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NEW PELTOGYNOIDS OF *GONIORRHACHIS MARGINATA**

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Key Word Index—*Goniorrhachis marginata*; Leguminosae; peltogynoids; peltochalcone; mopanone.

Abstract—A re-examination of the heartwood of *Goniorrhachis marginata* disclosed the presence of additional peltogynoids: mopanone and peltochalcone.

THE HEARTWOOD of *Goniorrhachis marginata* Taub. (Leguminosae–Caesalpinioideae) contains the 5-methoxylated flavanones **1a** and **2a**, besides peltogynone (**1b**) and mopachalcone (**4a**).[2] The isolation of peltochalcone (**3a**) and mopanone (**2b**) from the same plant material, reported in the present paper, completes the list of possible simple oxidative derivatives of peltogynol (**5**) and mopanol (**6a**).

The spectral data, including the ORD curve, of the novel **2b** and the known **1b**[2] are very similar. Thus, the PMR spectrum of the triacetate **2c** [$C_{16}H_9O_3(OAc)_3$], differs from the analogous spectrum of the triacetate **1c**[2] solely with respect to the two aromatic protons of ring B. Though benzylic coupling of the proton at C-2′ persists, the signal is now represented substantially by a doublet (*J* 8·5 Hz), thus demonstrating the vicinal relationship of the ring B protons. The structural proposal was confirmed by conversion, via the trimethyl ether **2d** [identical with the oxidation product of tri-*O*-methylmopanol (**6b**)], to the chalcone **4b** (identical with the trimethyl ether of mopachalcone). The reference cmpds. were obtained by methylation respectively of mopanol (**6a**) *ex Peltogyne* spp.[3] and of mopachalcone (**4a**) *ex Goniorrhachis marginata.*[2]

Analogously, the spectral data of the novel **3a** [$C_{16}H_8O_2(OH)_4$] and the known **4a**[2] are very similar. The sole significative difference refers again to the PMR signals attributed to the two ring B protons. Instead of two *ortho* split doublets, two singlets appear, indicating the *para* relation of these protons. The UV spectrum of **3a** changes spontaneously with time, or more rapidly upon addition of HCl, to the spectrum of peltogynone (**1b**).[2] The structural proposal was confirmed by methylation which led, successively, to the trimethyl ether **3b** and to the tetramethyl ether **3c**, identical respectively with the chalcone obtained by alkaline treatment of tri-*O*-methylpeltogynone (**1d**)[1] and its methylation product.

The MS fragmentation pathways of mopanone (**2b**), peltochalcone (**3a**) and their derivatives again conform to the pattern interpreted in our previous paper[2] on constituents of *Goniorrhachis marginata.*

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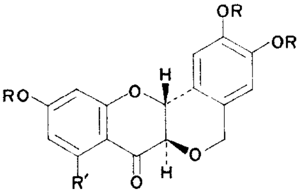
* Part XLII in the series "The Chemistry of Brazilian Leguminosae". For Part XLI see Ref. 1. Taken, in part, from the Doctorate thesis submitted by J.R. de S. to the Universidade Federal de Minas Gerais (1973).

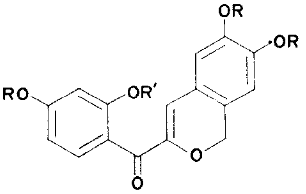
[1] VIEGAS ASSUMPCÃO, R. M. and GOTTLIEB, O. R. (1973) *Phytochemistry* **12**, 1188.

[2] GOTTLIEB, O. R. and REGO DE SOUSA, J. (1972) *Phytochemistry* **11**, 2841.

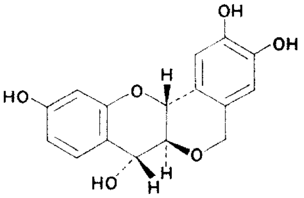
[3] ALMEIDA, M. E. DE, GOTTLIEB, O. R., RÊGO DE SOUSA, J. and TEIXEIRA, M. A. (1973) *Phytochemistry* **12**, 1225.



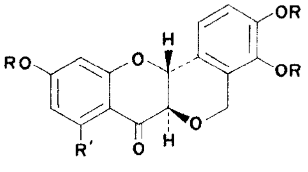
(1a) R = H; R' = OMe 5-Methoxypeltogynone
(1b) R = H; R' = H Peltogynone
(1c) R = Ac; R' = H
(1d) R = Me; R' = H



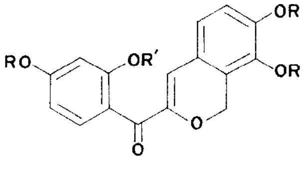
(3a) R = H; R' = H Peltochalcone
(3b) R = Me; R' = H
(3c) R = Me; R' = Me



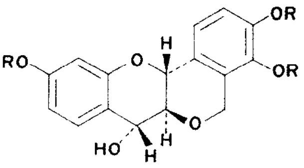
(5) Peltogynol



(2a) R = H; R' = OMe 5-Methoxymopanone.
(2b) R = H; R' = H Mopanone
(2c) R = Ac; R' = H
(2d) R = Me; R' = H



(4a) R = H; R' = H Mopachalcone
(4b) R = Me; R' = H



(6a) R = H Mopanol
(6b) R = Me

EXPERIMENTAL

Isolation procedure. The mother liquor of mopachalcone (**4a**) (*ex* fraction F_1, see Experimental, Ref. 2) was chromatographed on silica. $CHCl_3$–MeOH 97 : 3 eluted a fraction which, upon slow evaporation of the solvent, gave crystals of **3a** (55 mg). Impure fractions and mother liquors of F_2, F_3 and F_4[2] were chromatographed on silica. The eluate obtained with $CHCl_3$–MeOH (24 : 1) was evaporated. The residue was washed with MeOH and recrystallized from MeOH giving **2b** (95 mg).

Mopanone (**2b**). m.p. 255–260° (MeOH) (Found: C, 63·80; H, 4·01. Calc. for $C_{16}H_{12}O_6$: C, 64·00; H, 4·03%). λ_{max}^{EtOH} (nm): 240 inf., 284, 325 inf., 347 inf. (ε 21 300, 8700, 6900, 4500), $\lambda_{max}^{EtOH+NaOH}$ (nm): 230 354 (ε 28 500, 14 100), $\lambda_{max}^{EtOH+NaOAc}$ (nm): 215, 284, 343 (ε 27 300, 5700, 8700), $\lambda_{max}^{EtOH+H_3BO_3+NaOAc}$ (nm): 220, 286, 320 inf. (ε 29 400, 8700, 4500), $\lambda_{max}^{EtOH+AlCl_3}$ (nm): 216, 240 inf., 284 (ε 25 500, 13 500, 8400, 4500). ν_{max}^{KBr} (cm^{-1}): 3460, 3340, 3250, 1675, 1608, 1575, 1502, 1472, 1369, 1335, 1304, 1250, 1216, 1158, 1110. ORD (EtOH, 400–300 nm): $[\theta]_{335}$ pos., $[\theta]_{315}$ 0, $[\theta]_{310}$ neg., $[\theta]_{307}$ 0.

Triacetate (**2c**). m.p. 212–215° (MeOH). ν_{max}^{KBr} (cm^{-1}): 1760, 1705, 1606, 1435, 1374, 1220, 1200, 1144, 1110. PMR (60 MHz, $CDCl_3$, τ): 2·00 (*d*, *J* 8·0 Hz, H-5), 2·40 (*d*, *J* 8·0 Hz, H-2'), 2·75 (*d*, *J* 8·0 Hz, H-3'), 3·05 (*s*, H-8), 3·10 (*dd*, *J* 8·0 and 2·5 Hz, H-6), 4·60 (*dd*, *J* 12·2 and 0·5 Hz, H-2), 5·02–5·10 (broad, $C\underline{H}_2$), 5·50 (*d*, *J* 12·2 Hz, H-3), 7·65 (*s*, two $COC\underline{H}_3$), 7·70 (*s*, $COC\underline{H}_3$), MS: M 426 (17%), *m/e* (%) 384 (40), 383 (10), 342 (36), 300 (28), 248 (15), 247 (12), 206 (47), 179 (28), 164 (87), 163 (14), 137 (100), 136 (17), 135 (10).

Trimethyl ether (**2d**). m.p. 210–212° (MeOH) [lit.[4] m.p. 210°]. ν_{max}^{KBr} (cm^{-1}): 1695, 1612, 1492, 1455, 1422, 1275, 1210, 1155, 1145, 1106, 1020. PMR superimposable on lit.[4] spectrum. Direct comparison proved this cmpd. to be identical with tri-*O*-methylmopanone, prepared according to Drews and Roux.[4] **2d**, submitted to the procedure of flavanone–chalcone conversion described in the previous paper,[2] gave yellow crystals of **4b**, m.p. 123° (MeOH). ν_{max}^{KBr} (cm^{-1}): 1625, 1585, 1560, 1500, 1350, 1262, 1230, 1150, 1025. MS: M 342 (36%), *m/e* (%) 192 (26), 152 (11), 151 (100). Direct comparison proved this compound to be identical with the methylation product (Me_2SO_4–K_2CO_3–Me_2CO, reflux, 1 hr) of natural mopachalcone (**4a**).[2]

Peltochalcone (**3a**). Yellow crystals, m.ps. 125° and 232–236° ($CHCl_3$–MeOH). (Found: C, 63·77; H, 3·99. Calc. for $C_{16}H_{12}O_6$: C, 64·00; H, 4·03%). λ_{max}^{EtOH} (nm): 255, 350 inf., 402 (ε 900, 12000, 15 300), $\lambda_{max}^{EtOH+NaOH}$ (nm): 250, 344, 450 (ε 8100, 23 700, 1500), $\lambda_{max}^{EtOH+NaOH+HCl}$ (nm): 232, 283, 325 (ε 12000, 14 100, 9600), $\lambda_{max}^{EtOH+NaOAc}$ (nm): 255, 350, 402 (ε 9000, 14 400, 12 900), $\lambda_{max}^{EtOH+NaOAc+H_3BO_3}$ (nm): 255, 291, 340 inf., 426 (ε 8100, 11 100, 8500, 9900), $\lambda_{max}^{EtOH+AlCl_3}$ (nm): 282, 320, 414 (ε 10 800, 9600, 8100), λ_{max}^{EtOH} 3 days after prep. of soln. (nm): 237, 284, 325 (ε 9600, 12 800, 8100). ν_{max}^{KBr} (cm^{-1}): 3525, 3150, 1630, 1600, 1575, 1500, 1450, 1310, 1258, 1248, 1155, 1144, 1105, PMR [220 MHz, $(CD_3)_2CO$, τ]: −2·80 (*s*, O$\underline{H}$), 1·85 (*d*, *J* 9·0 Hz, H-6'),

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[4] DREWS, S. E. and ROUX, D. G. (1966) *J. Chem. Soc.* C, 1644.

3·20 (*s*, H-β), 3·23 (*s*, H-2), 3·30 (*s*, H-5), 3·60 (*dd*, 9·0 and 2·5 Hz, H-5′), 3·66 (*d*, *J* 2·5 Hz, H-3′), 5·11 (*s*, $C\underline{H}_2$), 6·80 (*s*, three $O\underline{H}$). MS: M 300 (90%), *m/e* (%) 164 (17), 163 (31), 138 (23), 137 (100), 136 (14), 135 (39).

Trimethylether (**3b**). Treatment of **3a** with Me_2SO_4–K_2CO_3–Me_2CO (reflux, 1 hr), and purification of the reaction product by TLC, gave yellow crystals, m.p. 126° (MeOH). ν_{max}^{KBr} (cm^{-1}): 2600 (broad), 1620, 1610, 1587, 1555, 1520, 1500. Direct comparison proved this compound to be identical with an authentic sample prepared from **1d**, the trimethyl ether of natural peltogynone (**1b**),[2] by the technique of flavanone–chalcone conversion described.[2]

Tetramethyl ether (**3c**). Exhaustive methylation of **3b** by Me_2SO_4–K_2CO_3–Me_2CO, and purification of the reaction product by TLC, gave yellow needles, m.p. 135–138° (MeOH). ν_{max}^{KBr} (cm^{-1}): 1647, 1600, 1575, 1510, 1470, 1385, 1335, 1320, 1260, 1210, 1120, 1110, 1025. MS: M 356 (98%), *m/e* (%) 191 (36), 166 (46); 165 (100), 164 (14), 163 (32), 122 (19).

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