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THE STRUCTURES OF INDACONITINE AND PSEUDACONITINE

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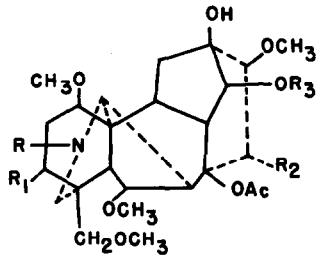
ACONITINE, $C_{34}H_{47}O_{11}N$ (I, R = Et; $R_1 = R_2 = OH$; $R_3 = C_6H_5CO$)[1,2] and delphinine, $C_{33}H_{45}O_9N$ (I, R = Me; $R_1 = R_2 = H$; $R_3 = C_6H_5CO$)[3] both when heated lose the elements of acetic acid and give rise to pyro-derivatives. Pyroaconitine is a ketone[4] because R_2 = OH in aconitine while pyrodelphinine contains a double bond[3,5] because R_2 = H in delphinine.



I

Both the alkaloids indaconitine, $C_{34}H_{47}O_{10}N$[6] and pseudaconitine $C_{36}H_{51}O_{12}N$[7] give rise similarly to pyro-derivatives and, therefore,

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1 K. Wiesner, M. Götz, D.L. Simmons, L.R. Fowler, F.W. Bachelor, R.F.C. Brown and G. Büchi, Tetrahedron Letters (2), 15 (1959).

2 M. Przybylska and L. Marion, Canad. J. Chem. 37, 1116 (1959).

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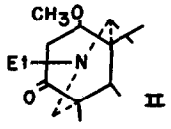
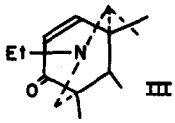
assuming that they have the same carbon-nitrogen nucleus as aconitine, they must contain an acetyl ester group in the same position.

In delphinine R_1 = H while in aconitine R_1 = OH and this secondary hydroxyl is oxidized by chromic acid to form a ketone, aconitinone (partial formula II), which readily loses methanol[8] to form aconitoline III.



II



III

Pseudaconitine is also oxidized by chromic acid to form a weakly basic substance containing one methoxyl less than the original base,[9] and this oxidation may be interpreted as indicating that indaconitine and pseudaconitine (which both give pseudaconine on hydrolysis) contain a secondary hydroxyl at R_1.

Since pseudaconine contains an ethylimino group[10] it was assumed as a working hypothesis that indaconitine had structure I (R = Et; R_1 = OH; R_2 = H; R_3 = C_6H_5CO) and to prove or disprove this, an attempt was made to convert indaconitine into delphinine by removal of the R_1 hydroxyl and replacement of the N-Et group by N-Me as previously carried out in the study of hypaconitine.[11]

Indaconitine on refluxing with thionyl chloride for 3 hr was converted into anhydroindaconitine, $C_{34}H_{45}O_9N$ (IV), perchlorate, m.p. 190-200° (dec.), $[\alpha]_D^{27}$ +31° (c, 0.5 in ethanol). Catalytic hydrogenation of IV in absolute ethanol over platinic oxide yielded deoxyindaconitine, $C_{34}H_{47}O_9N$ (V), m.p.

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8 H. Mayer and L. Marion, Canad. J. Chem. 37, 856 (1959).

9 T.A. Henry and T.M. Sharp, J. Chem. Soc. 1105 (1928).

10 R. Konovalova and A. Orekhov, Bull. Soc. Chim. Fr. 7, 95 (1940).

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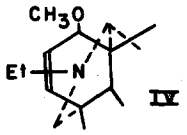
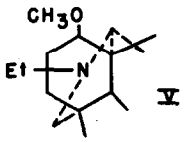


IV



V

175-180° (dec.), $[\alpha]_D^{25}$ +14° (c, 0.6 in ethanol). Deoxyindaconitine was refluxed for 5 hr in 3 per cent acetic acid with mercuric acetate to remove the imino-ethyl group. The amorphous N-desethyldeoxyindaconitine thus produced had an NMR spectrum that contained no ethyl group signal. A small quantity of the product was converted back to deoxyindaconitine by the action of ethyl iodide.

Refluxing N-desethyldeoxyindaconitine for 1 hr with methyl iodide gave N-methyl-(N-desethyl)-deoxyindaconitine, m.p. 185-191° (dec.), $[\alpha]_D^{25}$ +26° (c, 0.6 in ethanol). (Found: C, 66.30; H, 7.66. Calc. for $C_{33}H_{45}O_9N$: C, 66.09; H, 7.56%).[12] The melting point was not altered by mixture of the product with an authentic sample of delphinine. The behavior of the product on a chromatoplate was identical with that of delphinine, and a mixture of the two gave only one spot. The infrared spectra of both were identical and so were the X-ray powder patterns.

In view of this conversion of indaconitine into delphinine, it follows that the structure of indaconitine is I (R = Et; R_1 = OH; R_2 = H; R_3 = C_6H_5CO). Since pseudaconitine on hydrolysis yields acetic acid, veratric acid and pseudaconine, it also follows that pseudaconitine is I [R = Et; R_1 = OH; R_2 = H; R_3 = $(CH_3O)_2C_6H_3.CO$].

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[12] Satisfactory analytical data were obtained for all the intermediates described in the course of this conversion.