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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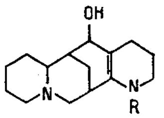
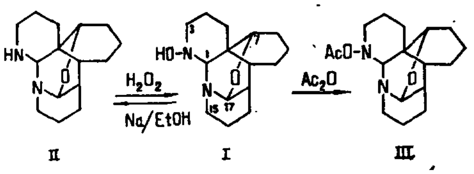
($\Delta\delta \sim 0.20$ ppm) was also experienced by the signals of the protons of the α-methylene groups. The chemical shift of the broadened signal from the C_7–H proton at 4.16 ppm scarcely changed its value with a change in the solvent.



Ia. R = OH
Ib. R = H



When (I) was acetylated with acetic anhdyride in the presence of pyridine at room temperature, a mono-O-acetyl derivative (III, M^+ 306) was obtained, in the IR spectrum of which, in place of the band of active hydrogen, intense absorption had appeared at 1747 cm^{-1}.

Reduction of (I) by the Bouveault–Blanc method with sodium in absolute ethanol led after 30 min to the formation of nitraramine (II, M^+ 248, IR spectrum). The reverse reaction was performed by oxidizng (II) with a 5% solution of hydrogen peroxide at room temperature for a day.

Thus, the facts given above on the chemical transformations and spectral characteristics of nitraramine N-oxide, and also the correlation with nitraramine, permit the conclusion that this base has the structure of 2-hydroxynitraramine (I). Since the previous name does not reflect the actual structure of the alkaloid, we consider it desirable to introduce a new name — nitraroxine.

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