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DIHYDROCINNAMIC ACIDS FROM *HORTIA BADINII**

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Key Word Index—*Hortia badinii*; Rutaceae; quinazolines; dihydrocinnamic acids.

Abstract—Hortia badinii (Rutaceae) contains rutecarpine and hortiacine in the bark, as well as coumurrayin, methyl 3-[2-methoxy-6′,6′-dimethylpyrano(2′,3′:3,4)phenyl]-propionate, 3-[2,6-dimethoxy-6′,6′-dimethylpyrano(2′,3′:3,4)phenyl]-propionic acid, methyl 3-[2,6-dimethoxy-6′,6′-dimethylpyrano(2′,3′:3,4)phenyl]-propionate and methyl 3-[2,4-dimethoxy-3-prenylphenyl]-propionate in the wood.

Branches of *Hortia badinii* M.A. Lisboa (Rutaceae) were collected at Morro do Fraga, near Santa Rita Durão, Minas Gerais, from a tree identified by the author of the original description of the species [1]. Rutecarpine and hortiacine [2] were isolated from the bark. The wood gave sitosterol, stigmasterol, coumurrayin (**1**) [3], **2**, **3a**, **3b** and **6**. Efforts to separate **2** and **3b**, obtained as a *ca* 1:1 mixture, were not successful.

Pure **3b** being available by CH_2N_2-methylation of **3a**, assignment of MS peaks and PMR signals of **2** by difference was nevertheless possible. The high resolution parent ion peak revealed the molecular formula $C_{16}H_{20}O_4$. The PMR signals, together with the IR maximum at 1735 cm^{-1}, demonstrated the existence of a methyl dihydrocinnamate unit, substituted by an aromatic methoxyl and fused to a 6,6-dimethylpyran system. The chemical shift value (τ 3·52) for one of the *ortho* related (J 8·5 Hz) aromatic protons is compatible only with the existence of oxy-functions at the *ortho* and *para* positions. Since the methoxyl, however, cannot be vicinal to an unsubstituted position in veiw of its relatively small benzene induced solvent shift (Δ 0·20 ppm, the same order of magnitude as the shift for the ester methoxyl) only structure **2** can represent the compound.

Indeed, **3b**, $C_{17}H_{22}O_5$, to which by analogous evidence a methyl 6,6-dimethylpyranodihydrocinnamate structure can be assigned, possesses, besides an equally *ortho*, *ortho*-flanked methoxyl (Δ 0·19 ppm), an additional methoxyl which must be vicinal to an unsubstituted position, since the aromatic ring is clearly of the phloroglucinol type (τ_{ArH} 3·82, *s*). As expected this methoxyl is characterized by a larger solvent shift (Δ 0·38 ppm). Only structure **3b** is compatible with these data.

The concomitantly isolated 6,6-dimethylpyranodihydrocinnamic acid, $C_{16}H_{20}O_5$, whose methyl ester is identical with **3b**, is consequently represented by **3a**. The unequal benzene induced solvent shifts of the methoxyl resonances for dihydro-**3a** (**4**) confirm the previous assignments. The methoxyls in the alternative **5** occupy, for the present purpose, rigorously comparable surroundings and would be subject to identical solvent shifts.

The structural analogies and differences between **2** and an additional isolate, $C_{16}H_{24}O_4$, are obvious upon comparison of their spectral data, and lead to structure **6** for the latter compound.

EXPERIMENTAL

Isolation of the constituents. Branches were separated into bark and wood. Powdered bark (1·2 kg) was ext. successively

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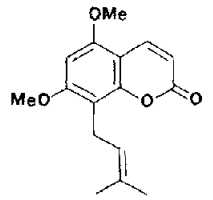
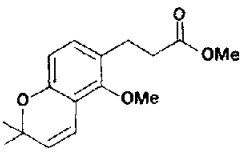
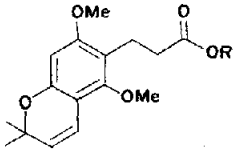


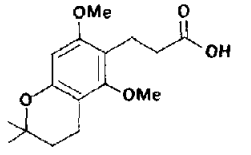
(1)



(2)



(3a) R = H
(3b) R = Me



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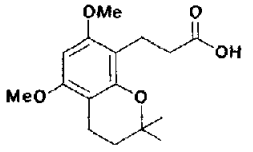

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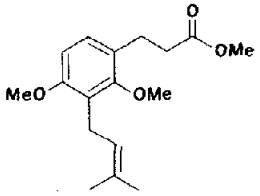

(6)

with $CHCl_3$ and EtOH. The $CHCl_3$-ext. (7 g), upon chromatography on a Si (200 g) column, gave the following fractions with the indicated eluants: A_1 (C_6H_6), A_2 (C_6H_6–$CHCl_3$ 1:1), A_3 ($CHCl_3$), A_4 ($CHCl_3$–MeOH 99:1), A_5 ($CHCl_3$ MeOH 97:3). A_2 (0·5 g) was washed with Et_2O and recryst. from EtOH giving a mixture of sitosterol and stigmasterol (20 mg). The presence of coumurrayin (**1**) [3] in the mother liquor was shown by TLC. A_3 (0·4 g) was rechromatographed on silica. The fraction eluted with C_6H_6 was crystallized from MeOH to give aliphatic material (7 mg). A_4 was washed with Et_2O and MeOH and the residue recrystallized from AcOEt to give rutecarpine [2] (150 mg). A_5 in $CHCl_3$ was repeatedly filtered through silica, before rechromatography on a silica column. The C_6H_6–$CHCl_3$ fraction was washed with MeOH to give hortiacine (14 mg) [2]. The EtOH-ext. (10 g), upon identical treatment, gave additional quantities of sitosterol + stigmasterol (20 mg), rutecarpine (85 mg), and hortiacine (10 mg). Powdered wood was ext. successively with C_6H_6 and EtOH. The C_6H_6-ext. (14 g), upon chromatography on a Si (220 g) column, gave the following fractions: B_1 (C_6H_6 and C_6H_6–$CHCl_3$ up to 1:6), B_2 ($CHCl_3$ and $CHCl_3$–MeOH 98:2), B_3 ($CHCl_3$–MeOH 9:1). The EtOH-ext. was separated into $CHCl_3$ sol. and insol. portions. The soluble portion (14 g), upon chromatography on a Si (220 g) column, gave the following fractions: C_1 ($CHCl_3$ and $CHCl_3$–MeOH up to 96:4), C_2 ($CHCl_3$–MeOH 93:7), C_3 ($CHCl_3$–MeOH 9:1). The insol. portion (21 g), upon chromatography on a Si (480 g) column, gave the following fractions: D_1 ($CHCl_3$–MeOH up to 9:1), D_2 ($CHCl_3$–MeOH 85:15), D_3 ($CHCl_3$–MeOH 8:2). After examination by TLC, B_1 (5 g), C_1 (1·7 g) and D_1 (0·3 g) were combined and rechromatographed on silica. The fractions eluted with C_6H_6 and $CHCl_3$ were combined and chromatographed on neutral alumina. The C_6H_6 fractions were rechromatographed several times on alumina giving a yellow oil (0·7 g). This was separated by TLC (SiO_2, C_6H_6–AcOEt–EtOH 75:25:3) into the more polar **6** (40 mg) and a less polar mixture of **2** and **3b** (300 mg). After examination by TLC, B_3 (2·7 g), C_2 (1·4 g) and D_2 (1·6 g) were combined and treated with Et_2O. The solid which pptd. was crystallized from EtOH giving **1** (134 mg). C_3 (2·7 g) was chromatographed on silica. The C_6H_6-fraction was separated into Et_2O soluble and insoluble portions. The sol. portions was washed with MeOH to give **3a** (3 mg).

3-[2,6-*Dimethoxy*-6′,6′-*dimethylpyrano*(2′,3′:3,4)*phenyl*]-propionic acid (**3a**), prisms, mp 164·5 166° (MeOH) [M found 292·1299. $C_{16}H_{20}O_5$ requires 292·1311]. ν_{max}^{KBr} (cm^{-1}) 2800–2400, 1710, 1630, 1610, 1480, 1370, 1310, 1140, 889. λ_{max}^{EtOH} (nm): 232, 238 inf., 278, 285, 307 (ε 22400, 16800, 6200, 6200, 4700). PMR ($CDCl_3$, τ): 3·50 (*d*, *J* 10·0 Hz, H-4′), 3·78 (*s*, ArH), 4·53 (*d*, *J* 10·0 Hz, H-5′), 6·25 (*s*, OMe), 6·27 (*s*, OMe), 6·90–7·25 (*m*, $ArCH_2$), 7·30–7·65 (*m*, CH_2CO), 8·60 (*s*, CMe_2). PMR (C_6D_6, τ): 6·47 (*s*, OMe), 6·68 (*s*, OMe). MS (*m/e*): 292 (17%) M, 277 (100), 233 (3), 217 (9), 201 (13). *Methyl ester* (**3b**) (**3a**, CH_2N_2–Et_2O) oil [M found 306. $C_{17}H_{22}O_5$ requires 306]. ν_{max}^{NaCl} (cm^{-1}): 1735, 1630, 1610, 1575, 1480, 1450, 1370, 1210, 885. λ_{max}^{EtOH} (nm): 230, 278, 286, 308 (ε 18400, 4000, 4000, 2800). PMR ($CDCl_3$, τ): 3·52 (*d*, *J* 10·0 Hz, H-4′), 3·82 (*s*, ArH), 4·55 (*d*, *J* 10·0 Hz, H-5′), 6·27 (*s*, OMe), 6·29 (*s*, OMe), 6·36 (*s*, CO_2Me), 6·90–7·28 (*m*, $ArCH_2$), 7·37–7·70 (*m*, CH_2CO), 8·60 (*s*, CMe_2). PMR (C_6D_6, τ): 6·46 (*s*, OMe), 6·56 (*s*, CO_2Me), 6·68 (*s*, OMe). *Dihydroderivative* (**4**) (**3a**, Pd/C, H_2, EtOH), mp 155–157° (cyclohexane) [M found 294. $C_{16}H_{22}O_5$ requires 294]. ν_{max}^{KBr} (cm^{-1}): 1710, 1615, 1585, 1480, 1465, 1215, 820. λ_{max}^{EtOH} (nm): 222 inf., 278, 286 (ε 11800, 2650, 2950). PMR ($CDCl_3$, τ): −0·30 (*s*, CO_2H), 3·81 (*s*, ArH), 6·27 (*s*, 2 OMe), 6·90–7·70 [*m*, $2(CH_2)_2$], 8·80 (*s*, CMe_2). PMR (C_6D_6, τ): 6·48 (*s*, OMe), 6·66 (*s*, OMe).

Methyl 3-[2-*methoxy*-6′,6′-*dimethylpyrano*(2′,3′:3,4) phenyl]-*propionate* (**2**) component of oily mixture with **3b**. Data obtained by difference [M found 276·1355, $C_{16}H_{20}O_4$ requires 276·1362]. ν_{max}^{NaCl} (cm^{-1}): 1735. PMR ($CDCl_3$, τ): 3·10 (*d*, *J* 8·5 Hz, H-6), 3·45 (*d*, *J* 10·0 Hz, H-4′), 3·52 (*d*, *J* 8·5 Hz, H-5), 4·42 (*d*, *J* 10·0 Hz, H-5′), 6·29 (*s*, *OMe*), 6·36 (*s*, *CO*$_2$Me), 6·90–7·60 [*m*, $(CH_2)_2$], 8·62 (*s*, CMe_2). PMR (C_6D_6, τ): 6·49 (*s*, OMe), 6·57 (*s*, CO_2Me).

Methyl 3-[2,4-*dimethoxy*-3-*prenylphenyl*]-*propionate* (**6**) oil, dec. upon heating [M found 292·1681. $C_{17}H_{24}O_4$ requires 292·1675]. ν_{max}^{NaCl} (cm^{-1}): 1735, 1600, 1530, 1485, 1460, 1090. λ_{max}^{EtOH} (nm): 220 inf., 275 (ε 16600, 2400). PMR ($CDCl_3$, τ): 3·00 (*d*, *J* 8·5 Hz, H-6), 3·41 (*d*, *J* 8·5 Hz, H-5), 4·80 (*m*, *J* 7·0 Hz, CH=), 6·22 (*s*, OMe), 6·27 (*s*, OMe), 6·34 (*s*, CO_2Me), 6·64 (*d*, *J* 7·0 Hz, $ArCH_2CH$=), 6·90–7·20 (*m*, $ArCH_2$), 7·30–7·60 (*m*, CH_2CO), 8·23 (*s*, Me), 8·33 (*s*, Me).

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