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.

LITERATURE CITED

1. N. B. Bondarenko, in: Third All-Union Congress of Pharmicists, Abstracts of Lectures [in Russian], Kishinev (1980), p. 197.
2. M. Susuki, B. Shimisu, J. Muraso, R. Hayashi, and H. Sanpei, J. Pharm. Soc. Jpn., 77, 1050 (1957).
3. B. Shimisu and M. Susuki, J. Pharm. Soc. Jpn., 79, 609 (1959).
4. N. V. Bondarenko, A. A. Shinkarenko and G. I. Gerashchenko, Tr. Vitebsk. Tekhnol. Inst. Legk. Promst., 1, 120 (1970).
5. N. V. Bondarenko, Zh. Obshch. Khim., 37, 332 (1967).
6. N. V. Bondarenko, in: The Phytochemical Study of the Flora of the Belorussian USSR and Biopharmaceutical Studies of Drug Preparations [in Russian], Leningrad (1975), p. 84.
7. N. V. Bondarenko, Khim. Prir. Soedin., 810 (1972).
8. N. V. Bondarenko, Khim. Prir. Soedin., 854 (1971).
9. N. V. Bondarenko, Khim. Prir. Soedin., 132 (1973).

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-γ-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 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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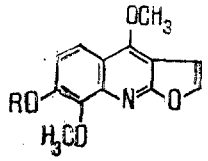
of the base (JNM-C-60 HL, $CDCl_3$, O — HMDS, δ scale, ppm) contained the signals of aromatic protons at 7.87 and 7.14 (doublets, 1 H each, J = 9 Hz, H_5 and H_6), 7.47 and 6.93 (doublets, 1 H each, J = 3 Hz, α- and β-protons of a furan ring), of the protons of two methoxy groups at 4.28 and 3.99 (singlets, 3 H each, and of the protons of a $-O-CH_2-CH-C(CH_3)_2$ side chain

at 4.20 (doublet, 2 H, J = 5 Hz, one component of the doublets superposed on the signal of a methoxy group), 3.11 (triplet, 1 H, J = 5 Hz), at 1.26 and 1.24 (singlets, 3 H each). These results permitted the conclusion that (III) was anhydroevoxine, isolated from *Evodia xanthoxyloides* F. Muell (family Rutaceae) [4]. A confirmation of this was the conversion of (III) into (I) by boiling it with 10% oxalic acid solution.

According to its IR spectrum, base (V), M^+ 389, contained a hydroxy group and an ester group (3235 and 1750 cm^{-1}, respectively). The NMR spectrum of (V) differed from that of (III) only by the presence of a three-proton singlet at 2.08 ppm ($OCOCH_3$) and of a one-proton multiplet at 5.12 ppm (CH—OAc) in place of the one-proton triplet at 3.11 ppm in the spectrum of (III). On the basis of the facts and of a direct comparison with an authentic sample obtained from (I), (V) was identified as the monoacetyl derivative of evoxine, isolated previously from *Haplophyllum hispanicum* Spach [5].



I. R = $-CH_2CH(OH)C(OH)(CH_3)_2$
II. R = $-CH_2CH=C(CH_3)_2$

III. R = $CH_2CH-C(CH_3)_2$ (O)

IV. R = $-CH_2CH(OH)C$ (CH_2, CH_3)

V. R = $-CH_2CH(OCOCH_3)C(OH)(CH_3)_2$
VI. R = rhamnose
VII. R = H

Thus, all the alkaloids of *H. ferganicum* are derivatives of 7-hydroxy-4,8-dimethoxy-furanoquinoline. It is interesting to note that this plant does not contain the simplest representative of this group of substances — skimmianine (R = CH_3), which is found in almost all other plants of the genus *Haplophyllum* [6].

LITERATURE CITED

1. D. M. Razakova and I. Bessonova, Khim. Prir. Soedin., 528 (1981).
2. Flora of the USSR [in Russian], Moscow—Leningrad, Vol. XIV (1949), p. 198.
3. Kh. A. Abdullaeva, I. A. Bessonova, and S. Yu. Yunusov, Khim. Prir. Soedin., 219 (1978).
4. D. L. Dreyer, J. Org. Chem., 35, 2420 (1970).
5. A. G. Gonzales, R. M. Ordonez and F. R. Luis, An. Quim., 68, 1133 (1972).
6. I. A. Bessonova and S. Yu. Yunusov, Khim. Prir. Soedin., 303 (1977).