

181. *Delphinium Alkaloids. Part III. Delpheline.*

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Delpheline has the formula $C_{25}H_{39}O_6N$ and not $C_{22}H_{33}O_6N$ previously assigned to it.

DELPHELINE, a base isolated from the alkaloids of *Delphinium elatum*, L., and assigned the formula $C_{22}H_{33}O_5N$ (Goodson, J., 1943, 139), has been found by potentiometric titration to have a molecular weight of 450, agreeing well with that required for the formula $C_{25}H_{39}O_6N$ and confirmed by the analytical figures found for the hydrochloride and nitrate previously recorded (Goodson, *loc. cit.*, p. 141) and by the fact that six oxygen atoms can now be accounted for. Of these, three were known to be present in methoxyl groups, two are now found in a methylenedioxy-group, and one is shown to occur in a hydroxyl group, by the preparation of a monoacetyl derivative. The substance, like aconine (Jacobs and Elderfield, *J. Amer. Chem. Soc.*, 1936, 58, 1059), contains an ethylimino-, not a methylimino-group as formerly assumed.

EXPERIMENTAL.

Detection of the Methylenedioxy-group.—Delpheline gives Gaebel's test for this group (Found by the method of Clowes and Tollens, *Ber.*, 1899, 32, 2847: CH_2O_2 , 9.7. Calc. for $C_{25}H_{39}O_6N$: CH_2O_2 , 10.2%).

Detection of the Ethylimino-group.—Delpheline was heated with hydriodic acid in a Herzig and Meyer apparatus and when all the methyl iodide arising from the action of the acid on the methoxyl groups had been removed the residue in the distillation flask was heated with hydriodic acid and ammonium iodide, and the evolved alkyl iodide collected in ice-cold dry alcohol. The solution was heated with excess of trimethylamine for 4 hours at 50°. Evaporation of the solvent left trimethylethylammonium iodide [Found: I, 58.8. Calc. for NMe_3EtI : I, 59.0%. Found for delpheline: NEt, 9.65; equiv., by potentiometric titration with $N/10$ -hydrochloric acid, 450. Calc. for $C_{25}H_{39}O_6N$: NEt, 9.58%; equiv., 449].

The following analytical figures previously recorded (Goodson, *loc. cit.*, p. 141) are given for comparison with those calculated for salts of a base having formula $C_{25}H_{39}O_6N$: Delpheline hydrochloride (Found: C, 59.5; H, 8.3; N, 3.1; Cl, 7.1; OMe, 18.6; NEt, 8.4. Calc. for $C_{25}H_{39}O_6N.HCl.H_2O$: C, 59.5; H, 8.4; N, 2.8; Cl, 7.0; 3OMe, 18.5; NEt, 8.5%). Delpheline nitrate (Found: C, 58.7; H, 7.8; N, 5.7; OMe, 19.8; NEt, 7.4. Calc. for $C_{25}H_{39}O_6N.HNO_3$: C, 58.5; H, 7.9; N, 5.5; 3OMe, 18.2; NEt, 8.4%).

Acetyl delpheline.—Delpheline (0.5 g.) was heated with acetyl chloride (4 c.c.) for 1 hour at 50°. The excess of acetyl chloride was removed, and the residue treated with water (20 c.c.) and excess of sodium bicarbonate. The acetyl compound, extracted with ether and recrystallised from dilute alcohol, gave anhydrous prisms (0.42 g.), m. p. 125° (sintering at 123°), $[\alpha]_D^{20} -34.5^\circ$ ($c = 2$ in dry alcohol) (Found: Ac, 8.75. $C_{25}H_{39}O_6N.Ac$ requires Ac, 8.8%).

Delpheline in acetic acid solution was not hydrogenated when shaken with palladium-black in the presence of hydrogen.

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