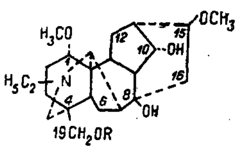
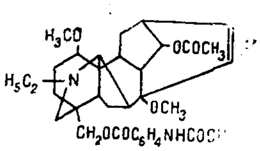


I R = $COC_6H_4NHCOCH_3$; II R = H



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-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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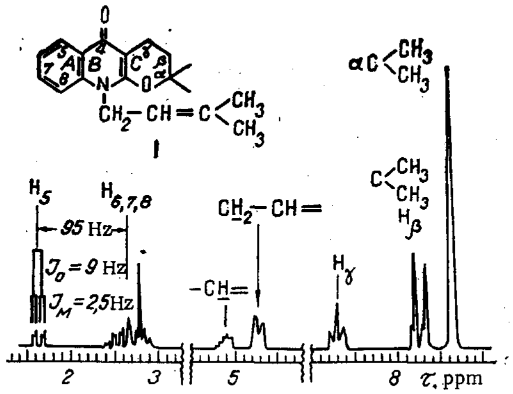

Fig. 1. NMR spectrum of haplobucharine.

The IR spectrum of (I) has maxima at (cm^{-1}) 1625, 1610, 1590, 1550, 1540, and 1500 of almost equal intensities, which is characteristic for the 2-alkoxy-4-quinolones [2]. Absorption maxima of active hydrogens are absent. The UV spectrum [λ_{max} 214, 238, 250 infl., 317, 329 nm (log ε 4.10, 4.12, 3.90, 3.74, 3.73)] almost coincides with that of N-methylhaplofoline [3]. Furthermore, in an acid medium the hypsochromic shift of the spectral curve that is characteristic for 4-quinolones [2] is observed.

Mass spectrum of (I) (m/e,%): 297 (M^+, 56), 229 (40), 228 (57), 214 (15), 212 (47), 200 (13), 186 (70), 174 (100), 69 (70). All the peaks with the exception of M^+ and that of the ion with m/e 69 are also present in the mass spectrum of haplofoline and that of dihydroflindersine [4].

In the NMR spectrum of (I) ($CDCl_3$, τ scale) (Fig. 1) there are the signals of four adjacent aromatic protons at 1.67 (1H, quadruplet, H_5) and 2.58 (3H, multiplet, $H_{6,7,8}$). The shift of the H_5 signal relative to the center of the multiplet of the other aromatic protons by 95 Hz in the downfield direction confirms the 4-quinolone structure of the base [5]. Also in the spectrum are signals at 4.90 (1H, triplet, J = 7.5 Hz), 5.25 (2H, doublet, J = 7.5 Hz), and 8.19 and 8.31 (singlets, 3H each) – isopentyl group attached to an aromatic system through a heteroatom. Chemical shifts of 7.31 (2H, triplet, J = 7 Hz, Hγ), 8.22 (2H, triplet, J = 7 Hz, Hβ), and 8.63 ppm [6H, singlet, $\alpha C(CH_3)_2$] are characteristic of an α,α-dimethyldihydropyran ring and almost coincide with those of N-methylhaplofoline [6]. The NMR spectrum of (I) shows that the side chain cannot be present in rings A and C, and the only position remaining for it is on the nitrogen atom. Consequently only structure (I) is possible for haplobucharine.

The remaining chloroform extract (A) after drying, was separated into basic, acidic, and neutral fractions. From the acid fraction by chromatography from alumina and then on silica gel we obtained bucharidine [1] (0.03%), and from the neutral fraction bucharaine [1] (0.004%) and flindersine [7] 0.007%). This is the first time that flindersine has been detected in this plant.

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