Phytochemistry, 1974. Vol. 13. pp. 2593 to 2595. Pergamon Press. Printed in England.

ISOFLAVONES FROM *PTERODON APPARICIOI**

ELIO GALINA and OTTO RICHARD GOTTLIEB†

Departamento de Química, Universidade Federal Rural do Rio de Janeiro, Brasil

(*Received* 7 *April* 1974)

Key Word Index—*Pterodon apparicioi*; Leguminosae; isoflavones.

Abstract—The trunk wood of *Pterodon apparicioi* contains five known compounds: 7-hydroxy-6,4′-dimethoxy-, 7-hydroxy-6-methoxy-3′,4′-methylenedioxy-, 6,7,2′,3′,4′-pentamethoxy-, 6,7,2′,4′,5′-pentamethoxy- and 6,7,2′-trimethoxy-4′,5′-methylenedioxyisoflavone. In addition, there are four new substances, namely 7,3′-dihydroxy-6,4′-dimethoxy-, 7-hydroxy-6,2′,4′,5′-tetramethoxy-, 7,2′-dimethoxy-4′,5′-methylenedioxy- and 7,8,2′-trimethoxy-4′,5′-methylenedioxyisoflavone.

INTRODUCTION

Pterodon apparicioi Pedersoli is a recently described species in the Leguminosae-Lotoideae, stated to be akin to *P. pubescens* Benth.[2] A sample of its trunk wood was collected at the bank of the Cipó River, Cipó Ridge, Minas Gerais State, from the formation which had served for the original botanical description of the species.

The isoflavones **1**a, **2**a, **3**a[3a] and **3**b[3b] have previously been shown to occur in *P. pubescens*. Three (**1**a, **3**a, **3**b) are accompanied in *P. apparicioi* by six additional isoflavones: **1**b, the well known afrormosin, and **2**b, both previously isolated from *Dalbergia riparia* (Mart.) Benth.,[4] as well as four new natural compounds. The identification of the five known isoflavones was confirmed by direct comparison with authentic samples.

Two of the new derivatives, $C_{15}H_6O_2(OH)_2(OMe)_2$ and $C_{15}H_5O_2(OH)(OMe)_4$, bear free phenolic hydroxyls and two, $C_{15}H_6O_2(OMe)_2O_2CH_2$ and $C_{15}H_5O_2(OMe)_3O_2CH_2$, are neutral. Methylation with dimethyl sulphate transformed the compounds of the former pair respectively into the known **2**a[3a,5] and **3**b,[5] establishing their oxygenation pattern. No UV shift was observed upon addition of H_3BO_3 + NaOAc to the dihydroxy derivative; the hydroxyls must thus be on different rings. The frequency shifts of the aromatic proton signals, observed upon comparison of the PMR spectra of the dimethyl ether (**2**a) and the diacetate (**2**c) of the compound (Table 1), not only confirmed this fact, but also located the hydroxyls on C-7 and 3′, as shown in **2**d. Comparably strong bathochromic shifts of

* Part XLVI in the series "The Chemistry of Brazilian Leguminosae". For Part XLV see Ref. 1. Taken from part of the M.S. thesis submitted by E.G. (on leave of absence from Cia. Souza Cruz Industria e Comercio) to the Universidade Federal Rural do Rio de Janeiro, 1974. Sponsored by Ministério do Planejamento (Financiadora de Estudos e Projetos S.A.) and Associação Brasileira da Indústria Farmacêutica through Academia Brasileira de Ciências.

† Instituto de Química, Universidade de São Paulo, Brasil.

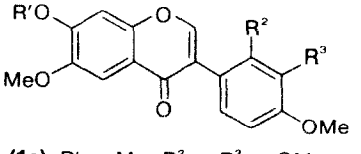
[1] ARAGÃO CRAVEIRO, A. and GOTTLIEB, O. R. (1974) *Phytochemistry* **13**, 1629.
[2] PEDERSOLI, J. L. (1970) *An. Acad. Brasil. Ciênc.* **42** (Supl.) 392.
[3] BRAZ FILHO, R., GOTTLIEB, O. R. and VIEGAS ASSUMPÇÃO, R. M. (a) (1971) *Phytochemistry* **10**, 2835; (b) unpublished result.
[4] BRAZ FILHO, R., LEITE DE ALMEIDA, M. E. and GOTTLIEB, O. R. (1974) *Phytochemistry* **12**, 1187.
[5] CAMPBELL, R. V. M., HARPER, S. H. and KEMP, A. D. (1969) *J. Chem. Soc.* (*C*) 1787.

the UV maxima were observed upon addition either of NaOH or of NaOAc to the monohydroxy derivative. The hydroxyl must thus be at C-7. The frequency shifts of the aromatic signals, observed upon comparison of the PMR spectra of the methyl ether (**3b**) and the acetate (**3c**) of the compound (Table 1) confirmed this fact and led to structure **3**d.

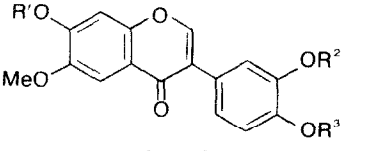
TABLE 1. PMR SPECTRAL COMPARISONS OF ETHERS AND ACETATES OF ISOFLAVONES IN $CDCl_3$

Position of H	2a	2c	Δ ppm	H/OH in 2d	3b	3c	Δ ppm	H/OH in 3d
5	2·33	2·22	−0·11	*m*	2·36	2·23	−0·13	*m*
8	3·10	2·70	−0·40	o	3·06	2·76	−0·30	o
2′	2·90	2·60	−0·30	o	—	—	—	—
3′	—	—	—	—	3·36	3·36	0·00	—
5′	3·06	2·98	−0·08	*m*	—	—	—	—
6′	2·68	2·53	−0·15	*p*	3·12	3·04	−0·08	

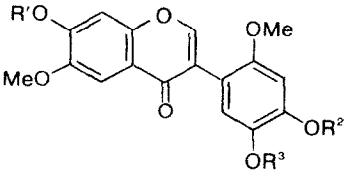
The two neutral compounds were also recognized as isoflavones through MR H-2 singlets (τ 2·01 and 2·07). The presence, in both spectra, of two additional one H singlets at τ 3·1 and 3·3 pointed to the existence of *para*-hydrogens on the B-rings, a requirement compatible with 2′-OMe-4′,5′-O_2CH_2 substitution. Since the remaining PMR signals clearly indicated the presence of hydrogens on C-5, 6 and 8 in the dimethoxy derivative and on C-5 and 6 in the trimethoxy derivative, the respective formulations **4**a and **4**b were considered to represent these compounds. The latter one has the m.p. given for 6,7,2′-trimethoxy-4′,5′-methylenedioxyisoflavone (**4**b) prepared from 4-methoxypterocarpin.[6] The alternative 7,8-O_2CH_2-2′,4′,5′-triOMe-substitution for **4**b is not favoured by the MS whose prominent fragment ions are compatible with dimethoxylation of ring A.



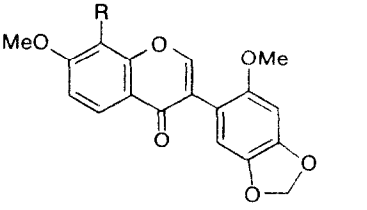
(1a) R′ = Me; R^2 = R^3 = OMe
(1b) R′ = R^2 = R^3 = H



(2a) R′ = R^2 = R^3 = Me
(2b) R′ = H; R^2 — R^3 = CH_2
(2c) R′ = R^2 = Ac; R^3 = Me
(2d) R′ = R^2 = H; R^3 = Me



(3a) R′ = Me; R^2 — R^3 = CH_2
(3b) R′ = R^2 = R^3 = Me
(3c) R′ = Ac; R^2 = R^3 = Me
(3d) R′ = H; R^2 = R^3 = Me



(4a) R = H
(4b) R = OMe

[6] BOUWER, D., BRINK, C. v. d. M., ENGELBRECHT, J. P. and RALL, G. J. H. (1968) *J. S. A. Chem. Inst.* **21**, 159.

EXPERIMENTAL

Isolation of the constituents of P. appariciol. Heartwood and softwood were not separated prior to grinding and extraction with C_6H_6. The extract (46 g, 1·9%) was separated by boiling light petrol. into two parts. The soluble part (4 g) was chromatographed on silica (85 g) giving the following fractions with the indicated eluants: A (C_6H_6–$CHCl_3$ 6:4), B (C_6H_6–EtOH 97:3). The insoluble part (42 g) in $CHCl_3$ was extd. with 5% aq. Na_2CO_3. The $CHCl_3$-layer was dried and evaporated. The residue (35 g) was chromatographed on silica (800 g) giving the following fractions with the indicated eluants: C (C_6H_6), D (C_6H_6–$CHCl_3$ 9:1), E (C_6H_6–$CHCl_3$ 7:3), F (C_6H_6–EtOH 96:4). The aq. soln. was acidified and extd. with $CHCl_3$. The $CHCl_3$-soln. was dried and evaporated. The residue (7 g) was chromatographed on silica (150 g) giving the following fractions with the indicated eluants: G (C_6H_6–$CHCl_3$ 1:1), H (C_6H_6–$CHCl_3$ 25:75), I (C_6H_6–EtOH 99:1), J (C_6H_6–EtOH 99:1). Crystallization of the fractions from the indicated solvents yielded the following cmpds.: A (EtOH) sitosterol (10 mg), B (EtOH) **3b** (22 mg), C (C_6H_6) **4a** (62 mg), D (C_6H_6–AcOEt) **4b** (71 mg), E (C_6H_6–AcOEt 8:2) **3a** (40 mg), F (C_6H_6) **1a** (320 g), G (EtOH–$CHCl_3$) **2b** (72 mg), H (EtOH) **1b** (30 mg), I (C_6H_6) **3d** (32 mg), J (EtOH) **2d** (52 mg).

6,7,2',3',4'-*Pentamethoxyisoflavone* (**1a**),[3] 7-*hydroxy*-6,4'-*dimethoxyisoflavone* (**1b**),[4] 7-*hydroxy*-6-*methoxy*-3',4'-*methylenedioxyisoflavone* (**2b**),[4] 6,7,2'-*trimethoxy*-4',5'-*methylenedioxyisoflavone* (**3a**),[5] 6,7,2',4',5'-*pentamethoxyisoflavone* (**3b**).[5] M.p., IR, UV, NMR and MS of these cmpds. were identical to lit. values.

7,3'-*Dihydroxy*-6,4'-*dimethoxyisoflavone* (**2d**), m.p. 213–215°, prisms (Found: C, 64·74; H, 4·41 $C_{17}H_{14}O_6$ requires: C, 64·97; H, 4·49%). ν_{max}^{KBr} (cm^{-1}): 3515, 3160, 1620, 1570, 1512, 1280, 1210, 1140, 1020, 880. λ_{max}^{EtOH} (nm): 261, 291 inf., 323 (ε 18200, 12550, 9100); no shifts upon add. of $AlCl_3$ or H_3BO_3 + NaOAc; $\lambda_{max}^{EtOH+NaOH}$ (nm): 263, 320, 355 (ε 19150, 9400, 15700); $\lambda_{max}^{EtOH+NaOAc}$ (nm): 258, 294 inf., 350 (ε 20100, 8150, 12250). MS *m/e* (%): 315 (20) M + 1, 314 (100) M, 313 (27), 299 (22), 285 (5), 271 (19), 243 (12), 192 (7), 167 (13), 141 (16), 133 (10), 127 (17), 106 (7), 105 (12). *Acetate* (**2c**), m.p. 185–187° (C_6H_6). ν_{max}^{KBr}(cm^{-1}): 1750, 1640, 1615, 1515, 1485, 1432, 1370, 1275, 1225, 1210, 1196, 1115, 1025, 810. PMR ($CDCl_3$, τ): 1·97 (*s*, H-2), 2·22 (*s*, H-5), 2·53 (*q*, *J* 8·0, 2·0 Hz, H-6'), 2·60 (*d*, *J* 2·0 Hz, H-2'), 2·70 (*s*, H-8), 2·98 (*d*, *J* 8·0 Hz, H-5'), 6·06 (*s*, OMe-6), 6·13 (*s*, OMe-4'), 7·65 (*s*, COMe), 7·68 (*s*, COMe). *Methyl ether* (**2a**), data as required by ref. 6.

7-*Hydroxy*-6,2',4',5'-*tetramethoxyisoflavone* (**3d**), m.p. 205–207°, needles (Found: C, 63·50; H, 5·02. $C_{19}H_{18}O_7$ requires: C, 63·68; H, 5·06%). ν_{max}^{KBr} (cm^{-1}): 3150, 1628, 1580, 1515, 1470, 1310, 1280, 1215, 1145, 1037, 874, 833, 814. λ_{max}^{EtOH} (nm): 254, 298, 331 inf. (ε 17000, 12550, 9650); no shift upon add. of $AlCl_3$; $\lambda_{max}^{EtOH+NaOH}$ (nm): 253, 298, 349 (ε 18600, 6100, 15400); add. of NaOAc produces similar spectrum. *Acetate* (**3c**), m.p. 166–168° (C_6H_6) needles. ν_{max}^{KBr} (cm^{-1}): 1760, 1643, 1620, 1513, 1470, 1435, 1215, 1180, 1160, 1140, 1030, 908, 822. PMR ($CDCl_3$, τ): 2·00 (*s*, H-2), 2·23 (*s*, H-5), 2·76 (*s*, H-8), 3·04 (*s*, H-6'), 3·36 (*s*, H-3'), 6·07 (*s*, 2 OMe), 6·15 (*s*, OMe), 6·25 (*s*, OMe-2'), 7·73 (*s*, COMe). *Methyl ether* (**3b**), data as required by Ref. 5.

7,2'-*Dimethoxy*-4',5'-*methylenedioxyisoflavone* (**4a**), m.p. 210–212°, prisms (Found: C, 65·99; H, 4·29. $C_{18}H_{14}O_6$ requires: C, 66·26; H, 4·32%). ν_{max}^{KBr} (cm^{-1}): 1640, 1628, 1600, 1502, 1447, 1320, 1268, 1253, 1195, 1040, 943, 835. λ_{max}^{EtOH} (nm): 240, 247, 267, 304 (ε 19900, 18900, 11400, 16150); no shift upon add. of NaOH. PMR ($CDCl_3$, τ): 1·77 (*d*, *J* 9 Hz, H-5), 2·07 (*s*, H-2), 2·97 (*q*, *J* 9 and 2 Hz, H-6), 3·06 (*d*, *J* 2 Hz, H-8), 3·13 (*s*, H-6'), 3·33 (*s*, H-3'), 4·01 (*s*, O_2CH_2), 6·07 (*s*, OMe-7), 6·27 (*s*, OMe-2'). MS *m/e* (%): 327 (21) M + 1, 326 (100) M, 325 (6), 309 (8), 297 (10), 296 (20), 295 (88), 283 (6), 281 (8), 280 (5), 253 (6), 252 (5), 189 (5), 176 (15), 175 (17), 161 (13), 151 (42), 148 (45), 147 (13), 134 (5), 133 (5), 131 (5), 107 (5), 103 (5).

7,8,2'-*Trimethoxy*-4',5'-*methylenedioxyisoflavone* (**4b**), m.p. 204–206° [lit.[6] m.p. 204°], prisms (Found: C, 63·91; H, 4·51. $C_{19}H_{16}O_7$ requires: C, 64·04; H, 4·53%). ν_{max}^{KBr} (cm^{-1}): 1640, 1620, 1600, 1323, 1290, 1212, 1192, 1173, 1108, 1080, 1062, 1042, 990, 940, 793. λ_{max}^{EtOH} (nm): 246, 251, 302 (ε 26250, 26700, 17800); no shift upon add. of NaOH. PMR ($CDCl_3$, τ): 1·97 (*d*, *J* 9·3 Hz, H-5), 2·01 (*s*, H-2), 2·92 (*d*, *J* 9·3 Hz, H-6), 3·14 (*s*, H-6'), 3·35 (*s*, H-3'), 4·01 (*s*, O_2CH_2), 5·99 (*s*, OMe-7,8), 6·26 (*s*, OMe-2'). MS *m/e* (%): 357 (21) M + 1, 356 (100) M, 343 (13), 342 (50), 341 (17), 327 (25), 326 (94), 325 (81), 313 (12), 312 (18), 311 (38), 310 (12), 309 (11), 297 (13), 296 (17), 295 (51), 283 (12), 281 (13), 181 (55), 176 (23), 175 (29), 171 (13), 167 (10), 163 (31), 162 (16), 161 (35), 152 (10), 151 (31), 149 (13), 148 (13), 147 (15), 137 (12), 134 (11).

Acknowledgement—The MS were registered by Dr. P. M. Baker, Universidade Federal do Rio de Janeiro.