LITERATURE CITED

1. M. N. Sultankhodzhaev and M. M. Tadzhibaev, Khim. Prir. Soedin., 406 (1976).
2. F. N. Dzhakhangirov and F. S. Sadritdinov, Dokl. Akad. Nauk Uzb. SSR, 3 (1977).
3. I. Gyenes, Titration in Nonaqueous Media, Van Nostrand, Princeton (1967).
4. S. Yu. Yunusov, Alkaloids [in Russian], Tashkent (1974), p. 72.
5. A. P. Orekhov, The Chemistry of the Alkaloids [in Russian], Moscow (1955), p. 14.

GLUCOHAPLOPINE — A NEW GLYCOALKALOID FROM *Haplophyllum perforatum*

Kh. A. Abdullaeva, I. A. Bessonova, and S. Yu. Yunusov

UDC 547.944/945

We have previously reported the isolation of new furanoquinoline alkaloids from the epigeal part of *Haplophyllum perforatum* (family Rutaceae) collection on the northern slopes of the Babatag range [1].

Continuing the separation of the combined chloroform-soluble alkaloids, we have treated them with water. The residue obtained from the water-soluble fraction was chromatographed on silica gel. Elution with chloroform–methanol (25:1) gave a crystalline base with the composition $C_{19}H_{21}NO_9$ (I) with mp 217-218°C (ethanol), $[\alpha]_D$ −41° (c 0.516; pyridine), R_f 0.36 [chloroform–methanol (8:1) system]. The substance is readily soluble in dilute acids and sparingly soluble in methanol, ethanol, and water and is insoluble in ether, chloroform, benzene, and ethyl acetate.

The UV spectrum of (I) ($\lambda_{max}^{C_2H_5OH}$ 250, 321, 334, 348 nm) is typical for 7,8-alkoxy-substituted 4-methoxyfuranoquinoline alkaloids [2]. The IR spectrum of (I) resembles that of glycoperine [3]. In the spectrum intense absorption is observed with maxima at 3470, 3340, 3320 cm^{-1} (hydroxy group), and at 3155 cm^{-1} (furan ring).

The acetylation of (I) with acetic anhydride in pyridine formed a tetraacetyl derivative (II), mp 135-137° (ethyl acetate–hexane), R_f 0.18 [chloroform–methanol (8:1)] and 0.24 [benzene–methanol (4:1)]. The mass spectrum of (II) contained, in addition to the peaks with m/e (%) 245 (100), 227 (23), 216 (9), and 202 (7) characteristic for the fragmentation of the molecular ions of haplopine [4], the peak of the molecular ion with m/e 575 (2.8) and the peaks of ions with m/e 331 (38), 271 (6), 169 (27), and 109 (16), which are characteristic for the fragmentation of the (M − 17) ion of 2,3,4,6-tetra-O-acetylglucopyranose [5].

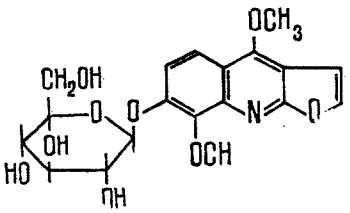
The facts given above permitted the conclusion that base (I) was a glucoalkaloid.

The enzymatic hydrolysis of (I) with snail pancreatic juice led to the formation of a base with mp 204-205°C (methanol), which was identified by TLC and by a mixed melting point with an authentic sample of haplopine [6], and D-glucose, the presence of which was confirmed by a chromatographic (TLC and PC) comparison with an authentic sample.

The results obtained gave grounds for calling the alkaloid isolated glucohaplopine.

The configuration of the glucosidic bond was established with the aid of Klyne's rule. The value of M_D = −225° shows that the D-glucose is attached to the haplopine by a β-glucosidic bond.

Thus, glucohaplopine has the structure of 7-β-D-glucopyranosyloxy-4,8-dimethoxyfuranoquinoline.



Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 6, p. 873, November-December, 1979. Original article submitted July 11, 1979.

 0009-3130/79/1506-0782$07.50

LITERATURE CITED

1. Kh. A. Abdullaeva, I. A. Bessonova, and S. Yu. Yunusov, Khim. Prir. Soedin., 684 (1974); 425 (1977); 219 (1978).
2. I. A. Bessonova and S. Yu. Yunusov, Khim. Prir. Soedin., 303 (1977).
3. V. I. Akhmedzhanova, I. A. Bessonova, and S. Yu. Yunusov, Khim. Prir. Soedin., 680 (1974).
4. D. M. Razakova, I. A. Bessonova, and S. Yu. Yunusov, Khim. Prir. Soedin., 791 (1976).
5. H. Budzikiewicz, C. Djerassi, and D. H. Williams, Structure Elucidation of Natural Products by Mass Spectrometry, Holden-Day, San Francisco, Vol. 2 (1964), p. 209.
6. G. P. Sidyakin and S. Yu. Yunusov, Dokl. Akad. Nauk Uzb. SSR, No. 4, 39 (1962).

ALKALOIDS OF *Fumaria vaillantii*. THE STRUCTURE OF NORJUZIPHINE

M. Alimova, I. A. Israilov, M. S. Yunusov, and S. Yu. Yunusov

UDC 547.943

Continuing the separation of the combined alkaloids of *Fumaria vaillantii* [1] collected in the Tashkent province in the period of flowering and incipient budding, in addition to the alkaloids mentioned previously we have isolated cheilanthifoline [2], parfumine [3], and d-stylopine [4], which were identified by direct comparison with authentic samples.

Base (I) with the composition $C_{20}H_{20}NO_4$, mp 264-266°C (chloroform–methanol), $[\alpha]_D$ −121.2° (c 0.28; methanol). The IR spectrum of (I) showed absorption bands at (cm^{-1}) 920, 940, 1045 (CH_2O_2), 1510 (aromatic ring), and 3150-3650 (OH). The UV spectrum of the base had two maxima, at 244 and 294 nm (log ε 3.90, 3.88). The NMR spectrum showed signals in the form of a three-proton singlet at 2.63 ppm from a N-CH_3 group and a four-proton singlet at 5.58 ppm from two methylenedioxy groups. The signals of aromatic protons appeared at 6.34 ppm (1 H) and 6.49 ppm (3 H).

The mass spectrum of the base lacked the peak of the molecular ion and showed peaks of ions with m/e 323, 174, and 148 (100%). The facts given above permitted base (I) to be identified as stylopine methohydroxide [5].

From the combined phenolic bases we isolated compound (II) with mp 198-199°C, $[\alpha]_D$ −18° (c 0.17; CH_3OH).

The UV spectrum of (II) had two maxima, at 228 and 285 nm (log ε 4.20, 3.56). The IR spectrum showed absorption bands at 3370 cm^{-1} (OH) and 1590 and 1610 cm^{-1} (aromatic ring). The mass spectrum of the base showed the peak of the molecular ion with m/e 285, and also the peaks of ions with m/e 178 (100%), 163, and 107. The NMR spectrum of the base recorded in methanol contained signals in the form of a three-proton singlet from a methoxy group at 3.79 ppm. In the aromatic region there were two two-proton doublets at 7.05 and 6.50 ppm (J = 8 Hz) from two pairs of equivalent ortho aromatic protons, and two one-proton doublets at 6.72 and 6.69 ppm (J = 8 Hz). Methylene protons appeared in the form of multiplets in the 2.50-2.90 ppm region.

At 4.19 ppm there was a one-proton quartet characteristic for the C_1 proton of a C_8-substituted benzyltetrahydroisoquinoline alkaloid [6]. According to the results of UV, IR, NMR, and mass spectroscopy, base (II) was a benzyltetrahydroisoquinoline alkaloid with methoxy and hydroxy groups in the isoquinoline moiety and a hydroxy group in the benzyl moiety of the molecule at C_4' [7]. When compound (II) was methylated by Craig's method [8] an N-methyl derivative was obtained which proved to be identical with juziphine (III) [6] according to TLC and a mixed melting point. Thus, the base (II) is norjuziphine

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 6, p. 874, November-December, 1979. Original article submitted July 11, 1979.

0009-3130/79/1506-0783$07.50