Tetrahedron Letters No.14, pp. 921-922, 1965. Pergamon Press Ltd.
Printed in Great Britain.

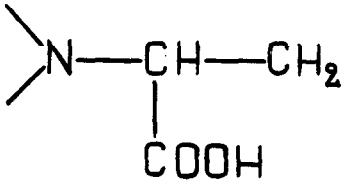
STUDIES ON ORCHIDACEAE ALKALOIDS II.[x]
STRUCTURE OF ALKALOIDS IN CHYSIS BRACTESCENS LINDL.

Björn Lüning and Hans Tränkner.
Institute of Organic Chemistry, University of Stockholm, Stockholm, Sweden.

(Received 19 February 1965)

Two alkaloids, Chysin A (I) and Chysin B (II), have been isolated from Chysis bractescens Lindl. Chysin A (n_D^{25} 1,4763, $[\alpha_D]$ +63.5°. M.wt. 169[xx]. Found: C, 64.0; H, 8.53; N, 8.11. Calc. for $C_9H_{15}NO_2$ C, 63.9; H, 8.94; N, 8.28.) gives a positive hydroxamate reaction and $\nu_{max}^{CCl_4}$ 1735 cm^{-1} (ester), does not decolourize Br_2 solution at room temperature and gives NMR signals at 6.27 τ (methyl singlet), 6.2 τ (1 H), 6.6-7.5 τ (5 H), 7.7-8.8 τ (6 H) in $CDCl_4$. The absence of N-H, N-CH_3 and alkene bands indicate that the compound is a tertiary aminoester containing two rings. The mass spectrum of I shows prominent peaks at m/e 169 (M^+), 154, 141, 138, 110, 108, 83 (base peak), 82, 59, 55.

The NMR signal at τ = 6.27 and the mass spectrum indicate that I is a methyl ester. In order to study the proton giving the NMR signal at τ = 6.2 the ester was saponified to the corresponding acid (III) (m.p. 244°-245°C, $[\alpha_D]$ +81.6°. Found: C, 61.7; H, 8.38; N, 8.90; O, 20.6. Calc. for $C_8H_{13}NO_2$: C, 61.9; H, 8.44; N, 9.03; O, 20.6.); NMR signals at 5.6 τ (1 H quartet J_1 7; J_2 16 c.p.s.), 6.0-7.4 τ (5 H) and 7.4-8.7 τ (6 H) in D_2O; prominent mass spectrum peaks at m/e 155 (M^+), 138, 127, 110, 108, 83 (base peak), 82, 55. The remarkable NMR signal at 5.6 τ (1 H quartet J_1 7; J_2 16 c.p.s.) indicates[2] the presence of the partial structure (a) in III.

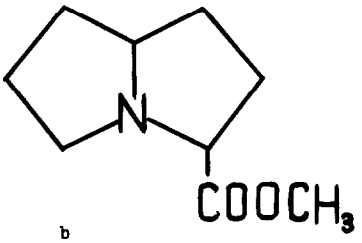


a

x For paper I of this series see Lüning[1].

(xx) Determined mass spectrometrically.

Decarboxylation of III gave as a main product pyrrolizidine (IV) identified as a picrate (m.p. 255°-258°C [3], identical with that of a synthetic sample); and with the aid of mass spectrum (peaks at m/e 111 (M^+), 83 (base peak), 55, 41.) which in all details was identical with that of a synthetic product obtained by ammonolysis of 1,4,7-tribromoheptane (c.f. ref[4].). Chysin A must therefore be 3-methoxycarbonyl-pyrrolizidine (b).



b

Chysin B gives the following mass spectra peaks: m/e 183 (M^+), 155, 154, 138, 110, 108, 83 (base peak), 82, 73, 55. This spectrum indicates that Chysin B is the ethyl ester of III.

A full report, including the synthesis and stereochemistry of Chysin A will be published later.

The authors are indepted to Dr. R. Ryhage for measurement of the mass spectra and to Dr. S. Forsén for measurement of the NMR spectra.

REFERENCES

1. Lüning, B. Acta Chem. Scand. 18, 1507 (1964).
2. Proline gives an NMR signal at τ 5.9 (1 H triplet J 7 c.p.s.).
3. Literature gives for pyrrolizidine picrate melting points varying from 240° to 258°C.
4. Seiwerth, R. and Djokić, S. Croatica Chemica Acta 29, 403 (1957).