

ALKALOIDS OF *Oxytropis*.

III. TRICHOPHYDINE

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A new alkaloid, which has been named trichophydine, has been isolated from the epigeal part of *Oxytropis trichophysa* growing in Mongolia. On the basis of the spectral characteristics of the hydrochloride, the structure of 2-O-benzoyl-2(β)-phenylethylamine, which has been synthesized previously, has been established for trichophydine.

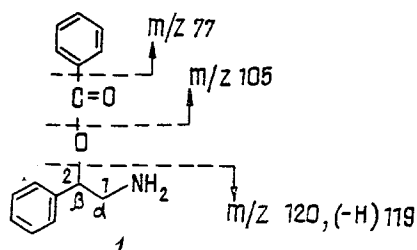
Continuing a study of the alkaloid composition of *Oxytropis trichophysa* [1] we have isolated a base (1) from the epigeal part of this plant by the production of its hydrochloride (2).

The UV spectrum of (2) was typical for aromatic compounds [2a], and its IR spectrum contained the absorption band of an ester carbonyl at 1730 cm^{-1} and a broad absorption band in the $3100\text{--}2800\text{ cm}^{-1}$ region characteristic for salts of primary amines [2b].

In the $^1\text{H NMR}$ spectrum of (2) (δ , D_2O), the signals of aromatic protons and two signals in a stronger field, at 6.28 and 3.68 ppm, were observed. The chemical shift of the two-proton multiplet at 3.68 ppm was characteristic for the α -protons of hydrochlorides of 2-hydroxy-2(β)-phenylethylamine derivatives unsubstituted at the nitrogen atom [3]. The one-proton signal at 6.28 ppm was shifted downfield by approximately 1.1 ppm in comparison with the chemical shifts of the β -protons of the above-mentioned derivatives, which is characteristic for protons geminal to an acylated secondary hydroxy group [2c].

The facts given above showed that (1) was an acyl derivative of 2-hydroxy-2(β)-phenylethylamine at the hydroxy group. The presence in the $^1\text{H NMR}$ spectrum of (2) of the signals of ten aromatic protons in place of five in the spectrum of 2-hydroxy-2(β)-phenylethylamine itself permitted the assumption that the acyl radical was a benzoic acid residue. This was confirmed by the electron-impact mass spectrum of (2), where the peak of a benzoyl cation with m/z 105, having the maximum intensity, was detected. The presence of a phenylethylamine fragment was witnessed by the peaks of ions with (m/z 120 and 119). The peak of the $(M - \text{HCl})^+$ ion with m/z 241, absent from the ordinary spectrum, was clearly recorded in the LSIMS(+) mass spectrum.

Thus, (1) had the structure of 2-O-benzoyl-2(β)-phenylethylamine. This compound has been synthesized previously and the melting point of its hydrochloride, agreeing with the corresponding constant of (2), has been given in the literature [4]. This is the first time that (1) has been found in nature, and it has been called trichophydine



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Huneck et al. [5] isolated a base with mp 38–40°C from the plant *Oxytropis pseudoglandulosa* and ascribed to it the structure (1), but this is contradicted by the spectral characteristics that they obtained for the alkaloid (3) and gave in their paper. Thus, the IR spectrum of (3) lacked the absorption band of an ester carbonyl. The chemical shifts of the α - and β -protons of (3) differed greatly from those given in the literature [3] for 2-hydroxy-2(β)-phenylethylamine derivatives and, as a comparative analysis shows, were characteristic for oxazoline compounds [6-8], i.e., (3) had a structure different from (1).

EXPERIMENTAL

UV spectra were taken on a Hitachi spectrophotometer, IR spectra on a UR-20, ^1H NMR spectra on a Tesla BS-567 A spectrometer (δ , 0 – HMDS), and mass spectra on a MKh 1310 instrument with a system for direct injection into the ion source, and with a LSIMS(+) source.

For column chromatography we used type KSK silica gel, and for thin-layer chromatography silica gel of the same type with the addition of 5% of gypsum, in the solvent system benzene–methanol (4:1); the spots were revealed with the Dragendorff reagent.

Isolation of the Alkaloid. The air-dry epigeal part of *O. trichophysa* (0.3 kg), gathered in Mongolia by D. Batsurén, was extracted with methanol. The dry extract was treated with hexane and, after the evaporation of the hexane, the residue was deposited on a column of silica gel (1:100) and was eluted with benzene–methanol (4:1). The first eluates yielded oxytriphine (50 mg) [1]. The following few eluates were combined and concentrated, and, with cooling, an acetone solution of hydrochloric acid was added to give a weak acid reaction. The precipitate of trichophydine hydrochloride that deposited in the cold (100 mg, mp 194–198°C) was washed with ethyl acetate and was crystallized twice from ethanol. This gave 25 mg of (2).

Trichophydine hydrochloride (2), mp 200–203°C. UV spectra (ethanol, λ_{max} , nm): 233, 284 (inflection). IR spectrum (KBr, ν_{max} , cm^{-1}): 3100–2800, 1730, 1600, 1275, 1105, 980, 770, 710.

Mass spectrum, m/z (%) 120 (5), 119 (33), 117 (37), 105 (100), 91 (13), 51 (34); LSIMS (+): m/z 242 [(M–HCl) + H] $^+$.

^1H NMR spectrum. (D_2O , δ , ppm, J, Hz): 3.68 (2H, m; α -H); 6.28 (1H, dd, J = 4.5; 6; β -H); 7.62 (8H, m, Ar–H); 8.18 (2H, m; Ar–H); ($\text{C}_5\text{D}_5\text{N}$): 3.78 (2H, m; α -H); 6.75 (1H, dd, J = 5; 6; β -H); 7.38 (m, Ar–H); 8.12 (2H, m; Ar–H).

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