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PRENYLATED FLAVONOIDS AS EVOLUTIONARY INDICATORS IN THE GENUS *DAHLSTEDTIA*

FERNANDA RODRIGUES GARCEZ,* SHIRLEI SCRAMIN,† MARIA CÉLIA DO NASCIMENTO and WALTER B. MORS

Núcleo de Pesquisas de Produtos Naturais, Universidade Federal do Rio de Janeiro, 21 941 Rio de Janeiro, Brazil

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Key Word Index—*Dahlstedtia pinnata*, *D pentaphylla*, Leguminosae, prenylated flavonoids, evolutionary indicators.

Abstract—Three chalcones, two β-hydroxychalcones, four flavanones, six flavones, four flavonols, one rotenoid and one pterocarpan were isolated from the roots of *Dahlstedtia pinnata* and *D. pentaphylla*. With the exception of the pterocarpan, all the compounds exhibit prenylation in the A ring, a characteristic of flavonoids produced by species of the Tephrosieae Of the 21 flavonoids identified, five (2 flavanones and 3 flavones) are new as naturally occurring compounds. A neat distinction in the biosynthetic capability of the two species, leading to the production of flavanones and flavonols in *D pentaphylla*, but not in *D. pinnata*, is observed. In this latter species, biosynthesis is totally oriented toward dehydrogenation, producing flavones. By both criteria—higher oxidation state and suppression of enzyme systems—*D pinnata* is the more advanced species.

INTRODUCTION

Prenylated flavonoids are characteristic constituents of a number of Leguminosae genera in the subfamily Papilionoideae, such as *Derris*, *Lonchocarpus*, *Milletia*, *Mundulea*, *Piscidia*, *Pongamia* and *Tephrosia*. Bentham [1] stressed the difficulty of neatly distinguishing these genera and this difficulty was acknowledged by most subsequent workers. Engler [2] placed them in two tribes Dalbergiae, subtribe Lonchocarpinae; and Astragalae, subtribes Tephrosinae and Psoraleinae Hutchinson [3] distributed them over four tribes: Milletieae, Lonchocarpeae, Tephrosieae and Psoralieae. Polhill and Geesink [4], on the other hand, united these genera into a single tribe, Tephrosieae, a decision maintained by Geesink [5], under Milletieae.

Dahlstedtia Malme, which has not previously been investigated chemically, belongs to this same complex. It is an exclusively Brazilian genus with only two known species: *D. pinnata* (Benth) Malme [6] and *D. pentaphylla* (Taub.) Burk. [7] Both have their centre of dispersion in the southern State of Santa Catarina, to which the latter species seems to be restricted, whereas *D pinnata* can also be found further to the north, occasionally as far as Rio de Janeiro, Minas Gerais and Goiás

In the present paper we describe the isolation and identification of 19 prenylated flavonoids from the roots of the two mentioned species, apart from two isoflavonoids (one rotenoid and one non-prenylated pterocarpan) Only two of these components—one chalcone, **1**, and one flavone, **7**, were isolated from both species. Five are described for the first time as naturally occurring substances. This prolific presence of compounds of a peculiar type in one small genus offers an interesting overview allowing for a number of conclusions with regard to biogenetic and evolutionary aspects, based on the metabolic pathways which govern the synthesis of these secondary products.

RESULTS AND DISCUSSION

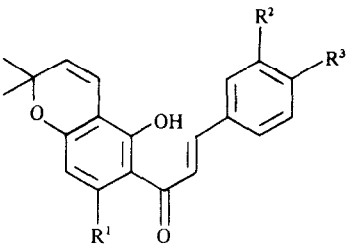
Charts 1 and 2 show the 21 identified flavonoid constituents of the two *Dahlstedtia* species Their structures were deduced by spectral methods Most of the compounds were known previously from plants in other genera of the tribe. Their names and the corresponding literature references are indicated in the Experimental Section. Flavones **3**, **4** and **12** and the flavanone **13** have been described as transformation products of the corresponding chalcones Consequently, **13** was known only as the optically inactive racemate Only flavanone **15** is new. Thus, almost all the structures, deduced from the spectral analysis, could be confirmed by comparison with physical constants and spectral data contained in the literature.

Inspection of the structures leads to a number of interesting deductions with regard to the synthetic sequences leading to the final products It is understood, of course, that the plants produce not only those compounds which could be isolated, but all intermediates on the synthetic route as well, such as would be expected to fill in the steps in the accepted biogenetic pathways

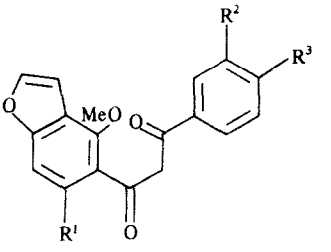
Comparison of the structural features with each Chart allows for the following conclusions: (i) all modifications incidental to ring A occur at least at the chalcone stage of biosynthesis. *O*-Methylation and, in the case of the re-

* Present address Departamento de Química, Universidade Federal do Mato Grosso do Sul, Caixa postal 649, 79 100 Campo Grande, MS, Brazil

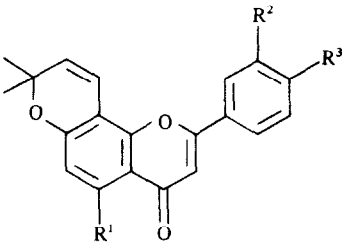
† Present address. Centro Nacional de Pesquisa de Defesa da Agricultura, EMBRAPA, Caixa postal 69, 13 280 Jaguariuna, SP, Brazil



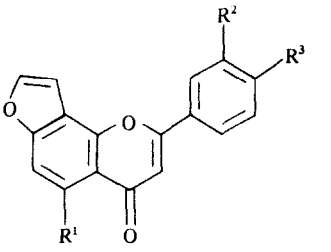
1 R^1 = OMe, R^2 = R^3 = H



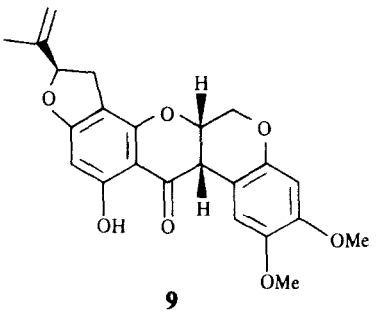
5 R^1 = R^2 = R^3 = H
6 R^1 = H, R^2 + R^3 = $-OCH_2O-$



2 R^1 = OMe, R^2 = R^3 = H
3 R^1 = OMe, R^2 + R^3 = $-OCH_2O-$
4 R^1 = H, R^2 + R^3 = $-OCH_2O-$



7 R^1 = R^2 = R^3 = H
8 R^1 = H, R^2 + R^3 = $-OCH_2O-$



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Compounds **3** and **4** have not previously been described as natural products
Chart 1 Flavonoid constituents of *Dahlstedtia pinnata*

sorcinol oxydation pattern, elimination of the hydroxyl group at C-6′ may happen even earlier, before cyclization, on the open polyketide chain Prenylation occurs after cyclization, since otherwise the C_5 substituent would isomerize to a Δ^1-isopentenyl group [8], (ii) Formation of β-hydroxychalcones (dibenzoylmethanes, e g **5** and **6**) is conditioned to the absence of a hydroxyl group suitable for closure of the pyrone ring (elimination at C-6′, *O*-methylation at C-2′); (iii) Where both C-2′ and C-6′ are oxygenated (phloroglucinol type) cyclization of the prenyl substituent toward the 'linear' disposition of the pyranochromene system (as found in many instances in *Pongamia*) rather than the 'angular' one (the only one present in *Dahlstedtia*) is also determined by the *O*-methylation pattern

Altogether, one observes a neat distinction in the synthetic capability of the two *Dahlstedtia* species Thus, *D pentaphylla* operates the complete biogenetic sequence of flavonoid biosynthesis up to flavanones and flavonols In *D pinnata*, on the other hand, biosynthesis is totally oriented toward dehydrogenation, producing flavones as final products By both criteria—higher oxydation state and suppression of enzyme activity—*D pinnata* is the evolutionary more advanced species

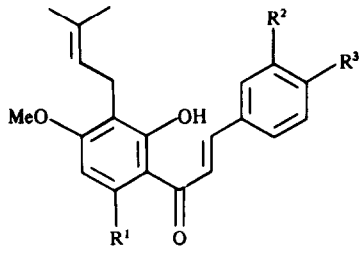
Discussion of the ^1H and ^{13}C NMR spectra of compounds **5** and **6** with a view on the structures involved in the respective keto–enol tautomerism in chloroform solution was the object of a previous paper [9] The ^{13}C spectra of a larger number of flavonoids, including the compounds here described, will be presented and discussed in a forthcoming publication An expansion of the method of reasoning here applied to the phylogenetic relationship between the two *Dahlstedtia* species to other genera of the tribe is being attempted

EXPERIMENTAL

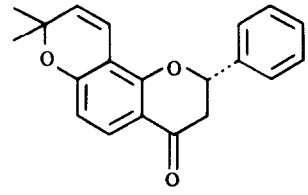
Root material of *D pinnata* and *D pentaphylla* was collected in the State of Santa Catarina, in the municipalities or Morretes and Rodeio, respectively Voucher specimens are deposited at the Museu Botânico Municipal in Curitiba, Paraná

Mps are uncorr UV spectra were obtained in MeOH or 95% EtOH and IR spectra in KBr pellets ^1H NMR spectra were recorded at 100 MHz in $CDCl_3$ with TMS as int standard,

1 and 7 as in Chart 1



10 R^1 = OMe; R^2 = R^3 = H
11 R^1 = OMe, $R^2 + R^3$ = $-OCH_2O-$



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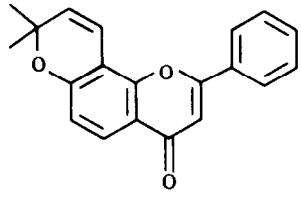

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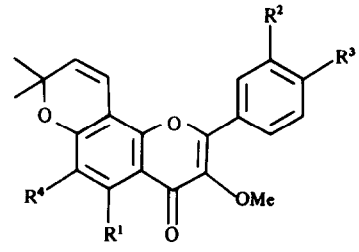
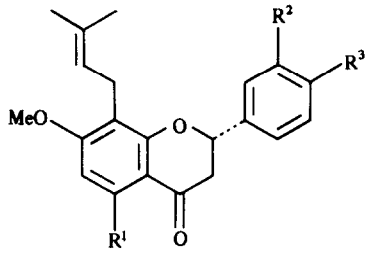
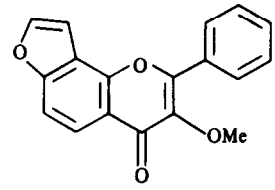


17 R^1 = R^2 = R^3 = R^4 = H
18 R^1 = R^2 = R^3 = H, R^4 = OMe
19 R^1 = R^4 = H; $R^2 + R^3$ = $-OCH_2O-$



13 R^1 = R^2 = R^3 = H
14 R^1 = OMe, R^2 = R^3 = H
15 R^1 = H, $R^2 + R^3$ = $-OCH_2O-$



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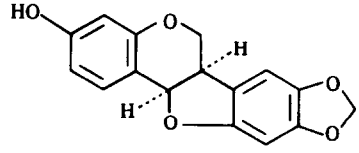

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Flavanone **15** is new in the literature; flavone **12** and flavanone **13** have not previously been described as natural products, the latter being formerly known only in the racemic form.
Chart 2 Flavonoid constituents of *Dahlstedtia pentaphylla*

chemical shifts are reported in δ (ppm) units MS were recorded on a Varian Micromass MM 12F instrument at 70 eV Silicic acid and silica-gel were used for CC, while silica-gel GF and PF_{254} were used for TLC Spots were visualized by exposing the plates to I_2 vapour, by spraying with $CeSO_4$ in 2N H_2SO_4 and by inspection under UV light (254 and 366 nm). Elution of the columns was started with petrol (bp 40–80°) and proceeded with solvent mixtures of increasing polarity.

Extraction Ground roots were exhaustively percolated first with petrol, then with Et_2O The extractives were redissolved in petrol and chromatographed as indicated above Of the nine flavonoids isolated from *D. pinnata*, eight were present in both extracts, one (**9**) was present in the petrol extract only. Of the 14 flavonoids isolated from *D pentaphylla*, **11** was present in the petrol extract exclusively, five (**12**, **14**, **16**, **19** and **21**) were present only in the Et_2O extract, and the remaining eight, in both Below, the compounds are listed in the order of their elution Our data not previously published are reported here.

2-Hydroxy-6'-methoxy-2'', 2''-dimethylpyrano (5'', 6''. 3', 4') chalcone (**1**, pongachalcone I). Eluted with hexane–EtOAC 99 1, orange-red crystals from hexane, mp 105–108° (lit. [10] 107–108°) UV λ_{max}^{MeOH} nm (log ε) 232 (4 29), 304 (4 36), 358

(4 30) UV $\lambda_{max}^{MeOH+AlCl_3}$ nm (log ε) 228 (4 26), 306 (4 24), 390 (4 33) MS 336 [M$^+$]

2-*Methoxy*-(2″, 3″ 3′,4′)-*furanodibenzoylmethane* [=2-*methoxy*-(2″, 3″ 3,4)-*furano*-β-*hydroxychalcone*] (**5**, pongamol) Eluted with hexane–EtOAc (98 2), red crystals from hexane–EtOAc (3 1), mp 134–137° (lit [11] 128–129°) UV λ_{max}^{EtOH} nm (log ε) 221 (4 18), 239 (4 29), 350 (4 24) MS *m/z* (rel int) 294 [M$^+$], (10), 263 (100), 175 (68), 160 (20), 105 (28), 77 (32)

2-*Methoxy*-3′,4′-*methylenedioxy*-(2″, 3″ 3,4)-furanodibenzoylmethane [=2-*methoxy*-3′,4′-*methylenedioxy*-(2″,3″ 3,4) *furano*-β-*hydroxychalcone*] (**6**, glabra-I, ovalitenone) Eluted with hexane–EtOAc (95 5), greenish-yellow crystals, mp 120–123 (lit [12] 123–126°) UV λ_{max}^{EtOH} nm (log ε) 221 (4 06), 240 (4 24), 367 (4 19) UV $\lambda_{max}^{EtOH+NaOH}$ nm (log ε) 221 (4 50), 350 (4 25) MS *m/z* (rel int) 338 (M$^+$] (18), 307 (100), 175 (76), 160 (21), 149 (41), 121 (13)

(2″, 3″ 7, 8)-*Furanoflavone* (**7**, lanceolatin B) Eluted with hexane–EtOAc (9 1), pale yellow crystals, mp 134–137° (lit [13] 138°) UV λ_{max}^{EtOH} nm (log ε) 224 (4 30), 264 (4 33), 297 (4 21) MS *m/z* (rel int) 262 [M$^+$] (61), 234 (5), 160 (100), 132 (12), 117 (9), 104 (7) ^{1}H NMR ($CDCl_3$) δ 6 88 (1H, s, H-3), 7 20 (1H, *d*, *J* = 2 0 Hz, H-β), 7 50–7 62 (4H, *m*, H-3′, H-4′, H-5′, H-6), 7 80 (1H, *d*, *J* = 2 0 Hz, H-α), 7 90–8 02 (2H, *m*, H-2′, H-6′), 8 16 (1H, *d*, *J* = 9 0 Hz, H-5)

3′, 4′-*Methylenedioxy*-(2″, 3″ 7, 8) *furanoflavone* (**8**, pongaglabrone) Eluted with hexane–EtOAc (9 1), colourless crystals, mp 228–230° (lit [14] 228–229°) UV λ_{max}^{EtOH} nm (log ε) 223 (4 47), 249 (4 52), 329 (4 32) MS *m/z* (rel int) 306 [M$^+$] (100), 278 (7), 160 (68), 146 (94), 132 (11), 104 (5) ^{1}H NMR ($CDCl_3$) δ 6 14 (2H, s, O–CH_2–O), 6 80 (1H, s, H-3), 7 0 (1H, *J* = 8 0 Hz, H-5′), 7 20 (1H, *d*, *J* = 2 0 Hz, H-β), 7 44 (1H, *d*, *J* = 2 0 Hz, H-2′), 7 59 (2H, *dd*, *J* = 8 0 and 2 0 Hz, H-6, H-6′), 7 82 (1H, *d*, *J* = 2 0 Hz, H-α), 8 22 (1H, *J* = 8 0 Hz, H-5)

3′, 4′-*Methylenedioxy*-2″, 2″-*dimethylpyrano*-(5″, 6″ 7, 8)*flavone* (**4**) Eluted with hexane–EtOAc (9 1), yellow crystals, mp 232–234° (lit [15] 233°) UV λ_{max}^{EtOH} nm (log ε) 237 (4 38), 270 (4 12), 339 (4 14) MS *m/z* (rel int) 384 [M$^+$] (15), 333 (100), 187 (47) ^{1}H NMR ($CDCl_3$) δ 1 52 (6H, s, *gem*-diMe), 5 73 (1H, *d*, *J* = 9 0 Hz, H-3″), 6 05 (2H, *s*, O–CH_2–O), 6 60 (1H, *s*, H-3), 6 82 (1H, *d*, *J* = 8 0 Hz, H-6), 6 87 (1H, *d*, *J* = 9 0 Hz, H-4″), 6 91 (1H, *d*, *J* = 8 0 Hz, H-5′), 7 29 (1H, *d*, *J* = 2 0 Hz, H-2′), 7 43 (1H, *dd*, *J* = 8 0 and 2 0 Hz, H-6′), 7 95 (1H, *d*, *J* = 8 0 Hz, H-5)

6a,12a,4′,5′-*Tetrahydro*-11-*hydroxy*-2,3-*dimethoxy*-5′-*isopropenylfurano*-(3′,2′ 8,9)-6*H*-*rotoxen*-12-*one* (**9**, sumatrol) Eluted with hexane–EtOAc (9 1), colourless crystals, mp 192–194° (lit [16] 194–195°), $[\alpha]_D^{25}$ −21 7 ($CHCl_3$, *c* 0 77), −187° (C_6H_6, *c* 0 5)

5-*Methoxy*-2″,2″-*dimethylpyrano*-(5″,6″ 7,8) *flavone* (**2**, isopongaflavone) Eluted with hexane–EtOAc (1 1), pale yellow crystals, mp 214–216° (lit [17] 214–216°) MS *m/z* 334 [M$^+$]

5-*Methoxy*-3′,4′-*methylenedioxy*-2″,2″-*dimethylpyrano*-(5″,6″ 7,8) *flavone* (**3**) Eluted with hexane–EtOAc (3 7), pale yellow crystals, mp 242–244° (lit [18] 242–244°) UV λ_{max}^{EtOH} nm (log ε) 236 (4 48), 276 (4 38), 331 (4 18) MS *m/z* (rel int) 378 [M$^+$] (53), 363 (100), 217 (70)

2′-*Hydroxy*-4′,6′-*dimethoxy*-3′-γ,γ-*dimethylallylchalcone* (**10**, ovalichalcone) Eluted with hexane–$CHCl_3$ (8 2), orange crystals from EtOH, mp 126–128° (lit [19] 123–124°)

(2S)-7-*Methoxy*-8-γ,γ-*dimethylallylflavanone* (**13**, (−)isoderricine A) Eluted with hexane–$CHCl_3$ (7 3) Colourless crystals from EtOH, mp 103–104° (lit for the racemic compound 123° [20]) Anal C 77 94, H 6 89 Calc for $C_{21}H_{22}O_3$ C 78 23, H 6 88 $[\alpha]_D^{28}$ −91 1° ($CHCl_3$, *c* 1 0) UV λ_{max}^{EtOH} nm (log ε) 220 (4 17), 237 (3 80, sh), 286 (3 82), 312 (3 40, sh) ^{1}H NMR δ 1 68 (6H, *s*, *gem*-diMe), 2 72–3 18 (2H, *m*, H-3), 3 36 (2H, *dl*, *J* = 7 Hz, –CH_2–CH=), 3 92 (3H s, 7-OMe), 5 20 (1H, *tl*, *J* = 7 Hz, –CH_2–CH=), 5 46 (1H, *dd*, *J* = 11 and 5 Hz, H-2), 6 63 (1H, *d*, *J* = 9 Hz, H-6), 7 38–7 48 (5H, *m*, C_6H_5), 7 83 (1H, *d*, *J* = 9 Hz, H-5) MS *m/z* 322 [M$^+$] (45), 307 (22), 279 (44), 267 (16), 218 (90), 203 (58), 190 (100), 175 (94), 163 (50), 131 (21), 104 (10), 103 (18) CD (MeOH, *c* 0 022 g l) $[\theta]_{352}$ = 0, $[\theta]_{333}$ = 23426, $[\theta]_{319}$ = 0, $[\theta]_{292}$ = −32211

2′-*Hydroxy*-4′,6′-*dimethoxy*-3′-γ,γ-*dimethylallyl*-3,4-*methylenedioxychalcone* (**11**, ovalichalcone A) Eluted with hexane–$CHCl_3$ (7 3), orange crystals from EtOH, mp 158–162 (lit [21] 158°) MS *m/z* (rel int) 396 [M$^+$] (87), 381 (19), 353 (57), 341 (25), 275 (4), 248 (15), 233 (58), 219 (12), 205 (33), 193 (66), 191 (30), 175 (100), 165 (6), 147 (12)

(2S)-7-*Methoxy*-8-γ,γ-*dimethylallyl*-3′,4′-*methylenedioxyflavanone* (**15**) Eluted with hexane–$CHCl_3$ (6 4), colourless crystals from EtOH, mp 120–122 Anal C 71 95 H 5 9 Calc for $C_{22}H_{22}O_5$ C 72 11, H 6 05 $[\alpha]_D^{28}$ −80 3 ($CHCl_3$, *c* 1 0) ^{1}H NMR δ 1 68 (6H, *sl gem*-diMe), 2 66–3 14 (2H *m*, H-3), 3 35 (2H, *dl*, *J* = 7 Hz, –CH_2–CH=), 3 91 (3H, s, 7-OMe), 5 18 (1H, *tl*, *J* 7 Hz, –CH_2–CH=), 5 35 (1H, *dd*, *J* = 11 and 5 Hz, H-2), 5 99 (2H, s, O–CH_2–O), 6 62 (1H, *d*, *J* = 9 Hz, H-6), 6 84–7 00 (3H, *m*, H-2′, H-5′, H-6′), 7 82 (1H *d*, *J* = 9 Hz, H-5) MS *m/z* (relat int) 366 [M$^+$] (100), 351 (12), 323 (88), 311 (31), 218 (40), 203 (36), 190 (60), 175 (73), 163 (62), 148 (65), 147 (29), 135 (14) CD (MeOH *c* 0 028 g l) $[\theta]_{334}$ = 24836, $[\theta]_{320}$ = 0 $[\theta]_{296}$ = −45752

3-*Methoxy*-(2″,3″ 7,8) *furanoflavone* (**20**, karanjin) Eluted with hexane–$CHCl_3$ (1 1), colourless crystals, mp 161-163° (lit [22] 161°)

3-*Methoxy*-2″,2″-*dimethylpyrano*-(5″,6″ 8,7) *flavone* (**17**, pongaflavone, karanjachromene) Eluted with hexane–$CHCl_3$ (1 1), colourless crystals, mp 148–150 (lit [22] 149)

3,6-*Dimethoxy*-2″, 2″-*dimethylpyrano*-(5″,6″,8,7) *flavone* (**18**) Eluted with hexane–$CHCl_3$ (25 75), colourless crystals from EtOH, mp 201–203 (lit [23,24] 203–205°)

(2S)-2″,2″-*Dimethylpyrano*-(5″,6″ 8,7) *flavanone* (**16**, (−)isolonchocarpine) Eluted from Et_2O extract with hexane–$CHCl_3$ (6 4), colourless crystals, mp 114–116 (lit [25, 26] 117–118) CD (MeOH, *c* 0 0325 g l) $[\theta]_{355}$ = 0 $[\theta]_{339}$ = 13207 $[\theta]_{329}$ = 0, $[\theta]_{305}$ = −37736

3-*Methoxy*-2″,2″-*dimethylpyrano*-(5″,6″ 8,7)-3′,4′-*methylenedioxyflavone* (**19**, pongachromene) Eluted from Et_2O extract with hexane–EtOAc (9 1), light yellow crystals from EtOH, mp 198–200 (lit [27] 195–196) MS *m/z* (rel int) 378 [M$^+$] (79), 377 (70), 363 (100), 187 (48), 159 (12), 149 (30)

2″,2″-*Dimethylpyrano*-(5″ 6′ 8,7) *flavone* (**12**) Eluted from Et_2O extract with hexane–EtOAc (8 2) Light yellow crystals from EtOH, mp 136–140° (lit [28] 142)

(6a*R*, 11a*R*)-3-*Hydroxy*-8,9-*methylenedioxypterocarpan* (**21**, maackiain, demethylpterocarpin) Eluted from Et_2O extract with hexane–EtOAc (85 15) Yellow amorphous solid Identification by spectral data (for mass spectrum see [29]) and acetylation (see below) ^{1}H NMR δ 3 34–3 80 (2H *m*, H-6a and H-6 axial), 4 13–4 30 (1H, *m*, H-6 equatorial), 5 50 (1H, *d*, *J* = 7 Hz, H-11a), 5 92 (2H, *m*, –O–CH_2–O–), 6 47 (1H, s, H-10), 6 52 (1H, *d*, *J* = 3 Hz, H-4), 6 67 (1H, *dd*, *J* = 8 and 3 Hz, H-2), 6 74 (1H, s, H-7), 7 38 (1H, *d*, *J* = 8 Hz, H-1)

(2S)-5,7-*Dimethoxy*-8-γ,γ-*dimethylallylflavanone* (**14**) Eluted from Et_2O extract with hexane EtOAc (7 3) Colourless crystals from $CHCl_3$–Me_2O, mp 97–100° (lit [30] 98°) $[\alpha]_D$ −33° ($CHCl_3$, *c* 1 0) CD (MeOH, *c* 0 0365 g/l) $[\theta]_{359}$ = 0, $[\theta]_{333}$ = 15384, $[\theta]_{310}$ = 0, $[\theta]_{280}$ = −47115

Acetylation of **21** (6a*R*, 11a*R*)-3-*acetoxy*-8,9-*methylenedioxypterocarpan* The material was acetylated with Ac_2O in pyridine in the usual way The product was recryst ×2 from EtOAc Colourless crystals, mp 177–180 (lit [31,32] 178) MS *m/z* (rel int) 326 [M$^+$] (39), 284 (100), 283 (17), 175 (7), 162 (13), 151

(7), 149 (5), 147 (6), 134 (12) ORD (MeOH, *c* 0 042 g/l) $[\theta]_{350} = -776$, $[\theta]_{320} = 3381$, $[\theta]_{312} = 0$, $[\theta]_{285} = -24062$, $[\theta]_{273} = -17852$, $[\theta]_{244} = -27943$

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REFERENCES

1. Bentham, G. (1860) *J. Linn. Soc. Bot.* **4** (Suppl.), 1.
2. Engler, A (1964) *Syllabus der Pflanzenfamilien* Borntrager, Berlin
3. Hutchinson, J (1964) *The Genera of Flowering Plants* Clarendon Press, Oxford
4. Polhill, R M and Geesink, R (1971) in *Chemotaxonomy of the Leguminosae* (Harborne, J B, Boulter, D and Turner, B L, eds) Academic Press, London
5. Geesink, R. (1984) *Scala Milletiearum* **8**, Leiden Bot. Series.
6. Malme, G O A N (1905) *Arkiv Botanik* **4**, 1
7. Burkart, A (1957) Darwiniana **11**, 269
8. Gonçalves, M L S and Mors, W B. (1981) *Phytochemistry* **20**, 1947
9. Scramin, S., da Silva, A J R. and Mors, W B (1983) *Anais do 2° Simpósio Nacional de Farmacologia e Química de Produtos Naturais*, Editora Universitária UFPB (João Pessoa, Brazil), 403
10. Chibber, S. S., Dutt, S. K., Sharma, R. P and Sharma, A. (1981) *Indian J Chem* **20B**, 626.
11. Narayanaswamy, S., Rangaswamy, S and Seshadri, T. R (1954) *J Chem Soc*, 1871
12. Gupta, R K and Krishnamurti, M. (1977) *Phytochemistry* **16**, 1104
13. Lira, L A, Mello, J F de, Delle Monache, G, Delle Monache, F and Marini-Bettòlo, G. B (1979) *Gazz Chim. Ital* **109**, 93
14. Khan, H and Zaman, A (1974) *Tetrahedron* **30**, 2811.
15. Subrahmanyam, K, Rao, J M. and Rao, K V J (1977) *Indian J Chem* **15B**, 105
16. Crombie, L and Peace, R. (1961) *J. Chem Soc*, 5445.
17. Roy, D, Sharma, N N and Khanna, R N. (1977) *Indian J Chem* **15B**, 1138
18. Malik, S B, Sharma, P and Seshadri, T R (1977) *Indian J Chem* **15B**, 493
19. Gupta, R K and Krishnamurti, M (1977) *Phytochemistry* **16**, 293
20. Nascimento, M C and Mors, W. B (1972) *Phytochemistry* **11**, 3023
21. Gupta, R K. and Krishnamurti, M (1979) *Indian J Chem.* **17B**, 291
22. Lakshmi, P, Srimannarayana, G and Subba Rao, N V. (1974) *Indian J Chem.* **12**, 8
23. Nascimento, M. C., Dias, R. L. V. and Mors, W. B. (1976) *Phytochemistry* **15**, 1553.
24. Nascimento, M. C and Mors, W. B. (1981) *Phytochemistry* **20**, 147.
25. Talapatra, S. K, Mallik, A K. and Talapatra, B (1980) *Phytochemistry* **19**, 1199
26. Venkata Rao, E and Ranga Raju, N (1979) *Phytochemistry* **18**, 1581
27. Mukerjee, S. K., Sarkar, S. C and Seshadri, T R (1969) *Tetrahedron* **25**, 1063.
28. Subrahmanyam, K., Madhusudhana Rao, J. and Jagannadha Rao, K V (1977) *Indian J Chem.* **15B**, 105.
29. Ingham, J L (1976) *Phytochemistry* **15**, 1989
30. Waterman, P G and Mahmoud, E N (1985) *Phytochemistry* **24**, 571
31. Cocker, W, Dahl, T, Dempsey, C and McMurray, T. B. H (1962) *J Chem Soc* 4906.
32. Harper, S H., Kemp, A D., Underwood, W. G E and Campbell, R V. M (1969) *J. Chem. Soc* 1109