ALKALOIDS OF Aconitum karakolicum

M. N. Sultankhodzhaev, M. S. Yunusov,
and S. Yu. Yunusov

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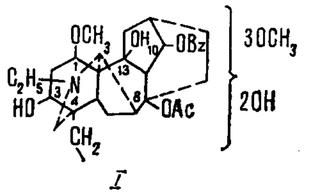
We have investigated the tubers of Aconitum karakolicum collected from two growth sites in the period of the withering of the epigeal part. From a sample collected in the upper reaches of the R. Tyup, Terskei-Alatau range of the Kirghiz SSR, in addition to aconitine and songorine [1] found previously, we have isolated napelline, a base with the composition $C_{19}H_{22}O_3N_2$, mp 120-122°C (methanol), and a new alkaloid $C_{34}H_{47}O_{12}N$ with mp 195-196°C (acetone), which we have called aconifine (I).

The base (I) contains a N-ethyl group, four methoxy groups, a benzoyl group, an acetyl group, and four hydroxy groups. Acetylation with acetyl chloride gave a tetraacetate. The mass spectrum of (I) is characteristic for alkaloids with the lycoctonine skeleton [2] and is similar to the spectrum of aconitine. The signal of the protons of the acetyl group appears in an unusually strong field at 1.26 ppm, which shows the presence of the acetyl group at C-8 and the benzoyl group at C-10 [3]. The maximum peak in the mass spectrum of aconifine is that of the ion M^+-91 $(M-60-31)$, and the next most intense is $M-109$ $(M-60-31-18)$. A similar pattern is found in the spectrum of aconitine. This is due to the presence of the acetyl group at C-8, a methoxy group at C-1, and a hydroxy group at C-3 [2, 4]. The one-proton doublet at 5.24 ppm (J 5 Hz) of the C-10 proton [3] in the NMR spectrum of (I) is shifted downfield by 0.44 ppm as compared with the same doublet in aconitine. The same shift of this signal is observed with the introduction of a hydroxy group into position 13 in eldeline, eldelidine, and dictyocarpine [5]. The presence of a doublet instead of the triplet characteristic for many Aconitum alkaloids shows the presence of a substituting group at C-9 or C-11.

On the basis of these facts, the partial structure (I) is proposed for aconifine.

From the tubers of Aconitum karakolicum collected in the Kirghiz SSR (Kungei-Alatau range) we have isolated songorine [1], karakoline (karacoline) [6], napelline, a base with mp 159-160°C (acetone), and a new alkaloid, $C_{22}H_{35}O_5N$, with mp 222-224°C (acetone), which we have called (karacolidine) (II).

Karakolidine contains N-ethyl, tertiary C-methyl, methoxy, and four hydroxy groups. Acetylation with acetyl chloride gave a tetraacetate. The mass spectrum of (II) corresponds to alkaloids with the lycoctonine skeleton [2]. The maximum peak in the spectrum is the M−17 ion, showing the presence of a hydroxy group at C-1 [2]. This was confirmed by the preparation of an internal α-carbinol amine ether $C_{22}H_{33}O_5N$, which has a characteristic mass spectrum [7]. The oxidation of (II) with Kiliani's solution gave didehydrokarakolidine, $C_{22}H_{31}O_5N$, mp 179-181°C (ether) in the IR spectrum of which absorption bands of carbonyl groups in five-membered (1760 cm^{-1}) and six-membered (1690 cm^{-1}) rings appeared. Consequently, in the base both hydroxy groups are secondary: one of them is located in one of positions 6, 10, and 12. The presence in the NMR spectrum of (II) of a one-proton triplet at 4.65 ppm (J = 4.5 Hz) excludes position 6 for a hydroxy group [8, 9]. This triplet is shifted downfield by 0.49 ppm as compared with karakoline, which shows the presence of a secondary hydroxy group at C-10 and a tertiary hydroxy group at C-13.



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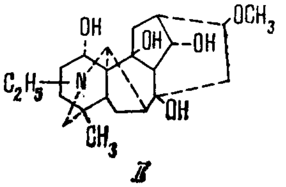

II

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Pyrolysis of the tetraacetate of (II) in vacuum, after the saponification of the reaction product, led to the formation of pyrokarakolidine, $C_{22}H_{33}O_4N$, with mp 174-186°C (ether–acetone, decomp.), which, on being boiled with a methanolic solution of perchloric acid, isomerized into isopyrokarakolidine with mp 118-122°C (hexane–chloroform). These facts permit the fourth hydroxy group to be assigned to C-8 and the methoxy group to C-15 [8, 9].

Consequently, karakolidine has the structure II.

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