4. M. V. Telezhenetskaya and A. L. D'yakonov, Khim. Prir. Soedin., 309 (1987).
5. L. E. Sutton, Tables of Interatomic Distances and Configuration in Molecules and Ions, Special Publication No. 18, The Chemical Society, London (1965).
6. G. V. Garner, O. Meth-Cohn, and H. Suschitsky, J. Chem. Soc. (C), 1234 (1971); A. M. Monro and M. J. Sewell, Tetrahedron Lett., 595 (1969).
7. S. R. Johns, J. A. Lamberton, and H. Suares, Aust. J. Chem., 38, 1007 (1985).
8. N. K. Hart, S. R. Johnes, and J. A. Lamberton, Aust. J. Chem., 24, 223 (1971).
9. V. I. Andrianov, Z. Sh. Safina, and N. L. Tarnopol'skii, Zh. Strukt. Khim., 15, 911 (1974).
10. M. Yang, Y. Chen, and L. Huang, Phytochemistry, 27, 445 (1988).

# ALKALOIDS OF Haplophyllum bungei

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The alkaloids dictamnine, skimmianine, folimine, robustinine, and 4-methoxy-2-quinolone, found for the first time in plants of the genus Haplophyllum and the new alkaloid haplobungine, for which the structure of 4,7,8-trimethoxy-2-quinolone has been established, have been isolated from the epigeal part of the plant Haplophyllum bungei Trautv. growing in the Moiynkumy desert, Chimkent province, Kazakh SSR.

Continuing a systematic study of plants of the genus Haplophyllum [1] we have subjected to chemical investigation the epigeal part of H. bungei Trautv, collected in the flowering period in the Moiynkumy desert, Chimkent province, Kazakh SSR. The plant H. bungei grows in Central Asia in sandy deserts [2] and belongs to the Haplophyllum species with low levels of alkaloids [3]. Skimmianine, dictamnine, robustinine and an unidentified base with mp 83°C have been isolated previously from this plant gathered on the territory of the Karakalpak Ust-Urt [5], where it forms pure thickets [4].

The comminuted raw material was extracted with methanol. The total alkaloids were obtained by the method generally adopted, these making up 0.08% of the mass of the dry epigeal part. Column chromatography of the mixture of alkaloids gave dictamnine, skimmianine, robustinine, folimine, a base with the composition $C_{12}H_{13}NO_4$, mp 174-175°C (I), and a substance with mp 254-255°C which was identified by spectral characteristics as 4-methoxy-2-quinolone.

Alkaloid (I) was new and was given the name haplobungine. Its UV spectrum had absorption maxima in the 219, 231, 251 (inflection), 288, 313, and 323 nm regions and did not change on acidification and alkylinization – properties characteristic for alkaloids of the 4-alkoxy-2-quinolone series. In the IR spectrum, a broad maximum was observed at 3175 $cm^{-1}$ (NH) and intense absorption at 1660 $cm^{-1}$ (amide carbonyl of a 2-quinolone). The NMR spectrum of haplobungine confirmed that it was a 4-alkoxy-2-quinolone derivative, since the spectrum contained the one-proton singlet at 5.74 ppm from H-3 that is characteristic for this group of substances [6]. The other signals – a one-proton broad signal at 8.65 ppm (NH), two doublets at 7.50 and 6.78 ppm with an ortho-splitting constant (J = 9 Hz), and two singlets at 3.90 (3 H) and 3.87 (6 H) – permitted the proposal of the structure of 4,7,8-trimethoxy-2-quinolone for the alkaloid isolated (see scheme on following page).

The results obtained do not exclude the alternative 4,5,6-trimethoxy-2-quinolone structure for haplobungine, and we therefore methylated (I) and obtained the N-methyl derivative (II), the spectral characteristics and melting point of which were identical with those published for 4,7,8-trimethoxy-N-methyl-2-quinolone isolated from Spathelia sorbifolia [7].

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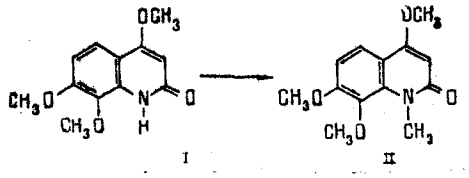

I II

The mass spectrum of the above-mentioned crystalline substance with mp 83°C obtained previously from this plant [5] show that it was a mixture of three compounds: 4-methoxy-2-quinolone, 4,8-dimethoxy-2-quinolone (robustinine) and 4,8-dimethoxy-N-methyl-2-quinolone (folimine). All three substances were isolated by the chromatography of this mixture and were identified by direct comparison with authentic samples. Consequently, all the alkaloids that we had isolated with the exception of haplobungine were present at the same low concentration in H. bungei plants gathered in Karakalpakia. It was thereby established that, in contrast to other plants of the genus Haplophyllum [8] the quantitative and qualitative composition of the alkaloids in Haplophyllum bungei varied little according to its growth site.

This is the first time that 4-methoxy-2-quinolone has been detected in plants of the genus Haplophyllum.

## EXPERIMENTAL

The spectra of the substances were obtained on the following instruments: Hitachi EPS-3T (ethanol); UR-20 (KBr); BS-567A, 100 MHz (δ scale, $CDCl_3$, O—HMDS): and MKh-1310. For TLC (alumina LSL 5/40 μm, neutral; silica gel LS 5/40 μm) the following solvent systems were used: 1) chloroform—acetone (6:1); and 2) toluene—ethyl acetate—acetic acid (5:4:1).

Isolation of the Alkaloids. The dry comminuted epigeal part (550 g) was extracted with methanol. The total alkaloids (0.47 g) were obtained from the evaporated extract in the usual way and they were chromatographed on alumina. The substances were eluted with system 1. This gave dictamnine, mp 132-133°C (12 mg); skimmianine, mp 176-177°C (28 mg); folimine, mp 139-140°C (67 mg); crystalline fractions containing robustanine and haplobungine; and 4-methoxy-2-quinolone, mp 254-255°C (23 mg). Treatment of the crystalline fractions (124 mg) with ethyl acetate led to the isolation of robustinine, mp 231-232°C (28 mg). The ethyl acetate mother liquor was chromatographed on a column of alumina. Crystals of haplobungine (32 mg) were obtained from the first eluates.

Haplobungine. mp 174-175°C (from ethyl acetate). Mass spectrum, m/z (%): 235 ($M^+$, 100). 234 (25), 220 (65), 206 (22), 192 (22).

N-Methylhaplobungine. Freshly calcined potash (0.1 g) and methyl iodide (1 ml) were added to a solution of haplobungine (10 mg) in dry acetone (15 ml), and the mixture was heated in the water bath for 20 h and was then cooled and filtered. The residue obtained after the solvent has been distilled off was chromatographed on silica gel with elution by system 1. The eluates yielded N-methylhaplobungine with mp 143-144°C (from petroleum ether). Mass spectrum, m/z (%): 249 ($M^+$, 81), 248 (37), 234 (100), 220 (25).

4-Methoxy-2-quinolone. mp 254-255°C (from ethanol), identified by direct comparison with a sample obtained from dubinidine [9].

The separation of the crystalline mixture with mp 83°C, obtained previously [5], by the method described above, gave folimine, robustinine, and 4-methoxy-2-quinolone.

## SUMMARY

The known alkaloids dictamnine, skimmianine, folimine, robustinine, and 4-methoxy-2-quinolone, and the new alkaloid haplobungine, for which the structure of 4,7,8-trimethoxy-2-quinolone has been established, have been isolated from the epigeal part of the plant Haplophyllum bungei Trautv, growing in the Moiynkumi desert, Chimkent province KazSSR.

## LITERATURE CITED

1. I. A. Bessonova and S. Yu. Yunusov, Khim. Prir. Soedin., 736 (1986).
2. The Flora of the USSR [in Russian], Izd. Akad. Nauk SSSR, Moscow—Leningrad, Vol. XIV (1949), p. 222.

3. G. P. Sidyakin, Author's abstract of doctoral dissertation [in Russian], Tashkent (1966).
4. A. Kholmuradov, Author's abstract of Candidate's dissertation [in Russian], Tashkent (1971).
5. D. Kurbanov and S. Yu. Yunusov, Khim. Prir. Soedin., 289 (1967).
6. T. P. Toube, J. W. Murphy, and A. D. Cross, Tetrahedron, 23, 2067 (1967).
7. R. Storer and D. W. Young, Tetrahedron, 29, 1721 (1973).
8. D. M. Razakova, I. A. Bessonova, Kh. A. Abdullaeva, and S. Yu. Yunusov, Khim. Prir. Soedin., 395 (1983).
9. G. P. Sidyakin, M. Eskairov, and S. Yu. Yunusov, Dokl. Akad. Nauk UzSSR, No. 8, 27 (1958).

# NMR INVESTIGATION OF ALKALOIDS.

## X. $^{13}C$ NMR SPECTRA AND STRUCTURE OF ALKALOIDS OF THE 5,6,7,8-TETRAHYDROFURANOQUINOLINE TYPE

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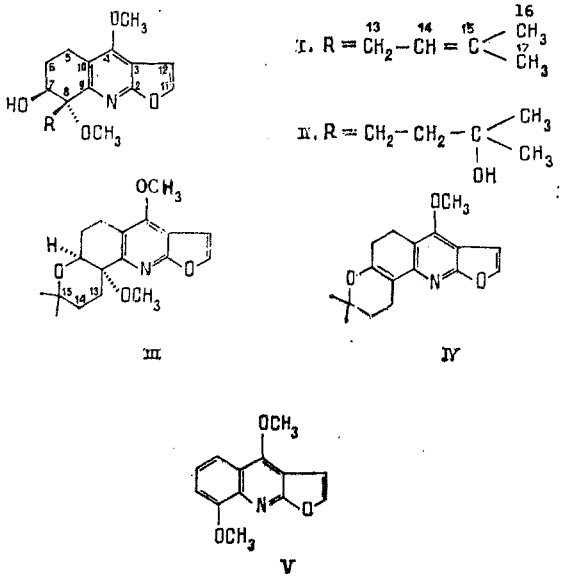
UDC 547.944.1.92

On the basis of a study of the spin-spin coupling constants $J_{CH}$ and the $^{13}C$ chemical shifts of haplophyllidine an assignment has been made of the signals of the carbon atoms of the 5,6,7,8-tetrahydrofuranoquinoline alkaloids haplophyllidine, perforine, anhydroperforine, their derivative (IV), and the furanoquinoline base γ-fagarine.

Haplophyllidine (I), perforine (II), and anhydroperforine (III) are the first derivatives of the new 5,6,7,8-tetrahydrofuroquinoline series of alkaloids. Their structures, established by chemical transformations, interconversions, and the method of spectral analysis [1-3] have been confirmed by the X-structural investigation of anhydroperforine [4].




There is information in the literature on a study of the $^{13}C$ NMR spectra of a number of furanoquinoline alkaloids [5, 7] and also of modified derivatives – perfamine and

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