

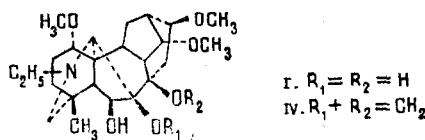
DEMETHYLENEDELPHINE - A NEW DITERPENE ALKALOID FROM
Delphinium corumbosum

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We have investigated the epigeal part of *Delphinium corumbosum* gathered in the flowering and the beginning of the fruit-bearing stage in the environs of the village of Topolevka, Dzhungarian Ala-Tau. The usual chloroform extraction gave 0.4% of total alkaloids, from which delcorine [1], methyllycaconitine [2], deoxydelcorine [3], base (I) with the composition $C_{24}H_{39}NO_6$, mp 78-80°C (ether), base (II) with the composition $C_{26}H_{39}NO_7$, mp 142-144°C (ether), and base (III) with the composition $C_{25}H_{39}NO_6$, mp 215-216°C (ether) were isolated. The IR spectrum (KBr) of base (I) contained absorption bands at 1100 and 3400-3600 cm^{-1} . Its PMR spectrum ($CDCl_3$, δ -scale) showed the signals of a tertiary methyl group (0.85 ppm, 3H, s), of an aminoethyl group (0.96 ppm, 3H, t, $J = 7$ Hz), of three methoxy groups (3.18, 3.30, and 3.39 ppm, 3H each, s), and of an α -H atom at C-6 [4] (4.24 ppm, 1H, br.s). Its mass spectrum contained the peaks of ions with m/z 437 (M^+) and 406 ($M^+ - 31$, 100%).

A comparison of the spectral characteristics and developed formulas of (I) and of delpheline (IV) and the difference in their molecular masses by 12 units permitted the assumption that alkaloid (I) was demethylenedelphine. In actual fact, when delpheline was heated with 10% sulfuric acid (steam bath, 15 h), demethylenedelphine was obtained, which was identical with the base isolated (mixed melting point, IR spectrum, and TLC). This is the first time that demethylenedelphine has been found in nature.



The IR spectrum of compound (II) contained absorption bands at 1100 and 1740 cm^{-1} (cyclopentanone). Its PMR spectrum ($CDCl_3$, δ -scale) exhibited the signals of an aminoethyl group (1.00 ppm, 1H, t, $J = 7$ Hz), of four methoxy groups (3.22, 3.25, 3.28, and 3.32 ppm, 3H each, singlets), of a β -H atom at C-14 (3.6 ppm, 1H, t, $J = 5$ Hz), and of a methylenedioxy group (5.00 and 5.43 ppm, 1H each, doublets, $J = 2$ Hz). Its mass spectrum was characteristic for the C_{19} -diterpene alkaloids and had the peaks of the following ions: M^+ 477 (6%), $M^+ - 15$ (4%), $M^+ - 31$ (100%), $M^+ - 45$ (6%), and $M^+ - 61$ (12.5%).

The properties described for (II) are close to those for dehydrodelcorine [5]. A direct comparison of the two bases (TLC, mixed melting point) showed their identity.

The physicochemical constants and spectral characteristics (IR, PMR, and mass spectra) of base (III) were identical with those of delpheline [6-8]. A direct comparison with delpheline [8] showed their identity.

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