

# THE ISOLATION OF *d*-SPARTEINE FROM *HOVEA* SPECIES\*

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[Manuscript received March 28, 1949]

## Summary

The fairly widespread alkaloid *d*-sparteine has been isolated from two *Hovea* species. The constants of four salts prepared from it agreed with those previously recorded.

## I. INTRODUCTION

The genus *Hovea* which belongs to the family Leguminosae, tribe Genisteae, is entirely Australian, some eleven species being found, six of which occur in Queensland. As far as the authors are aware no previous chemical examination of this genus has been made. *H. longifolia* R.Br. occurs in several distinct forms, one of which shades into *H. acutifolia* A. Cunn., and it has been suspected of poisoning stock(1). Both of the above species gave positive alkaloid tests (Webb, personal communication) and were found to contain the steam volatile liquid alkaloid *d*-sparteine which has been previously isolated from several sources (cf. 2, 3, 4).

## II. EXPERIMENTAL

### (a) *Hovea acutifolia* A. Cunn.

This sample was collected at Walton Bridge near Brisbane, Queensland, in July 1947 and extraction begun shortly after drying.

The dried milled leaves were extracted with methanol in a soxhlet, and after removal of the solvent, the residue was treated with 1% hydrochloric acid, and filtered. The filtrate was made alkaline with caustic soda, steam distilled, and the liquid alkaloid recovered by ether extraction and distillation *in vacuo*.

It was obtained as a colourless, viscous liquid, yield 0.5%, b.p. 134 °C./1.1 mm. (lit.(5), 133–135 °C./1 mm.);  $[\alpha]_D^{20}$ , 16.8°; *c*, 7.2 in alcohol (lit.(6), 16.3°, *c*, 2 in alcohol).

Found: C, 76.4; H, 11.1; N, 11.8%.

Calculated for  $C_{15}H_{28}N_2$ : C, 76.9; H, 11.1; N, 12.0%.

### (i) *d*-Sparteine Dipicrate

Prepared in alcohol and recrystallized from a large volume of the same solvent as needles, m.p. 203–204.5 °C. (lit.(3), m.p. 204–205 °C.).

Found: N, 15.9%.

Calculated for  $C_{27}H_{32}N_8O_{14}$ : N, 16.2%.

### (ii) *d*-Sparteine Methiodide

Prepared in benzene and recrystallized from chloroform-benzene as colourless prisms, m.p. 234–235 °C. (lit.(6), m.p. 236–238 °C.).

\* The plant material was collected by L. J. Webb, C.S.I.R.O., and the work is part of the survey being carried out by the C.S.I.R.O. and other institutions on the chemical constituents of Australian flora.

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Found: C, 50.3; H, 7.7; N, 7.4; I, 34.0%.

Calculated for  $C_{16}H_{26}N_2I$ : C, 51.0; H, 7.7; N, 7.4; I, 33.8%.

(iii) *d-Sparteine Dihydriodide*

The alkaloid was dissolved in 5% sulphuric acid and a saturated solution of potassium iodide added. On standing, the dihydriodide precipitated and was recrystallized from alcohol as large colourless prisms, m.p. 255–257.5 °C. (lit.(6), m.p. 255–257.5 °C.).

Found: I, 51.0%.

Calculated for  $C_{15}H_{26}N_2 \cdot 2HI \cdot H_2O$ : I, 51.0%.

(iv) *d-Sparteine Perchlorate*

Perchloric acid was added to an ethereal solution of the alkaloid and the precipitated salt recrystallized from alcohol as colourless cubes, m.p. 171.5–172.5 °C. (lit.(3), m.p. 171–172 °C.)

Found: N, 8.2%.

Calculated for  $C_{15}H_{26}N_2 \cdot HClO_4$ : N, 8.4%.

A pK determination by potentiometric titration using a glass electrode showed that there were two basic centres:

$$pK_{a1} = 11.4 \pm 0.1 \quad \text{conc.} = \frac{M}{100} \quad \text{in alcohol water (1:1) at 20 °C.}$$

$$pK_{a2} = 3.96 \pm 0.05 \quad \text{conc.} = \frac{M}{100} \quad \text{in alcohol water (1:1) at 20 °C.}$$

Kolthoff(7) found values for *d*-sparteine in water at 15 °C. to be  $pK_{a1} = 12.0$ ,  $pK_{a2} = 4.89$ .

(b) *Hovea longifolia R.Br.*

This material was collected between Kenmore and Moggill Ferry in October 1947, and after oven-drying worked up in the same way as above. The yield of *d*-sparteine varied between 1.1 and 1.4%, the higher yield being obtained from young plants. The derivatives prepared as above agreed in all respects. A small amount of amorphous material remained after steam distillation which gave strong alkaloid tests but it was insufficient for further examination.

### III. ACKNOWLEDGMENTS

The authors wish to thank Mr. G. K. Hughes, Chemistry Department, University of Sydney, and Mr. H. J. Hines, Physiology Department, University of Queensland, for their interest and advice. The authors are also indebted to Miss J. E. Fildes, microanalyst, University of Sydney, for the semi-microanalyses, to Miss Pam Rolfe for technical assistance, and to Mr. J. N. Phillips for the pK determinations.

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