ACETYLNAPELLINE – A NEW ALKALOID FROM Aconitum karakolicum

M. N. Sultankhodzhaev, L. V. Beshitaishvili,
M. S. Yunusov, and S. Yu. Yunusov

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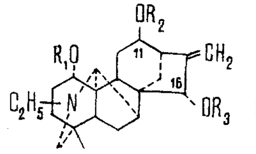
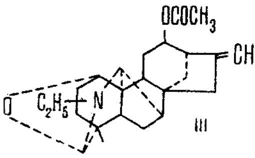
We have investigated the epigeal part of Aconitum karakolicum collected in the upper reaches of the R. Tyup (KirgSSR) in the budding period. The amount of combined alkaloids was 0.56% of the weight of the dry plant. The quantitative ratio and qualitative composition of the alkaloids of the epigeal part differed substantially from those for the tubers, in which the main component was aconitine [1]. By separating the mixture of bases we isolated songorine, napelline and a base with mp 205-206°C, but napelline proved to be the alkaloid present in greatest amount.

The base with mp 205-206°C had the composition $C_{24}H_{35}NO_4$ (I) and was readily soluble in chloroform and ethanol and less readily in acetone and ether. According to its NMR spectrum, the alkaloid contained a N-ethyl group (1.01 ppm, 3H, triplet), a tertiary C-methyl group (0.70 ppm, 3H, singlet), an acetoxy group (1.91 ppm, 3H, singlet), and a terminal methylene group. On acetylation with acetic anhydride in the presence of pyridine, it formed a diacetyl derivative (II) with mp 224-226°C (acetone) the NMR spectrum of which contained the signals of three acetoxy groups. Consequently, the developed formula of the base is: $C_{16}H_{20}(N-C_2H_5)\cdot(C-CH_3)(C=CH_2)(OCOCH_3)(OH)_2$. In the mass spectrum of the alkaloid, the maximum peak was that of the molecular ion, and there were also peaks of the ions M – 17, M – 43, and M – 59. Alkaline hydrolysis gave an amino alcohol which was identified as napelline. Consequently, the base was napelline monoacetate and it remained to determine the position of the acetoxy group. When (I) was oxidized with silver oxide, an anhydrohydroxy derivative was obtained with the composition $C_{24}H_{33}NO_4$ (III) the mass spectrum of which contained the peak of the ion M – 56, which is characteristic for analogous compounds [2]. The formation of this product shows that the hydroxy group at C-1 was not esterified. The choice between positions 11 and 16 was made by an analysis of the mass spectra of the base itself and of its diacetate.

It has been shown previously that an acetoxy group in position 16 leads to the intensive ejection of an acetyl radical [3]. In the mass spectrum of (II) a marked increase in the $M-CH_3CO$ peak (36%) was observed, while in the spectrum of (I) the peak of the ion $M-CH_3COO$ is second in intensity (41%) and the peak of the ion $M-CH_3CO$ has an intensity of 6%. These facts permit the acetoxy group to be located at C-11 and structure (I) to be suggested as the most probable one for the alkaloid





I. $R_1=R_3=H$; $R_2=COCH_3$
II. $R_1=R_2=R_3=COCH_3$

LITERATURE CITED

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