[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY OF THE NATIONAL RESEARCH COUNCIL

THE PAPILIONACEOUS ALKALOIDS. VI. *LUPINUS PUSILLUS*, PURSH.[1]

LÉO MARION AND STUART W. FENTON

Received June 8, 1948

In continuation of the investigation in this series, the isolation of the alkaloids of *Lupinus pusillus*, Pursh., is now reported. The plant was collected in southern Alberta and placed at our disposal through the generosity of Dr. R. H. F. Manske. It contains at least four alkaloids, three of which, *i.e.*, *d*-sparteine (1), anagyrine (rhombinine) (2, 3), and *l*-lupanine (4), have been isolated previously from other sources.

The fourth alkaloid appears to be new and it is proposed to designate it pusilline. Its empirical formula, $C_{15}H_{28}N_2$, differs from that of sparteine in containing two more H atoms. Its properties are closely related to those of sparteine from which it is difficult to separate and, in common with that alkaloid, it forms a monoperchlorate which crystallizes from an aqueous solution only after the addition of a little ammonia. Pusilline contains one methylimino group and it forms a methiodide which does not undergo the Hofmann degradation, but is converted back to the original base.

EXPERIMENTAL

The dried and ground plant material (1200 g.) was extracted with methanol in Soxhlet extractors. The combined extract was distilled until the solvent had been largely removed and the residue was diluted with water, acidified with hydrochloric acid, and kept on the steam-bath overnight. The crude alkaloid obtained according to the process already described (4), consisted of a viscous oil weighing 13.6 g. It was distilled *in vacuo* and the following fractions were obtained: I, b.p. 100–110° (0.2 mm.), a colorless oil, wt. 5.05 g.; II, b.p. 120–135° (0.2 mm.), a thick, colorless oil, wt. 0.72 g.; III, b.p. 140–155° (0.2 mm.), a thick colorless oil, wt. 2.15 g.; IV, b.p. 160–175° (0.2 mm.), a thick oil, wt. 1.46 g., and a residue.

Isolation of pusilline. The oil obtained as fraction I [b.p. 100–110° (0.2 mm.)] was dissolved in a small volume of methanol and the solution made just acid to Congo Red with 65% perchloric acid. A crystalline perchlorate, which separated during the addition of the acid, had all dissolved again when the addition was completed. Water was added to the solution, which was heated on the steam-bath until the methanol had evaporated. Even on long standing, no perchlorate separated from the aqueous solution, but the addition of a few drops of ammonium hydroxide caused immediate crystallization. The filtered perchlorate, after several recrystallizations from boiling methanol, consisted of fine, colorless needles, m.p. 219.5°.[2]

Anal. Calc'd for $C_{15}H_{28}N_2 \cdot HClO_4$: C, 53.49; H, 8.62; N, 8.32; Imino-CH_3, 4.46.
Found: C, 54.08, 54.13; H, 8.74, 8.62; N, 8.22, 8.37; Imino-CH_3, 4.41.

The free base, recovered from the perchlorate, could not be induced to crystallize; it is levorotatory, $[\alpha]_D^{32}$ −15.3° ($c = 2.3$ in abs. ethanol). No definitely crystalline picrate could be obtained.

---

[1] Published as National Research Council Bull. No. 1733.

[2] All melting points are corrected.

Isolation of d-sparteine. After concentration, the methanolic mother liquor from which pusilline perchlorate had separated, yielded a second perchlorate, m.p. 170–173°. A mixture of this salt with an authentic sample of *d*-sparteine monoperchlorate (m.p. 173°) melted at 172–173°. The base recovered from the perchlorate and distilled [b.p. 98–100° (0.2 mm.)], had $[\alpha]_D^{20}$ + 16.6° (*c* = 0.87 in abs. ethanol); when dissolved in methanol and added to a boiling methanolic solution of picric acid, it yielded a picrate. After several recrystallizations from boiling methanol, this picrate was obtained as pale yellow needles, m.p. 208.5°. The melting point was not altered by admixture of the picrate with *d*-sparteine dipicrate, but was depressed by admixture with *l*-sparteine dipicrate.

Isolation of l-lupanine. Fraction III could not be induced to crystallize. It was, therefore, dissolved in methanol and the solution made just acid to Congo Red by the cautious addition of 65% perchloric acid. A crystalline perchlorate separated immediately which, after several recrystallizations from boiling methanol, consisted of stout, colorless prisms, m.p. 213°, either alone or after admixture with *l*-lupanine perchlorate (2, 4). The identity is also confirmed by the optical rotation of the salt, $[\alpha]_D$ −40.1° (*c* = 1.3 in water), which agrees with that of *l*-lupanine perchlorate (2, 4). The oil obtained as fraction II, when neutralized with perchloric acid, yielded further quantities of pusilline perchlorate and *l*-lupanine perchlorate.

Isolation of anagyrine. Fraction IV, b.p. 160–175° (0.2 mm.), was converted to the perchlorate in the usual manner. After two recrystallizations from boiling methanol, from which it separated as fine, colorless needles, the perchlorate melted at 315° (dec.), either alone or after admixture with anagyrine perchlorate (m.p. 315°) (2, 3). A quantity of the perchlorate was decomposed with aqueous ammonia and the liberated base extracted with chloroform. After evaporation of the chloroform, the residual base was distilled, b.p. 165–170° (0.1 mm.), and converted in methanolic solution to the picrate which, after two crystallizations from boiling methanol, melted sharply at 253°, either alone or after admixture with anagyrine picrate (m.p. 253°).

Pusilline methiodide. To a solution of pusilline (0.244 g.) in ethyl acetate (5 cc.), methyl iodide (0.185 g.) was added and the solution allowed to stand at room temperature in a stoppered flask. A white, crystalline methiodide separated rapidly which, after three recrystallizations from ethyl acetate, melted at 260°.

Anal. Calc'd for $C_{15}H_{28}N_2 \cdot CH_3I$: C, 50.79; H, 8.26.
Found: C, 50.76; H, 8.07.

Pusilline methiodide does not undergo the Hofmann degradation, and on treatment with moist silver oxide gives a quantitative yield of pusilline.

SUMMARY

Lupinus pusillus, Pursh., contains at least four alkaloids, *i.e.*, *d*-sparteine, *l*-lupanine, anagyrine, and a new alkaloid, pusilline. Pusilline, $C_{15}H_{28}N_2$, differs from sparteine in containing two more H atoms, and it is similar to it in properties.

OTTAWA, CANADA

REFERENCES

(1) ORECHOFF, RABINOWITCH, AND KONOWALOWA, *Ber.*, **66**, 621 (1933).
(2) MARION AND OUELLET, *J. Am. Chem. Soc.*, in press.
(3) MANSKE AND MARION, *Can. J. Research*, **B21**, 144 (1943).
(4) MARION, *J. Am. Chem. Soc.*, **68**, 759 (1946).