HAPLATINE — A NEW ALKALOID FROM *Haplophyllum latifolium*

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We have investigated the leaves of *H. latifolium* collected in the period of vigorous flowering and the beginning of fruit bearing of the plant (May 13, 1974) in the Chimkent oblast, Ostantsovye mountains, Alimtau, "Syrdar'ya" sovkhoz [state farm]. The comminuted plant was extracted with methanol. The methanol was evaporated off and the residue was treated with 10% of sulfuric acid from which, after the addition of an excess of ammonia, the alkaloids were extracted with ether. When the ethereal solution was concentrated, crystals of skimmianine (I) deposited in an amount of 0.27% of the weight of the dry plant [1]. The mother solution after the isolation of (I) was chromatographed on alumina. The first eluates yielded another 0.03% of (I), and the subsequent ethereal fractions a new base (II) with the composition $C_{18}H_{19}O_5N$, mp 139-140°C (benzene), M^+ 329, which we have called haplatine. The alkaloid is readily soluble in organic solvents and dilute acids and is insoluble in water and aqueous alkali.

The IR spectrum of (II) showed maxima at (cm^{-1}) 3340 (OH group), 3170, and 3140 (furan ring). The UV spectrum [λ_{max} 252, 320, 335 nm (log ε 4.87, 3.82, 3.80)] resembled the UV spectrum of the furanoquinoline alkaloids of the skimmianine type [2]. The NMR spectrum of (II) ($CDCl_3$ τ scale) showed protons from a furanoquinoline nucleus at 2.15, 2.89, and 2.52, 3.08 (two pairs of doublets, J = 10 and 3 Hz, respectively, $H_{5,6}$ and $H_{\alpha,\beta}$), two methoxy groups at 5.69 and 5.95 (singlets, 3H each), and also a $-O-CH_2-CH=C(CH_3)(CH_2OH)$ side chain at 4.40 (triplet, 1H, J = 6.5 Hz), 5.25 (doublet, 2H, J = 6.5 Hz), 5.81 (singlet, 2H), 8.20 (singlet, 3H), and 7.14 ppm (broadened singlet, 1H, OH). Mass spectrum of (II), m/e (%): 329 (M^+, 18), 245 (100), 244 (52); 230 (30), 227 (98), 216 (35), 202 (20).

The properties given are similar to those for 7-isopentenyloxy-γ-fagarine [3], from which (II) differs by a hydroxymethyl group in place of a methyl group.

The acetylation of (II) with acetic anhydride in pyridine gave a monoacetyl derivative (III), with mp 87-88°C (acetone–ether), composition $C_{20}H_{21}O_6N$, mol. wt. 371 (mass spectrometry), ν_{max} 1740 cm^{-1} ($R-OCOCH_3$).

The NMR spectrum of (III) differs from that of haplatine only by the absence of the proton of the hydroxy group, by a downfield shift of the signal of the protons of the methylene group geminal to the acetyl group by 0.41 ppm, and by a signal at 8.00 ppm from the protons of the $O-CO-CH_3$ group. The maximum ion with m/e 127 in the mass spectrum of (III) arising as a result of β-cleavage confirms the structure of the side chain.

The hydrolysis of (III) with concentrated hydrochloric acid yielded haplopine (IV), identified by comparison with an authentic sample.

Consequently, haplatine has the structure (II). (See scheme on the following page).

Haplatine has not been found previously in the plant *H. latifolium* collected in the Tashkent oblast.

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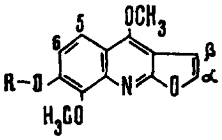

I. $R = CH_3$

II. $R = CH_2{-}CH{=}C\begin{smallmatrix}\nearrow CH_2{-}OH\\ \searrow CH_3\end{smallmatrix}$

III. $R = CH_2{-}CH{=}C\begin{smallmatrix}\nearrow CH_2{-}O{-}Ac\\ \searrow CH_3\end{smallmatrix}$

IV. $R = H$

LITERATURE CITED

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