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NEW PELTOGYNOIDS FROM THREE *PELTOGYNE* SPECIES*

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Key Word Index—*Peltogyne catingae*; *P. confertiflora*; *P. paniculata*; Leguminosae; peltogynoids; peltogynol; mopanol; 7-*O*-methylpeltogynol; 4-*O*-methyl-4′,5′-*O*,*O*-methylidenemopanol; fraxetin.

Abstract—Two novel peltogynoids, 7-*O*-methylpeltogynol and 4-*O*-methyl-4′,5′-*O*,*O*-methylidenemopanol were isolated respectively from the trunk wood of *Peltogyne paniculata* Benth. and *P. confertiflora* Benth. The latter species, as well as *P. catingae* Ducke, also contain the common peltogynoids peltogynol and mopanol.

A RECENT investigation of *Goniorrhachis marginata* Taub. (Leguminosae–Caesalpinioideae) revealed the existence in its heartwood of peltogynoid flavanones and chalcones.[1,2] The genus was, consequently, considered to have evolved into *Peltogyne*, the known species of which contain mainly peltogynoid flavonols.[2] Since *Goniorrhachis* is monotypic, the only way of placing this hypothesis on firmer ground and, eventually, to use it as basis of a phyletic classification of related genera, requires the analysis of additional *Peltogyne* species.

A search for peltogynoids in the bark of *Peltogyne confertiflora* Benth. (from Espirito Santo State), *P. catingae* Ducke and *P. paniculata* Benth. (both from Amazonas State) was unsuccessful. Only a glycoside of fraxetin (7,8-dihydroxy-6-methoxycoumarin) was located in *P. confertiflora*. The heartwoods, however, of *P. catingae* and *P. confertiflora* were found to contain peltogynol (**1a**) and mopanol (**2a**), typical constituents of *Peltogyne* and related genera. From the C_6H_6 extracts of *P. paniculata* and *P. confertiflora* two additional phenols, respectively $C_{17}H_{16}O_6$ and $C_{18}H_{16}O_6$, were isolated. Their UV spectra were very similar to those of peltogynol and mopanol, so they were considered to be closely related peltogynoids. Comparisons of the PMR spectra in the acetate series not only confirmed this (see chemical shifts of aliphatic protons with lit.[3] data), but also indicated identical relative configurations at the chiral centres 2, 3 and 4 (cf. $J_{2,3}$ and $J_{3,4}$). Attribution of the substitution pattern of peltogynol to $C_{17}H_{16}O_6$ and of mopanol to $C_{18}H_{16}O_6$ was based on the analysis of the aromatic spectral regions.

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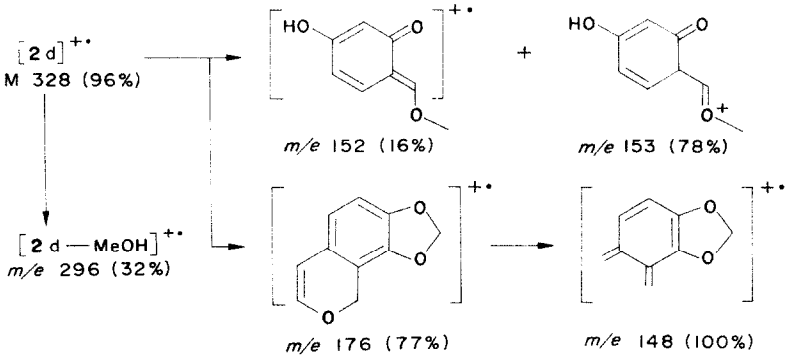
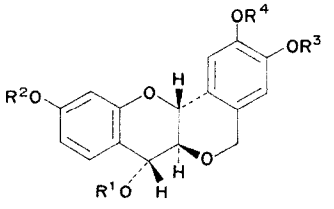
[1] GOTTLIEB, O. R. and RÊGO DE SOUSA, J. (1973) *Phytochemistry* **12**, 1229.
[2] GOTTLIEB, O. R. and RÊGO DE SOUSA, J. (1972) *Phytochemistry* **11**, 2841.
[3] DREWES, S. E. and ROUX, D. G. (1966) *J. Chem. Soc.* **C**, 1644.

The peltogynol derivative harbours a catechol system (UV shift by H_3BO_3 + NaOAc) and an aliphatic hydroxyl (ν_{max}^{KBr} of acetate 1730 cm^{-1}). Its methoxyl (τ 6·27, *s*) can thus occupy only position 7, as in **1c**, a proposition which is consistent with the MS of the triacetate **1d** which contains evidence for an aliphatic acetoxyl [$(M-AcOH)^{+\cdot}$ 382] and a methoxylated A-ring (retro-Diels–Alder fragments *m/e* 152, 153).



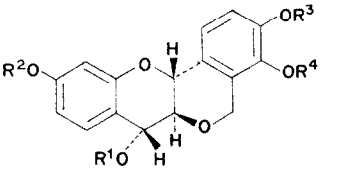
SCHEME 1. INTERPRETED MS OF 4-*O*-METHYL-4′,5′-*O*,*O*-METHYLIDENEMOPANOL (**2d**).

In agreement with this both peltogynol (**1a**) and the new (**1c**), yield tri-*O*-methylpeltogynol (**1g**) upon methylation either with Me_2SO_4–K_2CO_3 in boiling Me_2CO or with CH_2N_2 in ether at $-10°$. The CH_2N_2-methylation of peltogynol at $-10°$ is a stepwise reaction and, using appropriate reaction times, can be used to produce the natural compound **1c** (48 hr), a separable mixture of 7-*O*-methyl- (**1c**), 7,3′-di-*O*-methyl- (**1e**) and 7,3′,4′-tri-*O*-methyl ethers (**1g**) (96 hr), or mainly 7,3′,4′-tri-*O*-methylpeltogynol (250 hr). Two additional compounds, probably insertion products,[4] were also detected in trace amounts in these reaction mixtures. The substitution pattern of the novel 7,3′-di-*O*-methylpeltogynol (**1e**) was identified through PMR spectral comparison ($CDCl_3$) of two pairs of compounds: its monomethyl ether (**1g**) and its diacetate (**1f**) vs 7-*O*-methylpeltogynol triacetate (**1d**) and peltogynol tetraacetate (**1b**).[3] The 3′-positions in the first pair are substituted by methoxyls and in the second pair by acetoxyls. In consequence, H-2′ of **1g** and **1f** resonates at higher field (resp. τ 2·82 and 2·90) than H-2′ of **1d** and **1b** (resp. τ 2·49 and 2·53).



(**1a**) R^1=H; R^2=H; R^3=H; R^4=H Peltogynol
(**1b**) R^1=Ac; R^2=Ac; R^3=Ac; R^4=Ac
(**1c**) R^1=H; R^2=Me; R^3=H; R^4=H 7-*O*-Methyl-peltogynol
(**1d**) R^1=Ac; R^2=Me; R^3=Ac; R^4=Ac
(**1e**) R^1=H; R^2=Me; R^3=H; R^4=Me
(**1f**) R^1=Ac; R^2=Me; R^3=Ac; R^4=Me
(**1g**) R^1=H; R^2=Me; R^3=Me; R^4=Me

(**1**)



(**2a**) R^1=H; R^2=H; R^3=H; R^4=H Mopanol
(**2b**) R^1=H; R^2=Ac; R^3=Ac; R^4=Ac
(**2c**) R^1=Ac; R^2=Ac; R^3=Ac; R^4=Ac
(**2d**) R^1=Me; R^2=H; R^3–R^4 = —CH_2— 4-*O*-methyl-4′,5′-*O*,*O*-methylidene-mopanol
(**2e**) R^1=Me; R^2=Ac; R^3–R^4 = —CH_2—
(**2f**) R^1=H; R^2=Me; R^3=Me; R^4=Me

(**2**)

[4] BRANDT, E. V., FERREIRA, D. and ROUX, D. G. (1971) *Chem. Commun.* 116.

The methylenedioxy group (τ 4·06, *s*) of the mopanol derivative $C_{18}H_{16}O_6$ can, of course, occupy only the 4',5'-positions. Three pieces of evidence show that the methoxyl (τ 6·38, *s*) is at C-4 : (1). The H-4 chemical shifts of the acetate (**2e**) and of tri-*O*-acetylmopanol (**2b**) are comparable (τ 5·35 and 5·33), suffering the expected large downfield shift (Δ −1·59 ppm) if the hydroxyl at C-4 appears in acetylated form, as in **2c** (2). The MS of the derivative (Scheme 1) conforms to the pattern observed for other flavanols of this series,[2] with the exception of the $[M-H_2O]^{+\cdot}$ peak which is replaced by a strong $[M-MeOH]^{+\cdot}$ peak (3). While tri-*O*-methylmopanol (**2f**) and tri-*O*-methylpeltogynol (**1g**) readily give tri-*O*-methylmopanone and tri-*O*-methylpeltogynone with the Jones reagent, the novel phenol is quite stable under oxidizing conditions. Thus, the lone phenolic hydroxyl can only be situated at C-7, as in **2d**.

EXPERIMENTAL

Isolation of the constituents of P. confertiflora. *Bark* was reduced to powder (1 kg) and extracted, successively, with C_6H_6 which removed aliphatic material, and with EtOH. The EtOH extract (25g) was chromatographed on silica. $CHCl_3$–MeOH (1 : 1) eluted a product which, after acetylation (Ac_2O–C_5H_5N, reflux, 2 hr), was rechromatographed on silica. The C_6H_6–$CHCl_3$ (3 : 7) fraction gave the pentaacetate of a glycoside of fraxetin. *Softwood* was reduced to powder (5·5 kg) and extracted with C_6H_6. The soln was evaporated and the residue (13 g) chromatographed on silica. The C_6H_6–$CHCl_3$ (19 : 1) fraction was evaporated and the residue treated with MeOH to give sitosterol. The C_6H_6–$CHCl_3$ (7 : 3) fraction was evaporated and the residue treated with petrol. to give **2d**. *Heartwood* was reduced to powder (11 kg) and extracted, successively, with C_6H_6 which removed sitosterol and triterpenes, and with EtOH. The EtOH extract (35 g) was chromatographed on silica. Mopanol (**2a**) pptd. upon slow conc. of the $CHCl_3$–MeOH (49 : 1) fraction. The $CHCl_3$–MeOH (24 : 1) fraction was evaporated and the residue, which proved to be difficult to purify, was acetylated. The reaction product was crystallized from MeOH to give mopanol tetraacetate (**2c**). The $CHCl_3$–MeOH (47:3) fraction was evaporated to give peltogynol (**1a**). Several successive fractions were acetylated to give additional quantities of **2c**.

Isolation of the constituents of P. catingae *and* P. paniculata. Ground trunk wood was extracted with EtOH. The soln. was evaporated and the residue chromatographed on silica. In the case of *P. catingae*, $CHCl_3$–MeOH (19 : 1) eluted mopanol (**2a**) and $CHCl_3$–MeOH (9 : 1) eluted peltogynol (**1a**). In the case of *P. paniculata*, $CHCl_3$–MeOH (97:3) eluted 7-*O*-methylpeltogynol (**1c**).

Sitosterol. Identified by direct comparison with an authentic sample.

Pentaacetate of a glycoside of fraxetin. Colourless crystals, m.p. 175–177° ($CHCl_3$ MeOH). ν_{max}^{KBr} (cm^{-1}): 1750 (broad), 1635, 1620, 1580, 1495, 1475, 1450, 1420, 1370, 1350, 1300, 1250 1200, 1175, 1125, 900, 855. PMR ($CDCl_3$, τ): 2·38 (*d*, *J* 10·0 Hz, H-3), 3·22 (*s*, H-5), 3·65 (*d*, *J* 10·0 Hz, H-4), 4·73 (*s*, $O_2C\underline{H}$), 5·71–5·92 (*m*, $OC\underline{H}_2$), 6·18 (*s*, $OC\underline{H}_3$), 7·70, 7·82, 7·96, 8·00 and 8·02 (*s*, five $COC\underline{H}_3$). Hydrolysis (2N HCl–MeOH, 1:1, room temp., 2 hr) gave *fraxetin*, yellow needles, m.p. 227–229° (MeOH) [lit.[5] m.p. 227–228°]. ν_{max}^{KBr} (cm^{-1}): 3500–3300, 1702, 1610, 1587, 1520, 1458, 1425, 1389, 1320, 1292, 1238, 1160, 1127, 1089, 1031, 935, 852, 745, 727. λ_{max}^{EtOH} (nm): 260, 344 (ε 3350, 9800). MS: M 208 (90%), *m/e* (%) 193 (100), 180 (82), 165 (89), 152 (64), 147 (18), 137 (92), 123 (45), 119 (28).

Peltogynol (**1a**). Identified by direct comparison with an authentic sample. *Tetraacetate* (**1b**), spectral data as required by lit.[3]

7-O-*Methylpeltogynol* (**1c**). Slightly rose col. crystals, m.p. 200–205° dec. ν_{max}^{KBr} (cm^{-1}): 3450, 3250, 1620, 1580, 1515, 1520, 1505, 1350, 1310, 1280, 1200, 1160, 1110, 1075, 1025, 985, 940, 885, 835, 780. *Triacetate* (**1d**). White needles, m.p. 223–225° (EtOH–C_6H_6). ν_{max}^{KBr} (cm^{-1}): 1765, 1740, 1620, 1580, 1440, 1425, 1370, 1330, 1315, 1290, 1220, 1185, 1160, 1065, 1015, 970, 855, 805. PMR ($CDCl_3$, τ): 2·49 (*s*, H-2'), 2·97 (*d*, *J* 8·5 Hz, H-5), 3·13 (*s*, H-5'), 3·46 (*dd*, *J* 8·5 and 2·5 Hz, H-6), 3·57 (*m*, H-8), 3·73 (*d*, *J* 8·5 Hz, H-4), 5·07 (*d*, *J* 9·5 Hz, H-2), 5·15 (*s*, $OC\underline{H}_2$), 6·17 (*dd*, *J* 9·5 and 8·5 Hz, H-3), 6·27 (*s*, $OC\underline{H}_3$), 7·72 (*s*, $COC\underline{H}_3$), 7·75 (*s*, $COC\underline{H}_3$), 7·82 (*s*, $COC\underline{H}_3$). MS: M 442, *m/e* 382, 153, 152. Treatment of **1c** with CH_2N_2–Et_2O (−10°, 48 hr) or with Me_2SO_4–K_2CO_3 in refluxing Me_2CO (2 hr) gave the *dimethyl ether* (**1g**), slightly yellow plates, m.p. 154–156° (EtOH) (lit.[3] m.p. 155–156°). ν_{max}^{KBr} (cm^{-1}): 3500–3200, 1620, 1590, 1515, 1475, 1450, 1360, 1340, 1280, 1235, 1210, 1170, 1125, 1100, 1035, 990, 950, 885, 860, 840, 800, 790. PMR ($CDCl_3$, τ): 2·61 (*d*, *J* 8·5 Hz, H-5), 2·90 (*s*, H-2'), 3·45 (*dd*, *J* 8·5 and 3·0 Hz, H-6), 3·53 (*m*, H-8, H-5'), 5·13 (*d*, *J* 10·0 Hz, H-2), 5·16 (*s*, $OC\underline{H}_2$), 5·27 (*d*, 8·6 Hz, H-4), 6·07 (*s*, $OC\underline{H}_3$), 6·17 (*s*, $OC\underline{H}_3$), 6·23 (*s*, $OC\underline{H}_3$), 6·45 (*dd*, *J* 10·0 and 8·6 Hz, H-3), 7·70 (*s*, $O\underline{H}$). Direct comparison proved this cmpd. to be identical with 7,3',4'-tri-*O*-methylpeltogynol prepared by methylation of authentic peltogynol (**1a**).

[5] KARRER, W. (1958) *Konstitution und Vorkommen der organischen Pflanzenstoffe*, p. 541, Birkhäuser, Basel.

Selective methylation of peltogynol (**1a**). An Et_2O soln of **1a** was treated with CH_2N_2–Et_2O (−10°, 48 hr). The reaction product was separated by TLC into two cmpds, identified, by direct comparison, with starting material and natural **1c**. Upon extending the time interval to 96 hr, tri-*O*-methylpeltogynol was present in the reaction product. After 250 hr **1c** had disappeared. The reaction product, in $CHCl_3$, was extracted with 5% aq. $NaHCO_3$. The evaporated $CHCl_3$ soln gave **1g**, identified by direct comparison with the Me_2SO_4-methylation product of peltogynol. Acidification of the aq. soln gave **1e**.

7,3′-*Di*-O-*methylpeltogynol* (**1e**). PMR [$(CD_3)_2CO$, τ]: 3·29 (*d*, *J* 8·5 Hz, H-5), 3·52 (*s*, H-2′), 3·97 (*s*, H-5′), 4·17 (*dd*, *J* 8·5 and 3·0 Hz, H-6), 4·26 (*d*, *J* 3·0 Hz, H-8), 5·87 (*m*, H-2, H-4, $OC\underline{H}_2$), 6·84 (*s*, $OC\underline{H}_3$), 6·89 (*s*, $OC\underline{H}_3$), 7·11 (*dd*, *J* 10·0 and 8·6 Hz, H-3). *Diacetate* (**1f**). Colourless crystals, m.p. 183–186° (EtOH). ν_{max}^{KBr} (cm^{-1}): 1770, 1720, 1615, 1590, 1520, 1500, 1460, 1435, 1380, 1315, 1295, 1270, 1255, 1240, 1200, 1145, 1135, 1125, 1090, 1035, 980, 960, 900, 880, 805, 780, 760. PMR ($CDCl_3$, τ): 2·82 (*s*, H-2′), 3·03–3·87 (*m*, H-4, H-5, H-6, H-8, H-5′), 5·13 (broad, $OC\underline{H}_2$, H-2), 6·03 (*s*, $OC\underline{H}_3$), 6·10 (*s*, $OC\underline{H}_3$, H-3), 7·68 (*s*, $COC\underline{H}_3$), 7·74 (*s*, $COC\underline{H}_3$).

Mopanol (**2a**). Identified by direct comparison with an authentic sample. Acetylation (Ac_2O, C_5H_5N, room temp, 24 hr) gave a product which was separated by chromatography on silica into 4,7,4′,5′-*tetra*-O-*acetyl mopanol* (**2c**), m.p. 220° lit.[3] m.p. 220°, spectral data as required;[3] and 7,4′,5′-*tri*-O-*acetylmopanol* (**2b**), m.p. 219–220° (MeOH); ν_{max}^{KBr} (cm^{-1}): 3490, 1762, 1620, 1598, 1498, 1440, 1372, 1225, 1205, 970, 920, 895, 840, 795. PMR [$(CD_3)_2CO$, τ]: 2·46 (*dd*, *J* 9·0 Hz and indet., H-2′), 2·60 (*d*, *J* 8·0 Hz, H-5), 2·82 (*d*, *J* 9·0 Hz, H-3′), 3·34 (*dd*, *J* 8·0 and 2·0 Hz, H-6), 3·38 (*d*, *J* 2·0 Hz, H-8), 5·06 (*d*, *J* 10·0 Hz, H-2), 5·07 and 5·32 (*AB* system, *J* 14·0 Hz, $OC\underline{H}_2$), 5·33 (*d*, *J* 8·5 Hz, H-4), 6·22 (*dd*, *J* 10·0 and 8·5 Hz, H-3), 7·59 (*s*, three $COC\underline{H}_3$).

4-O-*Methyl*-4′,5′-O,O-*methylidenemopanol* (**2d**). m.p. 209–210°. λ_{max}^{EtOH} (nm): 216, 285 (ε 23600, 10500); $\lambda_{max}^{EtOH+NaOH}$ (nm): 245, 290 (ε 26250, 16400). ν_{max}^{KBr} (cm^{-1}): 3395, 1625, 1600, 1506, 1470, 1387, 1344, 1313, 1263, 1169, 1150, 1095, 1050. MS: M 328 (96%), *m/e* (%) 296 (32), 268 (54), 240 (14), 176 (77), 163 (28), 153 (79), 148 (100), 137 (56), 123 (52). Acetylation with Ac_2O–C_5H_5N (room temp, 24 hr) gives the *monoacetate* (**2e**), m.p. 137–139° (MeOH). ν_{max}^{KBr} (cm^{-1}): 1750, 1618, 1593, 1500, 1483, 1433, 1368, 1337, 1318, 1263, 1228, 1148, 1123, 1086, 1043. PMR ($CDCl_3$, τ): 2·56 (*dd*, *J* 9·0 and *ca* 1 Hz, H-2′), 2·85 (*d*, 8·2 Hz, H-5), 3·24 (*d*, *J* 9·0 Hz, H-3′), 3·28 (*d*, *J* 2·0 Hz, H-8), 3·30 (*dd*, *J* 8·2 and 2·0 Hz, H-6), 4·06 (*s*, $O_2C\underline{H}_2$), 5·13 (*d*, *J* 10·0 Hz, H-2), 5·07 and 5·15 (*AB*-system, *J* 5·0 Hz, $OC\underline{H}_2$), 5·35 (*d*, *J* 8·5 Hz, H-4), 6·17 (*dd*, *J* 10·0 and 8·5 Hz, H-3), 6·38 (*s*, $OC\underline{H}_3$), 7·73 (*s*, $COC\underline{H}_3$).

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