

porated off, and the residue was recrystallized from methanol. This gave 180 mg of cyclosieversigenin 3-O- β -D-xylopyranoside (IV) with mp 259-261°C, $[\alpha]_D^{20} +42.0 \pm 2^\circ$ (c 0.60; methanol), identical with an authentic sample [2] according to R_f value and IR spectral characteristics.

SUMMARY

Two new glycosides, cyclosieversiosides A and C, have been isolated from the roots of the plant *Astragalus sieversianus* Pall. It has been shown that cyclosieversioside A is cyclosieversigenin 3-O-(2',3'-di-O-acetyl- β -D-xylopyranoside) 6-O- β -D-xylopyranoside and cyclosieversioside C is cyclosieversigenin 3-O-(2'-O-acetyl- β -D-xylopyranoside) 6-O- β -D-xylopyranoside.

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ALKALOIDS OF *Nitraria komarovii*.

V. STRUCTURE AND SYNTHESIS OF KOMAROVICINE

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The new alkaloid komarovicine has been isolated from the epigeal part of the plant *Nitraria komarovii* Iljin et Lava. Its structure has been established on the basis of spectral and experimental results and its synthesis has been performed. A transition has been made to the alkaloids komarovine and komarovidine isolated previously.

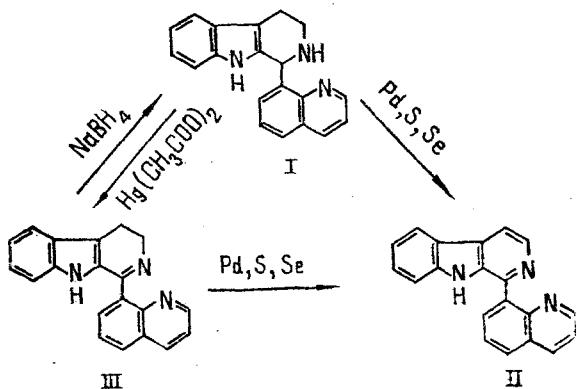
Continuing an investigation of the alkaloids of *Nitraria komarovii* Iljin et Lava [1], from the combined fractions with pH 5, 6, and 7 after the separation of komarovine [2] and komarovidine [3], by chromatography on a column we have isolated a base with mp 209-210°C (CH_2Cl_2) having the composition $\text{C}_{20}\text{H}_{11}\text{N}_3$, $[\alpha]_D \pm 0^\circ$, which we have called komarovicine (I).

In the mass spectrum of the alkaloid there are the peaks of the ions with m/z 299 (M^+ , 100%), 283 (20), 282 (52), 281 (44), 271 (30), 270 (28), 269 (54), 149.5 M^{++} .

In the UV spectrum there are absorption maxima characteristic for indole and quinoline: $\lambda_{\text{max}}^{\text{ethanol}} 220, 275-286, 294, 318$ ($\lg \epsilon 4.75, 4.14, 4.13, 3.68$), $\lambda_{\text{max}}^{\text{ethanol}+\text{H}^+} 225, 272, 283, 316$. The IR spectrum contains the absorption bands due to an indole nucleus (1460, 1505, 1580, 1620, cm^{-1}) and to methylene and methine groups (2860, 2940 cm^{-1}).

The PMR spectrum contains, in addition to a complex group of signals in the aromatic region, two two-proton multiplets at 2.81 and 2.99 ppm ($\text{Ar}-\text{CH}_2-\text{CH}_2-\text{N}^{\text{H}}-$) and two one-

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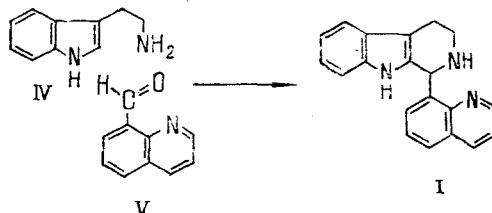


Scheme 1

proton signals at 3.21 and 6.28 ppm ($\text{N}-\text{H}$, $\text{Ar}-\text{C}-\text{H}$).

The composition of komarovicine differs from that of komarovine (II) [1, 2] by four hydrogen atoms. The dehydrogenation of the (I) led to (II). When komarovidine (III) [1, 3] was reduced with sodium tetrahydroborate, komarovicine was formed. The reverse reaction took place under the action of mercuric acetate (scheme 1).

On the basis of the experimental and spectral results we proposed for komarovicine the structure of 1-(quinolin-8'-yl)-3,4,5,6-tetrahydro- β -carboline. We synthesized a compound of this structure from quinoline-8-carbaldehyde and triptamine by the Pictet-Spengler method (scheme 2).



Scheme 2

Quinoline-8-carbaldehyde was obtained by the oxidation of 8-methylquinoline with selenium dioxide, the 8-methylquinoline having been synthesized from o-toluidine by the Skraup method.

The product (I) obtained proved to be identical in its physicochemical properties and spectral characteristics to the natural alkaloid komarovicine. Thus, the structure of 1-(quinolin-8'-yl)-3,4,5,6-tetrahydro- β -carboline has been established unambiguously for komarovicine.

EXPERIMENTAL

UV spectra were obtained on a Hitachi EPS-3T spectrophotometer in ethanol, IR spectra on a UR-20 spectrometer using KBr tablets, mass spectra on a MKh-1303 instrument, and PMR spectra on a JNM-4H-100/100 MHz spectrometer in CDCl_3 - CD_3OD with HMDS as internal standard.

For TLC we used silica gel L 5/40 μm and the following solvent systems: 1) chloroform-acetone-methanol (5:4:1); 2) chloroform-acetone-methanol-ammonia (5:4:1:0.1); 3) chloroform-acetone-ethanol-ammonia (7:2:1:0.1); and 4) benzene-ethyl acetate-diethylamine (7:2:1).

Komarovicine. The combined fractions with pH 5, 6, and 7 after the separation of the komarovine and komarovidine [1] were chromatographed on a column of silica gel, with elution by system 1. The fractions enriched with komarovicine were rechromatographed on a column using system 2. This gave 0.1 g (0.00035% of the weight of the dry raw material) of a base with mp 209–210°C (CH_2Cl_2), composition $\text{C}_{20}\text{H}_{17}\text{N}_3$. Here, and below, the analyses corresponded to the calculated figures.

Passage from Komarovicine to Komarovine. A ground mixture of 20 mg of (I) and 20 mg of Pd black was heated at 180-200°C for 30 min. After cooling, the mixture was dissolved in chloroform and the catalyst was filtered off. The filtrate was evaporated and the residue was recrystallized from methylene chloride to give 11 mg (56%) of (II) with mp 229-230°C.

Passage from Komarovidine to Komarovicine. Sodium tetrahydroborate was added portion-wise in a total amount of 100 mg to a solution of 25 mg of (III) in 5 ml of absolute ethanol. The mixture was stirred at room temperature for 1 h, and the solvent was distilled off, the excess of reagent in the residue was carefully decomposed with water, and the reaction product was extracted with ether. This gave 16 mg (60%) of an alkaloid with mp 208-210°C. The melting point of a mixture with komarovicine showed no depression. The analogous reaction using methanol as solvent gave a less satisfactory result.

Passage from Komarovicine to Komarovidine. A solution of 100 mg of mercuric acetate in 10 ml of 2% acetic acid was added to a solution of 50 mg of (I) in 5 ml of 10% acetic acid. The mixture was boiled under reflux for 20 h (chromatographic monitoring). The cooled solution was treated with 10% ammonia solution, and the product was extracted with ether and then with chloroform. This gave 20 mg (42%) of the base (III) with mp 218-219°C (CH_2Cl_2).

Quinoline-8-carbaldehyde [4]. A mixture of 10 g (0.07 mole) of 8-methylquinoline and 8.5 g (0.076 mole) of selenium dioxide was heated over a naked flame in a two-necked 250-ml flask fitted with a thermometer and a condenser for the direct distillation of the water formed and the excess of methylquinoline. A vigorous reaction began at 145-148°C. Heating was stopped, and the temperature rose to 220°C through the heat of the reaction. When the temperature had fallen to 190°C, the mixture was heated again, to 250°C, for 15 min. After cooling, the aldehyde was extracted from the residue with ether. This gave 7.45 g (68%) of aldehyde with mp 94-95°C (water).

1-(Quinolin-8'-yl)-3,4,5,6-tetrahydro- β -carboline (I). A mixture of 1 g of triptamine hydrochloride in 20 ml of water, 3.0 ml of 2N sulfuric acid, and 1.5 g of quinoline-8-carbaldehyde was gradually heated to 110°C in a sand bath and was kept at this temperature for 1 h. After cooling, a 15% solution of caustic soda was added and the product was extracted with ether and then with chloroform. The solvents were evaporated off to give 0.91 g (60%) of (I) with mp 209-210°C (CH_2Cl_2), composition $\text{C}_{20}\text{H}_{11}\text{N}_3$.

1-(Quinolin-8'-yl)- β -carboline (II). A ground mixture of 0.5 g of (I) and 0.2 g of sulfur was heated in the sand bath at 180-200°C for 35 min. After cooling, it was dissolved in 10% sulfuric acid and the acid solution was filtered and was washed with ether. Then it was decomposed with 15% caustic soda and the reaction product was extracted with ether and then with chloroform. This gave 250 mg (52%) of (II), with mp 228-230°C (CH_2Cl_2).

The use of selenium as dehydrogenating agent led to similar results.

SUMMARY

The structure of the new alkaloid from *Nitraria komarovii* Iljin et Lava, komarovicine, has been established. Its synthesis and also its conversion into komarovine have been performed. A mutual transition of komarovidine and komarovicine has been effected.

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