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MURICATISINE — A NEW ALKALOID FROM TWO SPECIES OF *Oxytropis*

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The new alkaloid muricatisine has been isolated from the epigeal parts of the plants Oxytropis muricata *(Pall.) DC. (Mongolia) and* O. puberula *Boriss. (Kazakhstan), which belong to the Fabaceae family, and its structure has been established on the basis of spectral characteristics as N-benzoyl-2-oxo-2-phenylethylamine and has been confirmed by a partial synthesis.*

Continuing a study of alkaloids of plants of the genus *Oxytropis* [1], from the epigeal part of *O. muricata* (Pall.) DC. growing in Mongolia we have isolated a new alkaloid, which has been called muricatisine (**1**). Because of its small amount, it was possible to record only the mass spectrum of (**1**). Its structure was established as a result of the detection of this alkaloid in, and its isolation from, the epigeal part of another species, *O. puberula* Boriss., collected at the end of fruit-bearing in the environs of the village of Koktal'skii, Balkashskii region of the Almatskii oblast.

Muricatisine is an optically inactive alkaloid with mp 124-125°C (from acetone), composition $C_{15}H_{13}NO_2$, M^+ 239 (mass spectrometry). The substance crystallizes from acetone in the form of white needles readily soluble in chloroform, sparingly soluble in methanol, and insoluble in water and alkalis.

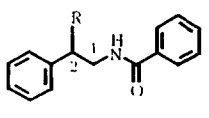
The UV spectrum of (**1**) contained maxima at 202 and 242 nm and was reminiscent of the spectra of N-acylated derivatives of 2-phenylethylamine [2], while its IR spectrum showed the absorption bands of active hydrogen at 3359 cm^{-1} and of conjugated and amide carbonyls at 1694 and 1635 cm^{-1}, respectively.

In the mass spectrum of muricatisine we observed a considerable peak of the molecular ion with m/z 239. The presence in the spectrum of intense peaks of ions with m/z 135, 134, 105, and 77 is characteristic for alkaloids of the 2-phenylethylamine group acylated at the nitrogen atom [2]. The fact that the peak of the molecular ion of (**1**) differed from that of N-benzoyl-2-hydroxy-2-phenylethylamine (**2**) by 2 a.m.u., and also the presence in the IR spectrum of muricatisine of an absorption band of a second carbonyl permitted the suggestion that (**1**) contained a keto group in place of the C-2 hydroxyl in (**2**). This agreed well with the ^1H NMR spectrum of the alkaloid isolated.

In the PMR spectrum of muricatisine we detected signals of the protons of a methylene group bound to a nitrogen atom at δ 4.97 ppm in the form of a two-proton doublet owing to interaction with a hydrogen atom on nitrogen, a broadened one-proton signal of a NH group at 7.35 ppm, and the signals of 10 aromatic protons at 7.50 (5H, m), 7.65 (1H, tt), 7.89 (2H, m), and 8.03 ppm (2H, m).

To confirm the structure of muricatisine, we oxidized compound (**2**) with the Jones reagent. The synthetic product obtained proved to be identical with (**1**) according to TLC, a mixed melting point, and its IR spectrum.

Thus, muricatisine has the structure (**1**) and is N-benzoyl-2-oxo-2-phenylethylamine.



1.R=O
2.R=OH

Compound (**1**) was known previously as a synthetic product for which the melting point and mass spectrum given in the literature [3] coincide with the corresponding characteristics of muricatisine.

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In addition to (1), the known alkaloids harmine and N-nicotinoyl-2-hydroxy-2-phenylethylamine, and β-sitosterol β-glucopyranoside, detected in this plant previously [4], were isolated from *O. puberula.*

EXPERIMENTAL

General Observations. For column chromatography we used type KSK silica gel, and for thin-layer chromatography the same type of silica gel with the addition of 5% of gypsum in the solvent systems benzene–methanol (4:1), chloroform–methanol (9:1), and toluene–ethyl acetate–formic acid (5:4:1). Revealing agents: the Dragendorf reagent and iodine vapor (for the alkaloids), and a 22% alcoholic solution of tungstophosphoric acid (for the glycoside).

UV, IR, PMR, and mass spectra were taken on a UV/VIS Lambda spectrometer, a Perkin–Elmer System 2000 FT-IR instrument, a UNITY-400 Plus instrument in $CDCl_3$ (δ scale, 0 — TMS) and a MKh 1310 instrument with direct injection into the ion source, respectively.

Isolation of Compound (1) from *O. muricata.* For the isolation of the total alkaloid fraction and its separation, see [1]. The ether–hexane (3:7) eluates following the muricatide fractions were combined, evaporated to dryness, and treated with acetone. The resulting crystals were recrystallized from acetone, which gave 2.5 mg of muricatisine with mp 121-122°C.

Isolation of Compound (1) from *O. puberula.* The air-dry epigeal part of *O. puberula* (1 kg) was wetted with 8% aqueous ammonia and extracted with chloroform. After elimination of the solvent, the extract was distributed between ether (A) and 10% aqueous sulfuric acid. The acid solution was alkalinized with concentrated ammonia and exhaustively extracted first with ether (1.5 g) and then with chloroform (1 g). The yield of the mixture of alkaloids amounted to 0.25% on the weight of the plant. The ether fraction of the mixture of alkaloids (1.5 g) was chromatographed on a column of silica gel (1:100), using gradient elution. Harmine (120 mg) and muricatisine (50 mg) deposited from the ether–chloroform eluates. The ethereal solution (A) was treated with 4% aqueous caustic potash, washed with water, dried, and concentrated. The dry residue was chromatographed on a column of silica gel (1:60). Chloroform–methanol eluates yielded 100 mg of β-sitosterol β-glucopyranoside.

Muricatisine (1), mp 124-125°C (from acetone).

UV spectrum (ethanol, λ_{max}, nm) 202, 242.

IR spectrum (ν_{max}, cm^{-1}): 3359, 1694, 1635, 1579, 1523, 1485, 1450, 1443, 1240, 1224, 980, 926, 800, 779, 756, 714.

Mass spectrum, m/z (%): 239 (M^+, 46), 211 (45), 135 (50), 134 (58), 105 (100), 77 (40).

^1H NMR spectrum ($CDCl_3$, δ, ppm: 4.97 (2H, d, J = 4.2 Hz, 2 × H-1), 7.35 (1H, br.s, NH), 7.50 (5H, m, 5 × Ar-H), 7.65 (1H, tt, J_1 = 7.4 Hz, J_2 = 1.9 Hz, J^3 = 1.3 Hz, Ar-H), 7.89 (2H, m, 2 × Ar-H), 8.03 (2H, m, 2 × Ar-H).

Synthesis of Muricatisine (1). With stirring, the Jones reagent [5] was added to an ice-cooled solution of (–)-N-benzoyl–2-hydroxyphenylethylamine (50 mg) until the solution had acquired a brownish coloration. After the addition of the reagent, the mixture was stirred for another 10 min and it was then diluted with 0.5 ml of methanol and poured into water (10 ml). The mixture was cooled, alkalinized with sodium carbonate, and extracted with chloroform. The chloroform solution was washed with water (2 ml) and filtered. The filtrate was concentrated, and the residue contained a white crystalline deposit in the form of needles, which were recrystallized from acetone, mp 124-125°C, yield 30 mg. A mixture with the natural sample gave no depression of the melting point and their IR spectra were identical.

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