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THE STRUCTURE OF ACONORINE

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From the total alkaloids of the roots of Aconitum orientale Mill. [1] collected in the flowering period in the environs of Lake Gek-Gel (Kirovabad region, AzerbSSR), we have isolated a new amorphous base which we have called aconorine, composition $C_{32}H_{44}N_2O_7$ (I), mol. wt. 568. The perchlorate of the base has mp 237°C (with effervescence).

The IR spectrum of (I) has absorption bands at 1695 cm^{-1} (ester carbonyl) and 1595 cm^{-1} (aromatic ring). The NMR spectrum of the alkaloid, (JNM-4H-100/100 MHz, $CDCl_3$, internal standard HMDS, δ scale) contains the signals of an ethyl group (1.03 ppm, 3H, triplet), and acetyl group (2.19 ppm 3H, singlet), and two methoxy groups (3.24 and 3.31 ppm, two three-proton singlets). In the weak-field region there are the signals from four aromatic protons at 6.9-8.7 ppm.

The alkaline hydrolysis of aconorine in a 10% solution of caustic soda in aqueous ethanol gave the amino alcohol of the base, $C_{23}H_{37}NO_5$ (III) with mp 140-141°C (hexane–acetone) and an acid $C_9H_9NO_3$ with mp 172°C which was identified as acetylanthranilic acid. The amino alcohol contains an ethyl group, two methoxy groups, and three hydroxy groups. The mass spectrum of (II) is characteristic for alkaloids with the lycoctonine skeleton [2]. The results of the pyrolysis of diacetylaconorine (III) are in harmony with this.

The NMR spectrum of the pyrolysis product contains signals from only two acetyl groups and has retained the signals of the aromatic protons. In the region of olefinic protons (6.06-5.59 ppm) there is an unresolved two-proton signal the nature of the splitting of which coincides with that in the spectrum of isopyroacetylthalatisamine [3]. Thus, the pyrolysis product that we isolated is isopyroacetylaconorine (IV), and, consequently, in aconorine there is a hydroxy group at C_8 and a methoxy group at C_{15} [4].

In the NMR spectrum of (II) at 4.11 ppm there is a poorly resolved triplet with an intensity of one proton unit, J = 5 Hz, shifting in the spectra of the acetyl derivatives of (I) and (II) to 4.76 ppm, which shows the presence of a hydroxy group at C_{10} in aconorine [5].

In the mass spectrum of (II), the maximum peak is that of the ion M − 31, due to the detachment of the methoxy group at C_1 [2]. The results of a comparison of the relative intensities of the peaks M^+(4.3%), M − 15 (3.2%), and M − 31 (100%) permits the methoxy group at C_1 to be assigned the α orientation [6].

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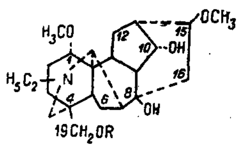
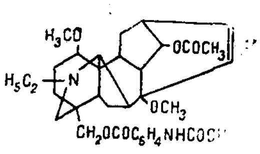


I R = $COC_6H_4NHCOCH_3$; II R = H



In view of the composition and the developed formula of (II) and the presence of a skeleton formed from nineteen carbon atoms, it may be assumed that there is a hydroxymethyl group at C_{19}. In the NMR spectrum of the diacetate of (I) at 3.96 ppm there is a broadened two-proton singlet, and in the NMR spectrum of the diacetate of (II) a two-proton singlet at 3.74 ppm. This signal is lacking from the NMR spectrum of (II), and therefore it can be assigned to the C_{19} methylene group.

The absence of NH and $N\text{-}CH_3$ groups from aconorine shows that the ethyl group is atached to the nitrogen atom.

The results of the pyrolysis reaction of (III) and the NMR spectra of (III) and of monoacetylaconorine show that the hydroxy groups at C_8 and C_{10} in aconorine are free and the acetylanthranilic acid is attached to the primary hydroxy group at C_{19}.

As Professor O. E. Edwards (Canada) has told us, a base which has been called columbianine, for which a structure identical with that of the amino alcohol (II) had been established had recently been isolated from Aconitum columbianum. A direct comparison of the two substances showed their identity.

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HAPLOBUCHARINE – A NEW ALKALOID FROM Haplophyllum bucharicum

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We have investigated the epigeal part of H. bucharicum collected in the fruit-bearing period (June 28–July 3, 1970) in the environs of Dekhkanabad, Kashkadar'inskaya oblast UzbSSR. The dry comminuted plant (85 kg) was wetted with 8% ammonia and extracted with chloroform. After the removal of the bucharaine [1] that had deposited (0.36% of the weight of the dry plant), the alkaloids were extracted from the concentrated chloroform extract (A) with 10% sulfuric acid. This gave the combined bases (0.04%), from which treatment with acetone isolated skimmianine [1] (0.009%). The dried acetone mother liquor was chromatographed first through alumina and then through silica gel. Ether eluates yielded a new base (I), with the composition $C_{19}H_{23}NO_2$ mp 126°C (ethyl acetate), mol. wt. 297 (mass spectrometry) which we have called haplobucharine. The alkaloid is readily soluble in organic solvents and dilute acids. On TLC in the toluene–ethyl acetate–formic acid (5 : 4 : 1) system it gives a single spot with R_f 0.55, it does not fluoresce in UV light, and it is revealed with the Dragendorff reagent.

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