

CONSTITUENTS OF BRAZILIAN LEGUMINOSAE*

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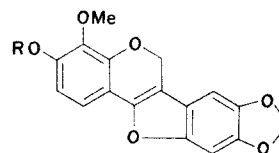
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Key Word Index—*Swartzia ulei*; *Dalbergia miscolobium*; *Machaerium secundiflorum*; *Vatairea heteroptera*; *Vatairea* spp.; *Vataireopsis* spp.; Leguminosae-Lotoideae; 3-hydroxy-4-methoxy-8,9-methylenedioxypterocarp-6-ene; flavonoids, anthraquinones; triterpenoids.

Plant. Swartzia ulei Harms [2] was collected in the vicinity of Manaus, Amazonas, and identified by the botanist W. Rodrigues. *Trunk wood*. The C_6H_6 extract (50 g ex 4.3 kg) was chromatographed on silica (750 g) giving, in succession, upon elution with C_6H_6 aliphatic esters (1 g), **1a** (recryst. C_6H_6 , 50 mg), a mixture of sitosterol and stigmaterol (recryst. C_6H_6 , 125 mg) and *O*-acetylleoanolic acid (recryst. AcOEt, 40 mg); upon elution with C_6H_6 -CHCl₃ 9:1 stearic acid (recryst. MeOH, 55 mg).

3-Hydroxy-4-methoxy-8,9-methylenedioxy-6a,11a-dehydropterocarpan (1a), crystals, mp 196–198° (found: C, 65.52; H, 4.00, $C_{17}H_{12}O_6$ requires: C, 65.38; H, 3.88%). The UV [λ_{max}^{EtOH} (nm): 245, 290 inf., 320 inf., 336 (ϵ 15600, 11800, 19000, 32400)]; $\lambda_{max}^{EtOH+NaOH}$ (nm): 250, 305 inf., 359 (ϵ 13700, 8100, 34600)] and IR [ν_{max}^{KBr} (cm⁻¹): 3500, 1650, 1600, 1500, 1470, 1380, 1335, 1200, 1050, 940, 900, 850, 810] spectra were compatible with the analogous spectra of 6a-11a-dehydropterocarpan [3–5]. Indeed, the PMR [τ (CD₃COCD₃): 2.89 (s, H-7), 2.90 (d, J 8.0 Hz, H-1), 3.04 (s, H-10), 3.45 (d, J 8.0 Hz, H-2), 3.97 (s, O₂CH₂), 4.40 (s, 2H-6), 4.47 (s, OH), 6.17 (s, Me)] spectrum contained the 2H singlet typical of the heterocyclic hydrogens of pterocarp-6a-ens [4, 5]. This system must be substituted by OH, OMe and O₂CH₂ [MS (*m/e*): 312 (100%) M, 313 (25), 311 (50), 296 (25), 281 (5), 269 (5), 241 (15), 212 (25), 157 (20)] as indicated in **1a**. All known natural pterocarpanoids show oxygenation at C-3 and C-9 [3–6], and it is an *ortho*-split doublet, located at higher field than all other aromatic H signals and thus corresponding to H-2, which suffers the strongest paramagnetic shift [Δ (ppm): H-1 0.06, H-2 0.18, H-7 0.04, H-10 0.04] by acetylation to **1b** [mp 185–187° (C_6H_6)].

Plant. Dalbergia miscolobium Benth. [7], trivial name “caviúna”, was collected in Belo Horizonte, Minas Gerais and identified by the botanist A. Pereira Duarte. *Leaves*. The C_6H_6 extract, washed with light petrol., gave crude prunetin (1.5% of the air-dried leaves) which was purified by precipitation from 3% aq NaOH and crystallizations from dioxane.



(1 a) R = H
 (1 b) R = Ac

Plant. Machaerium secundiflorum Mart., trivial name “canela de velho”, was collected at the Experimental Station of Água Limpa, Minas Gerais, and identified by the botanist A. Pereira Duarte. *Trunk wood*. The C_6H_6 extract (85 g ex 17.8 kg) was chromatographed on silica. Successive elution with C_6H_6 , C_6H_6 -AcOEt and MeOH and purification of the fractions by rechromatography and/or crystallization gave saturated aliphatic alcohols, sitosterol, 3-*O*-acetyl- β -amyirin, 3-*O*-acetylleoanolic aldehyde and 3-*O*-acetylleoanolic acid identified by direct comparison with authentic samples from other *M.* species [7, 8].

Plant. Vatairea heteroptera (Fr. Allem.) Ducke was collected at the Linhares Forest Reserve, Rio Doce, Espírito Santo, and identified by the botanist C. Mainieri. *Trunk wood*. The C_6H_6 extract (110 g ex 6 kg) was chromatographed on silica. Elution with solvent of increasing polarity gave, in succession, chrysophanol (0.5% of wood sample), saturated fatty acids (mainly $C_{26}H_{52}O_2$ and $C_{24}H_{48}O_2$), sitosterol plus stigmaterol, emodin, (2S)-7-hydroxyflavanone and formononetin. (2S)-7-Hydroxyflavanone was identified by direct comparison with an authentic sample from *Platymiscium praecox* Mart. [9]. Prof. J. W. Clark-Lewis kindly called our attention to the fact that in the paper on this species, the absolute configurations of this compound and of (2R,3R)-3,7-dihydroxyflavanone were wrongly given respectively as 2R and 2S,3S.

Note. A collection of the Rio de Janeiro Botanic Garden includes trunk wood samples of *Vatairea guianensis* Aubl.

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(source: Pará), *Vatairea macrocarpa* (Benth.) Ducke (Minas Gerais), *Vatairea paraensis* Ducke (Pará), *Vatairea sericea* Ducke (Pará), *Vataireopsis araroba* (Aguiar) Ducke (Espírito Santo), *Vataireopsis speciosa* Ducke (Amazonas) and *Vataireopsis pallidiflora* Rizz. (Goiás). Small, mostly heartwood, fragments were secured by courtesy of the botanist A. de Mattos. TLC (SiO_2 , C_6H_6 -AcOEt-MeOH 72:25:3) examination of their C_6H_6 extracts failed to reveal the presence of chrysophanol only in the extract from *V. pallidiflora*, prepared from a softwood sample.

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SITOSTEROL- β -D-GALACTOSIDE FROM *HIBISCUS SABDARIFFA**

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Key Word Index—*Hibiscus sabdariffa*; Malvaceae; karkade; sitosterol- β -D-galactoside.

Hibiscus sabdariffa (Malvaceae) or karkade is widely used in Egypt for curing heart and nerve diseases [1,2]. Previously [3] we reported the isolation of a steroidal compound of unknown structure from the leaves of this plant.

The neutral part of the non-volatile fraction of the Et_2O extract of defatted leaves deposited colourless rosettes which were recrystallised ($3 \times \text{CHCl}_3$) to yield sitosterol- β -D-galactoside, m.p. $275\text{--}277^\circ$ (decomp.), $[\alpha]_D -63^\circ$ (in pyridine), $\nu_{\max} 3450\text{ cm}^{-1}$ (b, OH), NMR (in deuterated pyridine) showed peaks at τ 4.68 (t, one olefinic H), τ at 6.29 (t, H α - to OH). Tetraacetate (needles, MeOH-CHCl_3), m.p. $149\text{--}151^\circ$, $[\alpha]_D -33.3^\circ$; MS; parent ion m/e 744 (agreeing with $\text{C}_{43}\text{H}_{68}\text{O}_{10}$); 331, 211, 229, 169 and 109 (characteristic for glycoside tetraacetates [4]); and at m/e 414 and m/e 396 (base peak), NMR showed sharp peaks at τ 7.9–8.0 (four

acetate groups), τ at 4.72 (t, one olefinic H). Tetra-benzoate (MeOH-CHCl_3), mp $196\text{--}198^\circ$, $[\alpha]_D +10.5^\circ$.

Acid hydrolysis [5] of the glycoside gave sitosterol (mp, mmp 132° , $[\alpha]_D -34^\circ$, IR, $\text{M}^+ 414$) plus galactose (R_f PC 0.12; $\text{BuOH-AcOH-H}_2\text{O}$, 4:1:2.2).

Sitosterol- β -D-galactoside was synthesized [6] from acetobromogalactose pentaacetate [7] and HBr gas in Ac_2O , to obtain a green gum which was dissolved in dry dioxane and added dropwise over 1 hr to a slurry in dioxane of sitosterol, Ag_2CO_3 and MgSO_4 . After 20 hr at room temp., the product was chromatographed over alumina to give sitosterol- β -D-galactoside tetraacetate identical in all respects (IR, mp, mmp and specific rotations) with the natural compound tetraacetate.

It is interesting to note that whereas sitosterol- β -D-glucoside has been isolated from several plant sources, this is the first report of the galactoside.

* Part XIII in a series. For Part XII see Ref. [8].