

The composition of the alkaloids of *Veratrum oxysepalum* Turcz. has been studied incompletely [1-3]. We have investigated the ester alkaloids protoverine of the hypogea part of the plant collected in the state of dormancy (August 14, 1977) in the environs of the town of Magadan.

By chromatography on a column of cellulose impregnated with formamide [4], from the sum of the alkaloids obtained by extraction of the raw material with diethyl ether we have isolated three alkaloids with  $R_f$  0.1 (I), 0.4 (II), [system 1: chloroform saturated with formamide; Leningrad type M paper impregnated with formaldehyde in ethanol (1:2)] and 0.47 (III) [system 2: chloroform-benzene (1:1), saturated with formamide].

Alkaloid (I),  $C_{37}H_{59}O_{12}N$ , mp 202-204°C (benzene),  $[\alpha]_D^{22} -18.5^\circ$  (c 0.75; pyridine). IR spectrum:  $1738\text{ cm}^{-1}$  (ester carbonyls),  $1248\text{ cm}^{-1}$  (ester band). The UV spectrum of the alkaloid in concentrated sulfuric acid (0.4 mg in 10 ml), taken 24 h after dissolution, had  $\lambda_{\text{max}}^{250, 291, 370, 540\text{ nm}}$  and a region of coincidence of 350 nm with the spectrum taken after 1.5 h (the amino alcohol protoverine) [5]. The products of the hydrolysis of the alkaloid (102 mg of alkaloid, 4 ml of 85% methanol, and 42 mg of potassium carbonate, 20-24°C, 24 h) were found by paper chromatography with markers to contain the amino alcohol protoverine [system 3: butan-1-ol-acetic acid-water (4:1:5)] and (l)- $\alpha$ -methylbutyric and (d)- $\alpha$ -hydroxy- $\alpha$ -methylbutyric acids [system 4: butan-1-ol-1.5 N aqueous ammonia (1:1)]. In accordance with the biogenetic nature of the *Veratrum* ester alkaloids [6], the acids found must occupy positions 15 and 3 in protoverine, which corresponds to dideacetylprotoveratrine A [7]. The  $R_f$  of the alkaloid coincided with that of the sample in system 1, and a mixed melting point gave no depression.

Alkaloid (II),  $C_{39}H_{61}O_{13}N$ , mp 191-192°C (benzene),  $[\alpha]_D^{22} -15.1^\circ$  (c 0.48; pyridine). IR spectrum (KBr):  $1740\text{ cm}^{-1}$  (ester carbonyls),  $1250\text{ cm}^{-1}$  (ester band). The UV spectrum of the alkaloid dissolved in concentrated sulfuric acid had  $\lambda_{\text{max}}^{250, 290, 370, 540\text{ nm}}$ . The spectra of the solution obtained after 1.5 and 24 h had a region of coincidence at 360 nm, which shows the presence of the amino alcohol protoverine [5]. By paper chromatography with markers, the products of the hydrolysis of the alkaloid were found to contain protoverine (system 3) and acetic, (l)- $\alpha$ -methylbutyric and (d)- $\alpha$ -hydroxy- $\alpha$ -methylbutyric acid (system 4).

On methanolysis, the alkaloid formed dideacetylprotoveratrine A. The  $R_f$  value of the alkaloid coincided with that of deacetylprotoveratrine A and a mixed melting point showed no depression. The results of analysis permitted the alkaloid to be identified as deacetyl-protoveratrine A [8].

Alkaloid III,  $C_{11}H_{63}O_{14}N$ , mp 260-262°C (ethanol),  $[\alpha]_D^{20} -43.7^\circ$  (c 0.321; pyridine). IR spectrum (KBr):  $1750\text{ cm}^{-1}$  (ester carbonyls),  $1245\text{ cm}^{-1}$  (ester band). The UV spectrum of the alkaloid in concentrated sulfuric acid had  $\lambda_{\text{max}}^{250, 330, 370, 530\text{ nm}}$ . The spectra of the solution taken by Bondarenko's method [5] had a region of coincidence at 360 nm (protoverine). In the products of the alkaline hydrolysis of the alkaloid (100 mg of alkaloid, 4 ml of 85% methanol, 42 mg of potassium carbonate, 20-22°C, 24 h) were found by paper chromatography with markers to contain the amino alcohol protoverine (system 3) and acetic, (l)- $\alpha$ -methylbutyric, and (d)- $\alpha$ -hydroxy- $\alpha$ -methylbutyric acids (system 4).

On methanolysis, the alkaloid formed deacetylprotoveratrine A and dideacetylprotoveratrine A, as was established by paper chromatography in system 1. The  $R_f$  value of the alkaloid coincided with that of protoveratrine A in systems 1 and 2, and a mixed melting point showed no depression.

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The results of analysis and the biogenetic nature of the structure of the *Veratrum* ester alkaloids [6] permits the alkaloid isolated to be identified as protoveratrine A [9].

This is the first time that alkaloids (I), (II), and (III) have been isolated from *Veratrum oxysepalum* Turcz.

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#### ALKALOIDS OF *Haplophyllum ferganicum*

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Continuing the chemical study of plants of the genus *Haplophyllum* [1], we have investigated another species (*H. ferganicum* Vved.) This subshrub grows on clayey and stony slopes in the foothills of the Fergana valley [2].

Stems of *H. ferganicum* were collected by R. S. Sakhobiddinov in the Sadkak foothills in the Fergana province in the flowering phase on May 23, 1980. The alkaloids were isolated from the air-dry comminuted stems (550 g) by extraction with methanol followed by treatment of the concentrated extract with acid. From the acid solution by the usual method a crystalline mixture of alkaloids was obtained. The yield was about 1% (on the mass of the dry stems).

Treatment of the mixture of alkaloids with acetone followed by crystallization of the residue from a mixture of acetone and benzene gave evoxine (1.76 g), mp 154–155°C (I). The residual mother liquor was chromatographed on a column of alumina (1:100). Gradient elution (hexane, petroleum ether, ether, chloroform, methanol) eluted 15 mg of 7-isopentenyloxy- $\gamma$ -fagarine, mp 105–106°C (II), 50 mg with a base with mp 136–138°C (III), 80 mg of evodine, mp 151–152°C (IV), 1.12 g of evoxine, 38 mg of a base with mp 160–162°C (V), and 0.95 g of glycoperine, mp 223–224°C (VI). The chloroform eluates containing, according to TLC, evoxine and haplopine, were separated into phenolic and nonphenolic fractions. Treatment of the phenolic fraction with acetone gave haplopine (20 mg), mp 204–205°C (from methanol) (VII). Alkaloids (I), (II), (IV), and (VII) were identified by direct comparison with authentic samples obtained previously from the epigeal part of *H. perforatum* [3].

The IR spectrum of base (III) (UR-20, tablets with KBr) contained absorption bands at 3138 and 3170  $\text{cm}^{-1}$  (stretching vibrations of the C–H bonds of a furan ring); there was no absorption of active hydrogen. The mass spectrum of (III) contained the peaks of ions with  $m/z$  329 ( $M^+$ , 100%), 314 (33), 300 (12), 258 (19), 245 (90), and 227 (83). The NMR spectrum

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