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ALKALOIDS OF *Nitraria sibirica*

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Continuing the separation of the combined alkaloids of the epigeal part of the plant *Nitraria sibirica* Pall. collected in the environs of the village of Rybach'e, Kirghiz SSR, we have isolated three more bases in addition to those obtained previously [1].

Base (I) with the composition $C_{15}H_{24}N_2O$, mp 82-84°C (petroleum ether), $\alpha[_D]+0°$ was isolated from the combined ether-extracted material of the plant collected in May, 1976 (yield of the total material 0.33%). The UV spectrum of (I) showed no absorption. In the IR spectrum of the alkaloid, together with other bands, the absorption of active hydrogen was seen (3535 and 3290 cm^{-1}). The PMR spectrum of (I) contained, in addition to a group of signals in the strong-field region (0-3.00 δ, $CDCl_3$), signals at 4.38 ppm (br.s) and 4.01 ppm (d). The mass spectrum of (I) showed the peaks of ions with m/z 248 (M^+ 100%), 231, 219, 205, 204, 191, 190, 177, 176, 163, and 150. The facts given above permitted (I) to be identified as nitraramine [2], previously isolated from *Nitraria schoberi*. A mixed sample gave no depression of the melting point.

Extraction of the epigeal part of *Nitraria sibirica* collected on September 9, 1978, yielded 0.28% of combined alkaloids. From the water-soluble fraction of the total ether-extraction material, by chromatography on a column of silica gel we isolated a base (II) with the composition $C_{11}H_{10}N_2O_2$, mp 204-205°C, $[\alpha]_D$ −91° (c 0.32; chloroform). The IR spectrum of (II) contained absorption bands of active hydrogen (3200 cm^{-1}), of an amide carbonyl group (1640 cm^{-1}), and others. The PMR spectrum contains signals at 8.10 and 7.61 ppm (aromatic protons), and also a group of multiplets in the medium-field region which are characteristic for a pyrrolidinoquinazoline nucleus. The mass spectrum of (II) showed the peaks of ions with m/z 202 M^+ (100%), 185, 174, 168, 146, 130, 129, 119, 103, and 102. Such fragmentation is characteristic for pyrrolidinoquinazoline alkaloids of the vasicinone type [3]. In actual fact, a comparison of the elementary composition, spectral characteristics, and R_f values of compound (II) with those of the alkaloid L-vasicinone showed their identity. A mixture gave no depression of the melting point. This is the first time that L-vasicinone has been isolated from plants of the genus *Nitraria*.

We isolated the same alkaloid from an extract of the plant *Cynomorium songaricum*, which is parasitic on *Nitraria* (collected in the environs of the village of Kaktal, Taldy-Kurgan province, KazSSR, June 3, 1980).

By the extraction of 7 kg of leaves and 16 kg of stems of *Nitraria sibirica* (collected in May, 1980 in the budding stage), we obtained, respectively, 0.7% and 0.18% of total alkaloids on the mass of the dry raw material. From the water-soluble fraction of the combined ether-extracted material from the leaves we isolated base (III) with the composition $C_{10}H_{19}NO$, mp 75-76°C, $[\alpha]_D$ ±0°. The IR spectra of (III) showed the absorption band of active hydrogen (3320 cm^{-1}). The mass spectrum of (III) showed peaks of ions with m/z 169 M^+ (100%), 151, 150, 136, 123, 122, 110, and 96. Such fragmentation is characteristic for the alkaloids nitramine and isonitramine [1]. Since the composition and molecular weight agreed with those of nitramine and isonitramine but at the same time compound III was optically inactive, we assume that it is the racemic form of one of the two bases. The spectral characteristics (IR, PMR) of (III) proved to be identical with those of nitramine. Thus, base (III) is the previously undescribed racemic form of nitramine and has the structure (+)-2-azaspiro[5.5]undecan-7-ol.

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CHROMATOGRAPHIC BEHAVIOR OF HALIDE SALTS OF ALKALOIDS ON ALUMINA

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In medical practice, alkaloids are usually used in the form of salts of mineral acids. These salts are checked for foreign impurities, mainly accompanying alkaloids, by chromatographic analysis. The amount of impurities is evaluated from the sensitivity of their detection and the amount of substance in the sample deposited. With a low sensitivity of detection (50-100 μg), 1000 and more micrograms of substance is deposited in a single point on the starting line of the chromatogram in order to detect the minimum amount of impurities.

We have observed that in this case the halide salts of alkaloids, after chromatography on a nonfixed layer of alumina are revealed by the Dragendorff reagent in the form of two spots: a main spot and a spot at the start the shape and size of which are equal to the deposited spot. The longer the chromatogram with the deposited sample was dried the clearer did the spot at the start become. In view of the fact that alumina is an active ion-exchange material [1], we assumed that during the drying of the deposited sample a reaction takes place between the salt of the alkaloid and the solvent. The alkaloid formed as the result of the reaction migrates on the plate in the form of the free base and the halide ion remains at the start and is revealed by the Dragendorff reagent in the form of a yellow spot. This assumption was confirmed by a series of experiments, which showed the following facts. The halide salts of alkaloids (hydrochlorides, hydrobromides) and the bases obtained from these salts have the same R_f values.

The reaction between the salt of an alkaloid and the sorbent takes place quantitatively. To show this, a section of the sorbent from the start after chromatography and the elimination of the solvents was eluted with water until the reaction for the halide ion was negative. The amount of halide ions was determined in the eluate by the mercurimetric method. A control experiment was performed in parallel. In all cases an amount of halide ions equivalent to the amount deposited was found at the start. The decomposition of the alkaloid salts takes place on "for chromatography" alumina with different pH values of a 10% aqueous suspension: 4-5, 6.7-7.5, and 9-10.

The sensitivity of the detection of chloride and bromide ions by the Dragendorff reagent is 500 μg.

We used systems of solvents containing chloroform, acetone, and ethanol in various proportions. The above-mentioned observations were checked on the following salts: deoxypeganine hydrochloride, lycorine hydrochloride, and galanthamine hydrobromide.

Thus, when halide salts of alkaloids in amounts greater than 500 μg are chromatographed on alumina, the decomposition of the salt and the appearance of an additional spot of the halide ions at the start must be taken into account.

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