ALKALOIDS OF Dictamnus caucasicus

I. M. Kikvidze, I. A. Bessonova,
K. S. Mudzhiri, and S. Yu. Yunusov

UDC 547.944/945

We have investigated the roots of Dictamnus caucasicus Fisch. (family Rutaceae) growing in the environs of Tbilisi. The combined alkaloids obtained by methanolic extraction from 8 kg of the roots were separated into phenolic and nonphenolic fractions. By treatment of the nonphenolic mixture of alkaloids with acetone, a base was isolated with mp 132-133°C (acetone); this was identified by its melting point, IR spectrum, and TLC as dictamnine, which has been isolated from Haplophyllum ramosissimum [1]. The dried acetone mother liquors were chromatographed on a column of alumina. The first ethereal eluates yielded dictamnine and then a crystalline mixture of alkaloids showing on TLC two spots which proved to be identical with authentic samples of γ-fagarine and skimmianine. The repeated recrystallization of this mixture of bases from acetone and methanol gave skimmianine with mp 177°C, and the acetonic mother liquors yielded γ-fagarine with mp 140-141°C (acetone–water), identical with authentic samples with respect to their melting points, IR spectra, and TLC.

Two alkaloids were extracted from the ethereal–chloroformic eluates: (I) with mp 168-169°C (ethanol–acetone), mol. wt. 259 (mass spectrometry), and (II) with mp 207-209°C (ethanol–acetone), mol. wt. 229 (mass spectrometry).

The bases were insoluble in alkali and in water, and very sparingly soluble in acid. Their IR spectra lacked the absorption bands of hydroxy groups but had absorption bands typical for an unsubstituted furan ring (3110, 3145 cm^{-1}). On standing, the substances became colored pink. This property is possessed by isofuranoquinoline derivatives [2].

The UV, mass, and NMR spectra of the substances showed that (I) was a dimethoxyisodictamnine and (II) was a methoxyisodictamnine. The NMR spectrum of (I) coincided with the spectrum of isomaculosidine [3]; their melting points were also identical [4]. Thus, (I) was 6,8-dimethoxyisodictamnine. We obtained the picrate of (I) with mp 183-186°C and a tetrahydro derivative with mp 215°C.

The NMR spectrum of (II) shows a doublet in the weak field at τ 2.14 from the H_5 proton, the splitting constant of which ($J = 2.5$ Hz) shows the absence of a proton in the ortho position. Consequently, the OCH_3 group is at C-6. The spectrum has an unresolved three-proton signal at 2.70-2.90 from an α-proton of the furan ring and the H_7 and H_8 protons, a doublet at 3.00 ($J = 2$ Hz) from a β proton of a furan ring, and two three-proton singlets at 6.10 and 6.16 from OCH_3 and $N-CH_3$ groups. The melting point of (II) is close to that published for 6-methoxyisodictamnine (isopteleine) [5, 6].

From the combined phenolic alkaloids, treatment with ethanol extracted a base with mp 144-145°C which was soluble in alkali on heating. The IR, UV, and mass spectra of this base were identical with those of robustine, which has been isolated from H. robustum [7].

The chromatography of the combined phenolic alkaloids remaining after the isolation of robustine on alumina gave a base with mp 183°C identical in melting point and TLC with an authentic sample of isodictamnine.

Thus, from the roots of Dictamnus caucasicus we have obtained dictamnine, γ-fagarine, skimmianine, 6,8-dimethoxyisodictamnine, 6-methoxyisodictamnine, robustine, and isodictamnine. This is the first time that 6,8-dimethoxyisodictamnine, 6-methoxyisodictamnine, and isodictamnine have been isolated from this plant.

I. G. Kutateladze Institute of Pharmaceutical Chemistry, Academy of Sciences of the Uzbek SSR. Translated from Khimiya Prirodnykh Soedinenii, No. 5, p. 675, September-October, 1971. Original article submitted April 23, 1971.

LITERATURE CITED

1. D. Kurbanov, G. P. Sidyakin, and S. Yu. Yunusov, Khim. Prirodn. Soedin., 3, 67 (1967).
2. F. N. Laney, M. McCamish, and T. McEwan, Austr. J. Chem., 22, 447 (1969).
3. A. V. Robertson, Austr. J. Chem., 16, 451 (1963).
4. R. F. C. Brown, P. T. Gilham, G. K. Hughes, and E. Ritchie, Austr. J. Chem., 7, 181 (1954).
5. F. Werny and P. J. Scheuer, Tetrahedron, 19, 1293 (1963).
6. V. I. Frolova, A. D. Kuzovkov, and P. N. Kibal'chich, Zh. Obshch. Khim., 34, 3399 (1964).
7. I. M. Fakhrutdinova, G. P. Sidyakin, and S. Yu. Yunusov, Khim. Prirodn. Soedin., 1, 107 (1965).