ALKALOIDS OF Aconitum monticola

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From the roots of Aconitum monticola (Kuyandysai, Dzhungarian Ala-Tau), which has not previously been investigated, we have isolated songorine, norsongorine, bases with mp 146-151°C (acetone) and with mp 155-160°C (acetone), and also a new alkaloid with mp 208-210°C (acetone–methanol) with the composition $C_{25}H_{41}NO_7$, mol. wt. 467 (mass spectrometrically) which we have called acomonine(I).

The base (I) contains an ethyl, four methoxy, and three hydroxyl groups. The acetylation of (I) with acetic anhydride in pyridine gave a monoacetate (II) with mp 76-78°C (acetone), mol wt. 509. With p-toluenesulfonyl chloride, acomonine gave anhydroacomonine (III) with mp 129-132°C (acetone), IR spectrum: ν_{max}^{KBr} 3040 cm^{-1} (= CH); NMR spectrum: 5.82 ppm (1 H, multiplet) and 5.32 ppm (1 H, doublet, J = 10 Hz); mol. wt. 449. Substance (III) was hydrogenated by Adams method to deoxyacomonine (IV), mol wt. 451. Periodate oxidation of anhydroacomonine led to secodemethanolanhydroacomonine (V) with mp 155-158°C (hexane–acetone); mol. wt. 415. Consequently, in acomonine one hydroxy group is secondary and two are tertiary and they form an α-glycol system.

The results of a comparison of the empirical and expanded formulas of acomonine show that its skeleton consists of six rings. The IR spectrum of (V) shows the absorption bands of an α,β-unsaturated ketone in a six-membered ring and of a ketone in a five-membered ring at 1655 and 1735 cm^{-1}, respectively, and in the UV spectrum there is a maximum at 232 nm (log ε 3.87). The mass spectrum of (V) is very close to the spectrum of demethylenesecodemethanoldeoxydelcorine [1, 2]. These facts show that the base (I) contains the lycoctonine skeleton in which the ditertiary α-glycol system is located at C_7 and C_8 and one methoxy group at C_{15}.

The presence in the alkaloid of a skeleton consisting of 19 carbon atoms and of one ethyl group, and the absence of primary OH, NH, N$-CH_3$, and $>C-CH_3$ groups shows that the ethyl group (NMR spectrum: 1.13 ppm, 3 H, triplet) is attached to the nitrogen atom, and there is a methoxymethyl group at C_4. In the mass spectra of alkaloids of the lycoctonine type, the maximum peak is, as a rule, formed by the splitting off of the substituent from position 1 [3, 4]. In the mass spectrum of acomonine, the maximum is the peak of the M−15 ion, as in the spectrum of deoxycondelphine [3]. When (I) was treated with $KMnO_4$ in aqueous acetone solution, anhydrooxyacomonine (VI) was formed, with mp 204-206°C (acetone), mol. wt. 465, the IR spectrum of which showed absorption bands at 900 and 1000 cm^{-1}, which are characteristic for internal ethers of α-carbinolamines [5]. Substance (VI) was reduced by sodium tetrahydroborate to the initial base. Under the same conditions of oxidation, deoxyacomonine gave an oxo derivative (VII), mol. wt. 465, with a lactam carbonyl in a six-membered ring (ν_{max}^{KBr} 1630 cm^{-1}). The mass spectra of acomonine [M−15 (100%), M−17 (43%)], its anhydrooxy derivative [M−15 (100%)], and its monoacetate (II) [M−59 (100%)] and the facts given above permit the second hydroxy group to be located at C_3. This is confirmed by the NMR spectrum of (III) and also by the nature of the splitting of the signal of the hydroxy group of the geminal proton in the NMR spectrum of (II) (4.7 ppm, 1 H, quadruplet, $J_{AX} = 7$ Hz, $J_{BX} = 10$ Hz).

The NMR spectrum of acomonine has the signal of the geminal proton to the C_{10} methoxy group (3.6 ppm, 1 H, triplet, $J \approx 5$ Hz), showing the absence of substituents at C_9 and C_{11} [6].

On the basis of the above facts, the following partial structure is proposed for acomonine:

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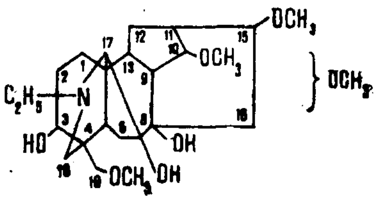

Work on determining the structure of acomonine is continuing.

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