# REVIEW ARTICLE

# WOOD PHENOLICS IN THE CHEMOTAXONOMY OF THE MORACEAE\*

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Abstract—Corner's recent taxonomic treatment of the Moraceae has shown that the family constitute a large taxa of over fifty genera and nearly 1400 species, including such important groups as Artocarpus, Morus and Ficus. A detailed study of the wood phenolics of six Artocarpus and five Morus species has led to the isolation of several flavonoids with the common features of hydroxyls in the 5,7,2',4'-positions and  $C-\gamma\gamma$ -dimethylallyl substituents in the 6-, 3,6- or 3,6,8-positions. The present state of our knowledge of the chemistry of the Moraceae is reviewed with particular reference to wood phenolics. The chemotaxonomy of the Moraceae is discussed in relation to flavonoids, flavonoids with isoprenoid substituents and stilbenes; the phenolic constituents can be useful in the taxonomy of the Moraceae if the investigation is extended to other genera and species.

#### THE GENUS ARTOCARPUS

THERE is no record in the literature preceding our work on the phenolics of Artocarpus species, except for morin, cyanomaclurin<sup>1</sup> and dihydromorin<sup>2</sup> in A. heterophyllus Lam. and oxyresveratrol in A. lakoocha Roxb.<sup>3</sup> The non-phenolics so far isolated from Artocarpus species are also few: the tetracyclic triterpenes cycloartenol (together with the corresponding ketone cycloartenone) and butyrospermol from the fruit of A. heterophyllus,<sup>4</sup> and acetylcholine from the seeds and leaves of A. integra Merrill,<sup>5</sup> cerotic acid and the pentacyclic triterpenes lupeol and a- and  $\beta$ -amyrin from the latex of A. elasticus Reinw. and A. communis <sup>6</sup>

In a recent series of papers Jarrett<sup>7</sup> has discussed the taxonomy of Artocarpus J. R. and G. Forster, consisting of about fifty species, Prainea King (four species), Parartocarpus Baillon (three species) and Hullettia King (two species). Jarrett has stated that "Members of the genus Artocarpus are the most commonly encountered representatives of the Moraceae in the lowland forests of the Old World tropics (Africa excepted) apart from the ubiquitous Ficus."

## Artocarpus heterophyllus

Artocarpus heterophyllus (A. integrifolia Linn.) is a large evergreen tree cultivated throughout India, Burma and Ceylon for its fruit (jack-fruit) and for its bright yellow

- \* Based on a paper read at the Wood Extractives Symposium, 161st Meeting of the American Chemical Society in Los Angeles, April 1971.
- <sup>1</sup> A. G. Perkin and F. Cope, J. Chem. Soc. 67, 937 (1895); A. G. Perkin, J. Chem. Soc. 87, 715 (1905).
- <sup>2</sup> G. CHAKRAVARTY and T. R. SESHADRI, *Indian J. Chem.* 2, 319 (1964); *Tetrahedron Letters* 787 (1962).
  <sup>3</sup> S. MONGOLSUK, A. ROBERTSON and R. TOWERS, *J. Chem. Soc.* 2231 (1957); also R. S. KAPIL and S. S.
- <sup>3</sup> S. Mongolsuk, A. Robertson and R. Towers, *J. Chem. Soc.* 2231 (1957); also R. S. Kapil and S. S. Joshi, *J. Sci. & Ind. Res.* 19B, 498 (1960).
- <sup>4</sup> For references see G. Ourisson, P. Crabbe and O. R. Rodig, *Tetracyclic Triterpenes*, Holden-Day, San Francisco (1964).
- <sup>5</sup> For references see W. Karrer, Konstitution und Vorkommen der Organischen Pflanzenstoffe, Birkhauser Verlag, Basel und Stuttgart (1958).
- <sup>6</sup> A. J. Ultee, Pharm. Weekblad 84, 65 (1949).
- <sup>7</sup> F. M. JARRETT, J. Arnold Arboretum 40, 1, 30, 113, 298 (1959); 41, 73, 320 (1960).

heartwood, which is moderately resistant to decay and is used for cheap furniture and building construction. Morin (I) and cyanomaclurin (II) were isolated from this wood by Perkin and Cope<sup>1</sup> in 1895, but it was only in 1963 that a study of the NMR spectrum of the acetate of cyanomaclurin trimethyl ether led to the correct structure (II) for cyanomaclurin. Perkin gave cyanomaclurin its name because of the intense blue colour it gives with aqueous alkali. Morin is well known as a reagent for aluminium, based on the brilliant bluish green fluorescence produced by the addition of an aluminium salt to a solution of morin in ethanol or water. Morin and cyanomaclurin in minute quantity can thus be readily detected, and are therefore useful as taxonomic markers. Dihydromorin, which occurs in the heartwood of some *Artocarpus* and *Morus* species, can be converted both to morin and to cyanomaclurin, although the formation of the latter is indicated only by the characteristic colour reaction.

Because of its similarity to old fustic in dyeing properties, Perkin isolated the colouring matters of jackwood from a water extract; the benzene-soluble pigments therefore escaped his notice. By the use of organic solvents, chromatography and several timber samples, the

- <sup>8</sup> D. Brandis, *Indian Trees*, Constable, London (1906); *Wealth of India* 1, Council of Scientific & Industrial Research, New Delhi (1948).
- <sup>9</sup> P. M. NAIR and K. Venkataraman, Tetrahedron Letters 317 (1963); also P. M. NAIR, P. C. PARTHA-SARATHY, P. V. RADHAKRISHNAN and K. VENKATARAMAN, Tetrahedron Letters 5357 (1966).

heartwood of A. heterophyllus has so far yielded the flavanone artocarpanone (IV) and eight flavones (V-XII).  $^{10-12}$  All are characterised by the  $\beta$ -resorcylic acid orientation of hydroxyl groups in the B-ring found only in morin and cyanomaclurin among the flavonoids.

The norartocarpetin structure (V) was once assigned erroneously to 'lotoflavin' occurring as a cyanogenetic glucoside in *Lotus arabicus* Linn.<sup>13</sup>; 5,7,2',4'-tetrahydroxyflavone (V) was synthesised in 1926.<sup>14</sup> 'Lotoflavin' was later shown to be quercetin contaminated with kaempferol.<sup>15</sup>

The structure of artocarpin (XI) was proved by classical methods, including the synthesis of tetrahydroartocarpin dimethyl ether. Since no flavone with an alkyl or alkenyl substituent in the 3-position was known at the time as a natural product, and such substitution of a preformed flavone chemically or biochemically was obviously impossible, a feasible biosynthetic route to artocarpin had to be considered. If the 1,3-diketone (XIII) is formed by the reactions shown in Scheme 1, attack of the methylene group by dimethylallyl pyrophosphate<sup>16</sup> can be readily imagined. A less likely, but not altogether impossible route, is substitution in the 3-position of the flavanone corresponding to the chalcone (XIV). One example of a naturally occurring dibenzoylmethane is pongamol in the seeds of *Pongamia glabra* Vent, <sup>17</sup> from which, however, neither the corresponding flavone nor any 3-alkyl-flavone has been isolated. In either case the attack of the highly nucleophilic phloroglucinol by the dimethylallyl cation very probably precedes the reactions in Scheme 1; this is supported by the isolation of artocarpesin (VII) and its derivatives (VIII) and (IX).

SCHEME 1. POSSIBLE BIOSYNTHETIC ROUTE TO ARTOCARPIN.

Cycloartocarpin (XII) is unique as the first flavone with an additional pyran ring D. Flavandiol derivatives with an isomeric ring system are peltogynol (XV) in the heartwood of *Peltogyne porphyrocardia*<sup>18</sup> and mopanol in *Colophospermum mopane*.<sup>20</sup> It has been suggested that peltogynol could arise biogenetically by condensation of formaldehyde (or its equivalent) with the corresponding flavan-3,4-diol.<sup>19</sup>

# Five Artocarpus Species

Five other Indian species of *Artocarpus* were then examined by Rathi<sup>21</sup> and the distribution of phenolics in the heartwoods of all six species is shown in Table 1.

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10 P. V. RADHAKRISHNAN, A. V. RAMA RAO and K. VENKATARAMAN, Tetrahedron Letters 663 (1965).
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<sup>&</sup>lt;sup>11</sup> P. M. NAIR, A. V. RAMA RAO and K. VENKATARAMAN, Tetrahedron Letters 125 (1964).

<sup>&</sup>lt;sup>12</sup> P. C. PARTHASARATHY, P. V. RADHAKRISHNAN, S. S. RATHI and K. VENKATARAMAN, *Indian J. Chem.* 7, 101 (1969); and earlier papers in this series.

<sup>&</sup>lt;sup>13</sup> W. R. Dunstan and T. A. Henry, Proc. Roy. Soc. London 68, 374 (1901).

<sup>&</sup>lt;sup>14</sup> R. Robinson and K. Venkataraman, J. Chem. Soc. 61 (1929).

<sup>&</sup>lt;sup>15</sup> T. S. Wheeler et al., J. Chem. Soc. 4249 (1955).

<sup>&</sup>lt;sup>16</sup> J. W. Cornforth and G. Popjak, Tetrahedron Letters (19), 29 (1959).

<sup>&</sup>lt;sup>17</sup> S. NARAYANASWAMY, S. RANGASWAMI and T. R. SESHADRI, J. Chem. Soc. 1871 (1954).

<sup>&</sup>lt;sup>18</sup> G. M. ROBINSON and R. ROBINSON, J. Chem. Soc. 744 (1935).

<sup>19</sup> W. R. CHAN, W. G. C. FORSYTH and C. H. HASSALL, J. Chem. Soc. 3174 (1958).

<sup>&</sup>lt;sup>20</sup> S. E. Drewes and D. G. Roux, J. Chem. Soc. C, 1644 (1966).

<sup>&</sup>lt;sup>21</sup> S. S. RATHI, Ph.D. Thesis, University of Poona (1970).

TARIE 1	DISTRIBUTION	OF PHENOLICS	IN THE	HEARTWOOD	OF SIX	Artocarpus SPECIES
IADLE I.	TO INTERVED	OF FRENULICS.	IN IDS	DEAL WOOD	OL SIV	mi tocurpus seecus

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Artocarpus species	Artocarpanone IV	Dihydromorin III	Morin I	Cyanomachurin II	Norartocarpetin V	Artocarpetin VI	Artocarpesin VII	Oxydihydroartocarpesin IX	Cycloartocarpesin VIII	Norartocarpin X	Artocarpin XI	Norcycloartocarpin	Cycloartocarpin XII	Chaplashin XVI	Reveratrol	Oxyresveratrol XXIX	Resorcinol	$\beta$ -Resorcylaldehyde
4. heterophyllus 4. hirsutus 4. gomezianus* 4. incisa 4. lakoocha 4. chaplasha	+ +	++	++++	++	+++	++	++++	+ +	+++	+ + -	+++++	- - - + -	+++++				<del>-</del> +++	- - - +

<sup>\*</sup> Mesoerythritol has been isolated from the heartwood of this species.

The unusually substituted flavones, artocarpin (XI) and cycloartocarpin (XII), occur in all six species, and this indeed is the only common feature. Except for the absence of norartocarpin (X), A. hirsutus is identical with A. heterophyllus in its flavonoid content; the two species are distinguished from the others by the presence of cyanomaclurin (III) and by the much greater complexity of flavonoid distribution. Artocarpus gomezianus Wall. and A. incisa Linn. (the breadfruit tree) form a second group with four of five flavones in common. Artocarpus lakoocha Roxb. and A. chaplasha Roxb. are in a third group, characterized by the presence of resorcinol and oxyresveratrol (2,4,3',5'-tetrahydroxystilbene, XXIX); the latter was earlier isolated from A. lakoocha by Robertson. 3 Erdtman<sup>22</sup> found oxyresveratrol in the heartwood of one out of about 60 species of Artocarpus, but Rathi encountered this stilbene in two of the six species examined by him. A. chaplasha contains  $\beta$ -resorcylaldehyde, a second stilbene, resveratrol (4,3',5'-trihydroxystilbene), and a new, uniquely constituted flavone, chaplashin (XVI). Except for the work on Morus species discussed later, this is the only recorded isolation of resorcinol and  $\beta$ -resorcylaldehyde from a plant; but Seikel et al. recently isolated resorcinol from the heartwood of Quercus rubra (northern red oak).23 The structure of chaplashin (XVI) was demonstrated by UV, NMR and MS data, and by the synthesis of racemic dihydrochaplashin from the compound (XVIII), obtained by the action of dichlorodicyanobenzoquinone (DDQ) on dihydroartocarpin (XVII). In the light of the DDQ reactions discussed later in connection with the Morus bark pigments, it was found that the DDQ reaction on (XVII) took a similar unexpected course leading to (XVIII), and not to dihydrocycloartocarpin.

The woods were obtained from different parts of India (Poona, Kerala, Dehra Dun, Assam, Jammu and Kashmir, and Andaman Islands). One of the Kerala varieties of A. heterophyllus, called vericca, was also obtained from Ceylon. Three samples of A. lakoocha

<sup>&</sup>lt;sup>22</sup> H. ERDTMAN, in *Chemical Plant Taxonomy* (edited by T. SWAIN), p. 100, Academic Press, New York (1963).

<sup>&</sup>lt;sup>23</sup> M. Seikel, F. D. Hostettler and G. J. Niemann, Phytochem. 10, 2249 (1971).

and several of A. heterophyllus from different localities were examined. It was found that different samples of the same species contained the same compounds, the only difference being a variation in the quantitative distribution of the phenolics. Artocarpus lakoocha from Andaman Islands, Kirkee (Poona) and Jammu contained 0.4, 0.3 and 0.15% of cycloartocarpin respectively; A. heterophyllus, 'vericca', from Ceylon and from Kerala showed no differences. A. heterophyllus types 'vericca' and 'koozha' differed sharply in fruit quality, but contained the same phenolics; 'koozha' yielded more cycloartocarpin (0.35%) than 'vericca' (0.2%).

Although chaplashin was only isolated from A. chaplasha, it is so obviously derived from artocarpin and is present in such a minute amount (0.017% of the wood) that its value as a taxonomic marker will depend on the establishment of an infallible method for its identification (and if possible, quantitative estimation). Artocarpus chaplasha is a good source of artocarpin (yield 1.3%).

Under the bark of the main trunk of A. heterophyllus, specially very old trees, a deep red-brown powder was noticed. From this powder or the whole bark two new flavones were isolated in very minute quantities, and the structure (XIX) of the relatively major pigment, cycloheterophyllin, was established on the basis of NMR and MS.<sup>24</sup> Cycloheterophyllin differs from cycloartocarpin in three structural factors; (1) an additional hydroxyl group in the B-ring, (2) an additional isoprenyl substituent in the 8-position, and (3) the replacement of the 6-isoprenyl A-ring by the chromene system (AE). The second pigment, heterophyllin, very probably has structure (XX).

The fragmentation of the artocarpin type of flavone with C-isoprenyl substituents by electron impact was studied by Rathi<sup>21</sup> in detail, because the mass spectrum provided valuable confirmation of the identity of a pigment deduced from its chromatographic behaviour.

#### MORUS SPECIES

Morus (mulberry) is a small genus of trees and shrubs, found in temperate and subtropical regions of the northern hemisphere. Four or five species occur in India, valued for

<sup>24</sup> A. V. RAMA RAO, M. VARADAN and K. VENKATARAMAN, Indian J. Chem. 9, 7 (1971).

their foliage as silkworm food, edible fruits, and useful timber. <sup>25</sup> In the older literature six Indian species are mentioned: *M. alba* Linn., *M. indica* Linn., *M. atropurpurea* Roxb., *M. nigra* Linn., *M. serrata* Wall. and *M. laevigata* Wall. Later authors regard the second and third, and also the Chinese and Japanese species (*M. multicaulis* Perr. and *M. latifolia* Poir.), introduced into India for rearing silkworms, as varieties of *M. alba*. The only difference between *M. alba* and *M. indica* is a slight variation in the habit. *Morus serrata* and *M. laevigata* also exhibit very minute differences from *M. alba* in floral and leaf characteristics; the former are trees of much larger dimensions, but the possibility of their being varieties of *M. alba* cannot be excluded. *Morus rubra* Linn. (red mulberry) and *M. microphylla* Buckl. (syn. *M. celtidifolia*) (Texas mulberry) are American species; *M. lactea* Poir. and *M. mesozygia* Stapf are African; *M. bombycis* Koidz, a Japanese plant, has been regarded as a variant of *M. alba* (var. *stylosa*).

Numerous organic compounds (acids, amino acids, proteins, tannins, carotenoids, vitamins, terpenes, sterols) have been isolated from the leaves of M. alba Linn.; the flavonoids so far detected are rutin and isoquercitrin. The fruits contain eriodictyol,  $\beta$ -carotene, nicotinic acid, riboflavin and ascorbic acid, all also found in the fruits of M. nigra. 26,27 Tannins, morin, maclurin and 2,4,6,4'-tetrahydroxybenzophenone<sup>28</sup> have been reported in the wood; but Laidlaw and Smith, 29 who isolated oxyresveratrol (2%), dihydrokaempferol and dihydromorin, and identified dihydroquercetin (taxifolin) by paper chromatography, were unable to confirm the presence of benzophenones. They found "at most, only traces of morin", and they considered that the divergence of results may be due to variations within the species or to the use of different parts of the tree. Their suggestion that morin may be an artefact produced from dihydromorin during extraction certainly does not apply to our results. From the bark  $\alpha$ - and  $\beta$ -amyrin, sitosterol, palmitic and stearic acids, and several sugars have been isolated,<sup>30</sup> but no phenolics. In the bark of M. nigra, sterols, fatty acids, tannins and phlobaphenes have been reported.<sup>31</sup> The wood of M. lactea contains morin, dihydromorin and dihydrokaempferol; <sup>29,32</sup> the wood of M. bombycis, morin, oxyresveratrol and sugars;33 the wood of M. mesozygia pinobanksin, morin and dihydromorin.34 There are no other references in the literature to the wood or bark constituents of Morus species.

## Four New Flavones from M. alba Bark

Deshpande<sup>35,36</sup> examined the stem bark and heartwood of *M. alba* Linn, *indica* Linn, *serrata* Wall, *laevigata* Wall and *rubra* Linn. After removal of a triterpene mixture which contained betulinic acid, he isolated from the bark of *M. alba*, four new flavones: mulberrin (XXI), mulberrochromene (XXII), cyclomulberrin (XXIII) and cyclomulberrochromene (XXIV) in yields of 0·15, 0·2, 0·02 and 0·015% respectively.

The general procedure was to chromatograph a benzene solution of the phenolics on a

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    The Wealth of India, Vol. 6, p. 429, Council of Scientific and Industrial Research, New Delhi (1962).
    B. BELAVADY and S. C. BALASUBRAMANIAN, Indian J. Agric. Sci. 29, 151 (1959).
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<sup>&</sup>lt;sup>27</sup> K. Ganju and B. Puri, *Indian J. Med. Res.* 47, 563 (1959).

<sup>&</sup>lt;sup>28</sup> A. Spada, R. Cameroni and M. T. Bernabei, Gazz. Chim. Ital. 86, 46 (1956).

<sup>&</sup>lt;sup>29</sup> R. A. LAIDLAW and G. A. SMITH, Chem. & Ind. 1325 (1958); 1604 (1959).

<sup>&</sup>lt;sup>30</sup> Y. Kashiwada, J. Sericult. Sci. (Japan) 24, 76 (1955).

<sup>31</sup> N. Froeschl, J. Zellner and E. Ziknunda, Montash. Chem. 56, 204 (1930).

<sup>32</sup> W. R. Carruthers, R. H. Farmer and R. A. Laidlaw, J. Chem. Soc. 4440 (1957).

<sup>33</sup> T. Kondo, H. Ito and M. Suda, Nippon Nogei-Kagaku Kaishi 30, 281 (1956).

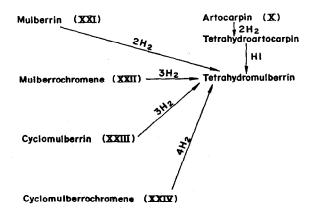
<sup>&</sup>lt;sup>34</sup> R. Paris, M. Debray and S. Etchepare, Ann. Pharm. Fr. 24, 745 (1966).

<sup>35</sup> V. H. DESHPANDE, Ph.D. Thesis, University of Poona (1970).

<sup>&</sup>lt;sup>36</sup> V. H. Deshpande, P. C. Parthasarathy and K. Venkataraman, Tetrahedron Letters 1715 (1968).

silica gel column, using benzene containing increasing amounts of acetone for elution; separation was monitored by TLC on silica gel and benzene-acetone. Three other pigments (A, B, C) are chromatographically homogeneous, but not yet crystalline. Colour reactions and NMR spectra show that one of them is a biflavonoid with two chelated hydroxyl groups and isoprenoid substituents. If the structure is confirmed, it will be the first biflavonoid found in the Moraceae and the first biflavonoid with isoprenoid substituents in any plant family.

The relation of the *Morus* bark flavones to each other and to artocarpin and cycloartocarpin was demonstrated by carrying out the conversions outlined in Scheme 2. The hydrogenations were carried out in presence of platinum oxide.



SCHEME 2. INTERCONVERSION OF Morus BARK AND Artocarpus FLAVONES.

The root bark of *M. alba* contained the same pigments as the trunk bark. From the stem bark of *M. indica*, *M. serrata* and *M. laevigata* mulberrin and mulberrochromene were isolated, as well as the three unidentified pigments A, B, C, but no cyclomulberrin or cyclomulberrochromene. None of these pigments was isolable from *M. rubra* bark, which contained three uncrystallisable pigments (D, E, F) whose colour reactions and NMR spectra indicated that they were flavones of similar type with the important difference, at least in one of them, that the 5,6-positions are unsubstituted, and that the A-ring is therefore derived from resorcinol and not phloroglucinol.

Mulberrin (XXI) is presumably the biosynthetic precursor of (XXII), (XXIII) and (XXIV), as well as artocarpin and cycloartocarpin. From this point of view, and also because larger amounts of XXIII and XXIV were required for chromatographic comparison, Deshpande attempted to convert XXII to XXIV by the action of DDQ. Campbell<sup>37</sup> and

<sup>&</sup>lt;sup>37</sup> I. M. CAMPBELL, C. H. CALZADILLA and N. J. McCorkindale, Tetrahedron Letters 5107 (1966).

Cardillo<sup>38</sup> have achieved the cyclodehydrogenation of o-allyl phenols (XXV) to chromenes (XXVI). The reaction proceeds by the abstraction of a hydride ion by DDQ; the formation of the intermediate quinone-methide (XXVII) as suggested by Ollis and Sutherland,<sup>39</sup> or by the alternative mechanism shown in Scheme 3, may then be involved. However, the

SCHEME 3. CYCLODEHYDROGENATION OF o-ALLYLPHENOLS TO CHROMENES.

product from mulberrochromene (XXII) was not (XXIV), but the 7-member heterocycle (XXVIII), the reaction taking the indicated course. When mulberrin (XXI) was treated with DDQ a mixture of mulberrochromene (XXII) and (XXVIII) was obtained; cyclomulberrin (XXIII) cyclised smoothly in the normal way to give cyclomulberrochromene (XXIV).

The distribution of flavones in the bark of five Morus species is shown in Table 2. Morus indica, M. serrata and M. laevigata are identical in their bark flavones; the only difference

TABLE 2. BARK FLAVONES OF FIVE Morus SPECIES

	Morus						
Compound	alba	indica	serrata	laevigata	rubra		
Mulberrin	+	4	+	+			
Mulberrochromene	+	÷	<u> </u>	+			
Cyclomulberrin	+	<u>-</u>	<u> </u>	<u>.</u>			
Cyclomulberrochromene	÷	-			_		
A	+	+	+	+	_		
В	+	<u> </u>	+	+	_		
C	+	+	+	<u>.</u>			
D	_	<del>-</del>	·	<u>.</u>	+		
E	_			_	<u>.</u>		
F	_	_			<u> </u>		

<sup>38</sup> G. CARDILLO, R. CRICCHIO and L. MERLINI, Tetrahedron 24, 4825 (1968).

<sup>&</sup>lt;sup>39</sup> W. D. Ollis and I. O. Sutherland, Recent Developments in the Chemistry of Natural Phenolic Substances, p. 84, Pergamon Press, London (1961).

in *M. alba* is the presence of cyclomulberrin and cyclomulberrochromene. *Morus rubra* is distinguished by the absence of the seven pigments of *M. alba* and by the presence of three other unidentified pigments.

# Phenolics of the Heartwood of Five Morus Species

Deshpande<sup>35</sup> found that the heartwoods contained a complex mixture of phenolics characterized by the total absence of flavones of the artocarpin type with isoprenyl sidechains, and they required a much more elaborate isolation procedure than the bark phenolics. By successive extraction with benzene (to remove waxes) and acetone, and treatment of the acetone extract with water, oxyresveratrol (XXIX) was separated. Extraction of the aqueous mixture with ethyl acetate, removal of tannins and polymeric material with polyamide, counter-current extraction (using a benzene-ethyl acetate-methanol-water system) of the solvent residue, and chromatography on silica gel and cellulose powder led to the phenols in the yields stated in Table 3.

TABLE 3. APPROXIMATE PERCENTAGE OF THE ISOLATED PHENOLICS IN THE HEARTWOOD OF Morus SPECIES

	Morus						
Compound	alba	indica	serrata	laevigata	rubra		
Norartocarpanone			_		0.04		
Dihydrokaempferol	0.01	0.005	0.01		0.04		
Dihydromorin	0.002	0.02	0.002		0.02		
Kaempferol		·			0.004		
Morin	0.003	0.007	0.002	0.004	0.02		
Ouercetin	0.0004	0.0007	0.001	0.001	0.005		
Resveratrol	0.01	0.02	0.004				
Oxyresveratrol	1.4	1.8	2.6	0.6	7.3		
Piceatannol					0.03		
3,4'-Dihydroxydihydro- stilbene	-			0.05			
3,2',4'-Trihydroxy- dihydrostilbene	_			0.04	_		
Dihydro-oxyresveratrol	0.02	0.007	0.007	0.02			
6,3',5'-Trihydroxy-2- phenylbenzofuran	<del>-</del>	-	<del>-</del>	0.02	_		
Resorcinol	0.002	0.01	0.003	0.002	0.002		
β-Resorcylaldehyde	0.0005	0.005	0.0004	0.001	0.000		

The only new compounds in Table 3 are norartocarpanone, 3,2',4'-trihydroxydihydrostilbene, and 6,3',5'-trihydroxy-2-phenylbenzofuran (XXX). Norartocarpanone was identified by the action of diazomethane which yielded artocarpanone dimethyl ether (5-hydroxy-7,2',4'-trimethoxyflavanone). The structures of the others were confirmed by synthesis. When the tetraacetate of oxyresveratrol was treated with bromine in chloroform, and the dibromide treated with methanolic potassium hydroxide, a complex mixture of products was obtained; chromatography on silica gel gave (XXX) in very poor yield. Although the furan ring is found in numerous natural products, only two naturally occurring 2-phenylbenzofurans are known: egonol in the seed oil of Styrax japonicus Seib. and 2-(2-hydroxy-6-methoxy-3,4-methylenedioxyphenyl)benzofuran in baker's yeast.<sup>5</sup> Dihydrooxyresveratrol was prepared earlier by catalytic reduction of oxyresveratrol;<sup>3</sup> and

3,4'-dihydroxydihydrostilbene by the degradation of hydrangenol; hydrangic acid, which can be converted to the dihydrostilbene, has also been synthesised.<sup>40</sup>

The only dihydrostilbenes isolated earlier from plants are dihydropinosylvin monomethyl ether (3-hydroxy-5-methoxy-dihydrostilbene) from the heartwood of *Pinus albicaulis* Engelm. and dihydropiceatannol (also as monoglucoside) from spruce bark.<sup>41</sup> Dihydropinosylvin, present in such small quantities that no effort was made to isolate it, was detected by paper chromatography in several other pine species.<sup>42</sup> Dihydrostilbenes have also been prepared by reduction of naturally occurring stilbenes.<sup>43-45</sup> The hydroxystilbenes and the corresponding dihydro derivatives examined in the present work have nearly the same  $R_f$  in silica gel TLC (benzene-acetone, 7:3), but different  $R_f$  in paper chromatography (15% acetic acid), and can be separated on cellulose columns.

From Table 3 it is clear that M. alba, M. indica and M. serrata have identical distribution of heartwood phenolics. M. laevigata shows characteristic differences: the absence of dihydrokaempferol, dihydromorin and resveratrol, and the presence of two additional dihydrostilbenes and trihydroxy-2-phenylbenzofuran. The American M. rubra differs from the Indian species in its kaempferol, norartocarpanone and piceatannol content. It should also be noted that all the five Morus species contain (in addition to quercetin) morin, oxyresveratrol,  $\beta$ -resorcylaldehyde and resorcinol. Erdtman<sup>22</sup> found oxyresveratrol in the heartwood of two out of 12 species of Morus; but in the present work it has been isolated in yields of 0.6-7.3% from all the five species examined.

## Chemistry of the Moraceae

Since chemotaxonomy depends on plant chemistry, our knowledge of the chemistry of the Moraceae, other than the genera *Artocarpus* and *Morus* which have already been discussed, is briefly reviewed.

The paucity of data on the wood extractives of plants belonging to the family Moraceae is indicated by the meagre references in a comprehensive 1962 survey of wood extractives. The genus *Ficus* and most other members of the Moraceae are not mentioned. The only references to *Morus* and *Artocarpus* species are the occurrence of oxyresveratrol in *M. alba* and *A. lakoocha*, shikimic acid and sucrose in *M. bombycis*, and the stilbene, chlorophorin (XXXI), in *Chlorophora excelsa* Gaudich. Dadswell and Hillis have drawn attention to dermatitis and asthma caused by the working of this timber and to the retardation of the rate of drying of polyester lacquers by the extractives.

- <sup>40</sup> Y. Asahina and J. Asano, Chem. Ber. 63, 2059 (1930); and earlier papers.
- <sup>41</sup> G. LINDSTEDT, Acta Chem. Scand. 4, 1246 (1950); H. ENDRES, Leder 12, 152 (1961).
- <sup>42</sup> G. LINDSTEDT and A. MISIORNY, Acta Chem. Scand. 5, 121 (1951).
- <sup>43</sup> D. E. HATHWAY and J. W. T. SEAKINS, Biochem. J. 72, 369 (1959).
- 44 H. ENDERS, W. GRASSMAN and W. PAUCKNER, Chem. Ber. 91, 134 (1958).
- 45 F. E. KING and M. F. GRUNDON, J. Chem. Soc. 3348 (1949).
- 46 W. E. HILLIS (editor), Wood Extractives, Academic Press, New York (1962).
- <sup>47</sup> H. E. DADSWELL and W. E. HILLIS in ref. 46, p. 48.

The root and bark of Streblus asper Lour. contain numerous cardenolide glycosides. As Broussonetia papyrifera Vent. and B. kazinoki Siebold have been examined as raw materials for paper and rayon manufacture.

Chlorophora tinctoria Gaudich (Morus tinctoria Linn.; Maclura tinctoria D. Don) is the source of old fustic. Morin and maclurin were isolated from the wood many years ago; it also contains dihydromorin and dihydrokaempferol.<sup>29</sup> At one time fustic was largely used for shading logwood and was regarded as the most important natural dyestuff;<sup>50</sup> it continues to be a commercial product. Commercial maclurin, extracted from Chlorophora tinctoria, contains a small amount of 1,3,6,7-tetrahydroxyxanthone. When a boiling 1% alcoholic solution of maclurin is irradiated with UV light for 3 hr in a stream of oxygen, there is a 45% conversion to the xanthone.<sup>51</sup> In addition to chlorophorin, C. excelsa Benth. and Hook, and C. regia A. Chev. contain oxyresveratrol. The stilbenes appear to be responsible for the light-induced darkening of these woods.<sup>52</sup>

The wood of Toxylon pomiferum Rahn (Maclura pomifera Schneid; M. aurantica Nutt; Osage Orange), "noted for its great durability and resistance to decay", 53 contains oxyresveratrol (about 1%), morin 53 and dihydromorin, 29 but no maclurin. According to Barnes and Gerber 53 the identification of oxyresveratrol was "complicated by the fact that it is usually obtained as an amorphous partially hydrated material, which can be crystallised in an anhydrous form only with difficulty". They believed that the presence of oxyresveratrol was the main reason for the remarkable resistance of the wood to decay. Mongolsuk et al. 3 isolated this stilbene as the crystalline dihydrate, m.p. 201°, from water by merely concentrating an aqueous extract of the wood of Artocarpus lakoocha and ether-extracting the crude product. The fruits contain the isoflavones, osajin and pomiferin. 5

'Cudranin', C<sub>13</sub>H<sub>10</sub>O<sub>4</sub>, found in the wood of *Cudrania triloba* Hanie, and also *M. alba*<sup>54,55</sup> is considered by Laidlaw and Smith<sup>29</sup> to be probably identical with oxyresveratrol. The stem bark of *Treculia africana* Decne contains morin, an unidentified flavonol and flavanone, a cyanidin glucoside and a highly unsaturated quinone. <sup>56</sup> The latex of *Antiaris toxicaria* Leschen (upas or ipoh tree) contains cardenolides used at one time as arrow

<sup>48</sup> A. R. Manzetti and T. Reichstein, Helv. Chim. Acta 47, 2303 (1964).

<sup>&</sup>lt;sup>49</sup> S. R. D. Guha, *Indian Forester* 95, 579 (1969); S. Machida and S. Nishikori, *Kami-pa Gikyoshi* 17, 501 (1963); H. IKEDA et al., Br. Pat. 1,063,321.

<sup>&</sup>lt;sup>50</sup> A. G. Perkin and A. E. Everest, The Natural Organic Colouring Matters, Longmans, London (1918).

<sup>&</sup>lt;sup>51</sup> A. Jefferson and F. Scheinmann, Nature, Lond. 207, 1193 (1965).

<sup>&</sup>lt;sup>52</sup> J. W. W. MORGAN and R. J. ORSLER, Holzforschung 22, 11 (1968).

<sup>&</sup>lt;sup>53</sup> R. A. BARNES and N. N. GERBER, J. Am. Chem. Soc. 77, 3259 (1955).

<sup>54</sup> T. Kondo, H. Ito and M. Suda, Nippon Nogei-Kagaku Kaishi 32, 1 (1958).

<sup>55</sup> G. SUZUSHINO, Misc. Repts. Res. Inst. Resources (Japan) No. 34, 21; No. 35, 8 (1954).

<sup>&</sup>lt;sup>56</sup> L. N. Prista and A. C. Alves, Garcia Orta 9 (2), 283 (1961).

poisons. Other *Antiaris* species and species of *Antiaropsis* and *Ogcodeia* also contain cardiac glycosides, and their taxonomy from this point of view has been studied by Bisset.<sup>57</sup>

## FICUS SPECIES

The genus Ficus consists of trees and shrubs with widely varying habit. Brandis<sup>8</sup> mentions 79 Indian species. For obvious reasons one extensively studied species is F. carica Linn. The leaves, bark and fruit, said to be widely used in folk medicine, have been analysed for total alkaloids (0·17, 0·11 and 0·05% respectively), total glycosides, etc. <sup>58</sup> Psoralene, bergapten and a third unidentified furocoumarin are present in the leaves and root; <sup>59</sup> rutin has also been identified in the leaves. Psoralene and bergapten also occur in F. salicifolia Miq. leaves, and the former in F. sycomoras Linn. <sup>60</sup> Coumarin is found in F. radicans Roxb. <sup>61</sup> Hegnauer <sup>62</sup> records the presence of salicylic acid (or methyl salicylate) in several Ficus species. The fruit of F. bengalensis Linn. contains cyanidin rhamnoglycoside, and the leaves petunidin diglycoside. <sup>63</sup> Cycloartenol, butyrospermol and lupeol were isolated from the bark exudate of F. macrophylla Roxb. <sup>64</sup>

Russel<sup>65</sup> isolated three indolizidine alkaloids (tylocrebrine, tylophorine and septicine) from *F. septica* Forst.; the first two were isolated earlier from *Tylophora crebriflora* S. T. Blake and *T. asthmatica* Wight (Asclepiadaceae). Of special interest is the occurrence of two unique alkaloidal flavones (ficine XXXII and isoficine XXXIII) in *F. pantoniana* King;<sup>66</sup> the structures have been confirmed by synthesis.<sup>67</sup> Brahmachari and Augusti<sup>68</sup> found that an aqueous infusion of the bark of *F. bengalensis* Linn. had hypoglycemic activity in experimental animals; this was confirmed by Joglekar *et al.*,<sup>69</sup> but there was only mild hypoglycemic activity in diabetic patients. The "active principle" isolated by Deshmukh *et al.*<sup>70</sup> was less active than the crude extract.

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- <sup>58</sup> S. Kucharski, Farm. Polska 20, 581 (1964).
- <sup>59</sup> S. Fukushi, Nippon Nogei-Kagaku Kaishi, 33, 564, 1025 (1959); also A. K. Athanasios, I. E. S. El-Kholy, G. Soliman and M. A. M. Shaban, J. Chem. Soc. 4253 (1962); I. E. S. El-Kholy and M. A. M. Shaban, 1140 (1966).
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- <sup>61</sup> R. Paris, in Chemical Plant Taxonomy (edited by T. Swain), p. 349, Academic Press, New York (1963).
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- 64 E. RITCHIE et al., Colloq. Int. Centre Nat. Rech. Sci. (144), 107 (1966).
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- <sup>67</sup> B. Anjaneyulu and T. R. Govindachari, Tetrahedron Letters 2847 (1969).
- <sup>68</sup> H. D. BRAHMACHARI and K. AUGUSTI, J. Pharm. Pharmacol. 13, 381 ((1961); Indian J. Physiol. Pharmacol. 8, 60 (1964).
- <sup>69</sup> G. V. JOGLEKAR, D. S. SHROTRI, R. AIMAN and J. H. BALWANI, J. Indian Med. Assoc. 40, 11 (1963); and earlier papers.
- <sup>70</sup> V. K. DESHMUKH, D. S. SHROTRI and R. AIMAN, Indian J. Physiol. Pharmacol. 4, 182 (1960).
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- <sup>76</sup> M. Komatsu, Chem. Pharm. Bull. 17, 1302 (1969).
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- <sup>78</sup> For references see *The Chemistry of Flavonoid Compounds* (edited by T. A. GEISSMAN), Pergamon Press, Oxford, 1962.
- <sup>79</sup> W. Brune and T. A. Geissman, Austral. J. Chem. 18, 1649 (1965).
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- 81 B. F. Burrows and W. D. Ollis, Proc. Chem. Soc. 177 (1960).

TABLE 4. FLAVONOIDS (OTHER THAN ISOFLAVONOIDS) WITH ISOPRENOID SUBSTITUENTS\*

	Substitution*	Family	Genus	Species	Part of plant	Ref.
Chalcones						
Xanthohumol	4,2',4'-(OH) <sub>3</sub> -6'- OMe-3'-dma	Urticaceae	Humulus	lupulus	Leaf	73
Bavachalcone	4,2',4'-(OH) <sub>3</sub> -5'- dma	Leguminoseae	Psoralea	corylifolia	Seeds	74
Isobavachal- cone	4,2',4'-(OH) <sub>3</sub> -3'- dma	"	"	"	"	74
Sophoradin	4,2',4'-(OH) <sub>3</sub> - 3,5,3'-(dma) <sub>3</sub>	**	Sophora	subprostrata	Root	75
Sophora- dochromene	4,5(2,2-dimethyl- 5,6)-α-pyrano-2',4'- (OH) <sub>2</sub> -3,3'-(dma) <sub>2</sub>	,,	**			76
Flavanones Bavachinin	4'-OH-7-OMe-6-	>>	Psoralea	corylifolia	Seeds	74
Bavachin	dma					74
Isobavachin	7,4'-(OH) <sub>2</sub> -6-dma 7,4'-(OH) <sub>2</sub> -8-dma	**	"	**	,,	/4
Selinone	5,7-(OH) <sub>2</sub> -4'-O- dma	Umbellifereae	Selinum	vaginatum	,,	77
	5-OH-7,3'-(OMe) <sub>2</sub> - 4'-O-dma	Rutaceae	Melicope	sarcococca	,,	78
	5-OH-7,3'-(OMe) <sub>2</sub> - 4'- <i>O</i> -CH <sub>2</sub> CH=CMe- CH <sub>2</sub> CH <sub>2</sub> CHMe <sub>2</sub>	**	**	"		79
Sophoranone	$7,4'-(OH)_2-8,3',5'-(dma)_3$	Leguminoseae	Sophora	subprostrata	Root	75
Sophorano- chromene	7-(OH)-4',5'(2,2-dimethyl-5,6)-a-pyrano-8,3'-(dma) <sub>2</sub>	**	**	**	,,	76
Dihydroflavonol Phellamurin	3,5,4'-(OH) <sub>3</sub> -7- <i>O</i> -Gl-8(3-hydroxy)-isoamyl	Rutaceae	Phelloden- dron	amurense	Leaves	78
Flavones						
Amurensin Icariin	(as phellamurin) 5,7-(OH) <sub>2</sub> -4'-OMe-3- <i>O</i> -rhamnosidyl-8(3- <i>O</i> -Gl)-isoamyl	Berberidaceae	., Epimedium	3 spp."	Root & leaves	78 78
Noricariin Noricariside	4'-OH in icariin 3,5,7,4'-(OH) <sub>4</sub> -8- (3-O-Gl)-isoamyl	Rutaceae	,, Phelloden- dron	macranthum 6 spp.	Roots	78 80
Sericetin	$3,5-(OH)_2-7,6(2,2-dimethyl-5,6)-a-$	Leguminoseae		sericea	Root bark	81
Artocarpus	pyrano-8-dma	Moraceae	Artocarpus	6 spp.	Heart-	
pigments Morus pigmen	ıte	**	Morus	5 spp.	wood Bark	

<sup>\*</sup>  $dma = \gamma \gamma$ -dimethylallyl; O-Gl = glucosidoxy.

#### CHEMOTAXONOMY OF THE MORACEAE

## Flavonoids as Taxonomic Markers

Harborne<sup>71</sup> summarizes "the generally agreed requirements for a chemical character to be of use in plant taxonomy as follows: 'Chemical complexity and structural variability, physiological stability, widespread distribution, and easy and rapid identification.' "He then discusses the flavonoids in this context and concludes that they have considerable potentialities as taxonomic markers in plant classification, although their present contribution to the study of plant relationships is slight because surveys have so far been limited. The present work has shown that 2,4-dihydroxylation in the B-ring is restricted to some genera and species among the Moraceae, but it should be confirmed by a much wider survey. The slender thread supporting chemotaxonomic generalisations is illustrated by Bate-Smith's statement<sup>72</sup> that "morin, 2'-hydroxykaempferol, is peculiar to the Moraceae and is associated in that family with dihydromorin and cyanomaclurin (a catechin)". Cyanomaclurin has so far been detected only in two Artocarpus species, and dihydromorin in two Artocarpus species and four Morus species; there is no morin in any Ficus or Broussenetia and in two out of six Artocarpus species so far examined.

#### Flavonoids with Isoprenoid Substituents

Numerous benzoquinones, naphthaquinones, coumarins, xanthones, rotenoids and phenols carrying isoprenoid groups are known among plant products; but chalcones, flavanones and flavones of this type are relatively few (Table 4). The plants belong to five families in addition to the Moraceae. Considering that many of the compounds in Table 4 were isolated during the last 10 years, and that their biosynthesis involves acceptable processes, there is little doubt that many more will be disclosed when more plants are examined with the aid of modern techniques of separation. A scrutiny of the structural variations may then enable chemotaxonomic conclusions to be drawn; thus flavones with isoprenoid substituents in the 3-position characterize some species of the genera Artocarpus and Morus of the family Moraceae.

## **Isoflavones**

According to Harborne<sup>82</sup> isoflavones occur sporadically in two related families (Rosaceae and Moraceae); the only record in the literature of isoflavones in a Moraceae plant is the occurrence of osajin and pomiferin in the fruits of *Toxylon pomiferum*.

#### Stilbenes

The distribution of stilbenes and dihydrostilbenes in two Artocarpus and five Morus species was discussed earlier. The stilbenes offer some promise in the chemotaxonomy of the Moraceae, but they are probably more useful for following species variations in a genus. Hathway<sup>83</sup> found that the hydroxystilbenes were useful as taxonomic tracers in the genus Eucalyptus. Erdtman's table<sup>22</sup> of the distribution of natural stilbenes in the Pinaceae, Liliaceae, Myrtaceae, Leguminosae, Moraceae, Polygonaceae and Saxifragaceae also indicates the need for a thorough search for stilbenes as an aid in taxonomy. Subsequent to Erdtman's tabulation the few new stilbenes that have been isolated are from Eucalyptus or

<sup>&</sup>lt;sup>71</sup> J. B. HARBORNE, Comparative Biochemistry of the Flavonoids, p. 304, Academic Press, New York, 1967.

 <sup>&</sup>lt;sup>72</sup> E. C. BATE-SMITH in ref. 46, p. 139.
 <sup>82</sup> Ref. 71, p. 310.

<sup>83</sup> D. E. HATHWAY, Biochem. J. 83, 80 (1962).

Table 5. Hydroxylation patterns in natural stilbenes (includes Me ethers and glucosides)

Stilbenes	
4-OH	Pinaceae
3,5-(OH) <sub>2</sub>	Pinaceae; Fagaceae
3,5,4'-(OH) <sub>3</sub>	Pinaceae; Leguminosae; Myrtaceae; Moraceae; Fagaceae; Liliaceae
3,5,2',4'-(OH) <sub>4</sub>	Moraceae (also 4-geranyi); Liliaceae
3,5,3',4'-(OH) <sub>4</sub>	Pinaceae; Leguminosae; Myrtaceae; Polygonaceae; Moraceae
3,5,3',4',5'-(OH) <sub>5</sub>	Leguminosae; Myrtaceae
3,4'-(OH) <sub>2</sub> -2-COOH	Saxifragaceae
Dihydrostilbenes	
3,5-(OH) <sub>2</sub>	Detected in 7 Pinus species.
	Me isolated from one
3,5,3',4'-(OH) <sub>4</sub>	Picea excelsa Link bark.
3,4'-(OH) <sub>2</sub>	
3,2',4'-(OH) <sub>3</sub>	4 Morus species
3,5,2′,4′-(OH) <sub>4</sub>	•

Picea spp. Table 5 gives the hydroxylation patterns of natural stilbenes and dihydrostilbenes.

In the hope of collecting preliminary chemotaxonomic data on a few more members of the family Moraceae, the bark and heartwood of the following species were submitted to a rapid screening procedure: Broussonetia papyrifera; Cudrania javanensis (C. cochinchinensis; Maclura ambioensis); Ficus carica Linn.; F. bengalensis Linn.; F. religiosa Forst.; F. retusa Linn.; F. Krishnae DC; F. glomerata Roxb. Except for p-coumaric acid in Broussonetia papyrifera Vent, the only phenolics isolated or identified were in the bark and heartwood of Cudrania javanensis Trec.: kaempferol, dihydrokaempferol, taxifolin, dihydromorin, morin and oxyresveratrol.

## Taxonomy of the Moraceae

The most recent taxonomic treatment of the Moraceae is by Corner.<sup>84</sup> Discussing the sub-division of Moraceae (Table 6) and the geographical distribution of Moraceous genera

TABLE 6. CLASSIFICATION OF THE MORACEAE (E. J. H. CORNER)84

Tribe	Tribe	Tribe
Moreae	Artocarpeae	Olmedieae
Ampalis	Artocarpus	Antiaris
Pachytrophe	Broussonetia	(17 species)
Morus	Maclura (Chlorophora;	Antiaropsis
Streblus	Cudrania)	-
(genus with 22 species)	Malaisia	
	Parartocarpus	Dorstenieae
	Plecospermum	
	Prainea	
Brosimeae	Treculia	Ficeae (Ficus)

<sup>&</sup>lt;sup>84</sup> E. J. H. Corner, The Gardens Bulletin, Singapore 19, 187 (1962).

TABLE 7. GEOGRAPHICAL TABLE OF MORACEOUS GENERA AND SPECIE	š
(E. J. H. CORNER) <sup>84</sup>	

Gen./spp.	America	Africa	Asia and Australasia	Tribes
10/68	4/19	6/13	4/36	Moreae
15/95	8/20	2/7	7/68	Artocarpeae
18/69	13/58	2/5	4/6	Olmedieae
8/44	1/6	7/38		Brosimeae
1/120	1/80?	1/40?	1/1	Dorstenieae
1/1000?	1/150?	1/250?	1/600?	Ficeae
53/1397	27/333	18/353	17/711	Total Moraceae

and species (Table 7) Corner states: "To the student of *Ficus* the classification, and therefore, the comprehension of Moraceae is confused with excessive genera. The fig (syconium) is so characteristic that no one is willing to make *Ficus* a tribe or family and raise its subdivisions to generic or tribal rank. Further there is a continuum through *Ficus* linking the first with the last. It is a genus which preserves a great deal of its evolution, and its products may still be strung together . . . Caution is needed in recombining the fragments of other Moraceae . . . Yet, the pieces of the puzzle are so strange, so splendidly different from the banalities of many other families, that the monography of the Moraceae is one of the most exciting chapters in angiosperm taxonomy."

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Key Word Index—Moraceae; chemotaxonomy; flavonoids, isoprenyl flavonoids; stilbenes.