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ALKALOIDS OF Nitraria komarovii.

IX. STRUCTURE OF KOMAROINE

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Continuing a study of the alkaloids of the epigeal part of the plant *Nitraria komarovii* Iljin et Lava [1], collected in June, 1978, in the environs of Krasnovodsk, the ethereal material of the pH 4 fraction from the polybuffer separation of the mixture of bases has been subjected to chromatographic separation. Chloroform, and then mixtures of chloroform and methanol in various proportions were used to elute the substances from the column. The chloroform eluate yielded a new alkaloid with the composition  $C_{28}H_{18}N_2$ , mp 144-145°C (petroleum ether-CH<sub>2</sub>Cl<sub>2</sub>), which has been named komaroine (I).

The mass spectrum of (I) contained, in addition to others, the peaks of ions with m/z 286 (M<sup>+</sup>), 271 (M - 15), 257 (M - 29), and 243 (M - 43), showing the presence of a propyl group in the molecule.

The PMR spectrum of the alkaloid contained, in addition to the signals in the aromatic region, signals at 0.85 ppm (triplet, 3 H,  $-CH_2-CH_3$ ), 2.58 ppm (triplet, 2 H,  $Ar-CH_2-CH_2-CH_3$ ), and 1.58 ppm (multiplet, 2 H,  $-CH_2-CH_2-CH_3$ ). These results permitted the conclusion that (I) contained a N-propyl group bound to an aromatic ring.

The UV spectrum of (I) taken in ethanol exhibited absorption maxima with  $\lambda_{max}$  215, 235, 235, 280, 290, 350 nm (log  $\varepsilon$  4.44, 4.42, 4.12, 4.12, 3.81), which in an acid medium underwent bathochromic shifts to  $\lambda_{max}$  216, 255, 265, 310-318, 382 nm. This behavior of the spectrum and the region of appearance of the maxima are characteristic for  $\beta$ -carboline derivatives.

The IR spectrum of (I) contained absorption bands of the bonds of a o-disubstituted benzene ring (750 cm<sup>-1</sup>), of an indole nucleus (1460, 1505, 1570, 1630 cm<sup>-1</sup>), and of saturated C-H bonds (2860, 2870, 2930, and 2965 cm<sup>-1</sup>).

When the dehydrogenation reaction of the alkaloid nitrarine (II) was studied, among the products a compound identical with komaroine was detected. It has been shown previously that the dehydrogenation of (II) with selenium takes place with the cleavage of the  $N_4-C_{21}$  bond in the initial stages of the reaction [2]. There is information in the literature that the dehydrogenation of decahydroquinolines takes place in some cases with the cleavage of the piperidine ring and the ejection of ammonia [3]. It is easy on the basis of these facts to explain the formation of komaroine from nitrarine when the latter is dehydrogenated with selenium or sulfur.

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No migration of the propyl group apparently takes place, otherwise we should have expected the formation of a substance with an isopropyl substituent.

Thus, the alkaloid komaroine has the structure of  $1-(3'-propylphenyl)-\beta$ -carboline.

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STRUCTURE OF STENANZAMINE

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The new alkaloid stenanzamine  $C_{2,7}H_{4,3}NO_2$  (I) has been isolated previously from the epigeal part of *Rhinopetaleum stenantherum* Regel [1]. The IR spectrum of the base contained absorption bands at (cm<sup>-1</sup>) 3400, 1070 (OH), 2940-2860, 1430 (-CH<sub>3</sub>; -CH<sub>2</sub>), 2775 (trans-quinolizidine), and 1660 (C=C). Stenanzamine instantaneously decolorized a dilute solution of potassium permanganate. As in korseveridine and severzine, the double bond in (I) was not hydrogenated in acetic acid in the presence of platinum black [2, 3].

The mass spectrum of (I) (taken on an MKh-1310 instrument) showed the peaks of ions with m/z 98, 111, 112, 125, 137, 138, 139, 149, 150, 164, 166, 178, 190, 358, 359, 384, 385, 386, 395 (M - 18)<sup>+</sup>, 396 (M - 17)<sup>+</sup>, 398 (M - 15)<sup>+</sup>, 413 M<sup>+</sup> (100%), which are characteristic for the C-nor-D-homosteroid alkaloids of the cevine group [2-4].

The PMR spectrum (CDCl<sub>3</sub>) contained a singlet at 0.93 ppm (3H, 19-CH<sub>3</sub>), doublets at 1.00 and 1.82 ppm (21-CH<sub>3</sub>; and 27-CH<sub>3</sub>), and the signals from two protons geminal to hydroxy groups at 3.78 and 3.58 ppm.

The action on (I) of acetic anhydride in the presence of pyridine formed diacetylstenanzamine (II), M<sup>+</sup> 497. In the IR spectrum of (II) there were absorption bands at (cm<sup>-1</sup>) 2775 (trans-quinolizidine), 1740, 1245, and 1030 (ester C=0) but no absorption bands of hydroxy groups. The PMR spectrum of (II) contained a singlet at 0.88 ppm (19-CH<sub>3</sub>), doublets at 0.93 and 0.82 ppm (21-CH<sub>3</sub> and 27-CH<sub>3</sub>); and signals from two methyls of acetyl groups at 1.95 ppm and from protons geminal to acetoxy groups at 4.65 and 4.92 ppm.

The results of a discussion of the IR, mass, and PMR spectra of compound (I) and (II) permitted us to suggest for (I) the heterocyclic skeleton of cevanine [2-4] with two secondary hydroxy groups and a tetrasubstituted double bond.

The absorption bands in the IR spectra of (I) and (II) at 1070 and 1030 cm<sup>-1</sup>, respectively, showed that one of the hydroxy groups was located at  $C_3$  and had the  $\beta$  orientation. This was confirmed by the presence of a multiplet at 4.65 ppm from the  $3\alpha$ -H atom in the PMR spectrum of diacetylstenanzamine [5, 6].

Stananzamine was not oxidized by periodic acid, which shows the absence of vicinal hydroxyls.

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