9. E. Wenkert, J. S. Bindra, C. J. Chang, D. W. Cochran, and F. M. Schell, Accounts Chem. Res., 7, 46 (1974).
10. L. Simeral and G. E. Maciel, Org. Magn. Res., 6, 223 (1974).
11. H. W. Avdovich and G. A. Neville, Can. J. Spectroscopy, 28, No. 1, 1 (1983).
12. F. W. Wehrli and T. Nishida, Fortschr. Chem. Org. Naturst., 36, 158 (1979).
13. F. W. Wehrli and T. Wirtlin, Interpretation of Carbon-13 NMR Spectra, Heyden, London (1976).
14. E. Breitmaier and W. Voelter, ^{13}C-NMR Spectroscopy, Verlag Chemie, Weinheim (1974).
15. F. I. Carrol, D. Smith, M. E. Waii, and C. G. Moreland, J. Med. Chem., 17, 985 (1974).
16. F. I. Caroll, A. Philip, and N. C. Coleman, Tetrahedron Lett., 1757 (1976).
17. M. Fuyita, M. Nagai, and T. Inoue, Chem. Pharm. Bull. (Tokyo), 30, No. 4, 1151 (1982).

ALKALOIDS OF Haplophyllum leptomerum.

I. THE STRUCTURE OF LEPTOMERINE

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From the epigeal part of the plant Haplophyllum leptomerum Lincz. et Vved. growing in the mountains of Babatag, Tadzhik SSR, which has not been studied previously, have been isolated β-sitosterol, the known alkaloids γ-fagarine, skimmianine, and N-methyl-2-phenyl-4-quinolone, and the new alkaloid leptomerine. On the basis of spectral characteristics, the structure of N-methyl-2-propyl-4-quinolone has been established for leptomerine.

Of 23 species of plants of the genus Haplophyllum growing on the territory of Central Asia, eight have not so far been studied by anyone. These include, in particular, Haplophyllum leptomerum Lincz. et Vved. We have begun the study of the alkaloid composition of the epigeal part of this plant collected by S. A. Khamidkhodzhaev in Babatag, Tadzhik SSR, in the budding period on May 20, 1984.

An ethanolic extract of the raw material was treated with ether, and from this the alkaloids were extracted in the usual way. The combined ether-extracted alkaloids were separated by chromatography on a column of silica gel. Ethereal eluates yielded the known alkaloids γ-fagarine, skimmianine, and N-methyl-2-phenyl-4-quinolone, and chloroform eluates, a new base which has been called leptomerine (I). β-Sitosterol was isolated from the neutral ether-soluble fraction of the extract with the aid of column chromatography. All the known substances were identified by TLC and mixtures with authentic specimens.

Leptomerine has mp 147-148°C (acetone) and is readily soluble in acids, chloroform, and ethanol and less readily in acetone and ether, and it is insoluble in water and alkalis.

The UV spectrum of (I) had the following absorption bands: λ_{max} 213, 230.5, 285.5, 294 nm (log ε 3.63, 3.61, 3.31, 3.40); λ_{min} 219, 246, 289 nm (log ε 3.42, 2.06, 3.24). On alkalinization the spectrum did not change, but in an acid medium the double maximum of the longwave band underwent a hypsochromic shift and was observed in the form of a single maximum at 273.5 nm. Such behavior is typical for the 2-alkyl-4-quinoline alkaloids containing an alkyl group at the nitrogen atom [1]. The IR spectrum of (I) contained absorption bands at 1635, 1600, and 1580 cm^{-1} of approximately equal intensity, which is characteristic for compounds of the 4-quinoline series [2].

In the PMR spectrum of leptomerine, the signals of the protons of an unsubstituted benzene ring of a 4-quinolone were observed at δ 8.34 ppm (q, 1H, J_{ortho} = 9 Hz, J_{meta} = 3 Hz; H_5) and 7.42 ppm (m, 3H, $H_{6,7,8}$); of a proton at C_3 with δ 6.11 ppm (s, 1H); of the protons of a

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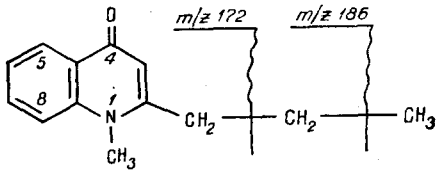
N-methyl group with δ 3.62 ppm (s, 3H) and of a propyl chain with δ 2.59 ppm (t, 2H, J = 7.5 Hz; Ar–CH_2), 1.63 ppm (m, 2H, CH_2), and 0.99 ppm (t, 3H, J = 7.5 Hz, CH_3). The shift of the H_5 signal relative to the center of the $H_{6,7,8}$ multiplet served as another confirmation of the 4 quinolone structure of (I) [3], and the presence in the leptomerine spectrum of the signal of a proton at C_3 in the form of a singlet indicated that the propyl substituent in its molecule was present at C_2. Consequently, leptomerine has structure (I), which agrees well with its mass spectrum.



I, M^+ 201

The main peaks in the spectrum of (I) are those of the molecular ion with m/z 201 (100%) and of an ion with m/z 173 (100%). The further fragmentation of the ion with m/z 173, corresponding to the molecular ion of 1,2-dimethyl-4-quinolone, took place in analogy with the breakdown of this compound [4], with the formation of the peaks of ions with m/z 145 (69%), 144 (56%), 130 (59%), and 77 (45%). The appearance in the spectrum of leptomerine of the peaks of ions with m/z 186 (38%) and 172 (19%) confirmed the presence of a propyl chain in its molecule. The mass spectrum of (I) also has the strong peak of an ion with m/z 158 (28%) formed from the ion with m/z 186 by the elimination of carbon monoxide.

EXPERIMENTAL

The UV spectrum was taken on a EPS-3T spectrophotometer (Hitachi) in ethanol, the PMR spectrum on a JNM-4H-100/100 MHz spectrometer in $CDCl_3$ with HMDS as internal standard, and the mass spectrum on a MKh-1310 instrument (temperature of the inlet system 100°C, ionizing voltage 50 V, emission current 40 μA). For TLC (silica gel 5/40 μm) we used the solvent system toluene–ethyl acetate–formic acid (5:4:1).

Isolation of the Substances. The raw material (2.5 kg) was extracted with ethanol. After the elimination of the ethanol, the extract was treated with ether (A). The ethereal solution was extracted with 10% aqueous sulfuric acid until the alkaloids had been removed completely. The acid solution was made alkaline with concentrated ammonia and was exhaustively extracted with ether (0.72 g) and then with chloroform (0.65 g). The combined ether-extracted alkaloids were separated on a column of silica gel. Ether eluted successively γ-fagarine (15 mg), mp 141-142°C (acetone), skimmianine (50 mg), mp 176-177°C (acetone), and N-methyl-2-phenyl-4-quinolone (10 mg), mp 118-119°C (acetone), and chloroform eluted leptomerine (20 mg). After the alkaloids had been extracted, the ethereal solution (A) was concentrated and the residue was chromatographed on a column of alumina. Ether eluted β-sitosterol (50 mg) with mp 139-140°C (acetone).

SUMMARY

1. From the epigeal part of the plant Haplophyllum leptomerum Lincz. et Vved. have been isolated β-sitosterol, the known alkaloids γ-fagarine, skimmianine, and N-methyl-2-phenyl-4-quinolone, and the new alkaloid leptomerine.

2. On the basis of spectral results, the structure of N-methyl-2-propyl-4-quinolone has been established for leptomerine.

LITERATURE CITED

1. R. Tschesche and W. Werner, Tetrahedron, 23, 1873 (1967).
2. I. A. Bessonova and S. Yu. Yunusov, Khim. Prir. Soedin., 303 (1977).
3. A. V. Robertson, Aust. J. Chem., 16, 451 (1963).
4. J. A. Lamberton, Aust. J. Chem., 19, 1995 (1966).