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ANTHRAQUINONES FROM *VISMIA* SPECIES*

MARIA DO CARMO M. MIRAGLIA, ANTONIO A. L. MESQUITA, M. DE JESUS C. VAREJÃO,† OTTO R. GOTTLIEB‡ and HUGO E. GOTTLIEB§

Instituto de Ciências Exatas, Universidade Federal de Minas Gerais, 30000 Belo Horizonte, MG, Brazil; †Instituto Nacional de Pesquisas da Amazônia, Conselho de Desenvolvimento Científico e Tecnológico, 69000 Manaus, AM, Brazil; ‡ Instituto de Química, Universidade de São Paulo, 05508 São Paulo, SP, Brazil; § Department of Organic Chemistry, The Weizmann Institute of Science, Rehovot, Israel

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Key Word Index—*Vismia cayennensis*; *V. japurensis*; Guttiferae; anthraquinones; physcion; vismiaquinone; vismiaketone.

Abstract—1,8-Dihydroxy-3-methyl-6-methoxyanthraquinone (physcion) and two derivatives, 7-(*trans*-3-methyl-1-butenyl)-physcion (vismiaquinone) and 7-(3-methyl-2-oxobutyl)-physcion (vismiaquinone B), were isolated respectively from *Vismia cayennensis* and *V. japurensis*.

Vismia cayennensis (Jacq.) Pers. [1] and *V. japurensis* Reich. (Guttiferae) [2] are large shrubs which occur in north-eastern South America. The latter species has recently been located also in central Brazil (Prof. José Badini, private information). Wood samples were found to contain respectively physcion (**1a**), besides sitosterol, lupeol and betulinic acid, and the two physcion derivatives **1b** and **1c**, besides sitosterol, friedelin and friedelan-3β-ol.

The structures of **1b** and **1c** resulted from a comparison of their spectral data with those of physcion (**1a**) [3]. The ^{1}H NMR spectra were very similar with respect to the signals of H-5 (δ 7.38 ± 0.04), H-4 (δ 7.59 ± 0.04), H-2 (δ 7.05 ± 0.03), Me-3 (δ 2.43 ± 0.02), OMe-6 (δ 3.98 ± 0.02) and two chelated hydroxyls. The only significant differences were that the signal of H-7 (δ 6.68) in **1a**, was replaced by signals assigned to a *trans*-3-methyl-1-butenyl group in **1b** and a 3-methyl-2-oxobutyl group in **1c**. All assignments and, most importantly, the fact that the C—Me group is flanked by two aromatic protons, were confirmed by double irradiation experiments. The IR spectra were consistent with the proposed structures indicating the existence in all three compounds of chelated ($\nu_{\max}^{\mathrm{KBr}}$ 1623 ± 2 cm^{-1}) and unchelated ($\nu_{\max}^{\mathrm{KBr}}$ 1666 ± 1 cm^{-1}) anthraquinone carbonyls and in **1c** additionally of an unconjugated ketone function ($\nu_{\max}^{\mathrm{KBr}}$ 1706 cm^{-1}).

Physcion (**1a**) is a well known natural compound and has been isolated for instance from *Harungana madagascariensis* Poir. which also belongs to the Guttiferae family [4]. 7-(3-Methyl-1-butenyl)-physcion (**1b**) has been reported previously as one of the alkaline decomposition products of vismione A, a constituent of the berries of *Vismia baccifera* (L.) Tr. et Pl. subsp. *dealbata* (H.B.K.) Ewan [5]. Gonçalves and Mors [6], who isolated **1b** while our work on *V. japurensis* was in progress and who named the compound vismiaquinone, demonstrated, however, that the product is a genuine constituent of the leaves of *V. reichardtiana* (O. Ktze.) Ewan.

In addition to vismione A and vismiaquinone, only the flavones artocarpin, norartocarpin [7] and chaplashine [8] from *Artocarpus* (Moraceae) species have been reported to contain 3-methyl-1-butenyl side chains. Delle Monache *et al.* [5] postulated that these groups may be formed from the more usual γ,γ-dimethylallyl chains by shift of the double bond into conjugation with the aromatic nucleus. The isolation of the novel vismiaquinone B (**1c**) reveals a possible mechanism for this shift. Oxygenation of the β-carbon of γ,γ-dimethylallyl groups does occur in Guttiferae, as demonstrated by psorospermin (**2**) [9], and an analogous intermediate substituted by $-CH_2.CHOR.CHMe_2$ may be a common

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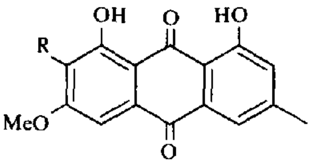
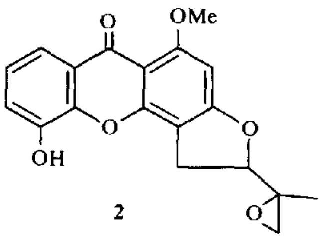


1a R = H
1b R = CH=CH.CHMe$_2$
1c R = CH$_2$.CO.CHMe$_2$



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precursor to both **1b** and **1c**.

EXPERIMENTAL

Isolation of the constituents of Vismia cayennensis. Plant material was collected near km 63 of the Manaus–Itacoatiara road (Amazonas State) and identified by Dr. William A. Rodrigues, INPA, Manaus. Air-dried, powdered bark (700 g) was extracted with C_6H_6. The extract (62 g) was chromatographed on Si gel (300 g). Elution (50 ml fractions) was performed with C_6H_6 (fractions 1–6), C_6H_6–$CHCl_3$ mixtures (fractions 7–21), $CHCl_3$ (fractions 22–41) and $CHCl_3$–MeOH 5:1 (fractions 42–73). The initial fractions contained fatty material. Fractions 33–41, 42–49 and 50–65 were evapd and the residues purified, by rechromatography and crystallization from the indicated solvents, to give respectively **1a** (20 mg, EtOH–$CHCl_3$), β-amyrin (20 mg, EtOH) and sitosterol (40 mg, MeOH). Air-dried, powdered wood (5 kg) was extracted with EtOH. The extract (10 g) was chromatographed on Si gel (100 g). Elution (50 ml fraction) was performed with solvents of increasing polarity. Fractions 21–50 gave betulinic acid.

Isolation of the constituents of Vismia japurensis. Plant material was collected at Serra do Caraça near Ouro Preto (Minas Gerais State) and identified by Prof. J. Badini, Universidade Federal de Ouro Preto (voucher Herbarium, Escola de Minas de Ouro Preto No. 1379). Air-dried, ground wood (3.4 kg) was extracted with C_6H_6. The extract (25 g) was chromatographed on Si gel (150 g). Elution (25 ml fractions) was performed with C_6H_6 (fractions 1–49), C_6H_6–$CHCl_3$ 1:2 (fractions 141–189) and $CHCl_3$ (fractions 191–205). The initial fractions contained fatty material. Fractions 9–14, 31–37 and 38–49 were evapd and the residue purified, by rechromatography and crystallization from the indicated solvents, to give respectively **1b** (30 mg, EtOH–$CHCl_3$, 19:1), friedelin (25 mg, EtOH) and friedelan-3β-ol (20 mg, subl.). Fractions 141–189 were evapd. The residue was crystallized from MeOH to give sitosterol (40 mg). Fractions 191–205 were evapd. The residue was rechromatographed. A yellow fraction, crystallized from EtOH–$CHCl_3$ (19:1), gave **1c** (12 mg).

Vismiaquinone (**1b**), red needles, mp 201–203° (EtOH–$CHCl_3$, 19:1). [M^+ found 352.1331; $C_{21}H_{20}O_5$ requires 352.1311]. IR ν_{max}^{KBr} (cm^{-1}): 1667, 1625, 1594, 1556, 1475, 1372, 1361, 1220, 1030, 969; UV λ_{max}^{EtOH} (nm): 223, 249, inf., 263 inf., 296, 454 (log ε 4.6, 4.5, 4.5, 4.7, 4.5); $\lambda_{max}^{EtOH+NaOH}$ (nm): 276, 324, 418, 534 (log ε 4.8, 4.3 inf., 4.6, 4.1); ^{1}H NMR (60 MHz, $CDCl_3$): δ 12.87 (*s*, OH-1), 12.07 (*s*, OH-8), 7.55 (*s* (*br*), $\nu_{1/2}$ = 2.5 Hz, H-4), 7.34 (*s*, H-5), 7.02 (*s* (*br*), $\nu_{1/2}$ = 2.5 Hz, H-2), 6.95 (*dd*, *J* = 16, 6.5 Hz, =C$\underline{H}$.CH), 6.61 (*d*, *J* = 16 Hz, CH-7), 4.00 (*s*, OMe-6), 2.6 (*m*, C$\underline{H}$Me$_2$), 2.41 (*s*, Me-3), 1.13 (*d*, *J* = 7 Hz, 2Me); MS *m/z* (rel. int.): 353 $[M + 1]^+$ (7), 352 $[M]^+$ (13), 337 (9), 323 (5), 310 (22), 309 (100), 297 (30), 295 (7), 294 (8), 283 (5), 267 (11), 161 (37), 115 (33).

Vismiaquinone B (**1c**), yellow crystals, mp 266–268° (EtOH–$CHCl_3$ 19:1) [M^+ found 368.1275; $C_{21}H_{20}O_6$ requires 368.1260]. IR ν_{max}^{KBr} (cm^{-1}): 1706, 1665, 1623, 1599, 1559, 1479, 1381, 1368, 1325, 1270, 1230, 759; UV λ_{max}^{EtOH} (nm): 225, 275, 316, 450 (log ε 4.6, 4.5, 4.2, 4.2); $\lambda_{max}^{EtOH+NaOH}$ (nm): 225, 243, 264, 320, 544 (log ε 4.6, 4.4, 4.2, 4.0, 4.0); $\lambda_{max}^{EtOH+NaOAc}$ (nm): 225, 272, 315 (log ε 4.6, 4.5, 4.2); ^{1}H NMR (270 MHz, $CDCl_3$): δ 12.40 (*s*, OH-1), 12.06 (*s*, OH-8), 7.63 (*dq*, *J* = 1.5, 0.5 Hz, H-4), 7.42 (s. H-5), 7.08 (*dq*, *J* = 1.5, 1.0 Hz, H-2), 3.98 (*s*, OMe-6), 3.90 (*s*, CH$_2$-7), 2.79 (*septet*, *J* = 7 Hz, C$\underline{H}$Me$_2$), 2.45 (*s* (*br*), $\nu_{1/2}$ = 2 Hz, Me-3), 1.19 (*d*, *J* = 7 Hz, 2 Me).

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