b is the loss in weight on drying, %; and

K is a correction factor, equal to 1.12.

The metrological characteristics of the method are given below

f	$\bar{X}$	S^2	$\pm S$	P	$t(Pf)$	$\pm \Delta X$	$\pm E\%$	$\frac{Em\%}{m=3}$
9	0.0123	$7{,}85\cdot10^{-8}$	$2{,}81\cdot10^{-4}$	95	2,26	$6{,}34\cdot10^{-4}$	5,16	2 98

It was found that the amount of vincamajine in the herbage of the larger periwinkle in the phase of the second autumn flowering was 0.0123%, calculated on the absolutely dry raw material.

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HAPLAPHINE – A NEW ALKALOID OF Haplophyllum perforatum

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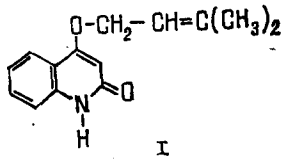
The epigeal part of the plant Haplophyllum perforatum (M.B.) Kar. et Kir. was collected by K. Taizhanov in the Dzhambul province, Kazakh SSR, close to the Kuyuk Pass in the flowering phase on June 17, 1984. The air-dry epigeal part (3100 g) was extracted by steeping with ethanol eight times. The treatment of a small amount of the evaporated ethanolic extract with 10% sulfuric acid showed that the alkaloids were not extracted by an acid solution, and the extract of the raw material, after the ethanol had been distilled off, was therefore boiled with ether. The concentrated ethereal extract was chromatographed on a column of silica gel. The first ethereal eluates yielded the lignan eudesmin, mp 105-106°C (acetone), and the later ones the alkaloid haplamine, mp 201-202°C (decomp., ethanol), with yields of 0.02 and 0.07%, respectively, on the weight of the dry raw material. The mother liquor from the haplamine, after its recrystallization, was chromatographed twice on silica gel. Ethereal eluates yielded 15 mg of a substance with mp 159-160°C (acetone), M+ 229 (mass spectrometry), which we have called haplaphine (I).

The IR spectrum of (I) contained absorption bands at 3160 and 1665 cm^{-1} (–NH–CO–). UV spectrum of (I), λ_{max}, nm: 215, 225, 229, 238 shoulder, 267, 277, 317, 328, which is typical for 4-alkoxy-2-quinolone alkaloids and, like the latter, did not change on acidification and alkalinization [1].

In the PMR spectrum of (I) ($CDCl_3$, 0 – HMDS, taken on a BS 567A 100 Mz instrument) there were signals at the following δ values (ppm): 1.73 and 1.79 (s, 3 H each, $=C(CH_3)_2$); 4.62 and 5.50 (d, 2 H, J = 6.8 Hz and t, 1 H, J = 6.8 Hz, $O-\underline{CH_2}-CH=$); 5.97 (s, 1H, proton at C-3 of a quinolone nucleus); 7.27 and 7.86 (m, 3 H, and dd, 1 H, aromatic protons at C-6, 7, and 8 and at C-5); 12.11 (br.s, 1 H, NH).

The facts given above indicate that haplaphine has has the structure of 4(γ,γ-dimethylallyloxy)-2-quinolone (I).



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This was confirmed by the mass spectrum of the alkaloid, in which the strongest peaks belonged to the molecular ion (m/z 229, 42%) and ions with m/z 162 (40%), 161 (100%), and 69 (70%), formed as the result of the cleavage of the O–C allyl bond, which is typical for allyl aromatic ethers.

The ether-insoluble fraction of the extract of the epigeal part was then treated with chloroform. Chromatography of the chloroform fraction yielded heplamine (0.026% on the dry weight of the raw material). Known substances were identified by direct comparison.

Thus, the epigeal part of the H. perforatum investigated contained 0.1% of alkaloids. The negative qualitative reaction for alkaloids that we recorded in an analysis of the plant is due to the absence of skimmianine and of other acid-soluble quinoline alkaloids that are characteristic of H. perforatum from other growth sites [1]. The main alkaloid quantitatively was the pyrano-2-quinolone alkaloid haplamine [1] (the new alkaloid haplaphine was present in trace amounts – less than 0.0005%), which, like amine alkaloids and other alkaloids of neutral character is insoluble in acid and is not detected by the usual method.

The results of this work form one more clear example of the fact that the question whether a plant contains alkaloids or not can be answered only after its complete investigation.

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ALKALOIDS OF Nitraria schoberi. STRUCTURE OF NITRAROXINE.

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Structure (Ia) has been proposed in [1] for the alkaloid nitraramine N-oxide (I) from the epigeal part of Nitraria schoberi, this being a hydroxylamine derivative of nitraramine (Ib). Recently [2], on the basis of an x-ray structural investigation of a crystalline salt, structure (II) was proposed for nitraramine. In the present communication we give the results of a chemical correlation of (I) with nitramine.

The composition of the molecular ion was established by high-resolution mass spectrometry as $C_{15}H_{24}N_2O_2$ (M^+ 264.1838), including one atom oxygen more than in nitraramine. A strong (~40% [1]) peak of the $(M - 17)^+$ ion in the spectrum of (I) was due to the ejection of a hydroxy group, since it had the composition $C_{15}H_{23}N_2O$ (247.1811). The rest of the fragmentation was similar to that in the spectrum of nitraramine.

The PMR spectrum of (I) ($CDCl_3$, 0 – HMDS, δ scale) contained signals due to: an equatorial proton at C_7 geminal to an ether oxygen (4.19 ppm, m, 1 H, $W_{1/2}$ = 7 Hz); a proton at C_{17} (4.00 ppm, d, 1 H, ^3J = 2.5 Hz); equatorial protons at C_3 and C_{15} in the α-positions to nitrogen atoms (3.20 ppm, d, 2 H, ^2J = –12 Hz); an axial proton at C_{15}(2.87 ppm, s, 1 H); and axial protons at C_3 and C_{15} (2.55 ppm, m, 2 H). The remaining protons gave a methylene hump in the 2.00-1.00 ppm region. It must be mentioned that the signal of the proton at C_7 was shifted upfield (Δδ 0.18 ppm) in relation to that in the spectrum of nitraramine [2] because of a decrease in the spatial descreening influence of the lone pair of electrons of the nitrogen atom in the hydroxylamine grouping of (I). Furthermore, in the spectrum of (I) the screening of the signal of the C_1 proton, as compared with that if nitraramine was observed (Δδ = 0.41 ppm).

In the spectrum of (I) taken in trifluoroacetic acid, there were considerable downfield shifts of the signals of the methine protons of the α-carbon atoms. The singlet C_1–H resonated in the 3.77 ppm region, and the signal from C_{17}–H appeared at 4.64 ppm. A small

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