

SHORT COMMUNICATION

THE BITTER PRINCIPLE OF *SPHENOCENTRUM JOLLYANUM*

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Abstract—Columbin has been isolated from the seeds of *Sphenocentrum jollyanum*, Pierre (Menispermaceae).

THE evergreen undershrub, *Sphenocentrum jollyanum* Pierre (Menispermaceae), indigenous to Nigeria and other parts of Western Africa, is used in native medicine as a bitter stomachic^{1,2}: the fruits are green when young and bright orange when ripe. Extraction of the defatted ripe fruits has yielded columbin (I) first isolated³ from the roots of *Jateorrhiza palmata*, also a member of the Menispermaceae. Identification of columbin was achieved by converting it into the following compounds, the melting points and (where asterisked) specific rotations (D line) of which were in agreement with literature values: decarboxycolumbin,⁴ isocolumbin,⁵ isocolumbin acetate*,⁶ decarboxyisocolumbin.*⁷ The i.r. spectrum of an authentic specimen of isocolumbin and a sample prepared from the bitter principle of *S. jollyanum* were identical. In addition, the two samples behaved as single substances when chromatographed on a thin layer of Kieselgel G using three different solvent systems.

TABLE 1

Position τ	Intensity	Multiplicity	Assignment
8.92	3	Singlet	Methyl groups on C.9 and C.5
8.78	3	Singlet	
4.7-4.9	1	Complex	H on C.12
3.42-3.62	3	Complex	H on β position of furan ring and olefinic protons on C.2 and C.3
2.43-2.55	2	Complex	H's on two α positions of furan ring
6.5 (columbin only)	1	Singlet removed by D ₂ O	H of hydroxyl
7.74 (isocolumbin acetate only)	3	Singlet	Acetate methyl

¹ J. M. DALZIEL, *The Useful Plants of West Tropical Africa*, p. 15. Crown Agents for Oversea Governments and Administration, London (1955).

² M. B. PATEL and J. M. ROWSON, *List of Plants in the Herbarium and Museum of Nigerian Medicinal Plants*. Nigerian College of Technology, Ibadan, Nigeria (1963).

³ WITTSTOCK, *Poggendorfs Ann.* 19, 298 (1830).

⁴ M. P. CAVA and E. J. SOBOCZENSKI *J. Am. Chem. Soc.* 78, 5317 (1956).

⁵ K. FEIST and W. VOLKSEN, *Ann.* 534, 41 (1938).

⁶ D. H. R. BARTON and D. ELAD, *J. Chem. Soc.*, 2085 (1956).

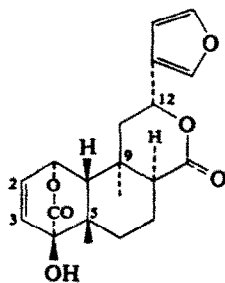
⁷ F. WESSELY, K. DINJASKI, W. ISEMAN and G. SINGER, *Monatsh. Chem.* 66, 87 (1935).

The main peaks in the NMR spectra of columbin⁸ and isocolumbin acetate (deutero-chloroform/internal TMS) together with their assignments are summarized in Table 1. In hexadeuteroacetone solution the olefinic protons on C.2 and C.3 were separated from the β proton on the furan ring, the resonances occurring at τ 3.88–3.78; the methyl resonance previously occurring at τ 8.92 is shifted upfield to τ 9.1. In decarboxycolumbin the methyl resonance, previously occurring at τ 8.92 shifts to 9.1. The olefinic protons (C₂ and C₃) also shift their resonance position upfield to τ 4.0.

EXPERIMENTAL

Ripe fruits of *S. jollyanum* were collected by one of us (M. B. P.) near Ibadan, Nigeria. Plants were authenticated by reference to Hutchinson and Dalziel⁹ and by comparing flowering and fruiting specimens with typed specimens in the Forest Herbarium, Ibadan.

Columbin: extraction and purification. Dried, powdered seed kernels of *S. jollyanum* (600 g) were defatted (24 hr) with light petroleum (b.p. 40/60) in a Soxhlet extractor.



(I)

Subsequent extraction (24 hr) with industrial methylated spirits gave a syrupy extract which was dissolved in methanol (150 ml) and allowed to stand overnight. Colourless crystals (9.4 g) were obtained and a further crop (3 g) resulted on concentrating the mother liquors. The crystals (1 g) in chloroform:methanol (9:1) were treated with charcoal and filtered through a column of Kieselgel G (10 g). Concentration of the filtrate and washings yielded a residue (920 mg) which on repeated crystallization from ethanol gave columbin, m.p. 195–196° (decomp.) $[\alpha]_D^{25} + 53^\circ$ (c 1.5 in pyridine). The i.r. spectrum of isocolumbin (in CHCl₃ and KBr) was identical with that of an authentic sample; the two samples also had the same R_f values in three solvent systems on a thin layer of Kieselgel G; (R_f 0.87 with ethyl acetate, 0.63 with acetone and 0.11 with chloroform).

Acknowledgement—We thank Professor D. H. R. Barton for an authentic specimen of isocolumbin.

⁸ E. J. COREY, G. SLOMP, SUKH DEV, S. TOBINAGA and E. R. GLAZIER, *J. Am. Chem. Soc.* **80**, 1204 (1958).

⁹ J. HUTCHINSON and J. M. DALZIEL, *Flora of West Tropical Africa*, Second Edition (revised by R. W. J. KEAY), Vol. 1, Part 1, p. 76. Crown Agents for Overseas Governments and Administration, London (1954).