Phytochemistry, 1974 Vol 13, p 1633 Pergamon Press Printed in England

FLAVANS FROM *IRYANTHERA* SPECIES*

NIDIA C. FRANCA, PEDRO P. DIAZ DIAZ†, OTTO R. GOTTLIEB
and BEL DE PAULA ROSA

Laboratório de Produtos Naturais da Fundação de Amparo à Pesquisa do Estado de São Paulo,
Instituto de Química, Universidade de São Paulo,
São Paulo, Brasil

(*Received* 26 *October* 1973)

Key Word Index—*Iryanthera coriacea*; *I juruensis*, Myristicaceae; (±)-3′,4-dihydroxy-5,7-dimethoxyflavan, (±)-2′-hydroxy-7-methoxy-4′,5′-methylenedioxyflavan

Iryanthera coriacea Ducke and *I. juruensis* Warb. (Myristicaceae) grow in the Amazonian forest near Manaus. From the trunk wood extracts closely related phenols, resp. $C_{17}H_{18}O_5$ and $C_{17}H_{16}O_5$, were isolated. The PMR spectra allowed expansion of these formulae to $C_{15}H_{10}O.2OH.2OMe$ and $C_{15}H_{10}O.OH.OMe.O_2CH_2$ and indicated that in each case five of the undefined hydrogens are aromatic, requiring the presence of two aromatic rings, and five are aliphatic. Since the IR spectra do not register carbonyl absorption, the undefined oxygens must participate in ether functions. If these were cyclic, as is most probable, then all hydrogen deficiencies would have been pinpointed in both cases. Indeed, in the PMR spectra of both, signals of one aliphatic proton are completely analyzable (resp. τ 5·17, *dd*, *J* 8·5, 3·5 Hz; τ 4·90, *J* 7·5, 5·5 Hz) and represent a benzylic axial oxymethine hydrogen which is vicinal to two other hydrogens. These and the additional pair give rise to multiplets (resp. τ 8, 7·4 and τ 7·7, 7·1), one at a chemical shift value consistent with the benzylic nature of the corresponding methylene group. The combined data show both to be flavans, even if of different aromatic substitution and heterocyclic conformation.

The difference in conformation is portrayed by the difference in chemical shift and coupling constants of the H-2 signals and must, clearly, be due to absence or presence of a hydroxyl at C-2′ as depicted resp. in **1** and **2**. In **1**, the aryl group at C-2 is free to avoid interference of the hydrogens at C-6′ and C-3. Free rotation is not feasible in the hydrogen bonded derivative **2** and the interference can only be attenuated by diminution of the dihedral angle Heq-C(3)-C(2)-H, expressed by enhanced coupling constants. As expected, acetylation, destroying the H-bridge, equalizes chemical shift and coupling constants of the oxymethine signals of **1** and **2**.

If, as these data indicate, **1** lacks a hydroxyl at C-2′, the *ortho*-dihydroxy system of this cmpd. (UV shift upon addition of borate) must occupy C-3′,4′. The location of both these hydroxyls on ring B, and indeed, the general distribution of all substituents among the rings was given by MS: By far the most intense peaks appeared at *m/e* values interpreted to represent the molecular ions **1**: 302 (81%), **2**: 300 (100%), and the retro Diels–Alder ions

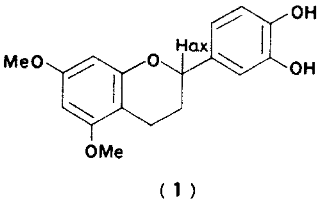
---

* Part III in the series "The Chemistry of Brazilian Myristicaceae" For Part II see Ref 1 Sponsored by Instituto Nacional de Pesquisas da Amazonia, Conselho Nacional de Pesquisas, Manaus

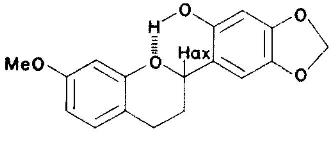
† Multinational Program in Chemistry, Organization of American States, graduate fellow, 1972–1973

[1] GOTTLIEB, O R, LOUREIRO, A A, SANTOS CARNEIRO, M DOS and ROCHA, A I DA (1973) *Phytochemistry* **12**, 1830

incorporating rings A after capture of a hydrogen **1**. 167 (100%), **2** 137 (90%) and B **1**: 136 (42%), **2**. 164 (80%).



(**1**)



(**2**)

Final proof for these structures was obtained through acetylation With **1** this produced a paramagnetic shift (Δ 0·43 ppm) of an aromatic 3-hydrogen multiplet in the PMR spectrum. The additional signal in the aromatic region, which was not affected, is located at high field (τ 3·92; AB system, J 3 Hz) and can represent only the *meta* related protons of the phloroglucinol-type, fully etherified, A-ring. Analogously, acetylation produced a paramagnetic shift (Δ 0·47 ppm) only of one of the aromatic proton singlets (τ 3·55) in the PMR spectrum of **2**. Neither the other singlet (τ 3·42) nor the 3 multiplets were affected One of these, an *ortho* split doublet (τ 3·05, J 8 Hz), appears at considerably lower field than all other signals (τ 3·42–3 60) and must, consequently, represent a proton which is *meta* related to oxyfunctions, a requirement satisfied by H-5 if the methoxyl is placed at C-7

FXPERIMENTAL

Isolation procedures. Iryanthera coriacea Identified by the botanist Rodrigues. Dried, powdered trunk wood (3 5 kg) was extd with EtOH The $C_6H_6/CHCl_3$-soluble portion (22 g) of the extract (180 g) was chromatographed on silica, $CHCl_3$ - MeOH 95 5 eluting (±)-3′,4′-dihydroxy-5,7-dimethoxyflavan (4 g) *I juruensis* Identified by the botanist Rodrigues INPA, Manaus, Herbaria Chem 40, 72, conf with Bot 35391 Dried powdered trunk wood (4 4 kg) was extd with $C_6H_6/CHCl_3$ The extract (16 g) was chromatographed on silica C_6H_6-$CHCl_3$ 9 1 eluting (±)-2′-hydroxy-7-methoxy-4′ 5-methylenedioxyflavan (100 mg)

(±)-3′,4′-*Dihydroxy-5,7-dimethoxyflavan* (**1**) Colourless crystals, m p 98 100 (C_6H_6) (Found C, 67 33 H, 5 98 $C_{17}H_{18}O_5$ requires C, 67 52, H, 6%) IR ν_{max}^{KBr}(cm^{-1}) 3180, 1615 1595, 1515 1485 1440, 1430, 1410, 1364, 1330, 1265, 1190; 1140; 1100; 878; 870; 815 UV λ_{max}^{EtOH}(nm) 230 sh, 279 (ε 11000 3000), $\lambda_{max}^{EtOH+H_3BO_3+NaOAc}$(nm) 232; 286 (ε 8300, 3800), add of NaOH destroys cmpd add of NaOAc does not affect UV PMR (CDCl$_3$, τ) 3 1 3 25 (*m*, H-2′,5′,6′), 3 89 (AB system, J 3 Hz, H-5,7) 4 13 (broad s, 2 OH), 5 17 (*dd*, J 8 5 3 5 Hz H-2), 6 23 6 27 (singlets, 2 OCH_3), 7 2 7 5 (*m*, 2 H-4) 7 65 - 8 35 (*m* 2 H-3) MS (*m/e*) 303 (7%) M + 1, 302 (81) M 180 (24) 179 (27), 168 (8) 167 (100), 166 (12), 154 (26), 149 (16), 148 (36) 147 (7) 138 (23) 137 (23) 136 (42), 123 (17), 110 (7), 109 (15) *Acetate* Colourless crystals, m p 122 - 124 (CCl_4) IR ν_{max}^{KBr}(cm^{-1}) 1770, 1625, 1595, 1485 1415, 1360, 1195, 1145, 1105, 1010, 820 PMR (CDCl$_3$, τ) 2 7–2 8 (*m*, H-2′, 5′, 6′) 3 89 (AB-system J 3 Hz, H-5,7) 5 03 (*dd*, J 8 5, 3 5 Hz, H-2), 6 23, 6 25 (singlets, 2 OMe), 7 2–7 45 (*m*, 2 H-4) 7 73 (*s*, 2 COMe), 7 65 - 8 1 (*m*, 2 H-3)

2′-*Hydroxy-7-methoxy-4′ 5′-methylenedioxyflavan* (**2**) Colourless scales, m p 164–166 (MeOH) (Found C, 67 85, H, 5 35 $C_{17}H_{16}O_5$ requires C, 67 99, H, 5 37%) IR ν_{max}^{KBr}(cm^{-1}) 3400, 1610, 1590 1500, 1440 1320 1260, 1205, 1170, 1120, 1040, 940 840 UV λ_{max}^{EtOH}(nm) 225, 284, 289, 300 (ε 15000, 7500, 9050 8400) PMR (CDCl$_3$, τ) 3 05 (*d*, J 8 Hz, H-5), 3 42 (s, H-6′), 3 45 (s, OH), 3 48 (*dd*, J 8, 2 Hz H-6), 3 55 (s, H-3′), 3 60 (*d*, J 2 0 Hz H-8), 4·10 (*s*; O_2CH_2); 4·90 (*dd*; J 7·5, 5·5 Hz, H-2); 6·28 (*s*; OMe); 6·95–7·25 (*m*; 2 H-4); 7·6–8 (*m*; 2 H-3) MS (*m/e*) 300 (100%) M, 178 (10), 175 (13), 164 (80), 163 (32), 151 (30), 150 (60), 138 (32) 137 (90) 135 (18) 133 (25), 121 (14), 115 (10), 109 (24), 108 (25), 107 (12), 106 (10), 105 (14)

Acetate Colourless needles, m p 131 - 133 (MeOH) IR ν_{max}^{KBr}(cm^{-1}) 1760 1610, 1570 1500 1470, 1210 1160, 1135, 1030, 860 UV λ_{max}^{MeOH}(nm) 225, 282, 287 (ε 12900 7950, 8250) PMR (CDCl$_3$ τ) 3 05 (*d*, J 8 Hz H-5), 3 08 (s, H-3′), 3 45 (*s*, H-6′), 3 50 (*dd* J 8, 2 Hz, H-6), 3 62 (*d*, J 2 Hz, H-8), 4 03 (s, O_2CH_2), 5 (*dd*, J 8, 4 Hz, H-2), 6·28 (s, OMe), 6·95–7·25 (*m*, 2 H-4), 7·75 (*s* COMe), 7·70–8·10 (*m* 2 H-3) MS (*m/e*) 342 (45%) M, 300 (39) 164 (59), 150 (44), 137 (100)

Acknowledgement—The MS were registered by Dr A Aragão Craveiro by courtesy of Prof E Wenkert Indiana University Bloomington U S A