- and ellagitannins. Both anthranilate-derived alkaloids and gallic and ellagic acid-derived tannins are widely distributed throughout the basic groups of the remaining dicotyledons, forming the *rosiflorean block* in the terminology of KUBITZKI & GOTTLIEB (1984).

The gradual transition from woody to herbaceous growth, occurring in parallel in several lineages of angiosperms, corresponds chemically to a decrease in quantitative importance of the shikimate pathway. Cinnamate surplus, from reduced consumption for the production of lignins, may account for a certain abundance of lignans, coumarins and even flavonoids, although the latter are subjected to selective forces different from those governing the presence of other secondary metabolites (GOTTLIEB 1982; KUBITSKI 1984) in herbaceous forms. One instructive case in point is provided by the Araliales which contain the closely allied families Araliaceae and Apiaceae. While the latter are mainly herbaceous and make ample use of cinnamate in the synthesis of coumarins, no such substances have been detected so far in the predominantly woody counterpart, the Araliaceae. Nevertheless, in such advanced angiosperm lineages shikimate derived secondary metabolites play a relatively minor role. In these lineages, the full potential of mevalonate utilization has led to steroid alkaloids, iridoids, iridoid alkaloids and sesquiterpene lactones, that of acetate to polyacetylenes.

3. THE PARTICULAR OXIDATION-REDUCTION POTENTIAL OF ANGIOSPERMS

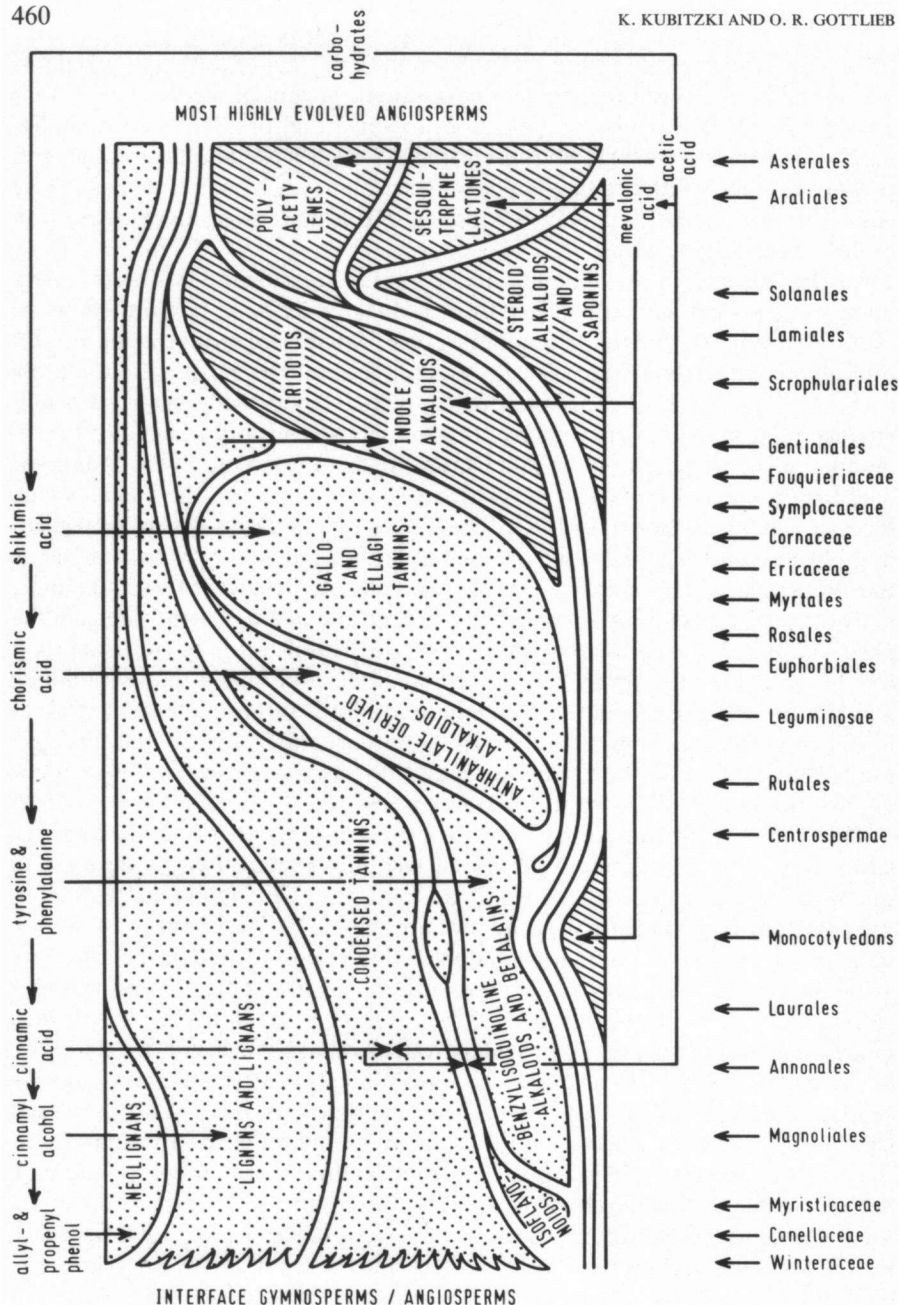Secondary metabolites, such as flavonoids, lignoids, polyketides, terpenoids and

Fig. 1. Distribution of major groups of allelochemicals in angiosperms, showing a gradual replacement of mainly shikimate derived constituents (dotted) by predominantly mevalonate and acetate-derived constituents (hatched) in advanced angiosperms. Condensed tannins, isoflavonoids and indole alkaloids are of mixed origin. Examples are given for different constellations of secondary compounds. No linear ancestor-descendant relationship is implied by the sequence of taxa.

steroids, as well as alkaloids, which are found in gymnosperms may also occur in angiosperms, where they are frequently accompanied by more highly oxidized, and occasionally by less highly oxidized, derivatives of the same biogenetic group. This observation was quantified for flavonoids (GOTTLIEB et al. 1982). Averaging the data for the oxidation patterns of all known flavonoids, both the triketide and the cinnamate derived moieties appear at conspicuously lower oxidation states for gymnospermous than for angiospermous compounds. Iso- flavonoids, which arise through oxidative transformation of chalcones, are restricted to angiosperms. The well known high relative proportion of coniferyl (4-hydroxy-3-methoxycinnamyl) alcohol versus sinapyl (4-hydroxy-3,5-dimethoxycinnamyl) alcohol in gymnosperm versus angiosperm lignins (SARKANEN & LUDWIG 1971) is viewed as further evidence for the higher oxidation level in angiosperms with respect to cinnamate derived moieties. The vast majority of lignans in gymnosperms stem from coniferyl alcohol, while in the angiosperms lignans and neolignans are frequently derived from trioxycinnamyl alcohols as well. In regard to polyketide moieties, accumulation of highly oxidized derivatives (e.g. acetophenones, polyacetylenes) is restricted to angiosperms. Terpenoids and steroids as highly oxidized as the monoterpenoid iridoids, the sesquiterpenoid lactones, the diterpenoid tanshinones, royleanones and coleones, the triterpenoid cucurbitacins and limonoids and the steroidal whithaferins are all known only from the angiosperms. The formation of indole (tryptophanemonoterpenoid) alkaloids as well as benzylisoquinoline alkaloids involves oxidative steps and is also restricted to the angiosperms. The transformation of the ubiquitous protein amino acids into cyanogenic glycosides also requires oxidative steps. Thus it is not surprising that the number of cyanophoric gymnosperms is so small in comparison to the number of such angiosperms (6 : 2,000 according to HEGNAUER 1977).

There can be little doubt that the origin of the angiosperms coincided with a substantial amplification of the oxidation-reduction potential of enzymatic catalysts for the formation of micromolecules. But what about the angiosperms themselves? Does the origin of new evolutionary lines within this plant division follow the same trend? Indeed, this seems to be the case for taxa of higher hierarchic levels, i.e. superorders and possibly also orders. *Table 1* lists some correlations of the mean oxidation levels of the compounds belonging to different biogenetic groups with SPORNE's (1980) evolutionary advancement indices of the angiosperm families (or the mean indices for the families of an order or superorder) in which they occur.

The existence of a positive correlation between oxidation levels of compounds and evolutionary advancement of the taxa which produce them means that, just as for the origin of the angiosperms themselves, the radiation of each major subgroup coincided with an abrupt amplification of the oxidation level of its micromolecules. A clear understanding of the evolutionary polarity of micromolecular oxidation states for taxa of lower hierarchic levels is yet less well documented due to the lack of advancement indices for genera and species, making quantitative correlations of morphology with chemistry impossible. Descriptive

Table 1. Biogenetic groups of compounds contained in plant taxa characterized by the correlation of mean oxidation level/evolutionary advancement indices *sensu* SPORNE (1980). The values of oxidation levels are internally comparable for each biogenetic group (see ref. for their determination in each case). Advancement indices are available for families. Advancement indices for orders and superorders are means from those of families. Classification after DAHLGREN (1980).

FLAVONOID-RING A (GOTTLIEB et al. 1982). Groups of Superorders R (Rosiflorae, Myrtiflorae, Rutiflorae, Santaliflorae, Malviflorae, Violiflorae, Theiflorae, Primuliflorae, Balanophoriflorae, Araliiforae, Corniflorae, Fabiflorae) 104.7/46.8; M (Magnoliiflorae, Nymphaeiflorae, Ranunculiflorae, Caryophylliflorae, Polygoniflorae) 113.7/50.4; A (Asteriflorae, Solaniflorae, Gentianiflorae, Lamiiflorae) 116.6/64.5.

BENZYLISOQUINOLINE ALKALOIDS (BARREIROS et al. 1984). Superorders: Magnoliiflorae (sine Aristolochiaceae) −0.27/45, Ranunculiflorae −0.20/48. Families of Magnoliiflorae: Magnoliaceae −0.31/25, Annonaceae −0.28/40, Monimiaceae −0.28/47. Lauraceae −0.25/52, Hernandiaceae −0.22/61, Aristolochiaceae +0.15/50; of Ranunculiflorae: Berberidaceae −0.21/45, Menispermaceae −0.22/47, Ranunculaceae −0.19/53, Papaveraceae incl. Fumariaceae −0.19/48.

IRIDOIDS (KAPLAN & GOTTLIEB 1982). Superorders: Corniflorae 9.8/51.6, Gentianiflorae 10.5/62, Loasiflorae 10.0/64, Lamiiflorae 10.0/64. Orders of Corniflorae: Eucommiales 10.8/40, Fouquieriales 10.3/47, Sarraceniales 9.3/48, Ericales 11.2/49.4, Cornales 10.3/56, Dipsacales 10.5/67; of Gentianiflorae: Gentianales 10.4/59.6, Oleales 10.9/62, Goodeniales 10.2/64.5; of Loasiflorae: Loasales 10.0/64; of Lamiiflorae: Lamiales 10.6/71, Scrophulariales 11.1/71, Hippuridales 11.5/83. Families of Eucommiales: Eucommiaceae 10.8/40; of Fouquieriales: Fouquieriaceae 10.3/47; of Sarraceniales: Sarraceniaceae 9.3/48; of Ericales: Ericaceae 11.3/45, Pyrolaceae 11.0/54; of Cornales: Davidiaceae 10.4/46, Symplocaceae 10.0/48, Garryaceae 10.7/50, Alangiaceae 9.0/52, Icacinaceae 10.3/56, Sambucaceae 10.3/56, Cornaceae 9.9/57, Stylidiaceae 11.3/62, Adoxaceae 9.8/78; of Dipsacales: Caprifoliaceae 10.6/60, Calyceraceae 10.5/67, Valerianaceae 9.2/83, Dipsacaceae 9.8/87; of Gentianales: Rubiaceae 10.2/48; Apocynaceae 10.4/57, Loganiaceae 9.4/61, Gentianaceae 9.9/63, Menyanthaceae 9.8/69; of Oleales: Oleaceae 10.9/62; of Goodeniales: Goodeniaceae 10.2/64; of Loasales: Loasaceae 10.0/64; of Lamiales: Verbenaceae 11.3/67, Lamiaceae 10.2/72, Callitrichaceae 11.5/74; of Scrophulariales: Myoporaceae 10.9/63, Scrophulariaceae 11.3/67, Plantaginaceae 10.8/69, Globulariaceae 10.8/69, Buddlejaceae 11.8/70, Pedaliaceae 12.0/70, Acanthaceae 11.0/72, Martyniaceae 10.6/75, Lentibulariaceae 11.8/75, Bignoniaceae 11.6/80; of Hippuridales: Hippuridaceae 11.5/83.

POLYACETYLENES (FERREIRA & GOTTLIEB 1982). Superorders: Rutiflorae −1.6/52, Santaliflorae −1.3/56, Araliiflorae −1.1/57, Asteriflorae −0.7/72. Orders of Rutiflorae: Rutales −1.6/49; of Santaliflorae: Santalales −1.3/61; of Araliiflorae: Araliales −1.1/56, Pittosporales −1.2/58; of Asteriflorae: Campanulales −0.8/61, Asterales −0.7/72. Families of Rutales: Simaroubaceae −1.6/40; of Santalales: Olacaceae −1.29/46, Santalaceae −1.30/64, Loranthaceae −1.40/65; of Araliales: Apiaceae −1.12/51, Araliaceae −1.10/55; of Pittosporales: Pittosporaceae −1.20/63; of Campanulales: Campanulaceae −0.80/63; of Asterales: Asteraceae −0.67/72.

Table 2. Reported cases for which a decrease of mean oxidation levels of compounds within biogenetic groups corresponds to a presumed evolutionary advancement in plant taxa.

FLAVONOIDS (GOMES et al. 1981): *Derris, Lonchocarpus.*
IRIDOIDS (KAPLAN & GOTTLIEB 1982): see families within orders in *table 1.*

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correlations for some micromolecular groups with evolutionary considerations based on morphological evidence for genera or species (*table 2*) could indicate the reversal of the trend, i.e. within each taxon or evolutionary line evolutionary diminution of the oxidation level occurs.

In conclusion, our working hypothesis states that an increase in the degree of reduction of micromolecules which constitutes the general trend in angiosperms, is opposed by a reverse oxidative trend which is most pronounced at the onset of each major phyletic line.

4. MICROMOLECULAR PATTERNS AND HERBIVORY

The wide-ranging replacement of gymnosperms by angiosperms in the Cretaceous was not a unique phenomenon in the history of plant life. Earlier, the upswing of novel major groups had been accompanied by the near displacement of the previously existing groups. This is documented by the statistical analysis of the sequence Silurian-Devonian early land plants → Devonian-Carboniferous pteridophytes → late Palaeozoic-Mesozoic gymnosperms → Cretaceous-Tertiary angiosperms (NIKLAS et al. 1983). While the floristic change in the late Palaeozoic coincided with profound environmental alterations, the appearance of the pteridophytes and angiosperms was associated with a decline in the number of species in the preceding dominant group. This suggests the competitive displacement of older taxa by newer ones. It has even been argued that competition, eventually leading to extinction, may have been more important in plant than in animal evolution (LEWIN 1983). This may be due to the fact that plants are all rather similar in their physical and nutritional needs and the general organisation that resulted therefrom. Because of this it is assumed that some of the factors that have determined the rise of the angiosperms were subtle traits that are today difficult to recognize. It is our conviction that the extreme chemical versatility of the angiosperms must have been such a trait.

In the foregoing, we have dealt with two phenomena: the sequential abbreviation of the shikimate pathway in the synthesis of primary precursors for secondary metabolites, and the extraordinarily high reduction-oxidation level that characterizes the secondary metabolism of angiosperms. We will now attempt to determine the evolutionary significance of these striking phenomena. It is widely agreed that selection of secondary metabolites by, and coevolution with, phytophagous and pathogenic organisms are the prime factors operational in shaping the diversity of natural products (EHRLICH & RAVEN 1965; SWAIN 1977). The acquisition of optical and olfactoric lures in coevolution with pollinators and seed dispersers may also have played an important role in this context. However, this interplay did not achieve its full expression until the appearance of the angiosperms. The defence chemistry of pteridophytes and gymnosperms, in contradistinction, is still unspecialized, either predominantly physical through

hard, lignified tissue[1] or impregnation with silica, or chemical through condensed tannins. The tanning action of the latter precipitates viral nucleoproteins, produces leaf protein-tannin complexes which are indigestible for microorganisms and insects, and inhibits the digestive enzymes of mammals as well as the degradative enzymes of fungi. This *general defence* (for defence theory see RHOADES 1979) requires that substantial amounts of chemicals be deposited in all organs that need protection. *Specialized defence* through toxic micromolecules, as it occurs on a broad scale in angiosperms, is energetically more favourable but has the drawback that selection can lead to detoxification mechanisms.

Coevolution with herbivores is widely accepted as the driving force behind phytochemical change at the level of populations and species, but this explanation has seldom been used in conjunction with phytochemical evolution in higher categories. Only CRONQUIST (1977) has hypothesized that the shifts from one major group of secondary constituents to the other reflect a succession of groups of secondary compounds that were used in plant defence, have diversified and, after being exhausted, were superseded by compounds of a novel group of secondary compounds. A similar view is held by GARDNER (1977) who is mainly concerned with the replacement of defences based on tannins and crystals, as occur in primitive Rosidae, by defences based on a variety of toxic and repellent substances. While this hypothesis is attractive in principle, there are some difficulties in its application because CRONQUIST (1977) implied a sequence from benzylisoquinolines to condensed and hydrolysable tannins, and farther to iridoids, polyacetylenes, sesquiterpene lactones and latex. To accept a systematic continuity or even an ancestor-descendant relationship in the sequence Magnoliidae → Rosidae and from there to the other major clusters of dicotyledons would imply that from the special defence of the Magnoliidae by benzylisoquinolines a reversal had occurred in the Rosidae to the use of the old bulk defence by condensed tannins, already employed by gymnosperms and pteridophytes. For these and other reasons, several authors (KUBITZKI 1969; BATE-SMITH 1972; MEEUSE 1970; SWAIN 1974) have argued that the magnolialean families, although harbouring the most archaic characters of the angiosperms, could hardly be considered to resemble the direct ancestor(s) of all other dicotyledons. It is more likely that the magnolialean and rosiflorean blocks, which must have an old origin, diverged at an early, as yet unknown stage of angiosperm evolution. Otherwise, the presence of winteraceous (WALKER et al. 1983), possibly proteaceous (SERLIN 1982), and other angiosperms as early as the Lower Cretaceous would be difficult to explain.

Once the existence of parallelisms, convergences and reticulations in the evolution of the angiosperms is accepted, the logic of natural selection as the major force responsible for the observed succession of "chemical weapons" becomes more obvious. However, this does not explain why the sequence of precursors of the shikimate pathway follows a reversed biosynthetic sequence rather than

[1] Lignins not only contribute to the compressive strength of the cell wall but may also act as a feeding deterrent (RHOADES 1979) and as a means of preventing fungal infection of epidermal cells (GRISEBACH 1981).

occurring at random. Chemical changes follow a fine-tuned hierarchy which at the population level begins with substitutional changes and is followed, after exhaustion of the possibilities of a given level, by configurational and constitutional changes. In this hierarchy, switch-overs to a novel primary precursor represent the most drastic innovation of secondary chemistry. In the case of the shikimate pathway, after the elaboration of the most highly reduced precursors, propenyl- and allylphenols, there is virtually no choice other than to retrace the biosynthetic sequence. Thus the use of primary precursors of the shikimate pathway in a sequence opposed to their biosynthetic origin follows the line of least resistance and exemplifies what STEBBINS (1974) has called "evolutionary canalisation". This retrograde biosynthetic sequence does not stop with the use of shikimic acid as the primary precursor for the synthesis of micromolecules. After the exhaustion of the shikimate theme, the enhancement of importance of mevalonate-acetate derived metabolites takes place. This decrease in the quantitative importance of the shikimate pathway is accompanied by a transition from woody to herbaceous growth. In light of our findings, the replacement of ligneous by herbaceous forms is a corollary of the coevolutionary relationship between plants and herbivores rather than reflecting increasing economy as often has been claimed.

Another instructive example of canalised evolution is provided by the sequential employment of hydroxycoumarins, linear furanocoumarins, and angular furanocoumarins in the Umbelliferae (BERENBAUM 1983). These groups of substances are progressively less suitable to polyphagous insects, yet some oligophagous species have counteradapted both physiologically as well as behaviourally. BERENBAUM (1983) finds the species diversity in coumarin-containing subgroups of the Umbelliferae greater than in subgroups that lack coumarins, and insect groups associated with coumarin-containing Umbellifers are more diversified than related groups on plants without coumarins. This corroborates the hypothesis that reciprocal evolutionary interactions, focusing on secondary plant chemistry, have been conducive in augmenting the diversity of plant and animal species since Cretaceaous times.

A similar explanation may be be envisioned for the extraordinarily broad range of oxidation-reduction levels that characterize angiosperm secondary metabolites. It has been shown that the rate of formation and the molecular properties of laccase in fungi depend upon the presence of inducers such as coumaric acid and gallic acid (MARBACH et al. 1983). Although the function of these oxidative enzymes is not yet clear, they may well operate in the detoxification of the host plant's allelochemicals. This function, together with the conversion of lipophilic compounds to water soluble, excretable compounds, is usually attributed to the mixed function oxidases (MFO) which are ubiquitous in animals (BRATTSTEN 1979). The potency of the MFO systems increases from monophagous to polyphagous species (KRIEGER et al. 1971; BRATTSTEN 1979) as well as with larval development and the concomitant increase of food consumption (AHMAD 1982). This suggests that the potency of the MFOs may also have increased evolutionarily, with the diversification of plant species and their secondary metabolites.

Thus it is to be expected that allelochemicals should be more and more reduced in order to be less and less easily oxidized, i.e., detoxified. Indeed, the sequence cinnamic acids → cinnamyl alcohols → allyl- and propenylphenols (*fig. 1*) accompanies the evolution of early land plants and there is no reason to suppose that this general reductive trend should cease with the appearance of the angiosperms. In this plant group, the origin of each new lineage coincides with the production of relatively higly oxidized compounds. Nevertheless, the general reductive trend persists, and in parallel in each lineage the oxidative power gradually decreases.

5. CONCLUSION

If the sudden appearance of more highly oxidized micromolecules has contributed to the success of angiosperm evolution and diversification, the relative ease of detoxification at the beginning of each major evolutionary line may constitute the attractive counterpoint of the plant-herbivore coadaptation. Thus the high oxidation state of secondary metabolites found in early angiosperms and at the onset of major lineages within the angiosperms may have intensified the relationship between plants and animals which, according to an attractive hypothesis (that can be traced to DOBZHANSKY 1950) was conducive in producing the diversity of plant and animal species since Cretaceous times. This would be at variance with the widely accepted ideas expressed by EHRLICH & RAVEN (1965) that the early radiation of angiosperms took place behind the biochemical "shield" formed by benzylisoquinolines. Subsequently, the diminishing oxidation level within different lineages could be expected to make detoxification more difficult and hence more selective.

Whatever the interpretation, the fact remains that a broad range of oxidation-reduction levels and a considerable number of precursors characterize the secondary metabolism of the angiosperms. Consequently, the existence of an ample oxidation-reduction potential and of a flexible activation-deactivation mechanism of enzymes in their cells must be important causes of the enormous diversity of angiosperm natural products and angiosperm species as well. This adds a fascinating new facet to the framework of hypotheses that have been erected around the question of why early angiosperms were so successful.

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