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A PHYLOGENETIC CORRELATION OF THE GENERA *DALBERGIA* AND *MACHAERIUM*[1,2]

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Abstract—A survey of the botanical and phytochemical characteristics of a number of species of *Dalbergia* and *Machaerium* has been made. This provides a phylogenetic basis for dividing these two genera into four species series: *Dalbergiae pantropicales, Dalbergia brasilianae, Machaeria scleroxyla*, and *Machaeria villosa.* The relation of these proposals to the theory of Continental Drift is considered.

THE BEAUTIFUL and durable heartwoods of several *Dalbergia* species have been articles of commerce[3,4] since the days of the early colonization of Brazil. *Dalbergia decipularis*[5] continues to be used commercially, but in more recent years the heartwood of *Machaerium scleroxylon*[6] has started to be adopted as a substitute for *Dalbergia nigra*, which is becoming scarce. In spite of this economic interest, however, the botanical information concerning *Dalbergia* and *Machaerium* is surprisingly meagre, and only classical descriptions are found in the literature;[7,8] these are frequently unreliable and have often been based only on dried herbarium specimens.

The results of our phytochemical examination of the genera *Dalbergia* and *Machaerium* are presently being published. A re-assessment of the botanical data in the light of present knowledge was therefore needed in order to assess the extent to which phytochemistry could be used as an aid in taxonomic determinations for this group of plants.

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[5] C. T. RIZZINI and A. DE MATTOS FILHO, *An. Acad. Brasil. Ciênc.* **40**, 231 (1968).

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BOTANICAL SURVEY

The generic distinction[7] between *Dalbergia* and *Machaerium* has been based upon the following morphological characters.

(1) Anthers terminal and dehiscent by a transverse or oblique slit. Legume slender, flat, oblong to linear, one to few-seeded. *Dalbergia* L.f.

(2) Anthers versatile, longitudinally dehiscent. Legume thick, with one seed at base and prolonged upwards into a large wing. *Machaerium* Pers.

These two genera do not present clear-cut, distinctive anatomical characters, but instead they show structural features which suggest either one genus or the other. Not even the specialist is always capable of distinguishing between the two genera on grounds of anatomical characters. The secondary wood in *Machaerium* species is much harder and heavier due to its more compact organization; the pores are minute, very numerous, and are either barely visible or invisible to the naked eye. The wood of *Dalbergia* species has a much more open structure, but the difference is one of degree and not of type. Another vegetative feature of *Machaerium* species is the production of thorns, which is observed in many species, principally during the juvenile stage or in the saplings; old trees may appear unarmed. An example of this situation can be found in *M. scleroxylon.*

The following discussion refers mainly to Brazilian species which have been chemically examined.

Seriation of Dalbergia *species*

The following natural series of *Dalbergia* species can be recognized.

I. *Inflorescences paniculate.* Pod one to few-seeded, the seminiferous nucleus slightly thickened. Wood, blackish-brown to almost black, irregularly striped or spotted. Rhytidoma thick, sulcate or fissured.

(1) Tree, medium-sized; bark thin and exfoliating in platy scales. Leaflets not coriaceous, the veins and nerves impressed, 7–15 mm long and 4–8 mm wide. Legume 1–2-seeded, 50–80 mm long and 12–15 mm wide. Wood odoriferous. Atlantic forest and coastal forest, from São Paulo to Southern Bahia. Local names: 'jacarandá', 'jacarandá-da-bahia'. *D. nigra* (Vell.) Fr. Allem.

(2) Tree small; bark very thick, furrowed. Leaflets leathery, almost nerveless, 18–25 mm long and 7–13 mm wide. Legume 1–2-seeded, 50–70 mm long and 15–20 mm wide. Wood odourless. Central Brazil, in the 'cerrado' (wooded savannah) and 'campo limpo' (grassy savannah). Local names: 'cabiúna', 'caviúna'. *D. miscolobium* Benth. [or *D. violacea* (Vog.) Malme]

(3) Tree resembling *D. nigra.* Leaflets subcoriaceous, 30–60 mm long and 15–30 mm wide. Legume 1–3-seeded (ovary 10–12 ovulate), 60–100 mm long and 17–25 mm wide. Wood odourless. 'Terra firme' (upland) forest, in the Amazonas and Pará States. Local name: 'jacarandá-do-pará'. *D. spruceana* Benth.

D. villosa Benth. and *D. barretoana* Hoehne are closely related species which belong, according to gross morphological data, to series I. A difference is, however, also evident since they show nine instead of ten stamens.

D. sissoo Roxb, may also be preferentially linked to series I. It shows, however, only eight stamens, a fact which places it in a rather distant position.

II. *Inflorescences cymose.* Pod one-seeded, the seminiferous nucleus thickened. Wood in various shades of red or purple, more or less regularly streaked. Rhytidoma very thin, smooth, or lamellated.

(1) Treelet or scandent shrub. Wood brown-purple or brown-red, lighter than in (2). Leaflets 5–13, obovate-oblong, the vesture variable. The species is of wide distribution throughout the rain forests from Argentina to the Amazon; it is particularly widespread in the South-Eastern forests. Local names: 'cipó-violeta' (Santa Catarina) and 'pau-de-estribo' (Rio de Janeiro). *D. frutescens* (Vell.) Britt. (= *D. variabilis* Vog.)

(2) Trees erect, small, in the 'caatinga' (semi-arid tract with shrubby vegetation) and medium-sized in the dry forest. Wood rose-red or purple, heavy and hard. Some well-defined local species are placed here which are only identified either by the above characters or by their locations.

(2a) Bark smooth. Leaflets 5–7, ovate, glabrous. Calyx hairless. Wood brownish-purple with deep-coloured stripes. Ceará, Bahia, and Pernambuco. Local names: 'violete' (Ceará) and 'violeta' (Bahia). *D. cearensis* Ducke

(2b) Bark breaking up into narrow plates. Leaflets 7 (5–9), oblong or ovate, pilose beneath. Calyx villose. Wood yellow-rose streaked with red, and with a fragrant scent when freshly cut. Central Bahia. Local name: 'sebastião-de-arruda'.
D. decipularis Rizz. & Matt.

D. ecastophyllum (L.) Taub. and *D. volubilis* (L.) Urb. are related. They differ from all previously mentioned species by the anatomy of their wood and the form of their fruit. *D. ecastophyllum* is of wide distribution over the seashores of both tropical America and tropical occidental Africa. *D. volubilis* grows in the Amazon forest.

These two species-series, I and II, differ considerably in their evolutionary status. Series II is dominated by *D. frutescens* which is a polymorphic species of wide geographic distribution. The numerous transitional forms of this species have made taxonomic determination difficult in the past. Close local forms have only recently been described in full, and only now may be recognized with certainty. The series II is therefore characterized by a state of current vigorous evolutionary differentiation.

On the other hand, series I is composed only of species with well defined characteristics, and its members are found in independent areas. Clearly, in relation to series II, the evolution of series I has already led to a high degree of differentiation. The conclusion that series I is of more ancient origin than series II is clearly indicated.

Both series are composed of vicarious species. Thus, *D. decipularis* and *D. cearensis* resemble each other understandably, since they both evolved in different dry regions from *D. frutescens*. Similarly, *D. miscolobium* is considered to be derived from *D. nigra*,[9] but a similar relationship between *D. spruceana* and *D. nigra* is less evident.

Seriation of Machaerium *species*

The following natural series of *Machaerium* species are recognized.

I. Leaflets small, mostly shorter than 3 cm, oblong and rounded at the apex.

(1) Stipules indurate and spinescent. Legume emarginate on one side and puberulous at the basal portion. Atlantic forest. *M. nictitans* (Vell.) Benth.

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[9] C. Rizzini, in *Simpósio Sôbre o Cerrado*, p. 125, Editora da Universida de de São Paulo, São Paulo (1963).

(2) Thorns unknown. Fruit as above. Calyx lobes almost linear. Inflorescence pilose. Atlantic forest. *M. kuhlmannii* Hoehne

(3) Stipules deciduous or reduced to small spines (these may be much larger in juvenile trees or the sprouts). Legume bullate at the seminiferous area. Atlantic forest and its inland stretches. *M. scleroxylon* Tul.

II. Leaflets larger, mostly longer than 3 cm, lanceolate and acute at the apex.

(1) Leaflets villose beneath. Legume reticulate at the base about the seed. Damp to rather dry forest; sometimes observed in the 'cerrado'. *M. villosum* Vog.

(2) Leaflets glabrous or puberulous beneath, the apex not or shortly mucronate. Legume bullate at the basal, seed-bearing portion. The same habitats as indicated above. *M. acutifolium* Vog.

(3) Leaflets puberulent beneath, the apex long-mucronate. Legume unknown. Forest and 'cerrado'; rare. *M. mucronulatum* Mart.

III. Leaflets as in series II, oval or oblong, the apex slightly attenuate or somewhat obtuse.

(1) Leaflets thick and firm, cordate at the base. Tree with an extremely thick bark, inhabiting the 'cerradões' and 'cerrados' of Minas Gerais and Goiás States. *M. opacum* Vog.

(2) Leaflets thinner and softer, obtuse at the base. Tree endowed with a normal rhytidoma, from the gallery forest in São Paulo State. *M. vestitum* Vog.

Clear-cut homogeneous series of related species occur in *Machaerium* and *Dalbergia*, but the interspecific relations within the series associated with *Machaerium* are not as clearly defined as in *Dalbergia.* No neat demarcation separates the regions of occurrence of species so that the concept of vicariism is not applicable.

Only slight differences are noted between *M. kuhlmannii* and *M. nictitans*, and between *M. mucronulatum* and *M. acutifolium*. Although the data available for these pairs of species are insufficient to validate any definite conclusion, it may well be that both pairs are represented by species at a little advanced stage of differentiation. Speciation is therefore considered to have begun at comparatively recent times, and the two series I and II to which these pairs of *Machaerium* species belong must thus be rather young. The situation in both series is similar to that prevailing in *Dalbergia* series II, where distinction between *D. frutescens*, *D. cearensis*, and *D. decipularis* is equally difficult without recourse to the wood anatomy and the morphology of the living tree.

The sole representative of the 'cerrado', *M. opacum*, does not show a close morphological affinity with any other species. Its classification in series III together with the little known *M. vestitum* is therefore an expedient which may well have to be modified in the future.

THE PHYTOCHEMICAL COMPARISON OF *DALBERGIA* AND *MACHAERIUM*

The association of neoflavanoids with *Dalbergia* species is now generally recognized,[10,11] and in view of the taxonomic proximity of the genera, *Dalbergia* and *Machaerium*, our

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[10] W. D. OLLIS, *Experientia* **22**, 777 (1966).

[11] W. D. OLLIS, in *Recent Advances in Phytochemistry* (edited by T. J. MABRY, R. E. ALSTON and V. C. RUNECKLES), Vol. 1, p. 329, Appleton-Century-Crofts, New York (1968)

studies were extended at an early stage to include the phytochemical examination of as many of the Brazilian *Machaerium* species as could be easily obtained. These studies are still in progress, but at the present stage some general chemotaxonomic trends are becoming apparent. The types of phenolic compounds which have been isolated are summarized in Table 1. This refers to those species where a detailed examination of the extractives has been made either by ourselves or by others.

The neoflavanoid class of natural products (see Fig. 1) includes the dalbergiquinols (I), the dalbergiones (II), the neoflavenes (III), and the dalbergins (IV). It has been suggested that these groups of structurally related natural products are formed by cinnamylation of a benzenoid or polyketide precursor and that they are inter-related by the bio-oxidative sequence:

Dalbergiquinol → dalbergione → neoflavene → dalbergin[12,13]

This bio-oxidative sequence may also be involved[11] in further oxidation of dalbergins (IV) to certain benzophenones (V) including cearoin, isolated from *D. cearensis*[14] and *D. spruceana*[14] and scleroin, isolated from *M. scleroxylon.*[12] Attempts to examine our biogenetic proposals[13] for the formation of neoflavanoids by the feeding of radio-labelled substances as possible precursors to plants have not been successful, but this is a common problem in trying to determine the biosynthetic routes associated with the formation of heartwood constituents. However, the proposals for neoflavanoid biosynthesis given in Fig. 1 are in accord with the biogenetic analysis of the constitutions of a quite large number of neoflavanoids isolated from various *Dalbergia* and *Machaerium* species. Strong support for the proposed formation of neoflavanoids (I–IV) by a cinnamylation process is provided by the discovery that neoflavanoids are often congeneric with cinnamylphenols (VI),[15] and in two cases their co-occurrence with 2,3-dihydrobenzofurans (VIII) has been detected.[16,17] Dalbergiquinols (I), cinnamylphenols (VI), and 2,3-dihydrobenzofurans (VIII) are consequences of different modes of reaction between the phenolic and cinnamyl precursors,[12,13] and just as a bio-oxidative sequence inter-relates the neoflavanoids (I → II → III → IV), so the quinonemethides (VII)[18] may be similarly derived from cinnamylphenols (VI).

The dalbergiquinols and dalbergiones have been isolated with either the R-configuration (Ia and IIa) or the S-configuration (Ib and IIb). The two 2,3-dihydrobenzofurans which have so far been described[16,17] have the chiralities designated in the formulae (VIIIa and VIIIb). Nine cinnamylphenols have so far been isolated,[15] of which three have been shown to have the *cis*-configuration (VIa) and six the *trans*-configuration (VIb).

Inspection of Table 1 shows a satisfying correlation between the extent and the positions of oxygenation of neoflavanoids (I–IV), cinnamylphenols (VI and VII), and 2,3-dihydrobenzofurans (VIII) isolated from *particular* species. Thus, the compounds isolated from

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[12] W. B. Eyton, W. D. Ollis, M. Fineberg, O. R. Gottlieb, I. Salignac de Souza Guimarães and M. Taveira Magalhães, *Tetrahedron* **21,** 2697 (1965).

[13] W. D. Ollis and O. R. Gottlieb, *Chem. Commun.* 1396 (1968).

[14] J. T. Cook, W. D. Ollis, I. O. Sutherland and O. R. Gottlieb, forthcoming publication; C. H. Souza Andrade, unpublished results.

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[17] B. J. Donnelly, D. M. X. Donnelly, A. M. O'Sullivan and J. P. Pendergast, *Tetrahedron* **25,** 4409 (1969).

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Table 1. Comparison of the frequency of occurrence of neoflavanoids and biogenetically related compounds (see Fig. 1), and isoflavanoids (see Fig. 2) in the genera *Dalbergia* and *Machaerium*. The numbers in this table refer to the occurrence in each species of the indicated type of natural product

		Occurrence of neoflavanoids and biogenetically related compounds						Occurrence of isoflavanoids					
		I–IV		VI, VII		VIII							
Specific series	Species from Asia, Africa, and America	$X = H$	$X = OMe$	$X = H$	$X = OMe$	$X = H$	$X = OMe$	Xa	Xb	XIa	XIb	XIIa	XIIb
Dalbergiae pantropicales	Asia												
	D. sissoo Roxb.[39–42]	3						3					
	D. latifolia Roxb.[30,43–49]	3											
	D. cochinchinensis Pierre [50]	3											
	D. lanceolaria L.f.[51]							1					
	Africa												
	D. melanoxylon Guill. & Perr.[17,52]	2				1							
	D. baroni Baker[52–54]	3							1				
	America												
	D. nigra (Vell.) Fr. Allem.[55–61]	4						1					
	**D. miscolobium* Benth.[15,58,62,63]	3		2					1				
	D. villosa Benth.[64]	1						1					
	D. barretoana Hoehne[64]	1						1	1				
	D. obtusa Lecomte[15,16,18,65]	2		3		1			1				
Dalbergiae brasilianae	America												
	D. spruceana Benth.[14]	2						3	2	5	2		
	†*D. frutescens* (Vell.) Britt.[22,23,66]								2	1	1	1	2
	D. cearensis Ducke[14]	2							1	1	1	1	
	D. decipularis Rizz. & Matt.[67]									1	1		
	D. ecastophyllum (L.) Taub.[31]								2	1	1		2
	D. volubilis (L.) Urb.[68]								1				
Machaeria scleroxyla	America												
	M. nictitans (Vell.) Benth.[69]		7						1		1		
	M. kuhlmannii Hoehne[15,69]	1	6		1				1		1		
	M. scleroxylon Tul.[12]	2	3										
Machaeria villosa	America												
	M. villosum Vog.[15,22,23,33,70]				2				5		1		2
	‡*M. acutifolium* Vog.[15,22,23]				1						1		2
	M. mucronulatum Mart.[15,22,23,71]				3				1		1		2
	M. opacum Vog.[22,23,72,73]												2
	M. vestitum Vog.[23,66,74]								2		2		2

* syn. *D. violacea* (Vog.) Malme.

† syn. *D. variabilis* Vog.

‡ formerly described as *M.* species (URB/18).[15]

each plant belong either to the types (see Fig. 1) in which $X = \mathrm{H}$ or to those in which $X = \mathrm{OMe}$. This indicates the operation of biosynthetic routes in particular plants involving precursors of limited oxygenation pattern. The reductive removal of one oxygen-containing group (Fig. 1, indicated by [O]) is also a common feature.

The mechanistic feasibility of the biochemical processes proposed to inter-relate the constitution of neoflavanoids (I–IV) and related natural products (VI–VIII) has been demonstrated by the formation, under mild conditions of acidic catalysis, of dalbergiquinols

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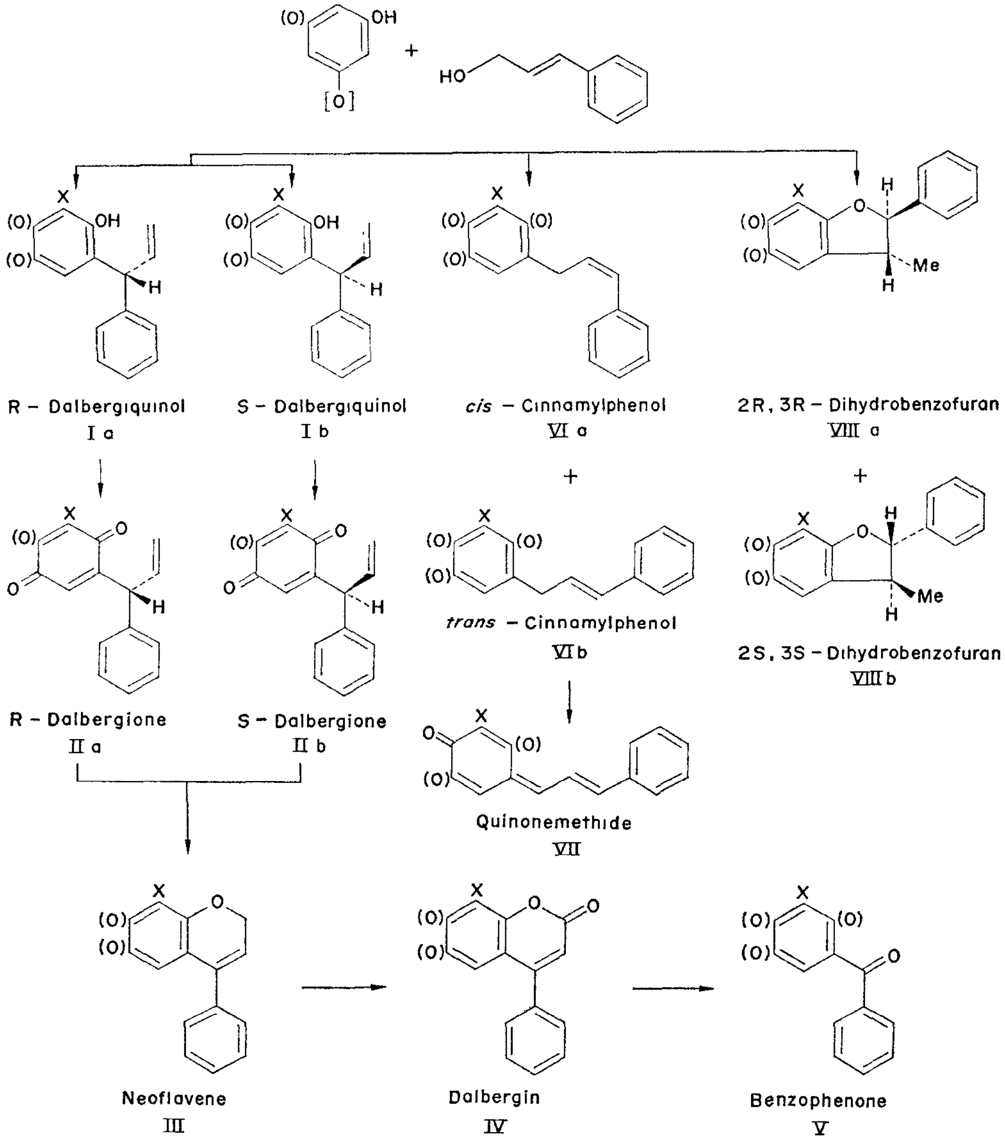

FIG. 1. POSSIBLE BIOGENETIC RELATIONSHIPS[13] AMONG THE NEOFLAVANOIDS (I–VI) AND RELATED NATURAL PRODUCTS (X = H OR OMe).

(I) and cinnamylphenols (VI) from phenols and cinnamyl alcohol.[19a–c,20] The postulated role of cinnamyl pyrophosphate in our biogenetic proposals[13] has recently been placed on even firmer ground by the important observation[19d] that cinnamyl pyrophosphate and

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[19] (a) L. JURD, *Experientia* **24**, 858 (1968); (b) *Tetrahedron* **25**, 1407 (1969); (c) *Tetrahedron Letters* 2863 (1969); (d) J. LARKIN, D. C. NONHEBEL and H. C. S. WOOD, *Chem. Commun.* 455 (1970).

[20] S. MAGESWARAN, W. D. OLLIS, R. J. ROBERTS and I. O. SUTHERLAND, *Tetrahedron Letters* 2897 (1969); O. R. GOTTLIEB, S. MAGESWARAN, W. D. OLLIS, R. J. ROBERTS and I. O. SUTHERLAND, Lecture at the Symposium on Natural Products of Tropical America, Academia Brasileira de Ciências, Rio de Janeiro, August 1969, *An. Acad. Brasil. Ciênc. Suppl.* in press.

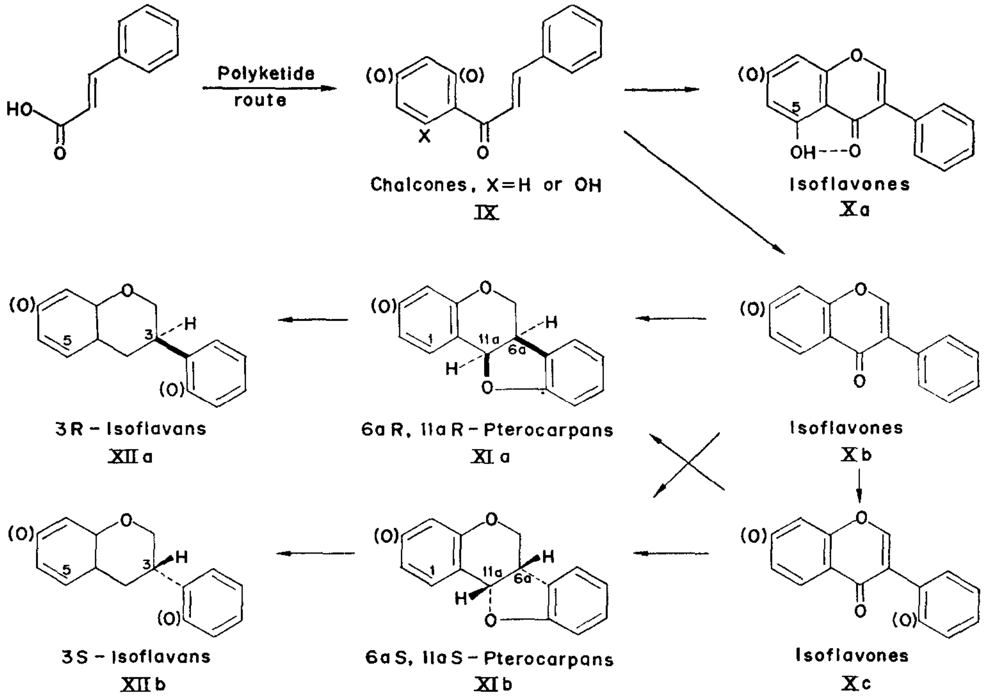

FIG. 2. POSSIBLE BIOGENETIC RELATIONSHIPS AMONG THE ISOFLAVANOIDS.

resorcinol interact in aqueous ammonium acetate at pH 7·2 yielding the corresponding neoflavanoid and cinnamyl-phenol.

As members of the Leguminosae family, the *Dalbergia* and *Machaerium* species might be expected to contain isoflavanoids which are phytochemically highly characteristic of the Leguminosae.[11,21] This is indeed the case (see Table 1). However, there are some interesting limitations upon the distribution and the oxygenation patterns of the isoflavanoids (see Fig. 2) that have been isolated from *Dalbergia* and *Machaerium*. This circumstance is now considered in relation to current knowledge regarding the biosynthesis of members of the isoflavanoid class of natural products.

The isoflavanoid class of natural products[21] includes the isoflavones (X), the pterocarpans (XI), and the isoflavans (XII). However, it may be noted that the isoflavans (XII) have been recognized only recently as a fairly widely occurring group of natural products.[22,23] The biosynthesis of isoflavones from chalcone precursors, formally represented as (IX) → (X), is now generally recognized,[24] but the appropriate experiments have not yet been done to define in detail the biosynthetic routes leading to pterocarpans (XI) and isoflavans (XII). However, some possibilities may be considered. The natural

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[21] W. D. OLLIS, in *The Chemistry of Flavonoid Compounds* (edited by T. A. GEISSMAN), p. 362, Pergamon Press, Oxford (1962).

[22] K. KUROSAWA, W. D. OLLIS, B. T. REDMAN, I. O. SUTHERLAND, A. BRAGA DE OLIVEIRA, O. R. GOTTLIEB and H. MAGALHÃES ALVES, *Chem. Commun.* 1263 (1968).

[23] K. KUROSAWA, W. D. OLLIS, B. T. REDMAN, I. O. SUTHERLAND, O. R. GOTTLIEB and H. MAGALHÃES ALVES, *Chem. Comm.* 1265 (1968).

[24] H. GRISEBACH, *Biosynthetic Patterns in Micro-organisms and Higher Plants*, p. 15, Wiley, New York (1967).

co-occurrence of isoflavones (X), pterocarpans (XI), and isoflavans (XII) suggests that they could be related in general terms by the biosynthetic sequence (X → XI → XII). In connection with this possibility, it may be noted that the known natural pterocarpans (XI)[11] are not oxygenated in position 1 and the known natural isoflavans (XII)[22] are not oxygenated in the corresponding position 5. With the exception of *D. spruceana* (see Table 1) the natural isoflavones which are found to be congeneric with natural pterocarpans (XI) and isoflavans (XII) are also not oxygenated at position 5. This clearly suggests that isoflavones (Xb and Xc) lacking a 5-hydroxyl group are more likely to be the direct precursors of the pterocarpans (XI) and the isoflavans (XII). Furthermore, it is probable that 5-hydroxyisoflavones (Xa) and 5-deoxyisoflavones (Xb) arise by different pathways originating with a bifurcation at the polyketide stage of their biosynthetic programmes. It is generally recognized[24] that isoflavones arise by the polyketide → chalcone → isoflavone route and that the operation, or otherwise, of a bio-reduction step at the polyketide stage[25] could well initiate two different routes (i and ii) leading either to the 5-hydroxyisoflavones (Xa) or to the 5-deoxyisoflavones (Xb). These two pathways may be formally represented as follows:

(i) Polyketide → Chalcones (IX; X = OH) → 5-Hydroxyisoflavones (Xa);
(ii) Polyketide → Reduced polyketide → Chalcones (IX; X = H) → 5-Deoxyisoflavones (Xb) → Isoflavanoids (XI and XII).

Various possibilities can be envisaged for the transformation (Xb → XI and XII) indicated in pathway (ii). Thus, a 5-deoxyisoflavone (Xb), after 2′-oxidation, which appears to be a fairly frequent feature of the biosynthesis of natural isoflavones,[11,21] could give an intermediate (Xc) which by reductive transformation to an isoflavan-4-ol could lead to a pterocarpan (XI) (cf. Ref. 26). Further biochemical reduction of either the pterocarpans (XI) or the isoflavan-4-ol intermediates could lead to isoflavans (XII). An alternative process which is possibly less reasonable, although it does have some distant photochemical analogy,[27] involves the isomerization of an isoflavone (type formula Xb) to a 6a,11a-dehydropterocarpan which could then be reduced to the pterocarpan (XI). In this connection, it may be noted that recently 6a,11a-dehydropterocarpans were postulated as possible intermediates in the biosynthesis of coumestones.[28]

These proposals, which are summarized in Fig. 2, must be regarded as only biogenetic possibilities until the appropriate definitive experiments have been done. However, at present they do have merit in providing a satisfying basis for correlating the constitutions of the large number of isoflavanoids (Table 1) which have been isolated from *Dalbergia* and *Machaerium* species.

With this background of possible biogenetic relationships between the neoflavanoids and isoflavanoids isolated from *Dalbergia* and *Machaerium* species, it is now possible to make a further examination of these natural products as chemotaxonomic pointers. In the sequel, the proposal is made that there is a phylogenetic correlation (Fig. 3) between the genera *Dalbergia* and *Machaerium* into the four species-series: *Dalbergiae pantropicales, Dalbergiae brasilianae*, *Machaeria scleroxyla*, and *Machaeria villosa*. The association of

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[25] E. WONG and C. M. FRANCIS, *Phytochem.* **7**, 2131 (1968) and references there cited.

[26] W. B. WHALLEY, in *Recent Developments in the Chemistry of Natural Phenolic Compounds* (edited by W. D. OLLIS), p 24, Pergamon Press, Oxford (1961).

[27] J. C. SHEEHAN and R. M. WILSON, *J. Am. Chem. Soc.* **86**, 5277 (1964).

[28] P. M. DEWICK, W BARZ and H. GRISEBACH, *Chem. Commun.* 466 (1966)

each species with one of these four species-series is indicated in Table 1 and this division correlates well with their neoflavanoid and isoflavanoid constituents and it obviously provides a dramatic encouragement for further phytochemical study of species belonging to the *Dalbergia* and *Machaerium*.

The members of the two series *Dalbergiae pantropicales* and *Machaeria scleroxyla* are characterized by an ability to produce neoflavanoids (I–IV), whereas this is obviously rare in the series *Dalbergiae brasilianae* and is apparently absent in the series *Machaeria villosa*. The species allocated to *Dalbergiae pantropicales* apparently produce only those neoflavanoids (I–IV), cinnamylphenols (VI), and 2,3-dihydrobenzofurans (VIII) in which $X = \mathrm{H}$, and on present knowledge there are no exceptions to this structural correlation. In contrast, species belonging to *Machaeria scleroxyla* apparently have a disposition towards the production of the more highly oxygenated neoflavanoids (I–IV; $X = \mathrm{OMe}$) and in the one case, *M. kuhlmannii*, from which a cinnamylphenol (VI) has been isolated, it also belongs to the more highly oxygenated class in which $X = \mathrm{OMe}$. Although no neoflavanoids (I–IV) have been isolated from species belonging to the series *Machaeria villosa*, the three plants which yield cinnamylphenols produce those of the type (VI; $X = \mathrm{OMe}$).

There is apparently an inverse correlation between the ability to produce either neoflavanoids and related compounds or isoflavanoids. This could be associated with a competitive or alternative involvement of cinnamic acid (or its equivalent) either directly *via* chalcones (IX) to give isoflavones (X), or indirectly after reduction to cinnamyl alcohol (or its equivalent) which then acts as the precursor of neoflavanoids (I–IV). Whether there is indeed competition between the production of neoflavanoids (I–IV) and isoflavanoids (X–XII) is a matter for conjecture. However, it is certainly clear on present knowledge that no neoflavanoids have been isolated from the species allocated to the series, *Machaeria villosa*, whereas these plants are excellent producers of isoflavanoids. Similarly, the species belonging to *Dalbergiae brasilianae* are poor producers of neoflavanoids, but their production of isoflavanoids is varied and extensive. In contrast, the species belonging to *Dalbergiae pantropicales* and *Machaeria scleroxyla* show a much more frequent occurrence of neoflavanoids in comparison with isoflavanoids.

The allocation of *Dalbergia* and *Machaerium* species to the four species-series indicated in Table 1 also emphasizes common structural features among their extractives including (i) the relative frequency of occurrence of 5-oxygenated (Xa) and 5-deoxygenated isoflavones (Xb) and (ii) a correspondence of chirality of the pterocarpans (XIa or XIb) and the isoflavans (XIIa or XIIb) when they occur in the same plant. The reductive sequence which has been postulated in order to account for the biosynthesis of pterocarpans (XI) and isoflavans (XII) from 5-deoxyisoflavone precursors (Xb) does not appear to operate among the members of *Dalbergiae pantropicales*. Thus, no pterocarpans or isoflavans have been isolated from the members of this species-series and 5-hydroxyisoflavones (Xa) appear to occur more frequently than 5-deoxyisoflavones (Xb). In contrast, 5-deoxyflavones (Xb) occur much more frequently in the other three series, *Dalbergiae brasilianae*, *Machaeria scleroxyla*, and *Machaeria villosa*. The members of these three species-series all produce pterocarpans (XI); isoflavans (XII) are also characteristic of *Dalbergiae brasilianae* and *Machaeria villosa*. The ability to operate the reductive process all the way through to the isoflavans is particularly marked for the members of *Machaeria villosa* and this is dramatically demonstrated by the extractives of *M. opacum* heartwood which consist almost entirely of the two isoflavans, duartin and mucronulatol.[22,23] It is striking that among the *Machaerium* species, which are divided between *Machaeria scleroxyla* and *Machaeria villosa*, only 5-deoxyisoflavones (Xb) have been isolated; there is also an obvious stereoselectivity operating which leads only to 6aS,11aS-pterocarpans (XIb) and only to the stereochemically corresponding 3S-isoflavans (XIIb).

On present knowledge, the phytochemical characteristics of the four species-series may be summarized as follows:

Dalbergiae pantropicales. High frequency of occurrence of neoflavanoids (I–IV) with, in some cases, cinnamylphenols (VI) and 2,3-dihydrobenzofurans (VIII); only the oxygenation pattern (X = H) is observed. Isoflavanoids are restricted only to isoflavones of which both types (Xa and Xb) have been isolated.

Dalbergiae brasilianae. Low frequency of occurrence of neoflavanoids (I–IV; X = H). High frequency of occurrence of isoflavanoids including 5-deoxyisoflavones (Xb), pterocarpans and isoflavans of both chiralities (XIa and XIb) and (XIIa and XIIb).

Machaeria scleroxyla. High frequency of occurrence of the more highly oxygenated (X = OMe) neoflavanoids (I–IV); the only cinnamylphenol (VI) isolated from this group is similarly oxygenated (X = OMe). Low frequency of occurrence of isoflavanoids as 5-deoxyisoflavones (Xb) and 6aS,11aS-pterocarpans (XIb). No isoflavans (XII) have been isolated.

Machaeria villosa. Neoflavanoids (I–IV) are absent and the cinnamylphenols (VI) isolated belong to the more highly oxygenated series (X = OMe). This series is very rich in isoflavanoids which include 5-deoxyisoflavones (Xb), 6aS,11aS-pterocarpans (XIb) and particularly 3S-isoflavans (XIIb).

Other phytochemical characteristics of the *Dalbergia* and *Machaerium* genera may be mentioned. During our studies we have also isolated various triterpenoids[29] from species belonging to both genera. These all contain 3-β-acetoxyl groups which is relatively unusual among natural triterpenoids. Chalcones and flavanones have been isolated from the following species with the indicated frequency of occurrence: *D. latifolia* (1),[30] *D. ecastophyllum* (1),[31] *M. mucronulatum* (2),[32] *M. villosum* (3),[33] *M. vestitum* (2).[34] A 2R,3R-3-hydroxyflavanone has also been isolated from *D. ecastophyllum.*[31]

THE PHYLOGENETIC CLASSIFICATION OF *DALBERGIA* AND *MACHAERIUM* SPECIES

The number of *Dalbergia* (17) and *Machaerium* (8) species which have been phytochemically examined (Table 1) is much less than the total number of *Dalbergia* (*ca.* 300) and *Machaerium* (*ca.* 150) species which have been claimed in the general botanical literature.[35] However, although it is appreciated that our present knowledge is limited, we nevertheless believe that it is useful to make a comparison of the conclusions which may be drawn from (i) the comparative phytochemistry of the species belonging to these two genera

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[29] H. MAGALHÃES ALVES, V. H. ARNDT, W. D. OLLIS, W. B. EYTON, O. R. GOTTLIEB and M. TAVEIRA MAGALHÃES, *Phytochem.* **5**, 1327 (1966).

[30] G D. BHATIA, S. K. MUKERJEE and T. R. SESHADRI, *Indian J Chem.* **3**, 422 (1965).

[31] F. J. DE ABREU MATOS, O R. GOTTLIEB, W. D. OLLIS and C. H. SOUZA ANDRADE, *An. Acad. Brasil. Ciênc. Suppl.* in press.

[32] A. BRAGA DE OLIVEIRA, R. CALDAS LINS, O. R. GOTTLIEB and W. D. OLLIS, unpublished results.

[33] A. BRAGA DE OLIVEIRA, O. R. GOTTLIEB and W. D. OLLIS, *An. Acad. Brasil. Ciênc.* **40**, 147 (1968).

[34] A. BRAGA DE OLIVEIRA, T. BRASILEIRO SILVA, O. R. GOTTLIEB, I. LACERDA MADRUGA and W. D. OLLIS, unpublished results.

[35] J C. WILLIS (Revised by H. K. AIRY SHAW), *A Dictionary of Flowering Plants and Ferns*, pp. 328 and 680, Cambridge University Press, Cambridge (1966).

(Table 1), (ii) their morphological characteristics (Botanical Survey), and (iii) their geographical distribution.

It is now proposed that the genus *Machaerium* evolved from the genus *Dalbergia*. This opinion of the direction of evolution is supported by the geographical distribution of the two genera in that *Dalbergia* species are widely distributed over tropical Asia, Africa, and America, whereas *Machaerium* species are locally restricted to the American continent and, more particularly, to Mexico, tropical South America, and the West Indies. This suggests that the evolutionary development of *Machaerium* from *Dalbergia* took place after the geographical or climatic interruption of intercontinental routes.[36,37]

The relatively ancient origin of a group of *Dalbergia* species (see Botanical Survey, *Dalbergiae*, Series I) is clearly indicated by the comparatively clear-cut morphological differentiation of its members and their endemic existence in unconnected areas of Asia, Africa, and America. The wide distribution of this series is indicated by our proposed description, *Dalbergiae pantropicales*. Its members are listed in Table 1 and their allocation is based upon botanical as well as phytochemical evidence. The phytochemistry of *Dalbergiae pantropicales* is particularly striking in that, although there is a very extensive geographical distribution of its species, there is nevertheless a rather limited structural variation among the neoflavanoids and isoflavanoids which have been isolated from its members. Their constitutions are closely related to the early stages of the biosynthetic programme (Figs. 1 and 2) proposed for their formation, and extensive additional structural alteration by further bio-oxidative or bio-reductive processes is not usually observed. It is therefore suggested (Fig. 3) that *Dalbergiae pantropicales* provided the evolutionary progenitors of *Dalbergiae brasilianae*, *Machaeria villosa*, and *Machaeria scleroxyla*.

On botanical and phytochemical grounds, it is also considered that there are some *Dalbergia* species (see Botanical Survey, *Dalbergiae*, Series II) which can be assigned to a second species-series, *Dalbergiae brasilianae*. This name has been selected because its allocated members (Table 1) are restricted to Brazil. The members of *Dalbergiae brasilianae* are not so clearly differentiated on morphological grounds, which suggests that they are of more recent evolutionary origin, but the general similarity of their phenolic constituents is

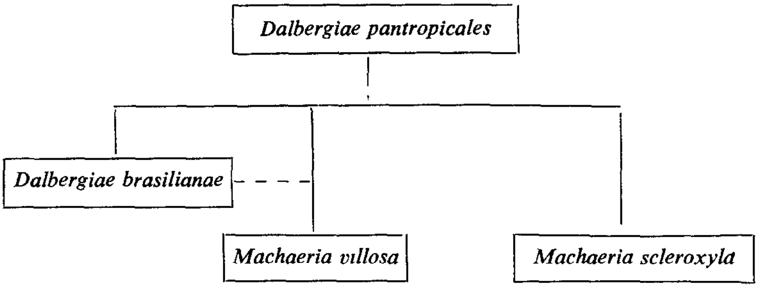

Fig. 3. A tentative phylogenetic correlation proposed for *Dalbergia* and *Machaerium*. The allocations of species to the four specific-series are given in Table 1.

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[36] O. R. Gottlieb, J. de Oliveira Meditsch and M. Taveira Magalhães, *An. Acad. Brasil. Ciênc.* **38**, *Suppl.* 303 (1966).

[37] J. Tuzo Wilson, *Scient. Am.* **208** (4), 86 (1963); Symposium on Continental Drift, *Phil. Trans. Roy. Soc.* A **258** vii–323 (1965); P. M. Hurley, *Scient. Am.* **218** (4), 53 (1968); B. Kurtén, *Scient. Am.* **220** (3), 54 (1969); E. Bullard, *Scient. Am.* **221** (3), 66 (1969); E. Orowan, *Scient. Am.* **221** (5), 102 (1969); J. Hutchinson, *Evolution and Phylogeny of Flowering Plants*, Academic Press, New York (1969); D. P. McKenzie, *Endeavour* **29**, 39 (1970).

clear. *Dalbergiae brasilianae* is therefore regarded as an evolutionary development from *Dalbergiae pantropicales*. It will be noticed that although *D. spruceana* was placed in series I (Botanical Survey, *Dalbergiae*), it has been included on phytochemical grounds (see Table 1) in *Dalbergiae brasilianae* rather than *Dalbergiae pantropicales*.

The relatively recent evolutionary development of the genus *Machaerium* is indicated by the occurrence of species which are poorly differentiated on morphological grounds. In the Botanical Survey it has been suggested that *Machaerium* should be divided into series I, II, and III, but on phytochemical grounds there is no obvious distinction between those allocated to series II and to series III. It is, therefore, provisionally suggested that *Machaerium* species should be divided into two species-series, *Machaeria scleroxyla* and *Machaeria villosa*. These names are derived from *M. scleroxylon*, the most abundant member of series I, and *M. villosum*, the most abundant member of series II and series III.

The species-series *Machaeria scleroxyla* forms a fairly well defined group on morphological as well as phytochemical grounds. On present evidence, the phytochemistry of *Machaeria scleroxyla* and *Dalbergiae pantropicales* are similar, whereas the phytochemical pattern of *Machaeria villosa* resembles that of *Dalbergiae brasilianae* rather more closely. Whether one is entitled to draw conclusions from these phytochemical similarities is a matter of opinion, but we are encouraged to suggest that *Machaeria scleroxyla* is more directly derived, in the evolutionary sense, from *Dalbergiae pantropicales*, whereas a more common line of evolution has provided *Dalbergiae brasilianae* and *Machaeria villosa*. It is even possible (see dotted line in Fig. 3) that *Dalbergiae brasilianae* has to some degree acted as the evolutionary progenitor of *Machaeria villosa*. These tentative phylogenetic correlations between the four species-series, *Dalbergiae pantropicales*, *Dalbergiae brasilianae*, *Machaeria scleroxyla*, and *Machaeria villosa*, are indicated in Fig. 3.

It will be apparent, even on present knowledge, that there is already a potentially satisfying correlation between the botanical and the phytochemical characteristics of the four species-series between which *Dalbergia* and *Machaerium* have been divided. It must be appreciated that these proposed correlations are based upon phytochemical information which is limited to a fraction of the total number of valid species of *Dalbergia* (180)[38] and *Machaerium* (121).[8] Many of the species are difficult to collect, but an attempt is being made to extend this phytochemical survey to other Brazilian *Dalbergia* and *Machaerium* species in order to test the generalizations now proposed.

The approach which has been used in the present study is novel in some respects, but its relevance to current extensive interest in the phenomenon of Continental Drift[37] will be appreciated. The probable arrangement of the African and South American continents and the adjacence of Africa and India within the supercontinent of Gondwanaland[75] could have provided a common location for the evolutionary source of *Dalbergiae pantropicales* now distributed widely in South America, Africa, and India. After the drifting apart of these continents and the formation of the Atlantic Ocean, some 120 million years ago, the subsequent separate evolutionary development leading to *Dalbergiae brasilianae*, *Machaeria scleroxyla*, and *Machaeria villosa* could have occurred.

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[38] G. J. H. AMSHOFF, *On South American Papilionaceae*, Utrecht (1939); A. DUCKE, *As Leguminosas da Amazônia Brasileira* (2nd Edition), p. 173, Boletim Técnico do Instituto Agronômico do Norte, Belém, Brasil (1949).

[75] E. BULLARD, J. E. EVERETT and A. G. SMITH, *Phil. Trans. Roy Soc.* **A258**, 41 (1965).