THE MAJOR ALKALOID OF *AOTUS SUBGLAUCA* (LEGUMINOSAE), *S*-(+)-N_b-METHYLTRYPTOPHAN METHYL ESTER

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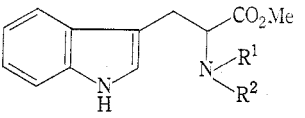
The alkaloids of *Aotus subglauca* Blakely & McKee are closely related to those of another Australian species, *Pultenaea altissima* F. Muell. ex Benth.,[1] which like *A. subglauca* belongs to the tribe Podalyriae of the family Leguminosae. *S*-(+)-N_b-Methyltryptophan methyl ester (1), which has now been shown to be by far the major alkaloid of *A. subglauca*, was isolated previously from the West Australian



	R^1	R^2
(1)	H	Me
(2)	Me	Me

species *Gastrolobium callistachys* Meissn.,[2] and *S*-(+)-N_b,N_b-dimethyltryptophan methyl ester (2) was isolated as the major alkaloid of *Pultenaea altissima* Benth.[1] Comparison by thin-layer chromatography indicates that the *A. subglauca* alkaloids contain a small proportion of (2) and *P. altissima* alkaloids a small proportion of (1), and this conclusion is supported by comparison of n.m.r. spectra of chromatographic fractions obtained in the separation of the alkaloids.

Experimental

Aotus subglauca (herbarium voucher number SN 7512) was collected near Stanthorpe in southern Queensland.

Crude alkaloids (30 g) were isolated from the milled, dried plants (35 kg) by the method described in the study of *P. altissima*.[1] Examination of the alkaloids by thin-layer chromatography on Kieselgel G in the system chloroform–methanol (9 : 1) and exposure of the developed plates to iodine vapour indicated the presence of a major constituent (R_F 0·31) and a minor constituent (R_F 0·51). The alkaloids of *P. altissima* showed major (R_F 0·51) and minor (R_F 0·31) constituents.

The crude *A. subglauca* alkaloids were chromatographed on alumina (Spence type H neutralized with ethyl acetate) and *c.* 85% of the total alkaloids was recovered as a series of fractions eluted from the column by benzene and by mixtures of benzene and chloroform. The n.m.r. spectra of selected fractions showed that all these fractions consisted largely of alkaloid (1) (R_F 0·31) with a small proportion of alkaloid (2) (R_F 0·51) in the fractions first eluted from the column. With ethanolic picric acid all fractions readily gave a crystalline picrate, which on crystallization from a small volume of ethanol gave S-(+)-N_b-*methyltryptophan methyl ester picrate* as reddish orange prisms, m.p. 151–153° (Found: C, 49·3; H, 4·0; N, 15·4. $C_{13}H_{16}N_2O_2,C_6H_3N_3O_7$ requires C, 49·5; H, 4·1; N, 15·2%).

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[1] Fitzgerald, J. S., *Aust. J. Chem.*, 1963, **16**, 246.

[2] Cannon, J. R., and Williams, J. R., unpublished data; Williams, J. R., Ph.D. Thesis, University of Western Australia, 1966.

Pure alkaloid (1), recovered from the crystalline picrate, was obtained as a colourless gum, ν_{max} 1735 and 3500 cm^{-1} in CCl_4, the n.m.r. spectrum of which showed ($CDCl_3$ solution) signals at δ 2·34 (s, 3H, NMe), 3·60 (s, 3H, CO_2Me), 9·00 (broad s, 1H, indolic NH), 1·80 (s, 1H, NHMe), 700–760 Hz (m, 4H, benzenoid ring protons), δ 6·84 (d, 1H, *J* 2 Hz, C 2–H), and at 303–320 Hz and 345–360 Hz (multiplets, 2H and 1H respectively, CH_2–CH). The presence of alkaloid (2) as a minor constituent in the fractions of alkaloid (1) first eluted from the chromatographic column is indicated by a sharp signal at δ 2·41 attributed to the NMe_2 group of (2). The hydrochloride of alkaloid (1) was prepared from the alkaloid recovered from the picrate and also directly from the chromatographic fractions. Crystallization of the hydrochloride from ethanol gave colourless needles, m.p. 171–172°, $[\alpha]_D$ +51° (*c*, 0·82 in methanol). The i.r. spectrum was identical with an authentic sample of *S*-(+)-N_b-methyltrytophan methyl ester hydrochloride,[2] and there was no depression of m.p. in a mixed m.p. determination. For the hydrochloride of (1), m.p. 171–172°, $[\alpha]_D$ +45·7° (*c*, 1·3 in methanol) has been recorded.[2]

Acknowledgments

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