KARACOLINE – A NEW DITERPENE ALKALOID FROM *Aconitum karacolicum*

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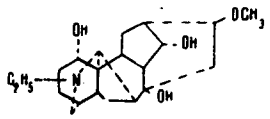
UDC 547.944/945

From the tubers of Aconitum karacolicum collected in the Kirghiz SSR (Kungei-Alatau range) we have isolated a new alkaloid with the composition $C_{22}H_{35}O_4N$, mp 183-184°C (acetone), mol. wt. 377 (mass-spectrometrically), which we have called karacoline (I).

The base contains a N-ethyl group, a tertiary C-methyl group, a methoxy group, and three hydroxy groups. The acetylation of karacoline with acetyl chloride gave a triacetate with mp 165-169°C. Its NMR spectrum had the signals of three acetyl groups (six-proton singlet at 1.96 ppm, three-proton singlet at 1.90 ppm). The acetylation of (I) with acetic anhydride in pyridine gave a diacetate with mp 119-122°C (hexane). This permitted the assumption that the base contains two secondary and one tertiary hydroxy groups. The mass spectrum of (I) is characteristic for alkaloids with a lycoctonine skeleton [1]. The maximum peak is that of the ion M−17, which shows the presence of a hydroxy group at C_1 [1]. This is confirmed by the production of an internal α-carbinolamine ether, $C_{22}H_{33}O_4N$, with mp 165-195°C (acetone), mol. wt. 375, with a mass spectrum characteristic for analogous compounds [2]. The hydrogenation of the product over a platinum catalyst led to the formation of the initial base. When karacoline was oxidized with chromium trioxide in acetone, a didehydro derivative, $C_{22}H_{31}O_4N$, was isolated the IR spectrum of which showed absorption bands of carbonyl groups in five-membered (1740 cm^{-1}) and six-membered (1665 cm^{-1}) rings, which limits the location of one of the secondary hydroxy groups to positions 6, 10, and 12. The presence in the NMR spectrum of (I) of a one-proton triplet at 4.16 ppm with a coupling constant of 4.5 Hz excludes positions 6 and 12 and permits the hydroxy group to be placed in the five-membered ring at C_{10} [3, 4]. The benzoylation of the alkaloid with benzoyl chloride in pyridine followed by acetylation formed a dibenzoyl-acetyl derivative with mol. wt. 627.

Its NMR spectrum had a ten-proton multiplet in the 7.97-7.41 ppm region. In this spectrum, the protons of the acetyl group appear in an unusually strong field at 1.30 ppm, which shows the presence of a hydroxy group at C_{10} and makes it possible to ascribe the tertiary hydroxy group to C_8 [5]. The presence in the mass spectrum of this product of the peak of an M−91 ion (M−59−32) shows that the methoxy group is located at C_{15} [6].

On the basis of the above facts, structural formula (I) is proposed for karacoline.



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