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ALKALOIDS OF *Buxus sempervirens*

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The alkaloids of *Buxus sempervirens* L. (common box) cultivated in the environs of the town of Kislovodsk had not been studied. We have begun an investigation of the alkaloids of this plant collected on May 21, 1978. The amounts of alkaloids were determined by chloroform extraction: in shoots of the first year — 2.39%; in young roots — 2.11%; in leaves and small branches — 1.64%: in the flowers 1.94%; and in branches several years old 1% of total alkaloids.

The etheral part of the total alkaloids isolated from 16 kg of thin branches and leaves was dissolved in benzene and was separated according to basicity by McIlvaine's solutions at pH 8.0-2.2 (pH interval 0.2).

The combined fractions of the total alkaloids with pH 8.0-7.4, 7.2-7.0, and 6.8-6.4 were chromatographed separately on a column of alumina (Brockmann activity grade II). Elution was carried out with ether—ethanol containing increasing concentrations of ethanol — 10, 20, 30, and 40%. In this way, bases were isolated with mp 241-243°C (ethanol), $[\alpha]_D$ +98.52°C (c 0.601; chloroform), $C_{25}H_{42}N_2O$ (I) mp 228-230°C (ethanol), $[\alpha]_D$ +68.78° (c 0.875; chloroform), $C_{26}H_{46}N_2O$ (II); and mp 200-202°C (ethanol); $[\alpha]_D$ +102.88° (c 0.522; chloroform), $C_{28}H_{50}N_2$ (III).

The mother liquor from the alkaloids (I), (II), and (III) was treated with acetone. The acetone-soluble part of the combined material was chromatographed on a column of alumina with eluation by ether—ethanol (4:3) and (1:1), fractions 1-8 were rechromatographed on a column of silica gel with elution by hexane—ether—ammonia (5:4:0.25) and (5:4:0.5).

The hexane—ether—ammonia (5:4:0.5) fraction yielded a base with mp 127-129° (ethanol) (IV).

Alkaloid (I) was identified as cyclobuxine D, (II) as cyclovirobuxine D, and (III) as cycloprotobuxine A (melting points and IR, NMR, and mass spectra of (I-III) and their derivatives) [1-3].

The IR spectrum of base (IV) contained absorption bands at 3030 and 1462 cm^{-1} (methylene of a cyclopropane ring), 3320 cm^{-1} (hydroxy group), and 2930 cm^{-1} (CH_2, CH_3). The main peaks in the mass spectrum are those of ions with m/z 57, 58, 70, 71, 72 (100%), 106, 365, 386, 400, and M^+ 430, which are characteristic for the mass-spectrometric fragmentation of the cycloprotobuxines [4]. From its spectral characteristics, this alkaloid was assigned to the bases of the 9β,19-cyclo-5α-pregnane type, which differs from the alkaloids of the *Buxus* genus isolated previously.

Thus, cyclobuxine D, cyclovirobuxine D, cycloprotobuxine A, and a base with mp 127-129°C have been isolated from *Buxus sempervirens* L.

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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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