A STUDY OF THE ALKALOIDS OF Glaucium fimbrilligerum

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Continuing a study of the alkaloid composition of G. fimbrilligerum [1] from different growth sites, we have investigated the plant collected on July 13, 1971, in the flowering period, in the environs of the village of Yurkun' (Pamir-Alai). Chloroform extraction gave 0.39% of combined alkaloids, and by separating these with respect to their solubility in organic solvents, by the preparation of salts, and by column chromatography on alumina, we isolated sanguinarine, chelenythrine, protopine, allocryptopine, isocorydine, corydine, isoboldine, and bases with mp 132-133°C and 200-201°C. The base with mp 132°-133°C (from methanol) has the composition $C_{18}H_{21}NO_3$, $[\alpha]_D$ −62.3° (c 0.78; chloroform) R_f 0.3 [benzene−chloroform−methanol (5:2:2) system]. The base is sparingly soluble in ether and benzene and readily soluble in alkalis. The IR spectrum shows absorption bands at 1510 and 1600 cm^{-1} (aromatic ring) and a broad band at 3200-3600 cm^{-1} (hydroxy group). UV spectrum, λ_{max} 228, 288 nm (log ε 4.14, 3.73). The mass spectrum of the base lacks the peak of the molecular ion, and the maximum ion is one with m/e 192, which is characteristic for the benzylisoquinoline alkaloids [2]. The NMR spectrum of the base taken in trifluoroacetic acid shows a three-proton doublet due to an N−CH_3 group at 2.64 ppm (J=4 Hz), a three-proton singlet (OCH_3) at 3.51 ppm, two one-proton singlets at 6.11 and 6.42 ppm from two para aromatic protons, and a four-proton quadruplet at 6.55 and 6.72 ppm (J=8 Hz) from two equivalent pairs of ortho aromatic protons. Methylation of the base with diazomethane gave the O,O-dimethyl ether with mp 59-60°C the methiodide of which, with mp 132-133°C (from methanol), was identical with an authentic sample of the methiodide of O-methylarmepavine [3].

The facts given above indicate that the base with mp 132-133°C is N-methylcoclaurine [4], first isolated from plants of the genus Glaucium.

From the combined nonphenolic alkaloids of G. fimbrilligerum collected in the village of Daraut-Kurgan (Pamir-Alai) [1] we have additionally obtained a base with the composition $C_{20}H_{19}NO_5$, mp 213-214°C (chloroform−methanol), $[\alpha]_D \pm 0°$. UV spectrum: λ_{max} 238, 290 nm (log ε 4.13, 4.01). The IR spectrum has absorption bands at 935 and 1040 cm^{-1} (methylenedioxy group, 1500 cm^{-1} (aromatic ring), and 3350-3600 cm^{-1} (hydroxy group). The NMR spectrum shows signals in the form of a three-proton singlet at 2.20 ppm from an N−CH_3 group, a four-proton signal at 5.95 and 5.99 ppm from two methylenedioxy groups, and signals from four aromatic protons at 6.66 and 6.70 ppm. The mass spectrum of the base shows the peak of the molecular ion with m/e 353 and those of ions with m/e 352, 335, 322, 304, and 294.

The spectral features given are characteristic for alkaloids of the chelidonine type. Acetylation of the base with acetic acid gave the O-acetyl derivative. The NMR spectra of the base and its O-acetyl derivative were identical with those of chelidonine and its acetate [5]. Thus, the base that we have isolated is dl-chelidonine.

LITERATURE CITED

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