

CONSTITUENTS OF BRAZILIAN LEGUMINOSAE*

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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-methylenedioxypoterocarp-6a-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 C₆H₆ extract (50 g ex 4.3 kg) was chromatographed on silica (750 g) giving, in succession, upon elution with C₆H₆, aliphatic esters (1 g), **1a** (recryst. C₆H₆, 50 mg), a mixture of sitosterol and stigmasterol (recryst. C₆H₆, 125 mg) and *O*-acetyloleanolic acid (recryst. AcOEt, 40 mg); upon elution with C₆H₆-CHCl₃ 9:1 stearic acid (recryst. MeOH, 55 mg).

3-Hydroxy-4-methoxy-8,9-methylenedioxypoterocarp-6a,11a-dehydropterocarpan (1a). crystals, mp 196-198° (found: C, 65.52; H, 4.00. C₁₇H₁₂O₆ requires: C, 65.38; H, 3.88%). The UV [$\lambda_{\text{max}}^{\text{EtOH}}$ (nm): 245, 290, inf., 320, inf., 336 (ϵ 15600, 11800, 19000, 32400); $\lambda_{\text{EtOH}+\text{NaOH}}^{\text{max}}$ (nm): 250, 305, inf., 359 (ϵ 13700, 8100, 34600)] and IR [$\nu_{\text{max}}^{\text{KBr}}$ (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-dehydropterocarpanos [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 (C₆H₆)].

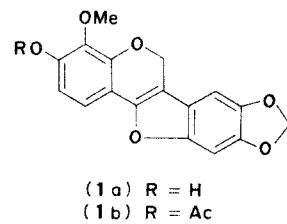
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Plant. *Dalbergia miscolobium* Benth. [7], trivial name "caivuna", was collected in Belo Horizonte, Minas Gerais and identified by the botanist A. Pereira Duarte. **Leaves.** The C₆H₆ extract, washed with light petrol., gave crude prunetin (1.5% of the air-dried leaves) which was purified by precipitation from 3% aq NaOH and crystallizations from dioxane.



(1a) R = H

(1b) 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 C₆H₆ extract (85 g ex 17.8 kg) was chromatographed on silica. Successive elution with C₆H₆, C₆H₆-AcOEt and MeOH and purification of the fractions by rechromatography and/or crystallization gave saturated aliphatic alcohols, sitosterol, 3-*O*-acetyl- β -amyrin, 3-*O*-acetyloleanolic aldehyde and 3-*O*-acetyloleanolic 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 C₆H₆ 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 C₂₆H₅₂O₂ and C₂₄H₄₈O₂), sitosterol plus stigmasterol, 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.

(source: Pará), *Vatairea macrocarpa* (Benth.) Ducke (Minas Gerais), *Vatairea paraensis* Ducke (Pará), *Vatairea sericea* Ducke (Pará), *Vataireopsis araroba* (Aguilar) 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 steroid 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 CHCl_3) to yield sitosterol- β -D-galactoside, m.p. 275-277° (decomp.), $[\alpha]_D -63^\circ$ (in pyridine), ν_{max} 3450 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. 149-151°, $[\alpha]_D -33.3^\circ$; 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). Tetrabenzoate (MeOH-CHCl_3), mp 196-198°, $[\alpha]_D +10.5^\circ$.

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].