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POROSIN: A NEOLIGNAN FROM *OCOTEA POROSA**

C. J. AIBA, R. BRAZ FILHO† and O. R. GOTTLIEB‡

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

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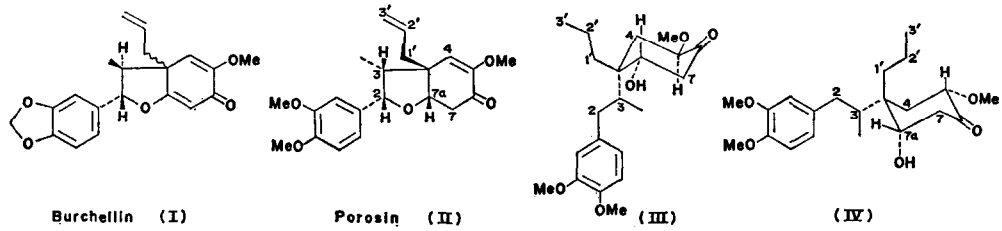
Key Word Index—*Ocotea porosa*; Lauraceae; neolignan; 3a-allyl-5-methoxy-3-methyl-2-veratryl-2,3,3a,6,7,7a-hexahydro-6-oxobenzofuran; porosin.

Abstract—The wood of *Ocotea porosa* (Nees) L. Barr. (Lauraceae) contains sitosterol, sesquiterpenes, *n*-octacosanoic acid, *n*-hexacosanoic acid and the neolignan porosin for which the structure of 3a-allyl-5-methoxy-3-methyl-2-veratryl-2,3,3a,6,7,7a-hexahydro-6-oxobenzofuran (II) is proposed.

Ocotea porosa (Nees) L. Barr., 'imbuia', is widely used in Brazil for the manufacture of furniture.[2] Its agreable woody smell was attributed to the presence of linalool,[3] a report we were not able to confirm. The colour of the wood varies from dark brown to greenish-yellow.[2] Equally variable is the presence of a new crystalline compound, porosin, which, occurring in some darker coloured samples, could not be detected in several others.



The formula $C_{18}H_{17}O_2(OMe)_3$ and spectral data classify porosin as a neolignan.[4] Indeed, a comparative study of the PMR spectra of burchellin (I)[1] and of porosin (Table 1) leads to formula II for this compound. In contrast to burchellin's piperonyl and dienone groups, porosin bears a veratryl substituent and an α,β-unsaturated keto function. The α',β'-bond is saturated, its H-β', linked directly to the carbon of an ether function (τ 5·98) and axial (*dd*, *J* 12 and 5 Hz), forming the *X* part of an *ABX* system. Again, as opposed to burchellin, the 2-aryl and 3-methyl groups of porosin must be *cis*-oriented, accounting for

* Part XXI in the series "The Chemistry of Brazilian Lauraceae". For Part XX see Ref. 1. Taken from the Doctorate thesis presented by Cacilda Junko Aiba to the Universidade de São Paulo (1972).

† On leave of absence from Instituto de Química, Universidade Federal do Ceará.

‡ Pesquisador-Conferencista, Conselho Nacional de Pesquisas.

[1] O. ARAÚJO LIMA, O. R. GOTTLIEB and M. TAVEIRA MAGALHÃES, *Phytochem.* **11**, 2031 (1972).
[2] W. B. MORS and C. T. RIZZINI, *Useful Plants of Brazil*, p. 125, Holden-Day, San Francisco (1966).
[3] T. R. M. MOLLAN, *Perf. Essent. Oil Record* **52**, 411 (1961).
[4] O. R. GOTTLIEB, *Phytochem.* **11**, 1537 (1972).

the appearance of the $C\underline{H}_3$-3 and H-3 signals at relatively high field, while the H-2 signal appears at relatively low field.[1] The methyl protons in *cis*-2-aryl-3-methyl-2,3-dihydrobenzofurans give rise to a signal at τ 9·26.[5] The additional shielding experienced by the methyl protons of porosin (τ 9·48) suggests their location in the magnetically protected region below the 5,6-double bond. Dreiding models of the stereochemical alternatives show that this requirement is met in the most efficient way if the relative configuration II is attributed to porosin.

TABLE 1. 220 MHz PMR SPECTRA OF BURCHELLIN (I) AND POROSIN (II)*

	I	II
Ar$\underline{H}$	3·17–3·25 *m*	3·07 *d* 3·17 *dd* 3·24 *d* 8·0 8·0, 2·0 2·0
$ArO_2C\underline{H}_2$	4·03	—
$ArOC\underline{H}_3$	—	6·10 6·10
H-2	4·83 *d*	4·11 *d*
	9·5	5·4
$C\underline{H}_3$-3	8·84 *d*	9·48 *d*
	6·9	7·5
H-3	7·12 *dq*	~7·4 *m*
	9·5, 6·9	
H-4	4·21	4·41
$OC\underline{H}_3$-5	6·32	6·38
H-7	4·57	7·78 *dt* 8·08 *t*
		12·0, 5·0 12·0
H-7a	—	5·98 *dd*
		12·0, 5·0
H-1′	7·45 *dd* 7·66 *dd*	7·31 *dd* 7·44 *dd*
	13·0, 6·8 13·0, 6·8	14·5, 7·0 14·5, 7·0
H-2′	4·45 *qt*	3·94–4·15 *m*
	6·8, 6·8, 9·5, 16·5	
H-3′	4·92 *dd* 4·99 *dd*	4·60–4·72 *m*
	9·5, 1·5 16·5, 1·5	

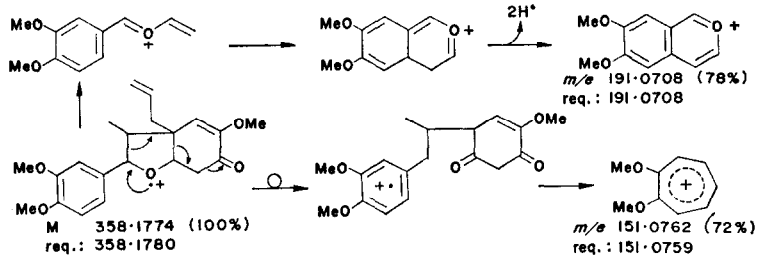
* Each signal is characterized from top to bottom by chemical shift (τ), multiplicity (*s*—singlet; *d*—doublet; *dd*—double doublet; *dq*—double quartet; *qt*—quadruple triplet; *m*—multiplet) and coupling constant in Hz. Solvent $CDCl_3$. Internal ref. TMS.

The MS of porosin is compatible with the proposed constitution (II), the origin of all peaks being easily interpretable. The two predominant fragmentation paths (Scheme 1) involve opening of the tetrahydrofuran moiety through a 1,4-hydrogen shift of a type already noted for burchellin (I);[1] and the concerted rupture of bonds, which are at the same time benzylic or allylic and α to an ether function, triggered by the α-cleavage of the ketone.

Since catalytic hydrogenation of II should take a predictable course, this reaction was performed on porosin in order to obtain additional evidence for the structural proposal. The preferred conformations III and IV for the epimeric hexahydroderivatives were established through analysis of the PMR double doublets at τ 7·9 and 8·0, attributed to the newly formed methylene protons at C-4. (For the sake of comparison with the parent compound, the carbons of III and IV were numbered according to their positions in the

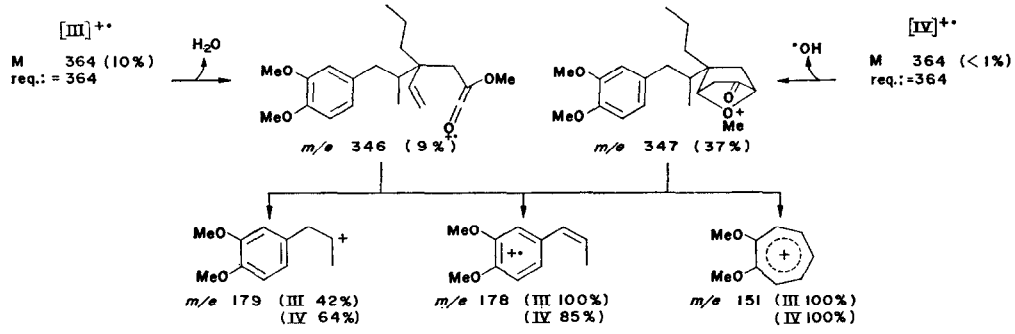
[5] M. GREGSON, W. D. OLLIS, B. T. REDMAN, I. O. SUTHERLAND and H. H. DIETRICHS, *Chem. Commun.* 1394 (1968).

benzofuran derivative II.) The coupling constants indicated the axial conformation of the neighbouring hydrogen in both compounds. All other spectral data of III and IV also proved to be consistent with the anticipated structures.



SCHEME 1. MS FRAGMENTATION PATHS OF POROSIN.

The *cis*-relation of the methoxyl and the hydroxyl in IV seems to make the attack of the methoxyl on C-9, with consequent expulsion of a hydroxyl radical and formation of a bridged oxonium ion, a facile electron impact reaction. The stability of the molecular ion is very low (Scheme 2). The *trans*-relation of these groups in III inhibits a similar reaction and a *cis*-1,4-elimination from the molecular ion in the boat form[6] may be evoked to explain the loss of the elements of water. All other fragmentation processes are of similar importance for both hexahydroporosins and clearly support the structural proposals.



SCHEME 2. MS FRAGMENTATION PATHS OF THE HEXAHYDROPOROSINS.

EXPERIMENTAL

M.ps were taken on the Kofler block and are uncorrected. Chromatography employed Merck's Kieselgel 0·05–0·20 mm for columns and G for plates. PMR spectra were recorded on Varian instruments, MS on an AEI MS9 instrument and ORD curves on a Cary 60 spectropolarimeter.

Isolation of the constituents of Ocotea porosa. Ground heartwood (7·5 kg) was extracted with benzene in a Soxhlet. A small portion (15 g) of the extract was chromatographed on silica giving a series of oily fractions. Two fractions, eluted respectively with benzene–AcOEt (9:1) and with benzene–AcOEt (8:1), were rechromatographed to yield sitosterol (150 mg) and crude porosin (50 mg). The rest of the extract (330 g) was washed with light petrol. The precipitate which appeared upon concentration of the petroleum solution was separated by filtration and crystallized from EtOH to give a mixture of aliphatic acids (3 g). The filtrate, freed from solvent under vacuum, consisted of a viscous oil (120 g), composed mainly of sesquiterpenes.

[6] H. BUDZIKIEWICZ, C. DJERASSI and D. H. WILLIAMS, *Mass Spectrometry of Organic Compounds*, p. 112, Holden-Day, San Francisco (1967).

The light petrol. insoluble portion of the original extract (205 g), chromatographed on silica, led to a sole crystalline fraction. This was rechromatographed on silica. Elution with benzene removed oily impurities. Elution with benzene–$CHCl_3$ (1:1) gave crystals which were recrystallized from benzene–light petrol. giving porosin (950 mg). This procedure was applied to 5 additional wood samples. While 3 failed to yield porosin, one yielded an equivalent amount (100 mg ex 650 g of wood) and one yielded more (350 mg ex 650 g of wood) than the sample described above.

Aliphatic acids. Crystals, m.p. 80–83° (EtOH). MS: *m/e* 452 (4%, $C_{30}H_{60}O_2$), 438 (2%, $C_{29}H_{58}O_2$), 424 (100%, $C_{28}H_{56}O_2$), 410 (5%, $C_{27}H_{54}O_2$), 396 (56%, $C_{26}H_{52}O_2$). Methylation with CH_2N_2–Et_2O gave *methyl ester*, crystals, m.p. 63–65° whose integrated PMR spectrum agreed with the formula $H_3C(CH_2)_{26}CO_2Me$.

Porosin (II). Crystals, m.p. 133–135° (benzene–light petrol.). γ_{max}^{KBr} (cm^{-1}): 1667, 1631, 1517, 1261, 1164, 1138, 1019, 924, 828, 769. λ_{max}^{EtOH} (nm): 237 inf, 258, 285 inf (ϵ 14 500, 21 800, 4600). MS: M+1 359 (25%), M 358 (100%), *m/e* (%) 329 (21), 328 (87), 313 (17), 300 (37), 287 (18), 286 (21), 272 (21), 259 (19), 231 (35), 192 (23), 191 (78), 190 (14), 189 (14), 178 (42), 177 (12), 165 (29), 164 (13), 163 (13), 152 (12), 151 (72), 149 (14), 138 (28), 107 (10). DOR (*c*, 0·46, EtOH, 400–240 nm): $[\phi]_{380}$ O, $[\phi]_{360}$ +9300, $[\phi]_{340}$ +9300, $[\phi]_{320}$ +3100, $[\phi]_{315}$ O, $[\phi]_{300}$ −15 000, $[\phi]_{295}$ −18 000, $[\phi]_{284}$ −31 000, $[\phi]_{280}$ −28 000, $[\phi]_{270}$ −15 000, $[\phi]_{265}$ O, $[\phi]_{263}$ +6200, $[\phi]_{250}$ +31 000.

Hexahydroporosins. II (170 mg) in AcOH (30 ml) was added to Pd–C (400 mg) and treated with excess H_2 (4 hr). The reaction mixture was separated by TLC (SiO_2, benzene–AcOEt, 1:1) into the more polar hexahydroporosin III (50 mg) and the less polar hexahydroporosin IV (80 mg). III: Oil, ν_{max}^{film} (cm^{-1}): 3510, 1709, 1595, 1513, 1263, 1156, 1143, 1105, 1033, 760, RMP ($CDCl_3$, τ): 3·14–3·27 (*m*, three ArH), 6·09 (*s*, $ArOCH_3$), 6·15 (*s*, $ArOCH_3$), ~6·2 (*m*, H-5), 6·35 (*dd*, *J* indet. and 4·0 Hz, H-7a), 6·48 (*s*, OCH_3-5), 7·25 (*dd*, *J* 13·2 and 4·0 Hz, H-7), 7·39 (*dd*, *J* 13·2 and 11·6 Hz, H-7), 7·5–7·7 (*m*, H-2), 7·94 (*dd*, 13·0 and 4·0 Hz, H-4), 8·07 (*dd*, *J* 13·0 and 10·0 Hz, H-4), 8·2–8·6 (*m*, H-3, H-1′, H-2′), 9·16 (*t*, *J* 7·2 Hz, H-3′), 9·28 (*d*, *J* 7·0 Hz, CH_3-3). MS: M 364 (10%), *m/e* (%) 346 (9), 288 (3), 179 (42), 178 (100), 168 (9), 164 (5), 163 (12), 152 (14), 151 (100), 139 (8), 138 (5), 137 (6), 136 (5), 135 (7), 125 (11), 121 (6), 109 (6), 108 (8), 107 (22), 106 (10), 105 (7). IV: Oil. IR spectrum practically superimposable on the IR spectrum of III. RMP ($CDCl_3$, τ): 3·11–3·27 (*m*, three ArH), 6·10 (*s*, $ArOCH_3$), 6·16 (*s*, $ArOCH_3$), ~6·15 (*m*, H-5), ~6·2 (*m*, H-7a), 6·59 (*s*, OCH_3-5), 7·53 (*dd*, *J* 12·0 and ~1·5 Hz, H-7), 7·57 (*dd*, *J* indet. and ~1·5 Hz, H-7), 7·5–7·8 (*m*, H-2), 7·96 (*dd*, *J* 13 and 4·0 Hz, H-4), 8·04 (*dd*, *J* 13 and 10·0 Hz, H-4), 8·2–8·6 (*m*, H-3, H-1′, H-2′), 9·17 (*t*, *J* 7·2 Hz, H-3′), 9·32 (*d*, *J* 7·0 Hz, CH_3-3). MS: M 364 (<1%), *m/e* (%) 347 (37), 179 (64), 178 (85), 170 (7), 164 (8), 163 (10), 152 (23), 151 (100), 138 (11), 137 (7), 136 (4), 135 (10), 127 (15), 121, (7), 109 (11), 108 (12), 107 (29), 106 (16), 105 (11).

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