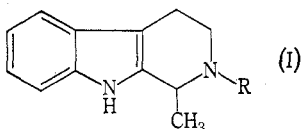


ALKALOIDS OF THE AUSTRALIAN LEGUMINOSAE*

VII.† *N*_b-METHYLTETRAHYDROHARMAN FROM *ACACIA COMPLANATA* A. CUNN. EX BENTH.

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Previous studies of *Acacia* species have led to the isolation of alkaloids of three distinct types. Phenylethylamine, *N*-methylphenylethylamine, and hordenine occur in many species,^{1,2a} tryptamine has been found in many species,^{2b} and *N*_b-methyl- and *N*_b*N*_b-dimethyl-tryptamine³ were shown to occur in *A. maidenii* F. Muell. A third class of *Acacia* alkaloid, represented by *N*^α-cinnamoylhistamine, has been isolated from *A. argentea* and *A. polystacha*.⁴



Examination of the alkaloids from the leaves and stems of *Acacia complanata* A. Cunn. ex Benth., a species found in southern Queensland, has revealed alkaloids of a further type. The major base, isolated in 0.3% yield, is *N*_b-methyltetrahydroharman (I; R = CH₃). A second alkaloid present in trace amounts only has been identified as tetrahydroharman (I; R = H) by thin-layer chromatography and gas chromatography.

Although harman type alkaloids have been isolated from many plant families *N*_b-methyltetrahydroharman appears to have been isolated previously only from *Arthropytum leptocladum*,^{5,6} family Chenopodiaceae. Tetrahydroharman has been found in the Leguminosae in *Petalostylis labicheoides*,⁷ and in trace amounts in *Petalostylis labicheoides* var. *casaeoides* Benth.⁸ No trace of tryptamine or its simple *N*_b-methyl derivatives could be detected in the alkaloids from *A. complanata*.

Experimental

Leaves and twigs of *Acacia complanata* were collected at Pine Mountain in southern Queensland, and a dried sample (1 kg) was extracted with methanol. Dilute sulphuric acid was added to the residue obtained on concentrating the methanol extract and, after filtration, the solution was basified by addition of ammonia. Chloroform extraction gave crude alkaloids

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³ Fitzgerald, J. S., and Sioumis, A. A., *Aust. J. Chem.*, 1965, **18**, 433.

⁴ Fitzgerald, J. S., *Aust. J. Chem.*, 1964, **17**, 375.

⁵ Yurashevskii, N. K., *Zh. obshch. Khim.*, 1939, **9**, 595.

⁶ Yurashevskii, N. K., *Zh. obshch. Khim.*, 1941, **11**, 157.

⁷ Badger, G. M., and Beecham, A. F., *Nature*, 1951, **168**, 517.

⁸ Johns, S. R., Lambertson, J. A., and Sioumis, A. A., *Aust. J. Chem.*, 1966, **19**, 893.

(4.3 g). To remove non-basic material the crude alkaloids were dissolved in chloroform, and the solution shaken repeatedly with 2*N* H₂SO₄, until the acid extract no longer gave a positive test with Mayer's reagent. The combined acid fractions were basified with ammonia and the alkaloids (3.4 g) extracted with chloroform.

When a 2.5-g sample of the alkaloids was chromatographed on weak neutral alumina, crystalline fractions totalling 2.1 g were eluted by chloroform. The crystalline material consisted of almost pure *N*-methyltetrahydroharman, which was converted into a picrate, m.p. 182–184°. The free base, recovered from the picrate, melted at 109–110°, and had $[\alpha]_D^{20}$ 0° (in ethanol) after crystallization from a small volume of xylene. A synthetic specimen of *N*-methyltetrahydroharman, prepared by methylating tetrahydroharman with methyl iodide, was shown to be identical by comparison of the infrared spectrum and by melting point and mixed melting point determinations.

The 60-Mc/s n.m.r. spectrum, measured in CDCl₃ solution with tetramethylsilane (δ 0.00) as internal reference standard, showed a broad one-proton peak at δ 7.88 (indole NH; exchangeable with D₂O), a four-proton multiplet at δ 6.85–7.55 (aromatic protons of benzenoid ring), a three-proton doublet at δ 1.30 and a one-proton quartet at δ 3.40 (*J* 6.5 c/s; CH₃-CH <), a three-proton singlet at δ 2.42 (NCH₃), and a broad four-proton multiplet extending from δ 2.60 to δ 3.15 (–CH₂CH₂–).

In thin-layer chromatograms the total alkaloids showed a strong spot (stained with iodine) due to *N*-methyltetrahydroharman, and a very faint one corresponding in *R_F* with tetrahydroharman. The respective *R_F* values were 0.37 and 0.03 on alumina plates with chloroform as developing solvent, and 0.75 and 0.65 with chloroform/methanol (2 : 1); and on silica gel plates 0.41 and 0.20 when developed in methanol. Preparative thin-layer chromatograms were run on silica gel plates and sufficient of the minor base was collected for gas chromatographic comparison with authentic tetrahydroharman. Identical retention times were observed for both samples.