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14-ACETYLNUDICAULIDINE AND 18-DEOXYLYCOCTONINE – NEW DITERPENE ALKALOIDS FROM Delphinium confusum

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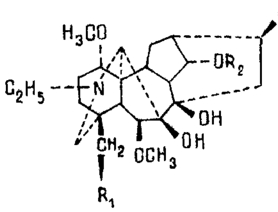
We have investigated the epigeal part of Delphinium confusum gathered in the flowering stage in the Kusavlisai gorge, Shakhristan Pass (Tadzhik SSR). Chloroform extraction in a Soxhlet apparatus gave 0.54% of total alkaloids, from which we isolated delphatine [1], base (I) with the composition $C_{26}H_{41}NO_7$, mp 206-208°C (hexane–ether), base (II) with the composition $C_{25}H_{41}NO_6$, mp 73-75°C (hexane–ether), and base (III) with the composition $C_{27}H_{43}NO_8$, mp 115-117°C (hexane–ether).

The IR spectrum (KBr) of (I) contained absorption bands at 1100, 1740, and 3400-3550 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 (1.00 ppm, 3H, t, J = 7 Hz), of an acetoxy group (2.1 ppm, 3H, s), of three methoxy groups (3.18, 3.26, 3.36 ppm, 3H each, singlets), and of a β-H at C-14 (4.7 ppm, 1H, t, J ≈ 4.5 Hz).

The PMR and mass spectra of (K) were characteristic for such C_{19}-diterpene alkaloids. In the mass spectrum, the maximum peak was due to the $M^+ - OCH_3$ ion, which agrees with the presence of a methoxy group at C-1 [2].

The molecular peak had an intensity of ∿1%, and the peak of the $M^+ - CH_3$ ion one of ~30%. This ratio of the intensities of these peaks in the mass spectrum of (I) is characteristic for lycoctonine alkaloids having a diol system at C-7 and C-8 and methoxy groups at C-1 and C-6 [3].

The acetoxy group in (I) was present at C-14, as was confirmed by the position of H-14β signal at 4.7 ppm [4]. The PMR spectrum also contained two one-proton broadened singlets at 3.87 and 3.81 ppm ($W_{1/2}$ ≈ 6 Hz), one of which was probably due to an α-proton geminal to a β-methoxy group at C-6 [5]. On the basis of the facts given above, structure (I) may be proposed for the alkaloid, from which it follows that the base (I) was the 14-acetyl derivative of nudicaulidine [6].



I. $R_1=H$; $R_2=COCH_3$
II. $R_1=H$; $R_2=CH_3$
III. $R_1=OCH_3$; $R_2=COCH_3$
IV. $R_1=OCH_3$; $R_2=H$

The IR spectrum of base (II) had absorption bands at 1100 and 3400-3600 cm^{-1}. Its PMR spectrum exhibited the signals of a tertiary methyl group (0.94 ppm, 3H, s), of an aminoethyl group (1.00 ppm, 3H, t, J = 7 Hz), and of four methoxy groups (3.34 and 3.36 ppm, 3H each, singlets; 3.45, 6H, s).

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The PMR mass spectra of (II) were characteristic for such C_{19}-diterpene alkaloids. The maximum peak of the $M^+ - OCH_3$ ion, and also the ratio of the intensities of the peaks of the M^+, $M^+ - CH_3$ and $M^+ - OCH_3$ ions, being similar to those in the spectrum of (I), showed the presence of a lycoctonine skeleton, of methoxy groups at C-1 and C-6, and of a diol system at C-7 and C-8. The presence of methoxy groups at C-14 and C-6 was responsible for a 1-proton triplet at 3.57 ppm with $J \approx 5$ Hz and a one-proton broadened singlet at 4.06 ppm ($W_{1/2} \approx 6$ Hz), respectively, in the PMR spectrum of (II). The results given permit us to consider that alkaloid (II) was 18-deoxylycoctonine, and this, so far as we are aware, is the first time that it has been found in nature [7].

IR spectrum of base (III): 1100, 1750, 3400-3600 cm^{-1}. Its PMR spectrum showed the signals of an aminoethyl group (0.95 ppm, 3H, t, $J = 7$ Hz), an acetoxy group (2.00 ppm, 3H, s), of four methoxy groups (3.17, 3.21, 3.24, and 3.30 ppm, 3H each, singlets), and of a H-14β atom (4.66 ppm, 1H, t, $J \approx 5$ Hz). The mass spectrum contained the peaks of ions with m/z 509 (M^+) and 478 ($M^+ - 31$, 100%). The characteristics given are close to those for browniine [8]. To confirm this hypothesis, we acetylated browniine (IV) with acetic anhydride in pyridine. The browniine acetate so obtained proved to be identical with the base (III) that had been isolated (mixed melting point, TLC, and mass, IR, and PMR spectra).

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