4-METHOXY-1-VINYL-β-CARBOLINE, A NEW ALKALOID FROM *PICRASMA JAVANICA* (SIMAROUBACEAE)

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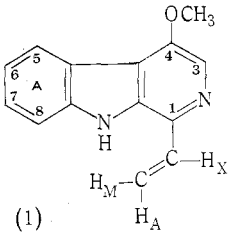
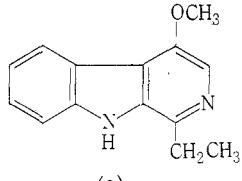
Picrasma javanica Bl., a large rain-forest tree of the family Simaroubaceae, occurs in New Guinea. The major bark alkaloid, 4-methoxy-1-vinyl-β-carboline (1), has been characterized spectroscopically, and its dihydro derivative is identical with the alkaloid crenatine (2) from the Argentinian species *Aeschrion crenata* Vell. (syn. *Picrasma crenata* [Vell.] Engl.).[1]



(1)



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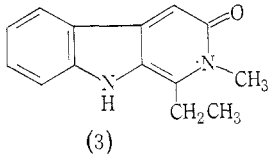

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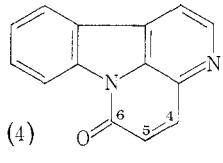

(4)

The 100-MHz n.m.r. spectrum of (1) in $CDCl_3$ solution shows an AMX system (δ_A 5·50, δ_M 6·21, δ_X 7·20; J_{AM} 1·5, J_{AX} 10·5, J_{XM} 17·2 Hz) from the vinyl group protons and a three-proton singlet at δ 4·08 assigned to the methoxy group. Analysis of the signals from the aromatic ring protons of (1) and (2) (Table 1) shows that there is no substituent on ring A, and on the basis of the assignments made for the C3 and C4 protons in harman, the methoxy group can be placed at C4 rather than C3. As in the case of crenatine,[1] the presence of a methoxy group in (1) is considered to cause an upfield shift of the signal from C3–H relative to the signal of C3–H in the spectrum of harman, whereas placing the methoxyl at C3 and assignment of the δ 8·08 signal to C4–H would involve a corresponding downfield displacement of the C4–H signal. The placing of the methoxy group at C4 in (1) and (2) depends on the assumption that

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[1] Sanchez, E., and Comin, J., *An. Asoc. quim. argent.*, 1969, **57**, 57.

introduction of a methoxy group will produce the usual upfield shift of the signal from the *ortho*-situated proton, and chemical confirmation of the structures of (1) and (2) has therefore been sought. The formation in high yield of a stable methiodide from (2) by reaction with methyl iodide is considered to support the structures shown, for a 3-methoxy substituted β-carboline might be expected, by analogy with 2-methoxypyridines and 2-methoxyquinolines, to be converted into (3).

Previous studies of alkaloids from *Picrasma* species have led to the isolation of canthin-6-one (4) from *P. crenata*,[2] and of 4,5-dimethoxycanthin-6-one from *P. ailanthoides*.[3]

TABLE 1

COMPARATIVE N.M.R. DATA FOR THE AROMATIC PROTONS OF ALKALOID (1), CRENATINE (2), AND HARMAN

In $CDCl_3$. Chemical shifts in p.p.m. (δ 0·00 from TMS); s, singlet; q, quartet; m, multiplet

	H 3	H 4	H 5	H 6, H 7, H 8	Coupling Constants (Hz)
Alkaloid (1)	s 8·08	—	q 8·34[a]	m 7·2–7·5	[a] J_{ortho} 7·2
Crenatine (2)	s 8·00	—	q 8·1[b]	m 7·2–7·6	[b] J_{ortho} 7·3
Harman	d 8·37[c]	d 7·81[c]	q 8·1[d]	m 7·2–7·5	[c] $J_{3,4}$ 5·4 [d] J_{ortho} 7·2

Experimental

Bark of *Picrasma javanica* Bl. was collected from a tree (40 ft high, 2 ft in diameter) growing in rain forest bordering Crooked Creek, about 4 miles south-west of Bulolo (long. 146° 39′ E., lat. 7° 11′ S.).

Extraction of the milled dried bark (3 kg) and work-up for alkaloids by the method previously described[4] afforded 3·62 g of crude alkaloids. Although thin-layer chromatography indicated the presence of other constituents, chromatography on neutral alumina afforded only one major series of fractions, which were eluted by benzene. These fractions, which crystallized readily on removal of the solvent, were combined and crystallization from ethanol gave alkaloid (1), *4-methoxy-1-vinyl-β-carboline*, as colourless crystals, m.p. 146–147° (Found: C, 75·1; H, 5·6; N, 12·5. $C_{14}H_{12}N_2O$ requires C, 75·0; H, 5·4; N, 12·5%). The mass spectrum showed a strong molecular ion peak at *m/e* 224 (base peak, 100%) and fragmentation peaks at *m/e* 223 (38), 209 (30), 181 (69), 154 (38), and 127 (23).

Catalytic hydrogenation of alkaloid (1) in ethanol solution over platinum oxide, and crystallization of the product from acetone, gave the dihydro derivative (2), colourless crystals, m.p. 181–183°. This hydrogenation product was identical in its i.r. and n.m.r. spectra with crenatine, and there was no depression of m.p. in a mixed m.p. determination with crenatine.

The dihydro derivative (2) (30 mg) was heated in a sealed tube at 100° with methyl iodide (1 ml) and chloroform (1 ml) for 4·5 hr. Crystallization of the product from aqueous methanol gave *crenatine methiodide* as pale yellow needles, m.p. 315° (dec.) (Found: C, 48·9; H, 4·6; N, 7·4. $C_{14}H_{14}N_2O,CH_3I$ requires C, 48·8; H, 4·7; N, 7·6%).

Acknowledgments

The authors are indebted to Dr T. G. Hartley for the collection of bark of *P. javanica* and to Dr J. Comin for a sample of crenatine.

[2] MacPhillamy, H. B., personal communication cited by W. I. Taylor in "The Alkaloids." (Ed. R. H. F. Manske.) Vol. VII, p. 252. (Academic Press: New York 1964.)

[3] Inamoto, N., Masuda, S., Simamura, O., and Tsuyuki, T., *Bull. chem. Soc. Japan*, 1961, **34**, 888.

[4] Johns, S. R., Lamberton, J. A., and Sioumis, A. A., *Aust. J. Chem.*, 1966, **19**, 2331.