3. I. A. Bessonova, V. I. Akhmedzhanova, and S. Yu. Yunusov, Khim. Prirodn. Soedin., 677 (1974).
4. L. H. Briggs and R. C. Cambie, Tetrahedron, 2, 256 (1958).
5. Beilstein, Hauptwerk, IX, 262 (1926).
6. A. A. Ryabinin and E. M. Il'ina, Dokl. Akad. Nauk SSSR, 76, 689 (1951).
7. E. F. Nesmelova, I. A. Bessonova, and S. Yu. Yunusov, Khim. Prirodn. Soedin., 815 (1975).

EVODINE AND EVOXOIDINE FROM Haplophyllum perforatum

V. I. Akhmedzhanova, I. A. Bessonova,
and S. Yu. Yunusov

UDC 547.944/945

We have continued a study of the alkaloid composition of the epigeal part of the plant H. perforatum growing in the Dzhungarian Ala-Tau, Kazakh SSR [1].

The ether-soluble part of the main fraction after the separation of evoxine was chromatographed on a column of alumina. From the ethereal eluate we isolated two bases with mp 152-153°C (from acetone), $[\alpha]_D - 60°$ (c 0.3; ethanol) (I) and 135-136°C (from acetone) (II), having the same composition – $C_{18}H_{19}NO_5$, mol. wt. 329 (mass spectrometrically). The substances dissolve readily in acid and chloroform, more sparingly in acetone and ether, and are insoluble in water and alkalis.

The UV spectrum of (I) is similar to the spectra of the furanoquinoline alkaloids of the skimmianine type [2]. Its IR spectrum has the absorption band of a hydroxy group at 3320 cm^{-1}, the presence of which is confirmed by the preparation of acetyl derivative (III) with mp 126-127°C (from cyclohexane), mol. wt. 371 (mass spectrometrically), ν_{max} 1745 cm^{-1}. The NMR spectrum of (I) ($CDCl_3$, τ scale) shows signals at 2.10 and 2.87 ppm (doublets, 1 H each; J = 9.4 Hz; ortho protons of a benzene ring); 2.48 and 3.04 ppm (doublets, 1 H each; J = 3 Hz, α- and β-protons of a furan ring); 4.91 and 5.07 (singlets, 1 H each; protons of a terminal methylene group); 5.66 and 5.91 ppm (singlets, 3 H each; 2 OCH_3); 5.46-6.06 ppm (multiplet, 3 H), 6.53 ppm (broadened signal, 1 H; OH); and 8.21 ppm (singlet, 3 H; $CH_3-C=$).

A comparison of the facts given with literature information furnishes grounds for considering that alkaloid (I) is evodine, which has been isolated from the plant Evodia xanthoxyloides F. Muell. (family Rutaceae) [3]. This was confirmed by the mass spectrum of (I) and the NMR spectrum of (III). The mass spectrum of (I) has the peaks of ions with m/e 258 (16%), 245 (50%), 244 (25%), 227 (100%), and 216 (25%), which are characteristic of all O-isoprenoid derivatives of haplopine, and the peak of an ion with m/e 71 (7%) having the structure $CH_2=C(CH_3)-CH=\overset{+}{O}H$. In the NMR spectrum of (III), unlike that of (I), the protons of the side chain geminal to the oxygen-containing substituent appear clearly at 4.44 ppm (triplet, 1 H; J = 5.5 Hz; $HO-\underline{CH}-CH_2O$) and 5.76 (doublet, 2 H; J = 5.5 Hz; $CH-\underline{CH_2}-O$).

The mass spectrum of (II) shows strong peaks of ions with m/e 329 (M^+; 54%), 258 (47%), 245 (17%), and 244 (100%). These characteristics, and also the melting point of (II) coincide with the properties of evoxoidine, isolated from E. xanthoxyloides [5]. A mixed melting point of (II) with a sample of evoxoidine obtained from evoxine gave no depression of the melting point.

This is the first time that evodine and evoxoidine have been detected in plants of the genus Haplophyllum.

LITERATURE CITED

1. V. I. Akhmedzhanova, I. A. Bessonova, and S. Yu. Yunusov, Khim. Prirodn. Soedin., 320 (1976).
2. A. W. Sangster and K. L. Stuart, Chem. Rev., 65, 97 (1965).
3. R. H. Prager, E. Ritchie, A. V. Robertson, W. C. Taylor, Aust. J. Chem., 15, 301 (1962).

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 2, pp. 289-290, March-April, 1977. Origina article submitted January 4, 1977.

4. V. I. Akhmedzhanova, I. A. Bessonova, and S. Yu. Yunusov, Khim. Prirodn. Soedin., 677 (1974), 272 (1975); E. F. Nesmeiova, I. A. Bessonova, and S. Yu. Yunusov, Khim. Prirodn. Soedin., 815 (1975).
5. F. W. Estwood, G. K. Hughes, and E. Ritchie, Aust. J. Chem., 7, 87 (1954).

CONVOLIDINE – A NEW ALKALOID FROM *Convolvulus krauseanus*

S. F. Aripova, V. M. Malikov,
and S. Yu. Yunusov

UDC 547.944

The roots of the previously unstudied species *Convolvulus krauseanus* Rgl. et Schmalh., collected at the end of the vegetation period on August 31, 1976 in the region of the village of Bakhmal (Turkestan range) contained 0.62% of total alkaloids. When the mixture of bases was separated, convolvine and convolamine [1], amounting to ~80% of the total, were isolated.

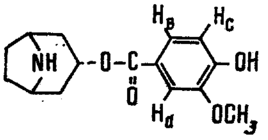
From the chloroform-soluble fraction of the total material we isolated a phenolic base with mp 214-215°C (methanol), composition $C_{15}H_{19}NO_4$ (mol. wt. 277) differing in its properties from those known hitherto, which we have called convolidine (I).

According to its IR spectrum, the alkaloid contains OH and NH groups (3620, 3200 cm^{-1}, an aromatic ester carbonyl group (1680 cm^{-1}), and a 1,2,4-trisubstituted benzene ring (825, 805, 880 cm^{-1}). The composition and spectral characteristics permit the conclusion that convolidine is based on a tropane skeleton, and subsequent chemical transformations of (I) confirmed this hypothesis.

The mass spectrum has the peak of the molecular ion with m/e 277 and the peaks of ions with m/e 167, 154, 151, 126, 123, 110 (100%), 108, and 97, which are characteristic for alkaloids of the tropane series.

Because of its poor solubility in the usual organic solvents, the NMR spectrum of the base was taken in trifluoroacetic acid. In the spectrum (JNM-4H-100/100 MHz), the signal of an aromatic H_c proton appeared at δ 6.65 ppm (doublet, $J_{ortho} = 9$ Hz), and the signals of H_a and H_b protons at 7.12-7.35 ppm; there were other signals at 5.08 (1 H, t) – $C_{3\alpha}$-H – and at 3.57 ppm (3 H, s) – aromatic OCH_3 group. The results of a comparison of the NMR and mass spectra of (I) with those of convolvine gave grounds for the assumption that (I) differs from convolvine only by the presence of a hydroxy group in place of one of the methoxy groups in the benzene ring. Thus, the methylation of (I) with diazomethane led to convolvine.

To determine the position of the hydroxy group, convolidine was subjected to alkaline hydrolysis, which led to the amino alcohol nortropine and an acid with mp 208-209°C, which proved to be vanillic acid [2]. On the basis of the facts given, the structure of (+)-3α-vanilloyloxynortropane is proposed for convolidine:



LITERATURE CITED

1. A. P. Orekhov and R. A. Konovalova, Zh. Obshch. Khim., 7, 646 (1937).
2. Beilsteins Handbuch der Organischen Chemie, 10, 392 (1987)

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 2, pp. 290-291, March-April, 1977. Original article submitted January 4, 1977.