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JURUENOLIDE: A γ-LACTONE FROM *IRYANTHERA JURUENSIS**

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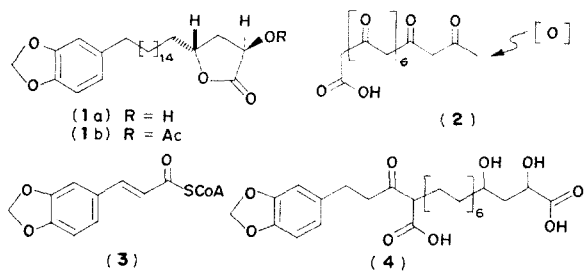
Key Word Index—*Iryanthera juruensis*; Myristicaceae; 2*R*,4*R*-dihydroxy-20-piperonyleicosanoic acid γ-lactone; juruenolide.

The chemical investigation of the trunk wood of a specimen of *Iryanthera juruensis* Warb. (Myristicaceae), revealed the presence of sitosterol, sitostenone, (±)-2′-hydroxy-7-methoxy-4′,5′-methylenedioxyflavan [1] and a lactone, $C_{27}H_{42}O_5$, designated juruenolide. The PMR spectra of the compound and of its acetate allowed expansion of the formula to **1**a. This contains a piperonylethyl unit (τ 3·3–3·5, 3ArH; 4·16, O_2CH_2; 7·53, *t*, *J* 7·5 Hz, $ArC\underline{H}_2CH_2$), a methylene chain (τ 8·2–8·8, 15 CH_2), whose signal covers an additional one H signal, and a hydroxy-γ-lactone unit (**1**a ν_{max} 1745 cm^{-1}; **1**b ν_{max} 1770, 1730 cm^{-1}). The allocation of the hydroxyl to C-2 and of the methylene chain to C-4 of this lactone was based on the analysis of the signals associated with its 2 oxymethine and 2 methylene protons. The latter can only be situated on C-3. Double irradiation experiments revealed one of them (τ 8·7) to be coupled to H-4 (τ 5·52) and the other one (τ 7·44) to H-2 (τ 5·88). Further correlation of the τ 5·88 doublet with the carbinolic proton was based on the paramagnetic shift (Δ − 0·86 ppm) of this signal upon acetylation.



The relatively high τ value (8·7) of one of the methylene proton signals indicated that the corresponding H-3 is situated well over the plane of the carbonyl. Coupling and absence of coupling was seen as evidence, respectively, for its *cis*-relation to H-4 and *trans*-relation to H-2. An identical conclusion about the relative stereochemistry of juruenolide was reached upon observing the coupling of the relatively deprotected (τ 7·44), and hence *quasi*-equatorial, H-3 to H-2 and the absence of coupling to H-4. According to the modified Hudson rule [2], formula **1**a represents also the absolute configuration of the lactone, since this is more dextrorotatory, $[\alpha]_D^{20}$ + 12·5 (MeOH), than its potassium salt $[\alpha]_D^{20}$ + 10·0 (MeOH).

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The biogenetic origin of juruenolide (**1a**) could involve condensation of a C_{18}-fatty acid precursor (**2**) with an activated cinnamic acid (**3**), via an intermediate such as **4**. The additional oxygenation of **2** has been postulated previously to explain the biosynthesis of the avocatins and the rubrenolides [3], constituents of the Lauraceae, a family which is morphologically closely related with the Myristicaceae.

EXPERIMENTAL

Isolation of the constituents of Iryanthera juruensis. A tree at the Ducke Forest Reserve, Manaus, identified by the botanist Rodrigues (Herbaria Chem. 40/72, conf. with Bot. 35391, INPA, Manaus) gave a trunk wood sample (4·4 kg) which was dried, powdered and extracted with C_6H_6. The $CHCl_3$ soluble portion of the extract (16 g) was chromatographed on silica. The following useful fractions were eluted with the indicated solvents: A_1 (C_6H_6–$CHCl_3$, 19:1), A_2 (C_6H_6–$CHCl_3$, 9:1), A_3 ($CHCl_3$). A_1 (425 mg) was fractionally crystallized from MeOH giving *sitostenone* (7 mg) and *sitosterol* (20 mg). A_2 (170 mg) was crystallized from MeOH giving (±)-*2′-hydroxy-7-methoxy-4′,5′-methylenedioxyflavan* (27 mg) [1]. A_3 (1·69 g) was recrystallized from MeOH giving *juruenolide* (80 mg).

Juruenolide (**1a**). Scales, m.p. 89–90° (MeOH). (M found: 446·3013; $C_{27}H_{42}O_5$ requires: 446·3032). IR: ν_{max}^{KBr} (cm^{-1}): 3420, 1750, 1505, 1490, 1470, 1440, 1365, 1248, 1190, 1040, 925, 810, 715. UV: λ_{max}^{MeOH} (nm): 233, 286 (ε 5600, 4950). PMR ($CDCl_3$, 220 MHz, τ): 3·35 (*d*, *J* 8 Hz, H-6′), 3·40 (*s*, H-2′), 3·48 (*d*, *J* 8·0 Hz, H-5′), 4·16 (*s*, O_2CH_2), 5·46 (*dt*, *J* 6·3, 6·3 Hz, H-4), 5·88 (*d*, *J* 6·0 Hz, H-2), 7·44 (*dd*, *J* 10, 6·0 Hz, H-3), 7·53 (*t*, *J* 7·5 Hz, CH_2-20), 7·87 (broad *s*, OH), 8·2–8·8 (m with strong s at 8·78, H-3, CH_2-5, CH_2-6 to 19). MS (*m/e*): 447 (14%) M + 1, 446 (53) M, 136 (23), 135 (100), 57 (23), 55 (16), 43 (18), 41 (16), 29 (11). ORD (*c* 8·0 mg/100 ml, MeOH, 220–300 nm): $[\phi]_{220}$ +11·1, $[\phi]_{225}$ +28·0, $[\phi]_{230}^{pk}$ +42·5, $[\phi]_{270}$ +17·9, $[\phi]_{300}$ 0. $[\alpha]_D^{20°}$ + 12·5 (*c* 80 mg/100 ml, MeOH). Acetylation (Ac_2O, C_5H_5N, room temp., 15 hr) gave the *acetate* (**1b**). Scales, m.p. 83–85° (MeOH). IR: ν_{max}^{KBr} (cm^{-1}): 1770, 1730, 1485, 1470, 1440, 1365, 1270–1230, 1040, 965, 940, 930, 808, 610. PMR ($CDCl_3$, 60 MHz, τ): identical to PMR of juruenolide, except band at 5·88 shifted to 4·94 (*d*, *J* 6·0 Hz, H-2) and band at 7·87 (OH) substituted by singlet at 7·88 ($COCH_3$). Double irradiation (a) at τ 8·7 (H-3): *dt* at 5·46 (H-4) collapses to a broad *s*; (b) at τ 7·5 (H-3): *d* at 4·94 (H-2) collapses to a *s*; (c) at τ 5·46 (H-4): no modification of *d* at 4·94 (H-2). MS (*m/e*): 488 (2·3%) M, 136 (23), 135 (100), 55 (14), 43 (65).

Sitosterol identified by direct comp. with an authentic sample. *Sitostenone*, m.p., IR and UV spectra as required by lit. [4] PMR ($CDCl_3$, τ): 4·28 (*s*, H-4).

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