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ALKALOIDS OF AQUILEGIA KARELINI

S. Abdizhabbarova, Z. F. Ismailov, and S. Yu. Yunusov

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Magnoflorine has been isolated from four species of Aquilegia [1, 2], and berberine and aquilegenine in the form of iodides, as well as magnoflorine, have been isolated from A. hybrida [1].

We have investigated the alkaloids of A. karelini (Baker), O. et B. Fedtsch., collected in the basin of the R. Nura (Alai valley) in the fruit-bearing period on 4 August 1965.

Methanolic extraction of the roots gave 1.5% (of the weight of dry roots) of crystals of an iodide of a tertiary base with mp 249°–251° C (decomp.), $[\alpha]_D^{14}$ + 100.6° (c 1.1; water). Its UV spectrum had the three maxima characteristic for aporphine bases. IR spectrum: 3100–3400 cm^{-1} (hydroxy group). The presence of two hydroxy groups in the iodide was confirmed by the preparation of an O, O-diacetyl derivative with mp 234°–235° C (decomp.), $[\alpha]_D^{13}$ + 115.2° C (c 0.9; methanol), and by the integration of the intensities of the bands in the IR spectrum [3]. Furthermore, the analytical results showed the presence of two methoxy groups. Consequently, the iodide of the base is a dihydroxydimethoxyaporphine.

The properties of this iodide are similar to those of the iodide of magnoflorine. Because we lacked a sample of magnoflorine, we methylated the iodide obtained with methyl iodide in the presence of sodium methoxide. A O, O-dimethyl derivative was formed which, by paper chromatography, a mixed melting point, and its IR spectrum, was identical with O-methylcorydine methiodide.

REFERENCES

1. Ch. L. Winek, J. L. Beal, and M. P. Cava, Lloydia, 27, 111, 1964.
2. Ch. L. Winek, J. L. Beal, and M. P. Cava, J. Pharmac. Sci., 53, 734, 1964.
3. Ya. V. Rashkes, ZhAKh, 20, 238, 1965.

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ISOLATION OF KOPSINILAM AND ERVINCINE

D. A. Rakhimov, V. M. Malikov, and S. Yu. Yunusov

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Continuing our investigation of the alkaloids of Vinca erecta Rgl. et Schmalh [1], by separating the total alkaloids with respect to their basicities and by chromatography on alumina we have isolated vincanine, vincanidine, kopsinine, vincamine, vincarine, tombozine, ervinidine, and two crystalline bases.

The first base with mp 248°–249° C, $[\alpha]_D$ −13.5° (c 2.30; chloroform) has a UV spectrum characteristic for indoline bases: λ_{max} (in ethanol): 246 and 295 mμ (log ε 3.39, 3.50). Its IR spectrum has bands of the stretching vibrations of an NH group (3260 cm^{-1}), an ester carbonyl group (1742 cm^{-1}), indoline (1612 cm^{-1}), and a five-membered lactam ring (1690 cm^{-1}). Acetylation of the base gave a N-acetyl derivative with mp 250°–251° C. The IR spectrum of the latter lacked the band of an NH group (3260 cm^{-1}) and showed the band of an amide carbonyl group (1670 cm^{-1}).

When the base was reduced with lithium aluminum hydride in ether, an amino alcohol with mp 155°–156° C (from ethanol) was formed. Its IR spectrum lacked the absorption bands of an ester carbonyl group and a lactam ring and had a broad band due to the adsorption of a hydroxy group (3400–3500 cm^{-1}). A comparison of the IR spectra, R_f values (TLC on silica gel), and a mixed melting point of the amino alcohol with authentic kopsinol showed their

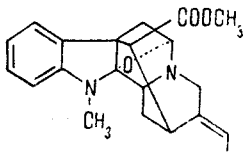
identity [1, 2]. Consequently, the alkaloid that we isolated is kopsinilam.

The second base had the composition $C_{21}H_{24}N_2O_3$ with mp 156°–157° C (methanol), $[\alpha]_D$ + 93° C (c 0.20; chloroform) and contained a methoxy and a $N-CH_3$ group. Oxidation of the alkaloid by the Kuhn-Roth method showed the presence of one $C-CH_3$ group. The IR spectrum of the base had absorption bands at 1750 cm^{-1} ($COOCH_3$), 1085 cm^{-1} (C—O—C), and 750 cm^{-1} (disubstituted benzene ring) and lacked bands characteristic for OH and NH groups.

These data permit the assumption of the following analytical formula for the base:

$$C_{18}H_{18}\,(=N-CH_3)\,(=N-)\,(COOCH_3)\,(-O-).$$

The IR spectrum of the base had three maxima: λ_{max} 228, 276, 316 (log ε 4.43, 3.97, 3.16) and was similar to the spectra of picrinine, picroline, and Ψ-akuammigine [3, 4]. Consequently, the base contains an analogous chromophore system and the following structural formula has been proposed for it as the most probable



This alkaloid proved to be new and has been called ervincine.

REFERENCES

1. V. M. Malikov and S. Yu. Yunusov, KhPS [Chemistry of Natural Compounds], 142, 1967.
2. C. Kump and H. S. Schmid, Helv. Chim. acta, 45, 1090, 1962.
3. A. Chatterjee, B. Mukherjee, and A. B. Roy, Tetrah. Let., 41, 3633, 1965.
4. M. M. Janot, J. Le Men, J. Levy, and L. Olivier, Bull. Soc. Chim. fr., 8–9, 1958, 1961.

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ALKALOIDS OF THE SEEDS OF HAPLOPHYLLUM DUBIUM

S. A. Sultanov, V. I. Pastukhova, and S. Yu. Yunusov

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The ripe seeds of H. dubium Eug. Kor., collected at the end of July in the Surkhandar Region, UzSSR, were defatted with gasoline, and the extract was treated with 10% sulfuric acid. Dubamine sulfate [1] separated out, and the mother liquor, after neutralization and elimination of the solvent by distillation, gave an oil. The yield of dubamine was 0.3% and that of the oil 10%. No other alkaloids were detected in the gasoline extract.

Chloroform extraction of the defatted seeds gave an additional 0.24% of combined bases. The total yield of alkaloids was 0.54%. Chromatography of the combined bases of the chloroform extract on alumina gave five alkaloids, which were identified with authentic samples: with haploperine from H. perforatum [2], with foliosine and skimmianine from H. foliosum [3], and with dubinidine and dubamine from the epigeal part of H. dubium [4].

The leaves of H. dubium, also gathered at the budding stage, contained 0.62% and the stems 0.21% of total bases. At the end of the flowering and the beginning of the fruit-bearing period, the amount of alkaloids in the epigeal part increased to 1.07% in the leaves and 0.3% in the stems. The separation of a mixture of bases from the epigeal part on alumina yielded, besides dubamine and dubinidine, foliosine and haploperine.