## ALKALOIDS OF THE AUSTRALIAN LEGUMINOSAE\*

V.† THE OCCURRENCE OF METHYLATED TRYPTAMINES IN ACACIA MAIDENII F. MUELL.

# By J. S. FITZGERALD<sup>‡</sup> and A. A. SIOUMIS<sup>‡</sup>

Acacia maidenii F. Muell., a member of the family Leguminosae, subfamily Mimosoideae, has not previously been examined for the presence of alkaloids. The bark has now been found to contain about 0.6% of the bases  $N_b$ -methyl- and  $N_bN_b$ dimethyl-tryptamine, in the proportions approximately 2:3. These have not previously been recognized in Acacia species but have been found in other genera of Leguminosae (Mimosa,<sup>1</sup> Piptadenia,<sup>1,2</sup> and Lespedeza<sup>1</sup>), in the Apocynaceae (Prestonia<sup>1</sup>), in the Chenopodiaceae (Arthrophytum<sup>1</sup> and Girgensohnia<sup>1</sup>) and in the Gramineae (Phalaris<sup>3</sup>).

Since the presence of  $N_b N_b$ -dimethyltryptamine in *Phalaris tuberosa* may be associated with toxicity to stock, the occurrence of these bases in genera such as *Acacia* which contain species used as forage merits further attention.

### Experimental

Microanalyses were made by the Australian Microanalytical Service, Melbourne.

## Isolation of Alkaloids

The crude alkaloid was extracted from the milled bark by percolation with warm methanol and recovered by the method described previously,<sup>4</sup> yielding 0.6% on the weight of dry bark.

Gas chromatography of the crude base in a column at 203° with Silicone E-301 as stationary phase gave a single peak, but it was found later that this phase did not separate mono- and di-methyltryptamines. Short-path distillation of the crude base at  $160^{\circ}/4$  mm and crystallization of the distillate from light petroleum gave the higher-melting (monomethyl) compound in a somewhat impure state. Separation was best effected by chromatography over alumina, chloroform eluting dimethyltryptamine and chloroform-methanol (1 : 1) eluting monomethyltryptamine. Thin layer chromatography of the mono- and dimethyl compounds on alumina gave  $R_F$  values 0.04 and 0.5 on elution by chloroform; 0.3 and 0.7 on elution by methanol; 0.3 and 0.7 on elution by chloroform-methanol (1 : 1).

## $N_b$ -Methyltryptamine

The second compound eluted from the alumina column crystallized from light petroleum in white prisms, m.p. 86-87° (lit.<sup>1</sup> m.p. 89°) (Found: C, 75·7; H, 8·0; N, 16·0; (N)-CH<sub>3</sub>, 7·5. Calc. for  $C_{11}H_{14}N_2$ : C, 75·8; H, 8·1; N, 16·1; (N)-CH<sub>3</sub>, 8·6%). Picrolonate, m.p. 240-243° (lit.<sup>1</sup> m.p. 243°) (Found: C, 57·5; H, 5·2; N, 18·7. Calc. for  $C_{11}H_{14}N_2, C_{10}H_8N_4O_5$ : C, 57·5; H, 5·1; N, 19·2%). Picrate, red needles, m.p. 193-195° (lit.<sup>1</sup> m.p. 190°) (Found: C, 50·7; H, 4·3; N, 17·2. Calc. for  $C_{11}H_{14}N_2, C_6H_3N_3O_7$ : C, 50·6; H, 4·3; N, 17·4%).

- \* Manuscript received October 27, 1964.
- † Part IV, Aust. J. Chem., 1964, 17, 375.
- ‡ Division of Organic Chemistry, CSIRO Chemical Research Laboratories, Melbourne.
- <sup>1</sup> Boit, H.-G., "Ergebnisse der Alkaloid-Chemie bis 1960." p. 478. (Akademie-Verlag: Berlin 1961.)
- <sup>2</sup> Legler, G., and Tschesche, R., Naturwissenschaften, 1963, 50, 94.
- <sup>3</sup> Culvenor, C. C. J., Dal Bon, R., and Smith, L. W., Aust. J. Chem., 1964, 17, 1301.
- <sup>4</sup> Fitzgerald, J. S., Aust. J. Chem., 1963, 16, 246.

Aust. J. Chem., 1965, 18, 433-4

### SHORT COMMUNICATIONS

No sample of N-methyltryptamine was available for comparison, but the infrared spectrum of the monomethyl compound was consistent with the structure.

#### $N_h N_h$ -Dimethyltryptamine

The first component eluted from the alumina column was crystallized from hexane and initially had m.p. 46-47°. A solution seeded with an authentic sample of NN-dimethyltryptamine (m.p. 56-58.5°) had m.p. 57.5-58.5°, not depressed on mixing (lit. m.p. 48-49°;<sup>1</sup> m.p. 47-49° changing to 71.73° on seeding<sup>5</sup>) (Found: C, 76.7; H, 8.4; N, 14.8. Calc. for  $C_{12}H_{16}N_3$ : C, 76.6; H, 8.6; N, 14.9%). Picrate, m.p. 170-171° (lit.<sup>1</sup> m.p. 170°). The picrate prepared in ethanol solution separated as red crystals but on recrystallization a mixture of red and yellow crystals was produced, the red crystals melting at 171-171.5° and the yellow ones at 170-171°. On further recrystallization only the yellow form was obtained (Found: C, 51.9; H, 4.7; N, 16.2; O, 28.7. Calc. for  $C_{12}H_{16}N_3C_6H_3N_3O_7$ : C, 51.8; H, 4.6; N, 16.8; O, 26.8%).

The infrared spectrum of the dimethyl compound extracted from A. maidenii was identical with that of an authentic sample.

The nuclear magnetic resonance spectra of the two compounds were in agreement with published data.<sup>6</sup>

## Acknowledgments

The authors thank Dr. C. C. J. Culvenor for helpful discussions and Mr. W. T. Jones for collecting the plant material.

<sup>5</sup> Fish, M. S., Johnson, N. M., and Horning, E. C., J. Amer. Chem. Soc., 1956, 78, 3668.
<sup>6</sup> Cohen, L. A., Daly, J. W., Kny, H., and Witkop, B., J. Amer. Chem. Soc., 1960, 82, 2184.