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A STILBENE AND TWO FLAVANONES FROM *DERRIS RARIFLORA**

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Key Word Index—*Derris rariflora*; Leguminosae; Lotoideae; stilbene, (2S)-flavanones.

Abstract—The wood of the vine *Derris rariflora* (Leguminosae–Lotoideae) contains 3,5-dimethoxy-4-prenylstilbene, (2S)-5,7-dihydroxy-6-prenylflavanone and (2S)-5-hydroxy-7-methoxy-6-prenylflavanone.

Derris rariflora (Mart.) Macbr. (Leguminosae–Lotoideae), trivial name "timbó-rana", can be found in vast regions of the Amazon valley, from the Guianas, the brazilian States of Pará and Amazonas to Peru [2]. The species is not used for fish poisoning and, indeed, TLC examination of extracts of subterranean and aerial parts of this vine revealed the absence of rotenone. Fractionation of the ethanolic wood extract led to 3 novel compounds, the stilbene (**1**) and the flavanones (**2a**) and (**2b**). The structure of the stilbene derivative, $C_{21}H_{24}O_{21}$, was deduced from its PMR and MS. Oxidation led to benzoic acid, confirming the presence of the phenyl group. The additional aromatic ring must be symmetrically substituted since its 2 aromatic and 6 methoxyl protons give rise to PMR singlets. Double resonance experiments established the lack of coupling between the aromatic and the benzylic methylene protons, eliminating one of the two symmetrical alternatives in favour of **1a**.

The structures of the (2S)-flavanones, $C_{20}H_{20}O_4$ (**2a**) and $C_{21}H_{22}O_4$ (**2b**), were deduced from ORD,

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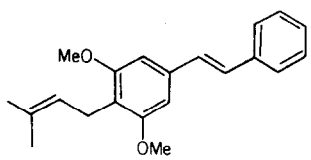
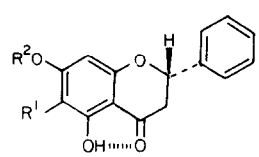
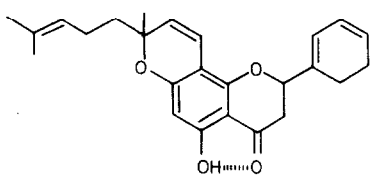


(1)



(2a) $R^1 = CH_2CH{=}CMe_2$, $R^2 = H$
(2b) $R^1 = CH_2CH{=}CMe_2$, $R^2 = Me$
(2c) $R^1 = H$, $R^2 = Me$



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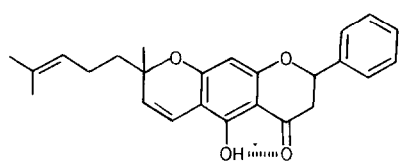

(4)

PMR and MS. Their interrelation was demonstrated by methylation of **2a** with CH_2N_2 which afforded **2b**. This methyl ether was used in the experiments which led to the allocation of the prenyl substituent to C-6 in preference to C-8. Although treatment with acid produced etherification of the C-5 hydroxyl by the side chain, as shown by the IR carbonyl frequency shift (ν_{max} 1642–1670 cm^{-1}), this test was not considered conclusive proof for the *ortho*-position of OH and prenyl groups. In the flavanone series acid catalyzed rearrangement could invalidate its significance. Pyridine-induced solvent shifts have been advocated to determine the location of hydrogen or alkyl substituents in the vicinity of phenolic hydroxyls [3]. The quantative conclusions of this work are, however, not applicable to cases in which the hydroxyl can chelate with an adjacent carbonyl. Thus the pyridine shifts for the flavanones (**3**) and (**4**), whose preparation [4], separation and identification [5] have been achieved, are very close, respectively −0·27 ppm (H-6) and −0·22 ppm (H-8). Absolute resonance values in pyridine, however, are more significant. While in $CDCl_3$ the H-6 and H-8 signals are very close (**2**, τ 4·04, **4**, τ 4·00), in pyridine the H-6 signal appears at lower field (τ 3·73) than the H-8 signal (τ 3·82). Thus in the pyridine spectrum of 7-*O*-methylpinocembrin (**2c**), the 3·73 signal must be attributed to H-6 and the 3·78 signal to H-8. The pyridine spectrum of the isolate shows of course only one of these signals. Since this occurs at τ 3·77, it can be correlated only with H-8. The strong pyridine solvent shift (Δ −0·21 ppm) of the prenylmethylene resonance is also consistent with the *ortho*-relationship of the 5-hydroxyl and alkyl groups in ring A of **2b**, and, consequently, also **2a**.

EXPERIMENTAL

Isolation of the constituents of Derris rariflora *wood.* A wood sample of a specimen, identified by the botanist W. Rodrigues, was collected near Manaus, Amazonas State, dried, powdered (2·4 kg) and extracted with EtOH. Evaporation of the solvent gave a residue (200 g) which was extracted exhaustively with hot petrol. The solution was filtered and the solvent evaporated. The residue was extracted with acetone. The solution was filtered and the solvent evaporated. The residue (30 g) was chromatographed on silica (500 g), giving the following products with the indicated solvents: oil (petrol.–C_6H_6, 9:1); (**1**) (80 mg, petrol.–C_6H_6, 8:2); (**2b**) (16 mg, petrol.–C_6H_6, 1:1); (**2a**) (110 mg, C_6H_6); sitosterol (80 mg, C_6H_6–$CHCl_3$, 8:2).

3,5-Dimethoxy-4-prenylstilbene (**1**), m.p. 84–86° (hexane). (Found: M, 308·1770; $C_{21}H_{24}O_2$ requires: M, 308·1776.) λ_{max}^{EtOH} (nm): 238, 312, 320, 333 (ε 23300, 48650, 49950, 30400). ν_{max}^{KBr} (cm^{-1}): 1638, 1600, 1595, 1582, 763, 702. PMR ($CDCl_3$, τ): 2·20–2·70 (*m*, C_6H_5), 2·86 (*s*, 2 CH), 3·23 (*s*, H-2, H-6), 4·70 (*t*, *J* 7·7 Hz), 6·11 (*s*, 2 OMe), 6·60, (*d*, *J* 7·7 Hz, CH_2), 8·18 (*s*, Me), 8·30 (*s*, Me). MS (*m/e*): 308 (100%) M, 293 (99), 278 (6), 277 (11), 263 (7), 253 (15), 240 (36), 239 (14), 179 (8), 178 (14), 165 (14), 152 (7), 115 (7), 105 (4), 104 (4). Oxidation ($KMnO_4$, Me_2CO) gave benzoic acid.

5,7-Dihydroxy-6-prenylflavanone (**2a**), m.p. 212–214° (C_6H_6). (Found: M, 324·1355. $C_{20}H_{20}O_4$ requires: M, 324·1362. λ_{max}^{EtOH} (nm): 297, 337 (ε 15950, 5500); $\lambda_{max}^{EtOH+NaOH}$ (nm): 250, 337 (ε 11450, 30500); $\lambda_{max}^{EtOH+NaOAc}$ (nm): 304, 337 (ε 12700, 20900); $\lambda_{max}^{EtOH+AlCl_3}$ (nm): 315, 392 (ε 20400, 2500). ν_{max}^{KBr} (cm^{-1}): 3120, 2700 (broad), 1644, 1634, 1592, 1496, 769, 699. PMR ($CDCl_3$, τ): −2·43 (*s*, OH), 2·50 (*s*, C_6H_5), 3·70 (*s*, *H*-8), 3·94 (*s*, *OH*), 4·54 (*dd*, *J* 4·3 and 8·6 Hz, H-2), 4·78 (*t*, *J* 6·8 Hz, =CH), 6·74 (*d*, *J* 6·8 Hz, CH_2), 7·12 (*dd*, *J* 8·6 and 18·9 Hz, H-3), 7·37 (*dd*, *J* 4·3 and 18·9 Hz, H-3), 8·27 (*s*, Me), 8·37 (*s*, Me). MS (*m/e*): 324 (100%) M, 309 (44), 281 (21), 269 (56), 256 (11), 255 (8), 220 (12), 219 (11), 205 (65), 192 (19), 191 (12), 179 (12), 177 (24), 165 (88), 131 (11), 123 (25), 104 (16), 103 (14). ORD (*ca* 2 mg/100 ml, MeOH): $[\phi]_{350}$ −5400, $[\phi]_{325}$ −10800, $[\phi]_{307}^{tr}$ −22600, $[\phi]_{290}$ 0, $[\phi]_{275}^{pk}$ +11100, $[\phi]_{258}$ +7100. The 7-*O-methyl derivative* was prepared by methylation with CH_2N_2 in Et_2O. It was found identical (m.m.p., IR, TLC) with the following isolate.

5-Hydroxy-7-methoxy-6-prenylflavanone (**2b**), m.p. 90–92° (petrol.). Found: M, 338·1525; $C_{21}H_{22}O_4$ requires: M, 338·1518. λ_{max}^{EtOH} (nm): 294, 343 (ε 22050, 3900); $\lambda_{max}^{EtOH+NaOH}$ (nm): 297, 370 (ε 8850, 9650); $\lambda_{max}^{EtOH+NaOAc}$ (nm): 294, 343 (ε 21600, 3650); $\lambda_{max}^{EtOH+AlCl_3}$ (nm): 312, 390 (ε 18150, 2300). Gibbs test: positive. ν_{max}^{KBr} (cm^{-1}): 2700 (broad), 1642, 1631, 1585, 1520, 1493, 765, 706. PMR ($CDCl_3$, τ): −2·08 (*s*, OH), 2·55 (*s*, C_6H_5), 3·89 (*s*, H-8), 4·59 (*dd*, *J* 4·5 and 11·0 Hz, H-2), 4·75 (*t*, *J* 8·0 Hz, =CH), 6·15 (*s*, OMe), 6·72 (*d*, *J* 8·0 Hz, CH_2), 6·90 (*dd*, *J* 11·0 and 18·9 Hz, H-3), 7·20 (*dd*, *J* 4·5 and 18·9 Hz, H-3), 8·22 (*s*, Me), 8·32 (*s*, Me). PMR (C_5D_5N, τ): 3·77 (*s*, H-8), 5·52 (*dd*, *J* 11·0 and 4·5 Hz, H-2, covers =CH signal), 6·25 (*s*, OMe), 6·50 (*d*, *J* 7·0 Hz, CH_2), 6·7–7·3 (*m*, 2 H-3), 8·18 (*s*, Me), 8·31 (*s*, Me). MS (*m/e*): 338 (100%) M, 323 (66), 296 (34), 284 (53), 271 (15), 270 (8), 235 (8), 234 (9), 220 (66), 207 (13), 206 (8), 194 (13), 192 (17), 179 (66), 166 (6), 149 (6), 131 (10), 105 (5), 104 (7), 103 (12). ORD (*ca* 2 mg/100 ml, MeOH): $[\phi]_{350}$ −5100, $[\phi]_{325}$ −11900, $[\phi]_{305}^{tr}$ −20000, $[\phi]_{291}$ 0, $[\phi]_{275}^{pk}$ +13600, $[\phi]_{258}$ +9000. *Cyclized derivative*. **2b** (11 mg) was dissolved in 0·3 ml AcOH containing 1 drop of H_2SO_4. After 24 hr at room temp. H_2O was added and the mixture extracted with $CHCl_3$. The $CHCl_3$-soln was washed, dried, filtered through silica and evaporated. The residue (8 mg) did not crystallize. λ_{max}^{EtOH} (nm): 280, 325. ν_{max}^{KBr} (cm^{-1}): 1670, 1600, 1580, 1500, 765, 700.

Model compounds. **3**, Gibbs test: negative. PMR ($CDCl_3$, τ): −2·11 (*s*, OH), 2·56 (*s*, C_6H_5), 3·40 (*d*, *J* 10·0 Hz, ArCH=), 4·00 (*s*, H-6), 4·55 (*dd*, *J* 11·0 and 5·0 Hz, H-2), 4·64 (*d*, *J* 10·0 Hz, ArCH=C<u>H</u>), 4·90 (*t*, *J* 7·0 Hz, CH=), 6·89 (*dd*, *J* 17·0 and 11·0 Hz, H-3), 7·25 (*dd*, *J* 17·0 and 5·0 Hz, H-3), 7·7–8·2 (*m*, 2 CH_2), 8·34, 8·44 and 8·59 (*s*, 3 Me). PMR (C_5D_5N, τ): 3·33 (*d*, *J* 10·0 Hz, ArCH=), 3·73 (*s*, H-6), 4·48 (*dd*, *J* 11·0 and 5·0 Hz, H-2), 4·52 (*d*, *J* 10·0 Hz, ArCH=C<u>H</u>), 6·78 (*dd*, *J* 17·0 and 11·0 Hz, H-3), 7·17 (*dd*, *J* 17·0 and 5·0 Hz, H-3), 7·6–8·2 (*m*, 2 CH_2), 8·37, 8·46, 8·59 (*s*, 3 Me). **4**, Gibbs test: positive. PMR ($CDCl_3$, τ): −2·31 (*s*, OH), 2·59 (*s*, C_6H_5), 3·34 (*d*, *J* 10·0 Hz, Ar CH=), 4·04 (*s*, H-8), 4·56 (*d*, *J* 10·0 Hz, ArCH=C<u>H</u>), 4·60 (*dd*, *J* 11·0 and 4·5 Hz, H-2), 4·92 (*t*, *J* 7·0 Hz, CH=), 6·87 (*dd*, *J* 17·0 and 11·0 Hz, H-3), 7·26 (*dd*, *J* 17·0 and 4·5 Hz, H-3), 7·6–8·2 (*m*, 2 CH_2), 8·34, 8·42 and 8·60 (*s*, 3 Me). PMR (C_5D_5N, τ): 3·15 (*d*, *J* 10·0 Hz, ArCH=), 3·82 (*s*, H-8), 4·50 (*d*, *J* 10·0 Hz, ArCH=C<u>H</u>), 4·52 (*dd*, *J* 11·0 and

4·5 Hz, H-2), 6·78 (*dd*, J 17·0 and 11·0 Hz, H-3), 7·13 (*dd*, *J* 17·0 and 4·5 Hz, H-3), 7·7–8·3 (*m*, 2 CH_2), 8·38, 8·47 and 8·62 (*s*, 3 Me). **2c**, Gibbs test: positive, PMR ($CDCl_3$, τ): −2·03 (*s*, OH), 2·56 (*s*, C_6H_5), 3·90 (*s*, H-6, H-8), 4·59 (*dd*, *J* 11·0 and 4·5 Hz, H-2), 6·20 (*s*, OMe), 6·97 (*dd*, *J* 17·0 and 11·0 Hz, H-3), 7·20 (*dd*, *J* 17·0 and 4·5 Hz, H-3). PMR (C_5D_5N, τ): 3·73 (*d*, *J* 2·0 Hz, H-6), 3·78 (*d*, *J* 2·0 Hz, H-8), 4·50 (*dd*, *J* 11·0 and 5·0, H-2), 6·32 (*s*, OMe), 6·92 (*dd*, *J* 17·0 and 11·0 Hz, H-3), 7·15 (*dd*, *J* 17·0 and 5·0 Hz, H-3).

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