COMPONENTS OF *Haplophyllum obtusifolium*

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Skimmianine, folimine, benzamide, and new alkaloid haplotusine (mp 118-119°C, $C_{11}H_{11}NO_3$, M^+ 205) have been isolated from the epigeal part of *Haplophyllum obtusifolium* Ledeb. growing in the environs of Kora-Koly, Turkmen SSR. By the analysis of spectral characteristics it has been established that haplotusine has the structure of 1,4-dimethoxy-2-quinolone.

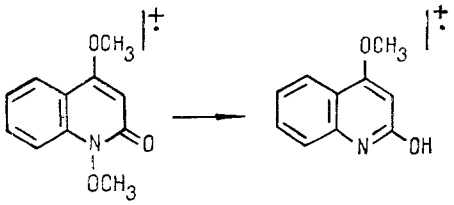
We have investigated the chemical composition of the epigeal part of *Haplophyllum obtusifolium* Ledeb. collected in the flowering phase in the environs of Kora-Koly, Turkmen SSR. By chromatographing the basic fraction of a methanolic extract of the plant, the known compounds skimmianine, folimine [1], and benzamide, and a new alkaloid with mp 118-119°C which has been called haplotusine, have been obtained.

Haplotusine (I) is optically inactive, has the composition $C_{11}H_{11}NO_3$, and contains no active hydrogen atoms. The presence of a strong band of an amide carbonyl at 1670 cm^{-1} in the IR spectrum of (I) and characteristic maxima in the 262-290-nm region of the IR-spectral curve which did not change on acidification and alkalinization, gave grounds for concluding that the alkaloid isolated was a derivative of the 4-alkoxy-2-quinolone series.

The PMR spectrum of haplotusine clearly showed the signals of four adjacent aromatic protons at 7.75 ppm (quadruplet, 1 H, J_{ortho} = 9 Hz, J_{meta} = 2.5 Hz, H_5), 7.41 ppm (multiplet, 2 H, $H_{6,7}$), 7.07 (multiplet, 1 H, H_8), of a proton at C_3 of a quinolone nucleus at 5.89 ppm (singlet, 1 H, H_3), and of two methoxy groups at 3.96 and 3.83 ppm (two singlets of 3 H each). The absence of substituents in positions 3, 5, 6, 7, and 8 permitted the conclusion that haplotusine had the structure of 1,4-dimethoxy-2-quinolone.

The proposed structure of haplotusine agrees well with the results obtained in a study of its mass spectrum and the spectrum of the direct analysis of daughter ions (DADI) of M^+ and a number of fragmentary ions. The main ion peaks in the mass spectrum of (I) were the following: m/z (%) 205 (M^+, 55), 175(100), 160(14), 146(28), 132(35), and 117(45). The spectrum of haplotusine did not contain the peak of the $(M - 15)^+$ ion that is characteristic for 2-quinolone alkaloids with methoxy substituents in various positions of the benzene ring [2].

The DADI spectrum of M^+ of haplotusine showed only one peak — of an ion with m/z 175 corresponding to the elimination of a formaldehyde molecule at the expense of a methoxy group attached to a nitrogen atom, with migration of the hydrogen atom to the amide carbonyl.



I, M^+ m/z 175

Other fragments arose in the fragmentation of the M — 30 ion and its daughter ions, as is observed in the fragmentation of the molecular ion of 4-methoxy-2-quinolone. The DADI

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spectrum of the ion with m/z 175 is characterized by the peak of ions formed on the ejection of a formyl radical (m/z 146), of a formaldehyde molecule (m/z 145), and of a methyl radical and a carbon monoxide molecule simultaneously (m/z 132), and by the peak of an ion with m/z 119.

Thus, the alkaloid haplotusine isolated from *H. obtusifolium* has the structure of 1,4-dimethoxy-2-quinolone with an unusual position, among quinoline alkaloids, of a methoxy group at the nitrogen atom.

EXPERIMENTAL

The spectra of the substances were obtained on Hitachi EPS-3T, UR-20 (KBr), MKh-1303, JNM-4H-100/100 MHz (δ scale, $CDCl_3$, HMDS), and Varian MAT-3H instruments. For TLC (type L 5/40 silica gel with the addition of 5% of gypsum), the toluene–ethyl acetate–formic acid (5:4:1) solvent system was used, and the substances were revealed with the Dragendorff reagent and with iodine vapor.

Isolation of the Alkaloids. The comminuted epigeal part (4 kg) was extracted with methanol. The solvent was driven off by distillation in vacuum. The extract was separated into basic (3 g), acidic (9 g), and neutral (150 g) fractions. The basic fraction was chromatographed on a column of alumina. The ethereal eluates yielded substances in the following sequence: skimmianine, folimine, haplotusine, and benzamide.

Skimmianine, mp 175-176°C, and folimine, mp 138-139°C, were identified by a direct comparison with authentic samples.

Benzamide, mp 120-121°C. UV spectrum: $\lambda_{max}^{C_2H_5OH}$ 227 nm (log ε 4.22). IR spectrum, ν_{max}: 1580, 1630, 1660, 3185, 3375 cm^{-1}. Mass spectrum, m/z (%): 121(M^+, 86), 105(100), 77(100).

Haplotusine, mp 118-119°C, was soluble in chloroform and dilute acid and, on heating in water and dilute alkali. UV spectrum: $\lambda_{max}^{C_2H_5OH}$ 230, 271, 280, 320 nm (log ε 4.77, 3.90, 3.90, 3.84). IR spectra: λ_{max} 1500, 1570, 1600, 1670 cm^{-1}.

Mass Spectrum of 4-Methoxy-2-quinolone: m/z (%) 175(M^+, 100), 146(15), 132(29), 117(30).

CONCLUSION

The epigeal part of *Haplophyllum obtusifolium* Ledeb. growing in the environs of Kora-Koly, Turkmen SSR, has yielded skimmianine, folimine, benzamide, and the new alkaloid haplotusine, for which the structure of 1,4-dimethoxy-2-quinolone has been established.

LITERATURE CITED

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