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EVOLUTION OF ANGIOSPERMS VIA MODULATION OF ANTAGONISMS

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Key Word Index—Quantitative phytochemistry; angiosperms; chemosystematics; acetate/shikimate relationships; evolutionary ecology; ecotones; evolutionary mechanisms; antagonisms.

Abstract—The controversies concerning the evolutionary mechanisms of flowering plants continue unabated in spite of the current trends toward the analysis of macromolecular data and of the growing body of distributional micromolecular data. The usual narrative approach to this latter effort is here replaced by a novel technique, quantitative phytochemistry. An evolutionary outline emerges and reveals modulation of antagonisms as the fundamental mechanism of angiosperm evolutionary ecology. Origin or operation of many systems can be rationalized analogously. It is concluded that the impact of opposing features possesses universal relevance. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

Great efforts have recently been made toward the inference of angiosperm phylogeny from macromolecular sequences [1]. However, even if this approach should eventually become fully successful, it will be of little use for the solution of practical ecology-based aspects. It is the purpose of the present work to introduce modulation of antagonisms as a fundamental mechanism of evolutionary ecology. To this end we first provide experimental evidence taken from our studies on quantitative phytochemistry, and then suggest the universality of the concept by the citation of cases selected from diverse fields of knowledge.

METHODOLOGY

Botanical abbreviations and comments

Dicotyledon subclasses: MAG Magnoliidae (families: Mag Magnoliaceae, Mon Monimiaceae, Ann Annonaceae, Lau Lauraceae, Her Hernandiaceae), RAN Ranunculidae (families: Men Menispermaceae, Ber Berberidaceae, Ran Ranunculaceae, Pap Papaveraceae, Fum Fumariaceae), CAR Caryophyllidae, HAM Hamamelidae, DIL Dilleniidae, ROS Rosidae, AST Asteridae. In Tables 1, 3-5, HAM, DIL and ROS are separated into 3 groups according to presence and absence of regulatory metabolites (GAL and CAF).

Cronquist [2] incorporated the subclass Ranunculidae into Magnoliidae, while for chemosystematic reasons in the present paper we prefer, following Takhtajan [3], to maintain the two subclasses apart.

Chemical abbreviations

SHI shikimic acid, CHO chorismic acid, PHE phenylalanine, TYR tyrosine, CAC cinnamic acids, CAL cinnamyl alcohols, APP allyl- and propenylphenols, GAL gallic acid, CAF caffeic acid, IND indole alkaloids, BIQ benzylisoquinoline alkaloids, LGN lignans, LIG lignins, NLG neolignans, PRO proanthocyanidins, ACE acetic acid, MEV mevalonic acid, POL polyacetylenes, PYR pyrrolizidine alkaloids, STE steroids, IRI iridoids, SIR secoiridoids.

Micromolecular categories—numbers of occurrences

Micromolecular categories in plant groups are represented by frequencies (= numbers) of occurrences (NO). The NO of a selected biosynthetic category known to occur in a family is established by the total

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Table 1(a). Numbers of shikimate-derived categories of angiosperm subclasses characterized by number of compounds and regulatory metabolites [36]

				GAL *sine* CAF			GAL and CAF			*sine* GAL			
No. of Cmpds	MAG	RAN	CAR	HAM	DIL	ROS	HAM	DIL	ROS	HAM	DIL	ROS	AST
1000	—	1	—	—	—	—	—	—	1*	—	—	—	1*
600	—	1	—	—	—	—	—	—	—	—	—	—	—
300	2	1	—	—	—	—	—	—	1	—	—	—	—
200	1	2	—	—	—	—	—	—	1*	—	—	—	—
150	1	—	—	—	—	—	—	—	1	—	—	—	2*
100	2	—	—	—	—	—	—	1*	—	—	—	—	—
< 50	7,1*	1	—	—	—	1*	1*	—	1,1*	—	1*	3	4

* Compounds derived from mixed biosynthetic pathways.

Table 1(b). Numbers of acetate-derived categories of angiosperm subclasses characterized by number of compounds and regulatory metabolites [36]

				GAL *sine* CAF			GAL and CAF			*sine* GAL			
No. of Cmpds	MAG	RAN	CAR	HAM	DIL	ROS	HAM	DIL	ROS	HAM	DIL	ROS	AST
2000	—	—	—	—	—	—	—	—	—	—	—	—	1
1000	—	—	—	—	—	—	—	—	—	—	—	—	1*
600	—	—	—	—	—	—	—	—	—	—	—	—	1
400	—	—	—	—	—	—	—	—	—	—	—	—	2
300	—	—	—	—	—	—	—	—	—	—	—	—	2
250	—	—	—	—	—	—	—	—	1	—	—	—	1
200	—	—	—	—	—	—	—	—	1*	—	—	—	1
150	—	—	—	—	—	—	—	—	1	—	—	—	2,2*
100	—	—	—	—	—	—	—	1,1*	1	—	1	—	4
< 50	1*	1	4	—	—	1*	1*	—	1*	1	1,1*	1	7

* Compounds derived from mixed biosynthetic pathways.

Table 2. Selected characteristics of angiosperm subclasses

Characteristics	MAG RAN CAR	HAM DIL ROS	AST
Metabolism	shikimate	shikimate + acetate	acetate
categories	few	many	few
alkaloids	frequent	rare	frequent
polyphenols	rare	frequent	rare
oxidative gradualism	frequent	rare	frequent
Morphology			
No. of families	29/10/14	25/78/116	49
No. of spp/family	276/375/740	135/316/540	1229
Ecogeography			
habitat	tropical	variable	temperate
distribution	restricted	vast	restricted

number of compounds registered for their species. The proportion of NLG/BIQ derivatives is given by:

$$\mathrm{NLG} = \frac{\mathrm{NO(NLG)} \times 100}{\mathrm{NO(NLG)} + \mathrm{NO(BIQ)}}$$

The proportion of micromolecular shikimate/acetate derivatives (SH) is established by the sum of the NO-values of the aromatic categories [NO(SH) = NO(NLG) + NO(LGN) + NO(PRO) + NO(CAF) + NO(BIQ) + NO(GAL)] vs the sum of the NO-values of the aliphatic categories [NO(AC) = NO(STE) + NO(IRI) + NO(POL) + NO(PYR)].

$$\mathrm{SH} = \frac{\mathrm{NO(SH)} \times 100}{\mathrm{NO(SH)} + \mathrm{NO(AC)}}$$

Table 3. Numbers of families of angiosperm subclasses for which metabolic profiles are available [36], characterized by Sporne indices and regulatory metabolites

				GAL *sine* CAF			GAL and CAF			*sine* GAL			
SI	MAG	RAN	CAR	HAM	DIL	ROS	HAM	DIL	ROS	HAM	DIL	ROS	AST
80	—	—	—	—	—	—	—	—	—	—	—	—	4
70	—	—	1	—	—	—	—	—	—	—	—	—	11
60	2	—	2	—	—	3	—	1	—	—	1	6	21
50	4	2	4	2	2	5	2	1	11	2	5	13	2
40	5	5	1	—	9	13	2	5	10	2	11	2	1
30	6	1	—	2	2	—	—	4	1	1	—	3	—
20	2	—	—	1	1	—	—	—	—	—	—	—	—
Mean	**39**	**41**	**54**	**36**	**39**	**45**	**45**	**39**	**46**	**42**	**44**	**49**	**64**

Table 4. Numbers of families of angiosperm subclasses for which metabolic profiles are available [36], characterized by woodiness indices and regulatory metabolites

				GAL *sine* CAF			GAL and CAF			*sine* GAL			
WI	MAG	RAN	CAR	HAM	DIL	ROS	HAM	DIL	ROS	HAM	DIL	ROS	AST
1	3	1	—	—	—	1	—	—	—	1	1	1	9
20	—	—	2	—	1	2	—	1	5	—	2	1	11
30	1	2	1	—	1	1	—	2	3	—	1	2	2
50	5	4	3	—	2	3	—	2	2	1	4	7	9
70	—	—	—	—	—	—	—	—	1	—	—	—	1
80	6	1	—	4	7	9	2	3	10	2	9	9	6
90	2	—	—	—	—	2	1	2	1	—	—	1	—
100	1	—	—	1	3	3	1	1	—	1	—	2	—

Table 5. Mean percentages of families of angiosperm subclasses based on 80 floristic inventories classified according to types of vegetation (f.forest) and range of latitudes in South America [26]

					GAL *sine* CAF			GAL and CAF			*sine* GAL			
Vegetation	Lat. (°S)	MAG	RAN	CAR	HAM	DIL	ROS	HAM	DIL	ROS	HAM	DIL	ROS	AST
Upland f.	2–12	8	2	2	—	6	11	2	9	20	2	10	6	10
Riverine f.	2–24	7	2	4	—	6	11	—	7	22	3	9	7	14
Cangas	6	7	2	2	—	3	1	3	7	20	3	11	4	13
Caatinga	6–9	3	—	5	—	7	9	1	5	14	1	9	7	17
Coast	6–28	6	2	7	—	5	7	1	5	15	1	7	5	19
Cerrados	13–22	5	2	3	—	8	9	1	6	22	2	7	3	17
Semidecid.f.	21–24	8	2	4	—	6	10	2	6	20	3	5	6	16
Atlantic f.	23–25	11	2	4	—	5	9	2	7	17	3	6	5	14
Open fields	23–30	4	3	6	—	5	10	1	9	17	2	6	5	24
Deciduous f.	30	4	1	6	—	5	8	1	6	20	2	8	3	22
Steppes	40–46	2	4	6	—	2	6	2	6	18	2	7	5	24

Oxidation state

The oxidation state of a compound (O) is determined by counting +1 for each C–X (X = heteroatom) and −1 for each C–H and dividing the sum by the number of carbons. Loss of a C-group is considered to operate through a carboxylated intermediate. The average of the O values of all compounds of the particular biosynthetic category is considered to represent the evolutionary advancement parameter of the species with respect to oxidation of the category (EA_O). The averages of the EA_O parameters of the species are considered to represent the EA_O parameter of their family.

Sporne indices

Morphological advancement in angiosperm families is represented by Sporne indices (SI). These indicate how infrequent is the presence of 30 characters regarded as primitive, in each of 291 families [4, 5].

Woodiness indices

Amount of lignin deposition in dicotyledonous families is represented by woodiness indices (WI). These are calculated by input values from 1–100, according to indications concerning the preponderant habit [6]. Thus, e.g. for families constituted only by "trees" WI = 100, and for families characterized by "herbs predominant over shrubs" WI = 12.5 [7].

Taxonomic uniqueness

Taxonomic uniqueness (TU) measures classificatory distances. The species listed in a biological inventory are compared pairwise in order to find the n-values characteristic of the highest classificatory ranks at which each pair diverges. Two species belonging to different genera, families, orders, subclasses (*sensu* [2]) and blocks (*sensu* [8]) respective n-value of 1,2,3,4 and 5 are assigned [9, 10]. The sequence of values can of course be extended to any level up to kingdom or domain. In the present context the highest n-value considered is 5. Hence TU = 5 corresponds to 100%.

$$\mathrm{TU} = \sum_{i}^{c} n/c \quad c = \text{number of pairwise combinations}$$

METABOLISM

The most obvious trend in the evolution of land plants concerns the oxygen dependence of woodiness [11]. Thus angiosperms, originating in the early Cretaceous [12], should have manifested at first trends toward woody forms and later, from K/T boundary times onward, toward herbaceous forms (Fig. 1). Biochemically lignification requires the reductive extension of the shikimate pathway beyond the ubiquitous phenylalanine stage toward cinnamyl alcohols, followed by the oxidative coupling of such monolignols. However, do these and other biosynthetic reactions of dicotyledons (Fig. 2) occur evolutionarily in the same direction?

The answer to this question is discerned by correlation of metabolic categories with the evolutionary advancement (Sporne) indices, SI, of the corresponding dicotyledonous families. According to analysis by this method (Fig. 3), the selected metabolic categories of angiosperms appear in the following order of increasing evolutionary advancement (as given by relevant SI ranges): NLG 28–61, LGN 34–72, GAL 37–57, BIQ 40–53, CAF 43–72, IND 48–61, STE 48–68, IRI 48–72, PYR 48–72, POL 57–72. Considering the early expression of NLG, LGN and BIQ (Fig. 3(a)), the former category is first enhanced and later replaced by the two further shikimate derived categories. LGN and BIQ in turn are followed by IND, and the acetate derived categories STE, IRI, PYR and POL (Fig. 3(c)).

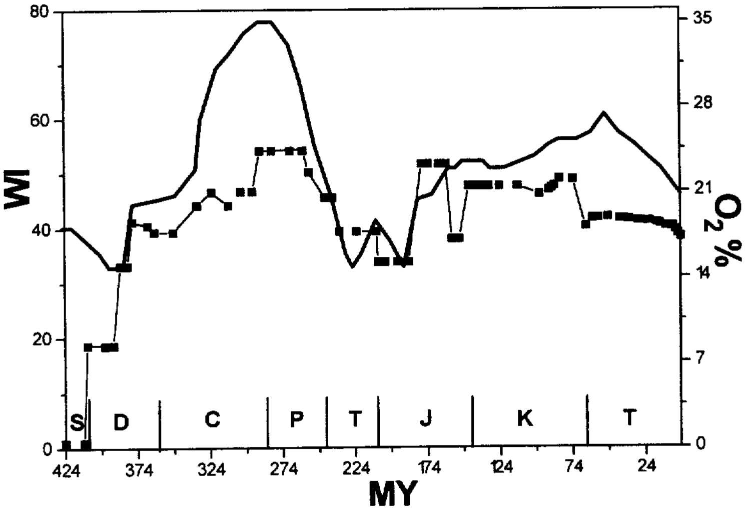

Fig. 1. Correlation of mean woodiness indices (WI) for divisions of vascular plants (■) per geologic stages (K Cretaceous, T Tertiary; MY millions of years before present) with the atmospheric oxygen content (thick line). Atmospheric oxygen content according to the model of Berner and Canfield [53]. The woodiness indices were determined considering the description of habit by Taylor and Taylor [54] and weighted according to indications of the relative abundance of each division[55]. Divisions: primitive vascular plants, lycopods, pteridophytes, progymnosperms, pteridosperms, conifers, angiosperms (dicotyledons only). Adapted from [56].

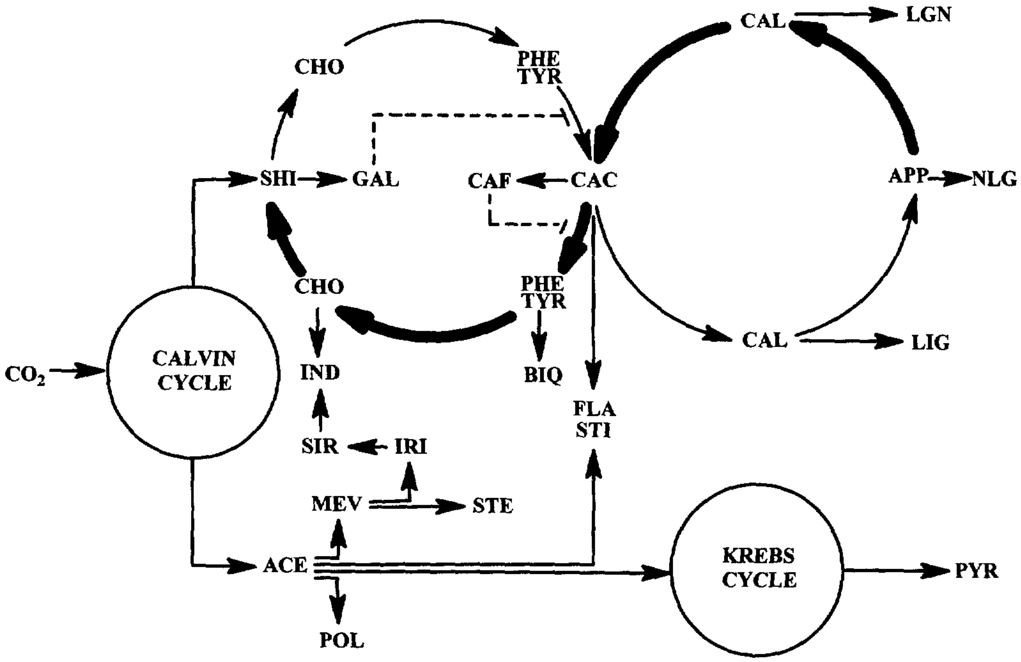

Fig. 2. Biosynthetic (thin arrows) and evolutionary (thick arrows) processes (i.e. activation/inhibition) leading to selected categories of secondary metabolites in angiosperms.

The order in which these categories are replaced by each other demonstrates this evolutionary process to run in reverse to the biosynthetic direction by successive step by step shortening of the shikimate pathway. The first stage of this evolutionary canalization [13–15] results in the accumulation of cinnamic acids; the second stage leads to the accumulation of GAL, while the third and last one is characterized by the trend toward replacement of shikimate by acetate derivatives.

GAL (Fig. 3(b)) appears in rather primitive (old) stock (SI = 37) in alternation to BIQ (Fig. 3(a)), a fact suggesting the early bifurcation of dicotyledons. Activator of the enzyme phenylalanine ammonia lyase (PAL) [16], GAL at the same time diminishes the rate of BIQ-synthesis and enhances the rate of cinnamic acid (CAC e.g. CAF)-synthesis, and thus opposes, via negative feedback, the trend of evolutionary canalization (Fig. 2).

Thus gallic acid plays a decisive regulatory role in this history. Restricted to families of lower evolutionary status (SI)(Fig. 4), it inhibits the major trend of angiosperm evolution from woody forms to herbaceous forms. Indeed, the proportions of woody (arbitrarily assigned WI > 65)/herbaceous (WI < 65) dicotyledon families *sine* GAL and *cum* GAL are respectively 70/89 and 21/15. In contradistinction, caffeic acid (Fig. 3(b)), an inhibitor of PAL [16], supplies positive feedback, i.e. revigorates the pathway in its original evolutionary direction by further debilitation of the shikimate route with concomitant strengthening of the acetate route for the production of secondary metabolites (Fig. 5).

Thus equalization of the attractive potency of both metabolic modes crosses an intermediate stage, seen to be coincident with modulation of GAL/CAF-expression (Fig. 3(b)), wherefrom metabolic novelty may, and indeed does (Tables 1(a, b)), arise. At this stage of low polarizations by internal factors, predictability of the resulting metabolic categories is low, and ecological influences are maximized.

An additional very conspicuous feature of gallic acid concerns its powerful antioxidant action. This is very significant, since secondary metabolites are mostly oxidation products of primary ones, i.e. the biosynthetic sequences usually start with condensations and reductions (to primary metabolites) and are finalized by oxidative steps. Confirming the systematic relevance of these results [17], additional examples concern steroids in angiosperms [18], lignins in vascular plants, flavonoid A-rings in plant groups, labdanes, iridoids and polyacetylenes in dicotyledons [19]. Indeed, the occurrence of neolignans [20] requires primitive angiosperms to possess a considerable redox potential. For this reason oxidatively differentiated secondary metabolites are accumulated in GAL-free (Fig. 6(a, b)); note the similarity with Fig. 3(a, c) but not in GAL-containing (Fig. 7(a, b)) families of identical SI-ranges. Only after the demise of such gallates, specific categories of secondary metabolites start to reappear.

Oxidative pathways within shikimate and acetate derived micromolecular categories mark respectively the subclasses Magnoliidae and Asteridae (*sensu* Cronquist [2]). The gradual enhancement of oxidation levels of BIQ in increasingly herbaceous Magnoliidae

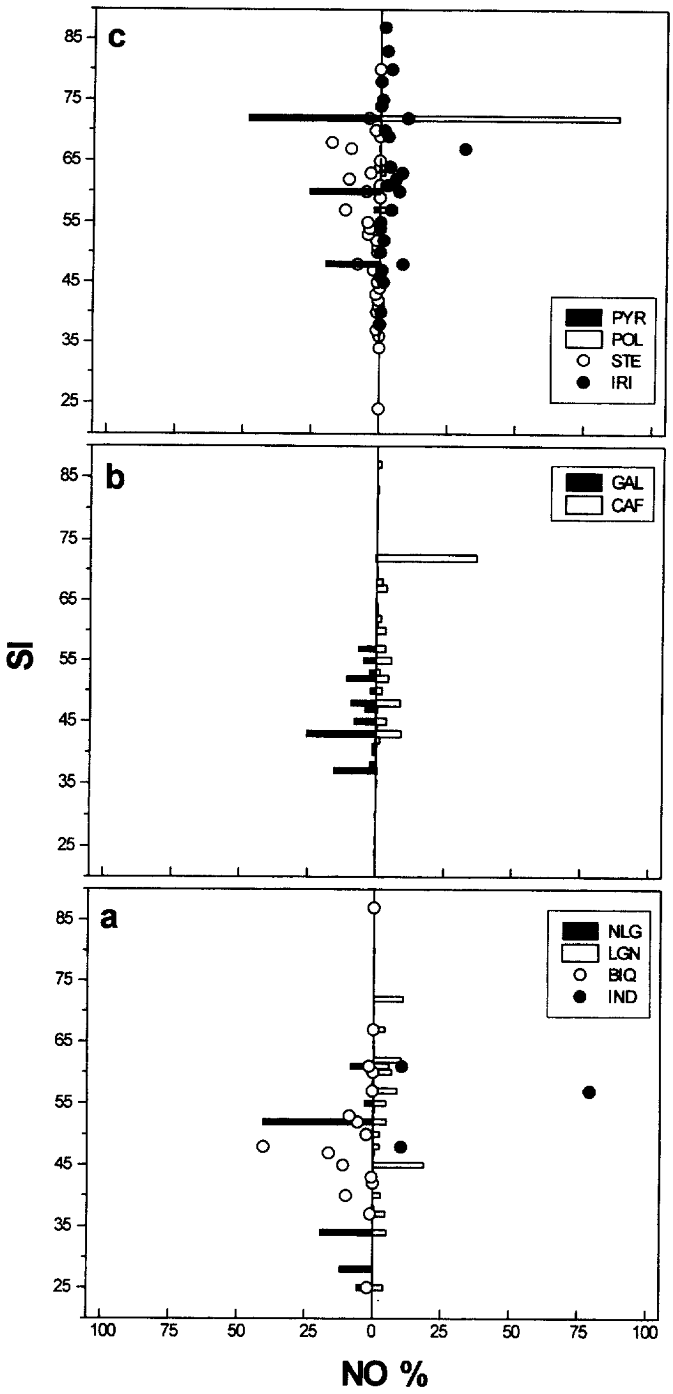

Fig. 3. Numbers of occurrences, in percentage values, of the indicated shikimate derived (a), gallic and caffeic acid derived (b) and acetate derived (c) micromolecular categories (each normalized to 100) per morphological advancement indices (SI) of chemically better known dicotyledon families [36].

families (Fig. 8) attains a climax within the predominantly herbaceous Ranunculidae. In the family Asteraceae, initially strongly oxidized sesquiterpene lactones suffer progressive reduction with evolutionary advancement of tribes [21, 22]. Oxidative pathways even yield clues for the connection of Magnoliidae and Asteridae through gallate-free families of Hamamelidae, Dilleniidae, and Rosidae, via the increasing mean oxidation levels of cucurbitacins, iridoids, polyacetylenes and pyrrolizidine alkaloids. In contrast, non-oxidative mixed pathways uniformly characterize gallate-rich families of the HAM, DIL,

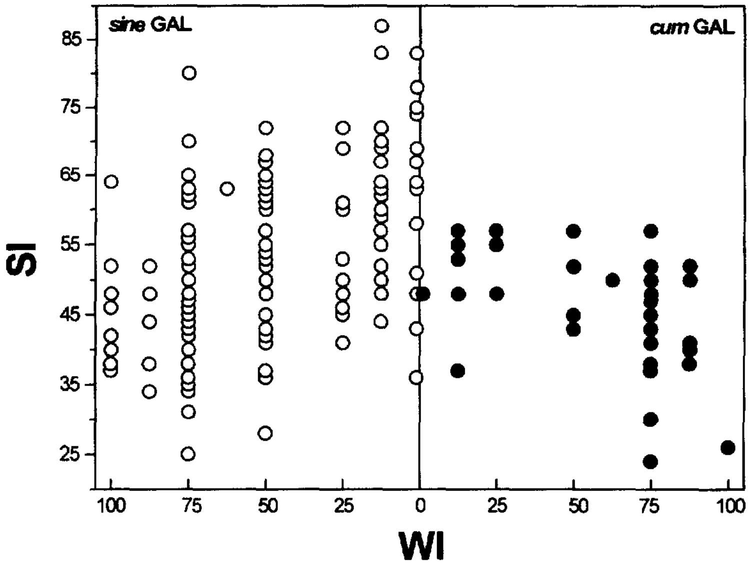

Fig. 4. Correlation of woodiness indices (WI) and Sporne indices (SI) for chemically better known dicotyledon families [36], without and with significant distribution of gallic acid, as gauged by numbers of occurrences (NO resp. < 9 and > 9 in % values of total NO).

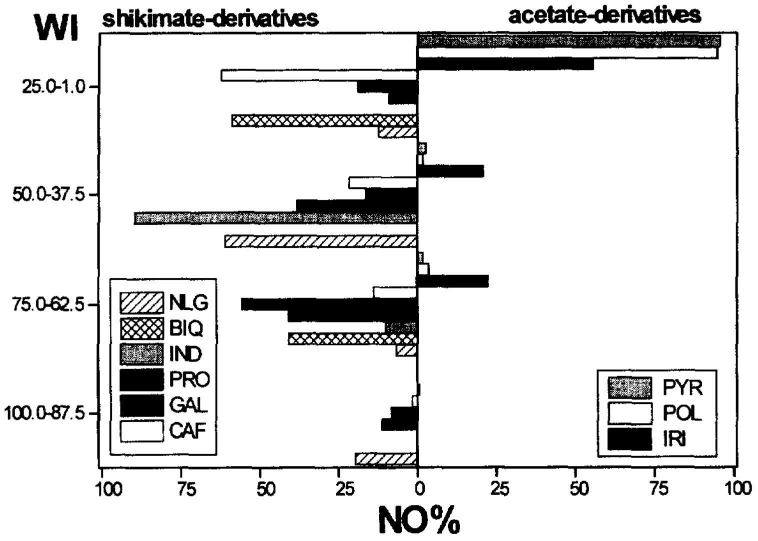

Fig. 5. NO (in % values of total NO) for 9 biosynthetic categories of chemical characters [36] per 4 ranges of WI.

ROS-complex (Table 2), and again gradual metabolic changes in angiosperms are interrupted by gallic acid.

MORPHOLOGY

Sporne indices for the measurement of morphology (Table 3), reveal the primitive Magnoliidae to be followed by Ranunculidae and Caryophyllidae, while Asteridae appear as the most modern outcrop. The HAM, DIL, ROS-complex *cum* gallic acid contains a larger proportion of more primitive families than the HAM, DIL, ROS-complex *sine* gallic acid. Additionally the two subclasses Magnoliidae and Ranunculidae lead via Rosidae *sine* gallic acid toward Asteridae. WI-oriented data (Table 4), for comparison with SI-oriented data (Table 3), reveal the internal chemical regulation by gallates toward lignification. Their introduction into the Magnoliidae (WI = 57), primitive gallic acid free angiosperm stock, enhances lignin accumulation from Hamamelidae (WI = 60 → 80), to gradually lesser extent over Dilleniidae (WI = 54 → 66) to Rosidae (WI = 61 → 64). The trend toward demise of gallic acid attains a maximum with the most herbaceous and again gallic acid poor Asteridae (WI = 32) (Fig. 9). The considerable proportion of woody Asteridae families may depend on the high

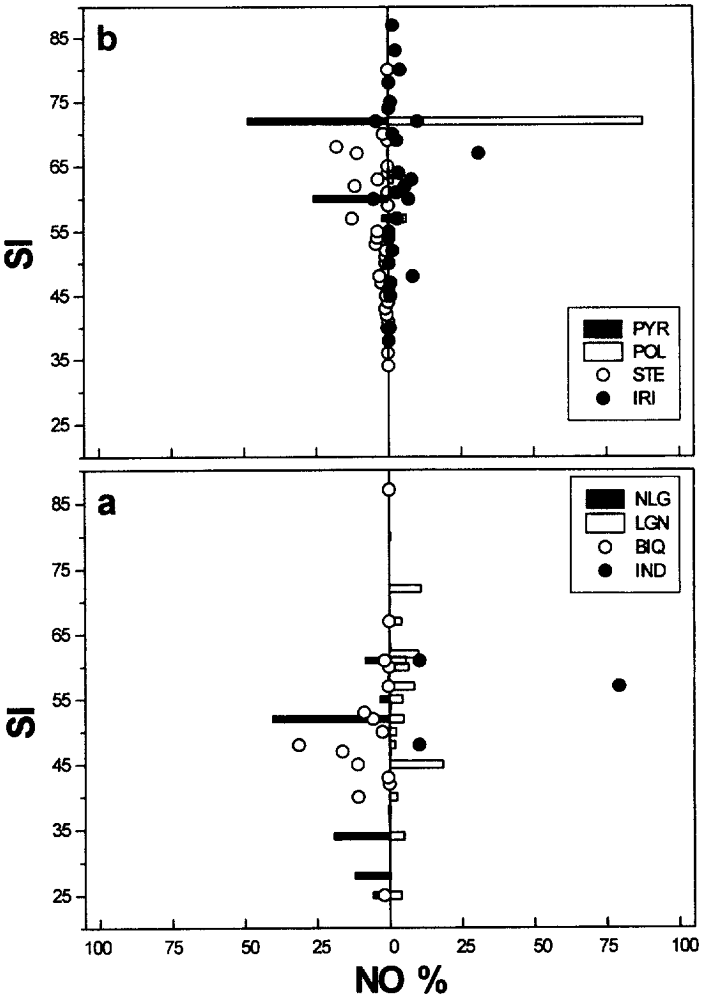

Fig. 6. As in Fig. 3 but for dicotyledon families without significant numbers of occurrences (NO < 9) of gallic acid.

oxygen content of the atmosphere, about 60 million years before the present [23], at the time of their origin (Fig. 1).

While shikimate-derived metabolic categories produce large numbers of micromolecules in the magnolialean block (Table 1(a), Fig. 10), acetate-derived categories are much better represented in the Asteridae (Table 1(b), Fig. 10) and the monocotyledons. The relative rarity of compounds in species of the HAM, DIL, ROS-complex is attenuated by CAF, which inhibits PAL-activation by GAL. This complex is characterized predominantly by categories of mixed (shikimate *plus* acetate) biosynthesis (Tables 1 and 2). Indeed correlation with an evolutionary scale based on WI, evidences twice the alternative predominance of NLG and BIQ, revealing at the same time the gradual substitution of gallic by caffeic acid (Fig. 5). Both these phenomena were examined in detail in order to evaluate their systematic potentialities.

NLG/BIQ proportions were postulated to represent the relative potency of the first and second stages of evolutionary canalization for the production of secondary metabolites in Laurales. The calculated values show NLG to be strongest for Trimeniaceae (100.0%) and weakest for Monimiaceae and Hernandiaceae (0.0%). Still within the NLG dominated field, but close to the critical transition (NLG = BIQ = 50%), Lauraceae (62.1%) assume an intermediate position.

Shikimate/acetate proportions were postulated to represent the relative potency of the shikimate pathway for the production of secondary metabolites. In the families without GAL (Fig. 11(a)), the calculated values show SH to be strongest for MAG (93.2%) and RAN (97.0%) and weakest for CAR (18.8%) and AST (19.9%). HAM (33.4%), DIL (51.8%), and ROS (40.8%) assume intermediate positions, preponderantly within the acetate dominated field, but close to the critical transition (SH = AC = 50%). By introduction of GAL (Fig. 11(b)), SH-potentials in HAM (92.7%), DIL (84.6%), and ROS (83.2%), suffer very strong changes (Δ respectively 59.3, 32.8, 42.4%), passing into the shikimate dominated field. Such substantial creative potential must lead to splin-

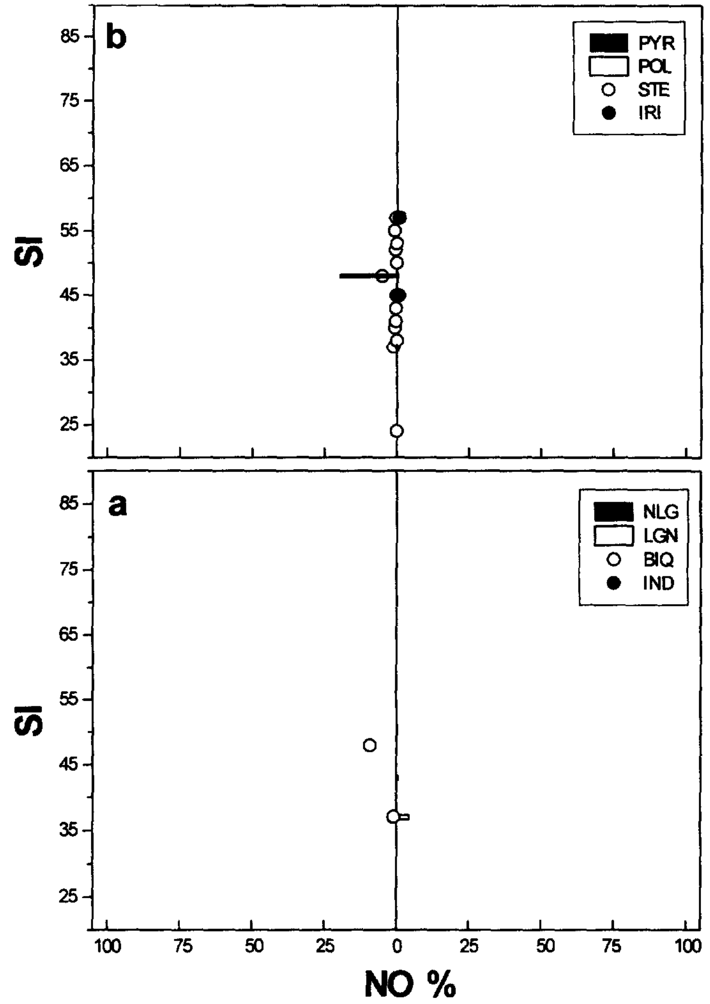

Fig. 7. As in Fig. 3 but for dicotyledon families with significant numbers of occurrences (NO > 9) of gallic acid.

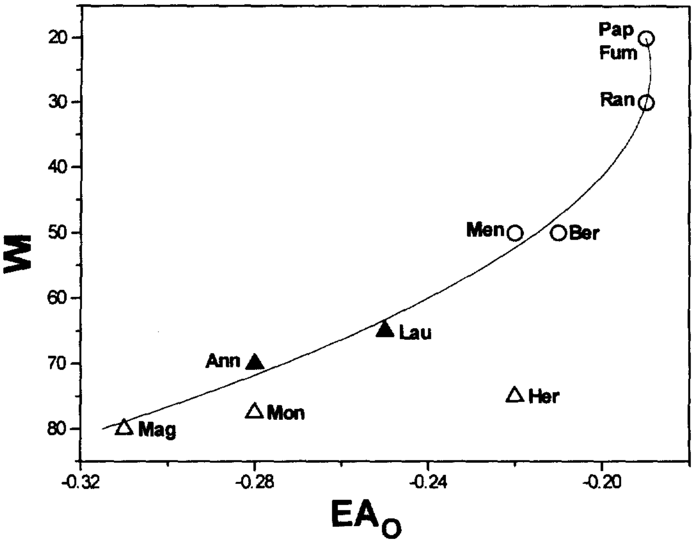

Fig. 8. Correlation of evolutionary advancement with respect to oxidation levels of benzylisoquinoline alkaloids (EA_O) and the woodiness index (WI) for families of Magnoliidae (Δ) and Ranunculidae (○). Dark and light symbols: proanthocyanidins resp. present and absent.

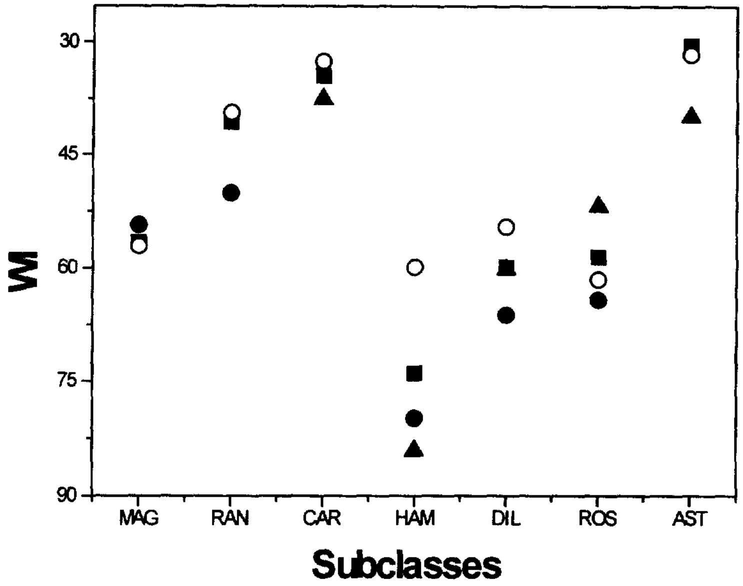

Fig. 9. Mean woodiness indices for all families (■), and for families characterized by regulatory metabolites [GAL *sine* CAF (●), GAL & CAF (▲) and *sine* GAL (○)] The plot justifies the separation of angiosperms into two blocks [8], the magnolialean block (with the subclasses MAG, RAN, CAR) and the rosiflorean block (with the subclasses HAM, DIL, ROS, AST).

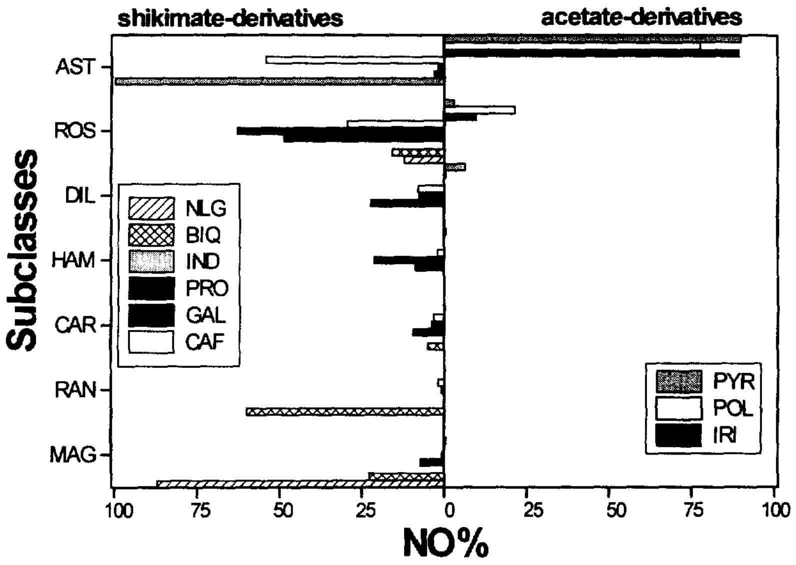

Fig. 10. NO (in % values of total NO) for 9 biosynthetic categories of chemical characters [36] per 7 subclasses of dicotyledons.

tering of the species into relatively many higher taxa such as orders or families (Table 2) and to the consequent differences in opinion on classificatory affinities [24] of plant groups in two blocks [8]. In contrast, MAG (100.0%), RAN (100.0%), and AST (24.9%) remain relatively stable (Δ respectively 6.8, 3.0, 5.0%). The pronounced trend toward shikimate metabolism for CAR (38.3%, $\Delta = 19.5$) is registered only if the families Polygonaceae and Plumbaginaceae (the former gallate containing) are included in CAR as in Cronquist's [2], but not in Dahlgren's [25] classification of angiosperms.

Gallic acid occurs preponderantly in plants of temperate regions (e.g. in oak and birch). Indeed ecogeographic considerations are of great interest for the rationalization of angiosperm evolution.

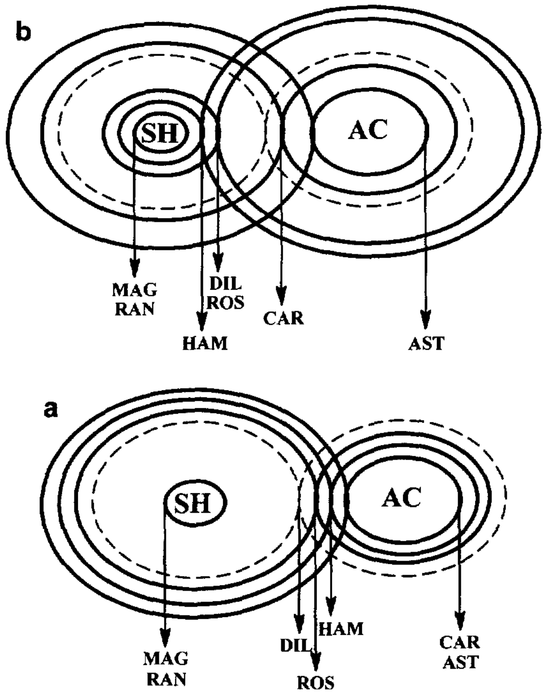

Fig. 11. Mechanical models representing shikimate derivation (SH) as metabolic attractors for angiosperm subclasses in absence of GAL (a) and in presence of GAL (b).

ECOLOGY

Many more families of Magnoliidae occur in forests, than in steppes (Table 5). Families of Ranunculidae, of Caryophyllidae, and very conspicuously of Asteridae, increase in importance countercurrently. In contrast to the irregular habitat-dependent distribution of the number of Magnoliidae and Asteridae families, the analogous distribution of families of the subclasses Hamamelidae, Dilleniidae, and Rosidae is strikingly uniform.

Biodiversity is usually expressed by the number of species in a given area. This will provide data on productivity, but not on taxonomic uniqueness, the relative importance of the area as a natural "genetic bank".

Correlations of taxonomic uniqueness of 80 South American areas [26] either with increasing southern latitude (Fig. 12(a)) or with decreasing woodiness (Fig. 12(b)) both show similar features. Lowest for the Amazonian forest species, habitat and habit (WI) transitions include strikingly abrupt disjunctions. In the former case these are situated at 10–15° and 30° southern latitude, in ecotones (tension zones), regions of transition between two or more communities, generally characterized by high biological diversity due to intense biotic-abiotic interactions [27]. In the latter case, lignin production in dense, and hence profoundly shaded forests, represses the formation of herbaceous plants, and hence the acetate derived biosynthetic pathway. The integration of ecology (impact of vegetation types) and evolution (liberation of the lignin promoted blockage) rationalize the abruptness in the increase of biodiversity.

EVOLUTIONARY MECHANISM

Edwards [28] refers to a "fascinating analysis of the evolution of secondary plant substances [29]. This shows the acquisition of new biosynthetic pathways to have contributed to a phase of rapid evolution within a taxon. However, biosynthetic breakthroughs occur infrequently. The evidence from oxidative modulation of secondary metabolites within biosynthetic categories tells us that the categories of many plant species have changed little over long periods of time, presumably because of the absence of suitable genetic variation. It is the evidence of stasis which is perhaps the most important lesson for ecologists."

General evolutionary trends for angiosperms are conveyed graphically by a sequence of partially superimposed gaussian patterns (Figs 3, 6) featuring the gradual replacement of shikimate-derived metabolic categories successively by shikimate-acetate and acetate-derived ones. While shikimate-derived categories are subject to rather neat replacements, most typically angiospermous acetate-derived categories appear at comparable, relatively high ranges of evolutionary status. This rise-and-fall pattern demonstrates the evolutionary mechanism to involve alternation of metabolic activation and inhibition.

Angiosperm evolution proceeds on all hierarchical levels by modulation of antagonistic pairs. Consisting of metabolic attractors, these pairs are necessarily interrelated by reaction sequences. Decreasing attractive power (100 → 0%) of one antagonist, implies in increasing attractive power (0 → 100%) of the other. When the attractive forces become of comparable potency (50%), creative situations, here exemplified by the cases of the Laurales and of the HAM, DIL, ROS-complex are expected to occur.

With respect to the first case, involving NLG/BIQ as metabolic attractors, cinnamic acids may either suffer reduction to lignoids, or diversify, through the use of mixed cinnamate-acetate intermediates, into products such as stilbenoids, arylpyrones and styrylpyrones [30]. In angiosperms, the champions of such trials toward modification of the flavonoid theme are Lauraceae, Piperaceae and monocotyledons. In Laurales, Lauraceae are about equally characterized by NLG and BIQ (see above). Hence, Piperaceae and monocotyledons might conceivably be rooted in the vicinity of Lauraceae. With respect to the second case, involving SH/AC as metabolic attractors, the equally intermediate HAM, DIL, ROS-complex also employs mixed biosynthetic pathways in striking frequency. Molecular flexibility in this complex is again evidenced by the relatively large range of WI-values caused by introduction of gallic acid (Fig. 9). Indeed it can be envisaged that the originally tropical magnolialean lineage would have been sufficiently woody to displace

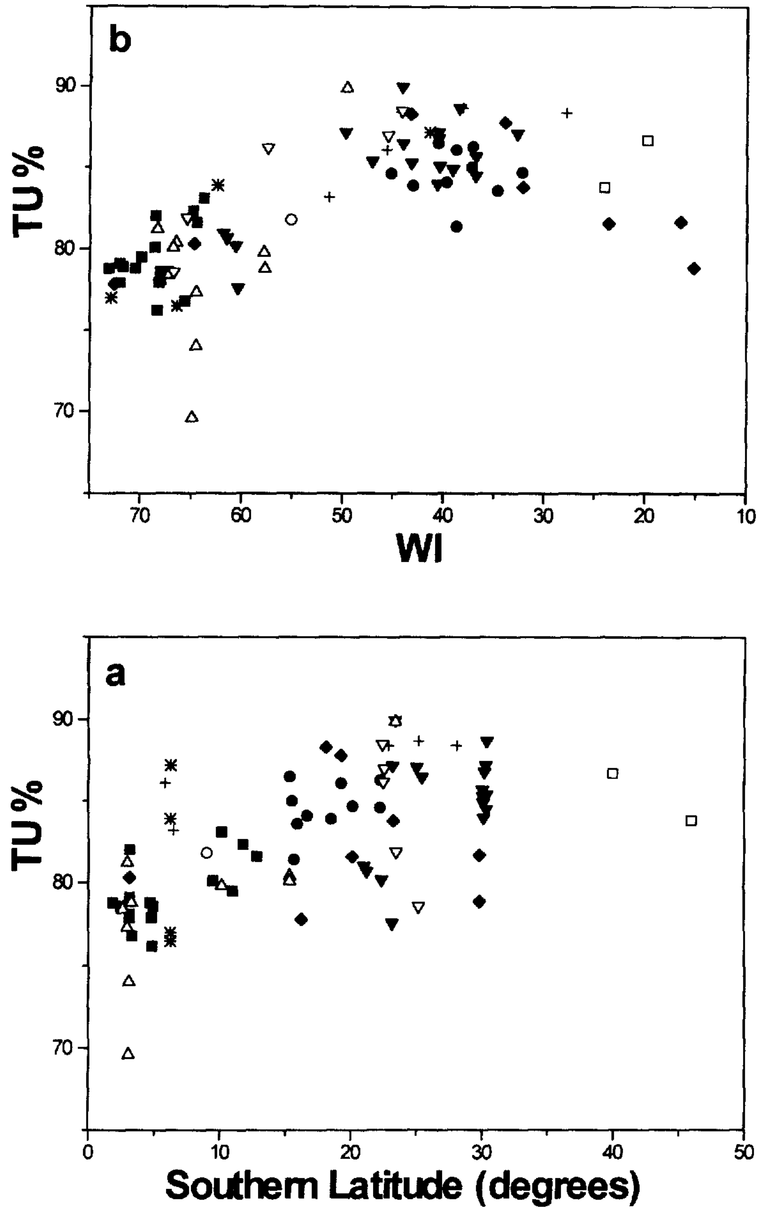

Fig. 12. Correlation of taxonomic uniqueness (in TU%) and southern latitude (a) and mean woodiness indices (b) of 80 neotropical areas [26]: Upland rain forests (■), cangas (vegetation on haematitic soils)(*), riverine forests (△), caatinga (○), cerrados (●), open fields (◆), forests (▼), Atlantic forests (▽), coasts (+), steppes (□).

shrubby (conceivably gnetalean [31, 32]) gymnosperms in tropical climates; but when in need of stronger lignified structures for the displacement of woody (conceivably coniferous [2]), gymnosperms in temperate climates achieved this goal by gallate induced strengthening of the shikimate route.

The often sporadic occurrence of the so called secondary metabolites in representatives of plant lineages has suggested to investigators for more than a century that, in contrast to the ubiquitous primary metabolites, secondary metabolites should have been selected for their functional advantage. However, in this case general dynamic trends of micromolecular expression and diversification, evidenced throughout the present work, should hardly be perceptible. Nevertheless, the organelles and their respective bacterial predecessors being specific and clearly differentiated producers of secondary metabolites, sporadic occurrence within homologous taxa could be rationalized by the serial endosymbiotic theory [33]. It is hoped that SET, together with modulation of antagonisms, may reveal the factors involved in the selection of phytochemicals, a task which so far has proved to be extraordinarily elusive. Indeed, as stated previously

[34] "answers as to *why* biochemical evolution has proceeded as it has are invariably clothed in ambiguity". Thus, the relevance of the present effort concerns the recognition of secondary metabolites in their long neglected role as dynamic markers of evolutionary ecology.

Table 6. Selected plant systems and corresponding antagonisms

Secondary metabolism: shikimate/acetate (Fig. 2); NLG/LGN/BIQ/IND (Figs 3(a), 5, 6(a), 7(a)); GAL-/CAF (Fig. 3(b)); STE/IRI/PYR/POL (Figs 3(c), 6(b), 7(b)); GAL/LIG (represented by WI)(Fig. 4); polyphenols/micromolecules (Figs 5–8); LIG-/micromolecules (Fig. 8); simple biosynthesis/mixed biosynthesis (Tables 1(a, b)).
Families: BIQ/LIG (Fig. 8)
Subclasses: GAL/CAF (Figs 9, 10); CAF/LIG (WI)(Fig. 9); GAL/micromolecules (Fig. 10); SH/AC (Tables 1(a, b), Figs 10,11).
Dicotyledons: MAG/HAM, DIL, ROS (Tables 1–5); HAM, DIL, ROS/AST (Tables 1–5).
Vascular plants: Magnoliales/Gnetales; angiosperms/gymnosperms; lignification/ecology (Fig. 1).
Regions: woodiness/biodiversity (Fig. 12(b)); ecogeography/biodiversity (Fig. 12(a)).

Table 7. Selected systems and corresponding antagonisms

Matter: quantum effects (Pauli exclusion principle)/electrical attractive force [37].
Universe: expansion/gravitation.
Star:outward pressures/gravitational attraction.
Evolution: chance/necessity (selection) [38].
Morphogenesis: short-range activation/long-range inhibition [38].
Metabolism: anabolism/catabolism, dehydration/hydrolysis, reduction/oxidation.
Cellular DNA: replication/mutation, UV-damage/blue-light photolyase repair [39].
Blood sugar control: glucagon/insulin [40].
Defective cells: tumor necrosis factor α/nuclear factor KB [41].
Cellular homeostasis: proliferation/apoptosis [42].
Leaf senescence: cytokinin/isopentenyl transferase [43].
Heart: neurocardiotoxins (lycotonine)/neuroprotectors (14-benzoyltalatizamine)[44].
Adaptive immunity: antigen/antibody.
Memory: excitatory synapsis (glutamic acid)/inhibitory synapsis (γ-aminobutyric acid)[45].
Cellular evolution: endosymbiosis of chemically antagonistic units (Calvin cycles/Krebs cycles).
Lichen: cyanobacterium/fungus.
Plant: insect attractor/insect antifeedant. Insect adaptability: juvenile hormones/ecdysones [46].
Drosophila leg: wingless/decapentaplegic [47].
Brain: endocrine system (corticosteroids)/immune system (interleukins)[48].
Biological systems: positive feedback/negative feedback [49, 50].
Lizards (*Uta stansburiana*): aggressive (testosterone rich) males/temperate (testosterone poor) males [51].
Cultural dynamics: competition/cooperation [52].

So far "investigation of the evolutionary history of the angiosperms has proved to be unexpectedly difficult" [1, 12]. Why? Consensus on the evolutionary *history* of a group of organisms will only be reached upon its evaluation against the background of a compatible evolutionary *mechanism*. Data based on morphology of fossilized fragments of organisms cannot provide conclusive evidence on this subject. Data based on metabolism, morphology and ecology of extant angiosperms reveal evolutionary mechanisms to operate at different organizational levels (systems) via interactive, inductive or alternative, antagonistic molecular categories or biological taxa, and, in the case of metabolism, even antagonistic cascades (Table 6).

Antagonistic pairs exert opposing actions on systems. Hence in the extreme case, the trend to annulment of one of the pairs would liberate the other to propel the system to extinction. However, in the general case, the effects of antagonists being interrelated, their transition should be amenable to mathematical analysis via duality transformations [35]. Antagonistic pairs characterize such a wide range of physical, chemical, biological and social systems (Table 7), that the concept of their modulation emerges as a fundamental mechanism of universal development.

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