1695 cm^{-1}; M^+ 316. In systems 1 and 3, the R_f values of compound (IX) coincided with those of the 14α-hydroxyandrost-5-en-1,4,17-trione obtained from (VII).

SUMMARY

Two withanolides have been isolated from the epigeal part of *Physalis viscosa* L. — 4β-hydroxywithanolide E and a new one which has been called physanolide. The latter has the structure of 14α,17β-20R-trihydroxy-1,4-dioxo-22R-witha-5,24-dienolide.

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ALKALOIDS OF *Nitraria komarovii*.

IV. TOTAL SYNTHESIS OF KOMAROVINE AND KOMAROVIDINE

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Two alkaloids of a new type — komarovine and komarovidine — have been isolated from the epigeal part of the *Nitraria komarovii*. Their structures — 3-(quinolin-8'-yl)-β-carboline and 3-(quinolin-8'-yl)-5,6-dihydro-β-carboline, respectively — have been established by synthesis.

The isolation of komarovine [1] and komarovidine [2] — alkaloids of the epigeal part of the *Nitraria komarovii* — and the determination of their structures have been reported previously. The identity of komarovine (V) with one of the products of the dehydrogenation of the main alkaloid of *N. schoberi*, nitrarine [3], with selenium and sulfur was shown. Nitrarine has also been isolated from this plant [4].

Analysis of the spectra (PMR, mass, IR, UV) of komarovidine (IV) showed that it is a dihydro derivative of komarovine. The dehydrogenation of (IV) with palladium black led to komarovine.

On the basis of the spectral characteristics of (V), and also taking into account its formation from 14,21-dimethylene-16-azayohimbane (nitrarine) in a dehydrogenation reaction, we put forward the structure of 3-(quinolin-8'-yl)-β-carboline for the alkaloid komarovine. We have synthesized a compound of this structure from quinoline-8-carboxylic acid and tryptamine.

Quinoline-8-carboxylic acid was obtained from anthranilic acid by the Skraup reaction [5]. Tryptamine was synthesized from indole in three stages by a known method [7], and was also obtained in part by the decarboxylation of tryptophan [8].

The amide (III) was synthesized by two methods: by the condensation of (I) and (II) with the participation of dicyclohexylcarbodiimide (DCC) at room temperature [9], and also by the direct thermal reaction of (I) and (II) [10]. It must be mentioned that the yields

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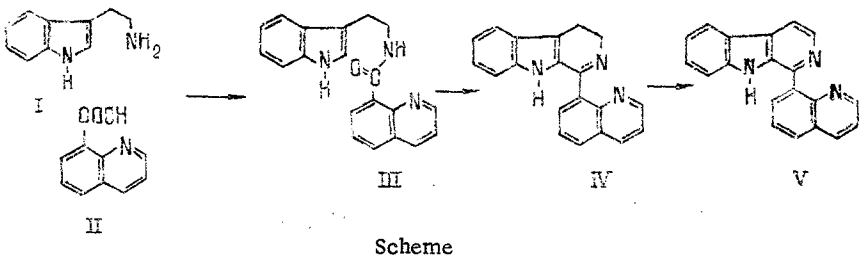

Scheme

here and in the stage of Bischler–Napieralski cyclization are comparatively low, apparently because of the conjugation of the carbonyl group with the quinoline system.

In their physicochemical properties, spectral characteristics, and mixed melting points, the synthetic 3-(quinolin-8'-yl)-β-carboline and 3-(quinolin-8'-yl)-5,6-dihydro-β-carboline proved to be identical with the natural alkaloids komarovine and komarovidine, respectively.

EXPERIMENTAL

UV spectra were taken in ethanol on a Hitachi spectrometer, mass spectra on an MKh-1303 mass spectrometer, NMR spectra on a JNM-4H 100/100 MHz instrument in a mixture of $CDCl_3$ and CD_3OD with HMDS as internal standard (δ scale), and IR spectra on a UR-20 instrument (tablets with KBr). For TLC silica gel L 5/40 μ was used with the following solvent systems: 1) chloroform–acetone (4:1); 2) chloroform–acetone–methanol (5:4:1); 3) system 2 + 0.1 conc. ammonia; 4) chloroform–acetone–ethanol–ammonia (10:8:1:0.2); and 5) chloroform–ethanol–ammonia (9:1:0.1).

Komarovine (V). The air-dry comminuted epigeal part of the plant (20 kg) moistened with 8% ammonia was extracted with chloroform. The concentrated chloroform extract was treated with 10% sulfuric acid. The acid extract was decomposed with concentrated ammonia, and the bases were extracted with ether and then with chloroform. This gave 50 g of combined alkaloids — 0.25% on the weight of the dry raw material.

The combined chloroform-extracted alkaloids (20 g) were separated according to basicity by citrate-phosphate buffer solutions into five fractions with pH 8-4. After the isolation of five known alkaloids [4], the mother liquors of the fractions with pH 5, 6, and 7 were combined and chromatographed on a column of silica gel with elution by chloroform–acetone–ethanol (20:50:1). The rechromatography of fraction 7-13 so obtained with system 3 gave 50 mg of technical (V). After crystallization from a mixture of petroleum ether (70–100°C) and benzene, and then from methylene chloride, it had mp 229–230°C.

Komarovidine (IV). After the separation of the (V), the subsequent fractions were treated with petroleum ether. This gave 40 mg of technical (IV). It was crystallized from a mixture of petroleum ether and benzene, and then from CH_2Cl_2; mp 219–220°C.

Passage from Komarovidine to Komarovine. A ground mixture of 20 mg of (IV) and 15 mg of Pd black was heated at 180–190°C for 30 min. After cooling, it was boiled with a mixture of benzene and petroleum ether, and the extract was filtered and concentrated. This gave 10 mg (50%) of (V) with mp 229–230°C.

Quinoline-8-carboxylic Acid (II) [5]. When 10.2 g of anthranilic acid, 7.5 g of o-nitrobenzoic acid, 25 g of glycerol, and 15 ml of concentrated H_2SO_4 were mixed, the temperature at first rose through the spontaneous evolution of heat, and after this the mixture was boiled for 7 h (sand bath). Isolation and crystallization of the product from ethanol yielded 6.15 g (48%) of compound (II) with mp 187–189°C.

Indole-3-carboxaldehyde (VI) [6, 7]. At –5°C, 15.34 g (0.1 mole) of phosphorus oxychloride was added to 44 g (0.6 mole) of dimethylformamide, and the mixture was stirred, the temperature not being allowed to rise above 10°C. Then 5.85 g (0.05 mole) of indole was added in portions at 25°C. The resulting mixture was stirred at 25°C for 30 min, and then 20 g of calcium carbonate was added and it was heated to 35°C. A further rise in temperature took place through the heat of the reaction. The mixture was stirred for another 30 min at 55–60°C. After it had been cooled to 10°C, 100 ml of 30% sodium acetate solution was added and it was diluted with water to 0.5 liter. Then 23.6 g (0.6 mole) of caustic

soda was added and the mixture was boiled for 3 h. The unchanged indole was distilled off with steam. The reaction mixture was diluted with water to 1.7 liters, boiled, and filtered. After cooling, 5.1 g (70%) of (VI) deposited with mp 193-195°C.

3-(2-Nitrovinyl) Indole (VII). A mixture of 4.5 g (0.03 mole) of (VI) in 120 ml of ethanol, 0.23 g of methylamine hydrochloride, 0.09 g of sodium carbonate, and 2 g of nitromethane was left for 6 days. Then the solution was concentrated in vacuum. On cooling, 2.9 g (45%) of (VII) deposited with mp 167-168°C (methanol).

Tryptamine (I). A. A solution of 2.5 g (0.013 mole) of (VII) in 70 ml of tetrahydrofuran was added dropwise to a suspension of 10 g of lithium tetrahydroaluminate in 150 ml of dry diethyl ether. The solution was boiled under reflux for 3 h and was left for 12 h. Then the product was decomposed with water, the mixture was made alkaline with dilute caustic soda solution, the ethereal layer was separated off, and gaseous HCl was passed through it. The hydrochloride that deposited (2.1 g, 81%) was filtered off; mp 248-249°C.

B. The method of Kametani et al. [8] was used. In an atmosphere of nitrogen, 0.5 g of D,L-tryptophan was boiled in 20 ml of diphenylmethane for 20 min. After cooling, 40 ml of a benzene solution of HCl was added. The precipitated hydrochloride of (I) was filtered off. Yield 350 mg (72%), mp 248-249°C.

3-[β-(Quinolin-8'-ylcarbonylamino)ethyl]indole (II). A. The method of Kametani et al. [9] was used. A suspension of 1.6 g (0.01 mole) of (I) and 1.73 g (0.01 mole) of (II) in 6 ml of methylene chloride was treated with 2.32 g (0.011 mole) of DCC. The mixture was stirred with a magnetic stirrer at room temperature for 15 h. Then the precipitate was filtered off and was washed with methylene chloride, the filtrate was evaporated, and the residue was chromatographed on a column of silica gel in system 2. The fraction enriched with the amide was rechromatographed, with elution by system 3. Crystallization of the product from acetone and then from methylene chloride gave 0.63 g (20%) of (III) with mp 191-193°C.

B. The method of Markaryan et al. [10] was used. A ground mixture of 1.6 g (0.01 mole) of (I) and 1.73 g (0.01 mole) of (II) was heated at 180-200°C (sand-bath) for 1.5 h. After cooling, the fused mass was boiled with acetone. The precipitate that deposited was filtered off and crystallized from methylene chloride, thus giving 1.42 g (45%) of (III) with the composition $C_{20}H_{17}N_3O$, mp 191-193°C. $\nu_{\underset{HN-C=O}{|}}$ 1645 cm^{-1}. PMR: 3.76 (triplet, 2 H); 3.05 ;t, 2 H) ($O=\underset{|\ H}{C}-N-CH_2-CH_2-Ar$). Here and below the analyses of all the compounds corresponded to the calculated figures.

3-(Quinolin-8'-yl)-5,6-dihydro-β-carboline (IV). A mixture of 1 g (0.0032 mole) (III), 1 g of phosphorus pentoxide, and 1 ml of phosphorus oxychloride in 25 ml of absolute toluene was boiled for 2.5 h. The excess of reagents was decomposed with water. The organic layer was separated off and extracted with 5% sulfuric acid. The acid extract was combined with the aqueous layer. The solution was decomposed with caustic soda, and the product was extracted with ether and then with chloroform. Crystallization from petroleum ether–benzene and then from methylene chloride gave 0.24 g (25%) of (IV), $C_{20}H_{15}N_3 \cdot H_2O$ mp 219-220°C.

3-(Quinolin-8'-yl)-β-carboline (V). A. A ground mixture of 0.25 g (0.0008 mole) of (IV) and 0.2 g of Pd black was heated at 180-200°C for 30 min. On cooling, the sintered mass was treated with 10% sulfuric acid and washed with ether. The acid solution was decomposed with concentrated ammonia, and the product was extracted with ether and chloroform. The solvents were evaporated off and the residue was crystallized from petroleum ether–benzene and then from methylene chloride, to give 0.125 g (50%) of (V), $C_{20}H_{13}N_3 \cdot 0.5H_2O$, mp 229-230°C.

B. A mixture of 0.1 g of (IV) and 0.1 g of sulfur was found in a test-tube and was then treated as in experiment A. The results were similar, but the product was less pure.

C. A mixture of 0.1 g of (IV) and 0.1 g of powdered selenium was subjected to a reaction under the conditions of experiment A. The results were similar to those obtained in experiment B.

SUMMARY

The structures of two alkalcids of a new type from the epigeal part of *Nitraria komarovii* have been established. Their synthesis has been performed. The 3-[β-(quinolin-8'-yl)carbonylamino]ethylindole obtained in the course of the synthesis, which has not beer described previously in the literature, has been characterized.

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STRUCTURE OF ISOREGELINONE

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From a fraction of the bases of *Colchicium kesselringii* Rgl., growing in the Tashkent Province, a new compound which has been called isoregelinone has been isolated. On the basis of spectral characteristics, especially the INDOR spectrum, and chemical transformations, a structure epimeric with that of regelinone has been proposed for it.

Information has been given previously [1-3] about the alkaloids of *Colchicium kesselringii* Rgl. (Kesselring's autumn crocus) growing on the left bank of the middle course of the R. Syrdar'ya. The main alkaloid in it is kesselringine — a phenolic base of the homoproaporphine series [4, 5]. Continuing an investigation of the autumn crocus collected in the Srednechirchikskii region, we have found a comparatively low content of total alkaloids (0.29%) and a qualitatively different composition of the fraction of strong bases. The main part of the total material here also consists of alkali-soluble bases. However, this fraction consists mainly of luteine [6] — an epimer of kesselringine — which we found somewhat unexpected. Luteine, isolated previously from *Colchicum luteum* Baker [7] has not been detected in *C. kesselringii* growing in the Syrdr'ya region.

From the same fraction of bases by chromatography on a column we have isolated a new compound with the composition $C_{19}H_{19}O_5N$, mp 321-323°C which has been called isoregelinone (I). The base possesses no phenolic character. Its passage into the alkaline solution during the separation of the alkaloids of basic nature is due to its relatively better solubility in water than in chloroform.

The IR spectrum of (I) has absorption bands at 3250 and 1690 cm^{-1} showing the presence of hydroxy and carbonyl groups. From the nature of its PMR spectrum (Fig. 1), the base differs from the homoproaporphine compounds that are characteristic for this plant [4, 8, 9] and is similar to regelinone [10]. In the low-field part of the spectrum a one-proton

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