ALKALOIDS OF *Nitraria komarovii.*

VII. STRUCTURE AND SYNTHESIS OF KOMAROVININE

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The new alkaloid komarovinine has been isolated from the total ether-extracted alkaloids of the epigeal part of *Nitraria komarovii*. It has also been found among the products of the dehydrogenation of nitrarine by selenium and sulfur. On the basis of the available facts, the structure of one of the isomers of 1-quinolinyl-β-carboline was proposed for komarovinine. A direct comparison with synthetic samples shows the identity of the alkaloid to 1-(quinolin-6'-yl)-β-carboline. 1-(Quinolin-7'-yl)-β-carboline, not previously described in the literature, has been characterized.

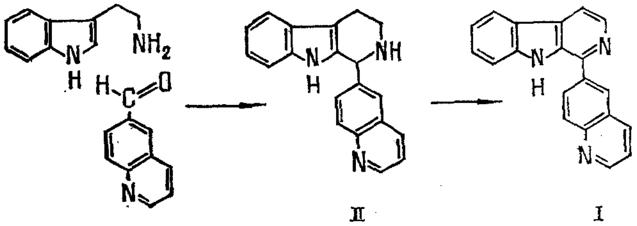
Continuing the separation of the mixture of alkaloids from the epigeal part of *Nitraria komarovii* Iljin et Lava [1], with the aid of the column chromatography of the combined ether-extracted alkaloids we have isolated a new optically inactive crystalline base with the composition $C_{20}H_{13}N_3$, mp 239-240°C (CH_2Cl_2) and have called it komarovinine (I).

The mass spectrum of (I) contains two main peaks (M^+ 295 and M^{++} 147.5). The UV spectrum of the alkaloid shows the following absorption maxima: λ_{max} 225, 272, 296, 370 nm (log ε 4.60; 4.31; 4.19; 4.00), which on acidification undergo bathochromic shifts, $\lambda_{max}^{ethanol + H^+}$ 225, 254, 284, 316, 400 nm.

Analysis of the PMR and IR spectra showed the total aromaticity of the molecule of (I). The composition and mass-spectrometric fragmentation of (I) coincide with those of the alkaloids komarovine [1, 2] and isokomarovine [3]. In addition, we have succeeded in detecting not only komarovine but also a substance identical with komarovinine among the products of the dehydrogenation of nitrarine [4] with selenium and sulfur.

It follows from what has been said above that (I) has the structure of one of isomeric β-carbolinylquinolines.

With the aim of a direct comparison, we have synthesized a number of such isomers. From a mixed melting point and spectral characteristics, (I) proved to be identical with 1-(quinolin-6'-yl)-β-carboline. The synthesis (see scheme) was carried out by Pictet-Spengler method from tryptamine and quinoline-6-carbaldehyde.



EXPERIMENTAL

UV spectra were recorded on a Hitachi EPS-3T spectrophotometer, IR spectra on a UR-20 instrument (KBr tablets), mass spectra on an MH-1310 spectrometer, and PMR spectra on a JNM-4H-100/100 MHz instrument in chloroform–methanol with HMDS as internal standard.

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For TLC we used type KSK silica gel. The following systems of solvents were used for chromatography: 1) benzene–chloroform (8:1); 2) chloroform–acetone–methanol (5:4:1); 3) benzene–methanol (4:1); and 4) chloroform–acetone–methanol–ammonia (5:4:1:0.1).

Komarovinine (I). The combined ether-extracted alkaloids (15 g) of the plant collected in May, 1976, were chromatographed on a column of silica gel in system 1. Fractions with a volume of 100 ml each were collected. Fractions 30-45, enriched with komarovinine, were rechromatographed with elution by system 2 (10-ml fractions). Base (I) was isolated from fractions 24-31. After recrystallization from petroleum ether–benzene and then from methylene chloride, it had mp 239-240°C, composition $C_{20}H_{13}N_3$. Here and below, the results of analyses corresponded to the calculated figures.

6-Methylquinoline was synthesized from p-toluidine by the Skraup method.

Quinoline-6-carbaldehyde. A mixture of 10 g of 6-methylquinoline and 8.5 g of selenium dioxide was heated to 170°C. After the burner had been removed, the temperature rose through the heat of the reaction to 215°C. When the mixture had cooled to 190°C, it was reheated to 210°C and was kept at this temperature for 20 min. After cooling, the aldehyde was extracted from the residue with benzene. The yield was 7.68 g (70%), mp 54-55°C.

1-(Quinolin-6'-yl)-3,4,5,6-tetrahydro-β-carboline (II). A mixture of 2 g of tryptamine hydrochloride, 4 g of quinoline-6-carbaldehyde, and 8 ml of 2 N sulfuric acid in 40 ml of water was heated at 110°C for 1.5 h. The cooled solution was made alkaline with 15% caustic soda and the reaction product was extracted with ether and chloroform, giving 1.85 g (62%) of technical (II).

1-(Quinolin-6'-yl)-β-carboline (I). A ground mixture of 800 mg of (II) and 400 mg of sulfur was heated at 180-200°C for 0.5 h. The cooled mass was dissolved in 10% sulfuric acid and filtered, the filtrate was washed with ether and was then made alkaline with a 15% solution of caustic soda, and the product was extracted with ether and then with chloroform. After recrystallization from methylene chloride, 400 mg (51%) of (I) was obtained with mp 238-240°C, composition $C_{20}H_{13}N_3$.

Quinoline-7-carboxylic Acid (III) [5]. By the Skraup reaction, from 20 g of m-aminobenzoic acid and 45 mg of glycerol we obtained 10.2 g of quinoline-5-carboxylic acid (IV) [3]. The filtrate after the separation of the (IV) was evaporated to a volume of 70-75 ml. The precipitate that then deposited was filtered off, and after recrystallization from ethanol 3 g (12%) of (III) with mp 250-251°C was obtained.

3-[β-(Quinolin-7'-carboxamido)ethyl]indole (V). A ground mixture of 1.6 g (0.01 mole) of triptamine and 2 g (0.012 mole) of (III) was heated in a sand bath at 200-210°C for 1.5 h. After cooling, the fused mass was treated with acetone. The precipitate that deposited was treated with methylene chloride, giving 1.5 g (46%) of technical (V).

1-(Quinolin-7'-yl)-5,6-dihydro-β-carboline (VI). A mixture of 1.5 g of (V) in 8 ml, or $POCl_3$ was boiled under reflux for 1.5 h. After cooling, the excess of $POCl_3$ was decomposed with ice water. The aqueous solution was made alkaline with 15% caustic soda and the reaction product was extracted with ether and then with chloroform. This gave 650 mg (42%) of technical (VI).

1-(Quinolin-7'-yl)-β-carboline (VII). A carefully ground mixture of 650 mg (0.0022 mole) of (VI) and 400 mg of sulfur was heated at 180-200°C for 30 min. The product was isolated in a similar manner to that described for the 8'- isomer [1]. This gave 300 mg (46.3%) of technical (VII). After recrystallization from CH_2Cl_2, mp 213-214°C, M^+ 295.

SUMMARY

The structure of a new alkaloid from the epigeal part of *Nitraria komarovii*, komarovinone, has been shown as 1-(quinolin-6'-yl)-β-carboline, and its synthesis has been performed.

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SUBHIRSINE — A NEW ALKALOID FROM THE ROOTS OF *Convolvulus subhirsutus*

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The roots of *Convolvulus subhirsutus* collected on the territory of the Chimkent Province (Kazakh SSR) have yielded a new dimeric alkaloid of the tropane series — subhirsine with mp 190-191°C, composition $C_{33}N_{40}O_9N_2$. Its structure has been established.

Previously, in a study of the alkaloids of the roots of *Convolvulus subhirsutus* Regel et Schmalh. collected in the environs of the village of Dzhilga, Chimkent Province, Kazakh SSR, in the phase of the vigorous growth of the plant, by separating the mixture of bases, into phenolic and nonphenolic fractions, we isolated five alkaloids: convolvine, convolamine [1], phyllalbine [2], convolidine [3], and confoline [4].

From the nonphenolic fraction of the combined material after separation by citrate-phosphate solution with pH 6.8 and with 10% sulfuric acid (fraction A), we obtained fraction B [4]. The latter was chromatographed on a column of silica gel. From ethereal eluates we isolated a base with mp 190-191°C (acetone), R_f 0.27 (system 1), readily soluble in chloroform and less readily in acetone and ether. We have called it subhirsine (I).

The mass spectrum of (I) shows the peak of the molecular ion (M^+ 608) and the peak of a doubly charged ion with m/z 304, confirming the molecular weight of the alkaloid can be seen, and also the peaks of ions with m/z 443, 426, 320, 304, 290, 261, 182, and 165, together with those characteristic for tropane nucleus.

The IR spectrum of the alkaloid shows the absorption bands of a conjugated ester carbonyl group (1710 cm^{-1}), of an amide carbonyl (1645 cm^{-1}), and of a 1,2,4-trisubstituted benzene ring (827, 880, 1600 cm^{-1}). The nature of the substitution in the aromatic nucleus was confirmed by the NMR spectrum of (I), which contains the signals from H_a and H_b protons in the 7.42-7.62 ppm region (4 H, m) and of H_c at 6.82 ppm (2 H, d). The signals of methine protons on the $C_{3\alpha}$ position (5.25 ppm, 2 H, t), from C_1 and C_5 protons (4 H, m), and from the protons of aromatic methoxy groups (3.84 ppm, 12 H, s) were also found.

The results of the mass spectroscopy of (I), its high molecular weight, and its even-numbered mass indicate the dimeric nature of the alkaloid. A comparison of the IR and NMR spectra of (I) and of convolvine shows that they are very similar, on which basis it may be assumed that subhirsine in all probability consist of two convolvine structural units. The absence from the IR spectrum of the absorption band of active hydrogen and the detection of a strong band of an amide carbonyl group indicates the nature of the bond of the two equivalent halves of convolvine through nitrogen atoms by means of a carbonyl group. Such a hypothesis required confirmation by chemical reactions, and for this purpose we performed the alkaline hydrolysis of subhirsine. On hydrolysis, an acid was isolated from the acid fraction and was identified from its R_f value and by a mixed melting point as veratric acid. From the amino alcohol fraction a substance (II) was obtained with mp 260°C and a molecular weight of 280 (mass-spectrometrically).

The IR spectrum of (II) showed bands of active hydrogen (3390 and 3455 cm^{-1}) and the absorption band of an amide carbonyl group (1615 cm^{-1}). A diacetyl derivative of the amino alcohol (II) was obtained, with mp 136-137°C (III).

Because of the poor solubility of the amino alcohol (II) in organic solvents, the NMR spectrum of its diacetyl derivative was taken, which clearly showed signals from the protons of a tropane nucleus and of the protons of two acetyl groups (2.01 ppm, 6 H, s). All these

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