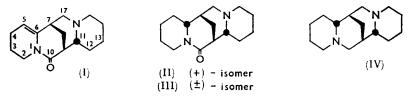
Alkaloids of the Leguminosae. Part XXVII.¹ The879. Structure of Monspessulanine.

By E. P. WHITE.

The structure (+)-5,6-dehydro-10-oxo- α -isosparteine is proposed for monspessulanine.

MONSPESSULANINE (I), C15H22N2O, from Cytisus monspessulanus L., its salts, and its reduction to dihydromonspessulanine (II), C₁₅H₂₄N₂O, have been described previously.² Both bases show carbonyl absorption typical of quinolizidine lactams in the 1630 cm.⁻¹ region, and are devoid of OH or >NH groups. The ultraviolet end-absorption of the dihydro-base is typical of saturated lactams of the series, such as lupanine and 17-oxosparteine.³ Lithium aluminium hydride reduction of dihydromonspessulanine gave (+)- α -isosparteine (IV), identified by comparison with the hydrate and picrate kindly supplied by Dr. L. Marion. This base has the hydrogens at C-6 and C-11 trans to the lone



pair on the nitrogens.⁴ The two lactams of this stereochemical series are known, (+)- α -isolupanine 5 with the carbonyl at C-2, clearly different from dihydromonspessulanine, and the synthetic (\pm)-lactam⁶ (III). Identity of the dihydro-base with (+)-10-oxo- α -isosparteine was suggested by the similarity of the infrared spectrum of the dihydro-base with that of lactam (III) (in CCl₄), and confirmed on detailed comparison, by Dr. Bohlmann.*

Comparison of infrared spectra of the bases shows that the major differences associated with hydrogenation of the double bond are the disappearance of peaks at 730, 733, 1420, and 1645sh cm. $^{-1}$ (the latter seen only in the perchlorate). A 5,6-position for the double bond is supported by identity of the ultraviolet absorption of monspessularine $[\lambda_{max}, 242 \text{ m}\mu]$ (log ε 4·1)], with that of aphyllidine ⁸ (5,6-dehydro-10-oxosparteine) and N-vinylpyrrolidone ⁹ $[\lambda_{max}, 240 \text{ m}\mu (\log \varepsilon ca 4)]$. This absorption, due to the chromophore •C:C•N•C:O, probably allows also a 2,3-position for the double bond. An $\alpha\beta$ -unsaturated lactam structure, which is not supported by infrared or ultraviolet evidence, would require a double bond in an inner ring, where it is not allowed on stereochemical grounds. Ultraviolet absorption close to that of monspessulanine is also reported for two bases which do not contain a conjugated system, 2,3-dehydro-17-oxosparteine ¹⁰ $[\lambda_{max}$ 243 m μ (log ε ca. 4)], and the 5,6-dehydro-analogue $10 \left[\lambda_{max}, 243 \text{ m}\mu \text{ (log } \epsilon 3.6) \text{ and } 210 \text{ m}\mu \text{ (log } \epsilon 4)\right]$. An 11,12double bond is excluded as the presence of strong "trans-bands" at 2700-2800 cm.⁻¹ in

- ¹ Part XXVI, White, New Zealand J. Sci. Technol., 1957, 38, B, 718.

- ² White, New Zealand J. Sci. Technol., 1931, 35, B, 110.
 ² White, New Zealand J. Sci. Technol., 1946, 27, B, 339; 1951, 33, B, 54.
 ³ Edwards, Clarke, and Douglas, Canad. J. Chem., 1954, 32, 235.
 ⁴ Leonard, in "The Alkaloids," ed. Manske, Academic Press, New York, 1960, Vol. VII, p. 273.
 ⁵ Marion, Turcotte, and Ouellet, Canad. J. Chem., 1951, 29, 22.
 ⁶ Bohlmann, Weise, Sander, Hanke, and Winterfeldt, Chem. Ber., 1957, 90, 653.

- ⁷ Labenskii, Zhur. obshchei Khim., 1958, 28, 547.
 ⁸ Galinovsky, Knoth, and Jarisch, Monatsh., 1957, 88, 143.
 ⁹ Breitenbach, Galinovsky, Nesvadba, and Wolf, Monatsh., 1956, 87, 581.
- ¹⁰ Bohlmann, Chem. Ber., 1958, 91, 2157.

^{*} The base,⁷ $C_{15}H_{24}N_2O$, prepared by pyrolysis of aphylline or aphyllic acid hydrochlorides has m. p. 105—106°, $[\alpha]_D + 25.9°$, picrate, m. p. 179—180° (decomp.), perchlorate, m. p. 233—234° (decomp.), suggesting identity with dihydromonspessulanine.

the low-resolution infrared spectrum of monspessulanine requires one quinolizidine ring to be free from a double bond at a ring junction, and from a lactam carbonyl group.^{10,11} The evidence favours a trisubstituted 5,6-double bond, but does not rule out the possibility of a disubstituted double bond.

Evidence for the double-bond substitution from the proton magnetic resonance spectrum is complicated by the presence, in the spectra of the saturated monolactams, dihydromonspessulanine, lupanine, 17-oxosparteine, and 13-oxylupanine, of a multiplet in the τ 5·1— 5.6 region, equivalent to one proton. In this region sparteine has no absorption and 2,17dioxosparteine shows a two-proton multiplet. The single proton likely to account for these absorptions is that at C-6(11), influenced by the -C(:O)·N< system. In monspessulanine there is a single proton multiplet at $\tau 4.80-5.07$, and no absorption at $\tau 5.1-5.6$; this is consistent with the absence of a proton at C-6, and with the interaction of a single proton at C-5 on a trisubstituted double bond, with protons at C-4.

EXPERIMENTAL

Infrared spectra were measured on a Perkin-Elmer Infracord 137 spectrophotometer, and identities established by infrared spectroscopy and mixed m. p. determinations.

Monspessulanine ² had m. p. 101° (from acetone–water), $[\alpha]_p + 176^\circ$ (c 0.6–1.0 in EtOH) (Found: C, 73·1; H, 8·7. Calc. for C₁₅H₂₂N₂O: C, 73·2; H, 8·95%), λ_{max} (MeOH) 241·5 mμ (log ε 4·05) decreasing to 210 mμ, ν_{max} (Nujol) 1645 (lactam C:O), 2820, 2780, ν_{max} (CHCl₃) 1635 (lactam C:O), 2830, 2780 cm.⁻¹, no peaks in the O-H or N-H stretching region. The *perchlorate*, from aqueous perchloric acid and sodium acetate, had m. p. 213° (from water), v_{max} (Nujol) 1620 (C:O), 1645sh (C:C), and the picrate had m. p. 242° (decomp.) (from ethanol) (Found: C, 53·4; H, 5·7; N, 14·5. $C_{21}H_{25}N_5O_8$ requires C, 53·1; H, 5·3; N, 14·8%).

Dihydromonspessulanine had m. p. 103° (from light petroleum), $[\alpha]_{n} + 27^{\circ}$ (c 1.3 in EtOH) (Found: C, 72.5; H, 10.0. Calc. for $C_{15}H_{24}N_2O$: C, 72.6; H, 9.7%), ultraviolet absorption increasing from 250 to 210 m μ (log ε ca. 3·9), ν_{max} (Nujol, CHCl₃) 1630 (lactam C:O), 2820, 2775, (in CCl₄) 1635 (C:O), 2810, 2760 cm.⁻¹, no peaks in the O-H or N-H stretching region. The picrate had m. p. 182° (from methanol-water) (Found: C, 51·1; H, 6·3. C₂₁H₂₇N₅O₈ requires C, 50.9; H, 5.9%), and the perchlorate had m. p. $220-227^{\circ}$ (from methanol-ethyl acetate), v_{max} (Nujol) 1640 (lactam C:O). A methiodide could not be prepared.

Reduction of Dihydromonspessularine to $(+)-\alpha$ -Isosparteine.—The dihydro-base (108 mg.) in ether was stirred at 25° for 48 hr. with an excess of lithium aluminium hydride. After addition of wet ether and water the base (105 mg.) was extracted with chloroform and steam-distilled. The distillate gave a hydrochloride (17 mg.), addition of sodium hydroxide forming needles which were extracted into ether and recrystallized from water, m. p. 95– 105° , [a]_p + 50° (c 0.7 in MeOH), $R_F 0.62$ [butan-1-ol-36% hydrochloric acid-water (50: 7.5: 17), disc method ¹²], close to sparteine, picrate, m. p. 222°. These values are close to those 13 of (+)- α -isosparteine, and identity was established by comparison with authentic base and picrate. The non-volatile base (58 mg.), chromatographed on Whatman No. 3 discs using the above solvent, gave more (+)- α -isosparteine (R_F 0.62), and two lower R_F zones.

The author thanks the Director, Dominion Laboratory, Wellington, for determination of proton magnetic resonance spectra (in CDCl₃) and for some comments.

RUAKURA AGRICULTURAL RESEARCH CENTRE, HAMILTON, NEW ZEALAND.

[Received, February 24th, 1964.]

¹¹ Wiewiorowski and Skolik, Bull. Acad. polon. Sci., Ser. Sci. chim., 1962, 10, 1. ¹² White, New Zealand J. Sci. Technol., 1957, 38, B, 707.

¹³ Cockburn and Marion, Canad. J. Chem., 1951, 29, 13.