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DIHYDROCINNAMYL ALCOHOLS FROM *HORTIA BADINII*

DIRCEU DE B. CORREA*, OTTO R. GOTTLIEB† and ADOLFO P. DE PÁDUA*

*Instituto de Ciências Exatas, Universidade Federal de Minas Gerais, Belo Horizonte,† Instituto de Quimica Universidade de São Paulo, c.p. 20780, São Paulo, Brasil

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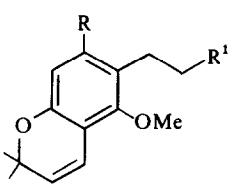
Key Word Index—*Hortia badinii*; Rutaceae; dihydrocinnamyl alcohols.

Abstract—*Hortia badinii* (Rutaceae) contains in the trunkwood skimmianine and 6,7-dimethoxycoumarin, as well as 3-[2-methoxy and 2,6-dimethoxy-6′,6′-dimethylpyrano(2′,3′ : 3,4)phenyl]-1-propanols.

Bark and wood of the branches from the rutaceous tree *Hortia badinii* M. A. Lisboa contain alkaloids, coumarins and dihydrocinnamic acids and esters (e.g. **1a**, **1b**, **1c**) [2]. Identical classes of compound, represented by skimmianine [1], 6,7-dimethoxycoumarin [1], **1a** and **1b** [2], accompanied by the novel dihydrocinnamyl alcohols **1d** and **1e**, have now also been isolated from the trunkwood of this species.

The structures of the alcohols $C_{14}H_{16}O.OH.OMe$ (**1d**) and $C_{14}H_{15}O.OH(OMe)_2$ (**1e**) follow directly from a consideration of spectra which, in connection with the bicyclic systems of the molecules, are closely comparable with the spectra of the corresponding carboxy-derivatives, **1a** and **1b** respectively. PMR data for the acyclic side chains are of course different for the two series of compounds, even if their interpretation for **1d** and **1e** is again trivial. PMR C_6H_6-induced shifts were used in order to probe the vicinity of the aromatic methoxyls in the same way, and with analogous results, as in the case of the dihydrocinnamates **1a** and **1b** [2].



1a R = H; $R^1 = CO_2Me$
1b R = OMe: $R^1 = CO_2Me$
1c R = OMe: $R^1 = CO_2H$
1d R = H: $R^1 = CH_2OH$
1e R = OMe, $R^1 = CH_2OH$

EXPERIMENTAL

Isolation of constituents. Powdered trunkwood (8 kg) of *Hortia badinii* from Morro do Fraga, Santa Rita Durão, Minas Gerais, was extracted successively with C_6H_6 and EtOH. The C_6H_6 extract (10 g), upon chromatography on a Si gel column (300 g), gave the following fractions with the indicated eluants: A_1 (C_6H_6), A_2 ($CHCl_3$), A_3 ($CHCl_3$–MeOH 1:1). A_1 gave aliphatic material, A_2 was rechromatographed on Si gel to give **1a**, **1d** and 6,7-dimethoxycoumarin and A_3 was rechromatographed on Si gel. The main fraction was crystallized from MeOH to yield skimmianine. The EtOH extract (140 g), upon chromatography on Si gel column (1 kg), gave the following fractions with the indicated eluants: B_1 (C_6H_6), B_2 (C_6H_6–$CHCl_3$ 1:0, 3:1, 3:2). B_1 gave **1a** and **1b**. B_2 was rechromatographed repeatedly on Si gel and Al_2O_3 to give **1a**, **1e** (20 mg) and **1d** (90 mg).

3-[2-*Methoxy*-6′,6′-*dimethylpyrano* (2′,3′:3,4)*phenyl*]-1-*propanol* (**1d**). Crystals, mp 96–99° (cyclohexane) (Found: M^+ 248.1406. $C_{15}H_{20}O_3$ requires: 248.1413). ν_{max}^{KBr} cm^{-1}: 3350 br, 1635, 1600, 1575, 1065, 1050, λ_{max}^{EtOH} nm: 226, 263 infl, 270, 275 infl, 317 (ε 28000, 5700, 6700, 5700, 1700). PMR (60 MHz, $CDCl_3$), τ 3.10 and 3.47 (AB system, J = 8 Hz, H-6 and H-5), 3.4 and 4.35 (AB system, J = 10 Hz, H-4′ and H-5′), 6.27 (*s*, OMe), 6.43 (*t*, J = 6 Hz, H-1), 7.35 (*t*, J = 7 Hz, H-3), 7.8 (*s*, OH), 8.2 (*dt*, J = 6, 7 Hz, H-2), 8.6 (*s*, CMe_2). PMR (C_6H_6): τ 6.52 (*s*, OMe). MS, *m/e* (%): 248 (90), 234 (83), 233 (100), 203 (20), 201 (19), 188 (13), 187 (43), 174 (73), 173 (46), 91 (19), 31 (27).

3-[2,6-*Dimethoxy*-6′,6′-*dimethylpyrano*(2′,3′:3,4)*phenyl*-1-*propanol* (**1e**). Oil (Found: 278.1512. $C_{16}H_{22}O_4$ requires: 278.1518). ν_{max} cm^{-1} 3400 br, 1625, 1605, 1570, 1115, λ_{max}^{EtOH} nm: 230, 278, 285, infl, 312 (ε 47200, 12200, 11700, 8900). PMR (60 MHz, $CDCl_3$): τ 3.45 and 4.47 (AB system, J = 10 Hz, H-4′ and H-5′), 3.76 (*s*, H-5), 6.2 and 6.24 (2*s*, 2 OMe), 6.45 (*t*, J = 6 Hz, H-1), 7.31 (*t*, J = 7 Hz, H-3), 7.63 (*s*, OH), 8.2 (*dt*, J = 6, 7 Hz, H-2), 8.58 (*s*, CMe_2). PMR (C_6H_6): τ 6.58 (*s*, OMe-2), 6.76 (*s*, OMe-6). MS *m/e* (%): 278 (17), 264 (19), 263 (100), 248 (6), 233 (48), 217 (9), 203 (14), 91 (12), 83 (100), 31 (13).

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