ALKALOIDS OF Veratrum lobelianum

ISOLATION OF γ-SOLANINE

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The present communication gives the results of a further study of the alkaloids of V. lobelianum growing in the Caucasus [1]. An ethanolic extract of 16 kg of the epigeal part of the plant was fractionated by Salzberger's method [2]. On concentration, an ether solution of the combined alkaloids deposited veralosine (I) [3]. The mother solution after the separation of the veralosine was separated by means of an acetate buffer with pH 4.0 into eight fractions. The fourth and fifth fractions were combined and chromatographed on a column of silica gel (KSK) with elution by benzene–acetone (10 : 1 and 4 : 1). At a ratio of 10 : 1, an alkaloid with mp 226-228°C (II), $[\alpha]_D$ −70.46°, was obtained, and at 4 : 1 a base with mp 220-222°C (III), $[\alpha]_D$ −65.46°.

The IR spectrum of (II) had ν_{max}, cm^{-1}: 3560, 3440 (OH), 1740, 1250 (ester C=O). The compound formed an acetyl derivative with mp 250-252°C. The IR spectrum of (III) had ν_{max}, cm^{-1}: 3540, 3450 (OH), 1750, 1250 (ester C=O). It gave a picrate with mp 244-246°C.

The alkaline hydrolysis of (II) gave the amino alcohol germine [1], α-methylbutyric acid, and acetic acid, and the saponification of (III) gave germine, α-methylbutyric acid, angelic acid, and acetic acid. The acetic acid was detected by paper chromatography [4].

It follows from the facts presented that compound (II) is identical with neogermitrine [5], and alkaloid (III) is germanitrine [6], which is confirmed by their NMR spectra. The NMR spectrum of (II) has singlets at 0.94 ppm (3 H, 19-CH_3), 1.13 (3 H, 21-CH_3), 2.01 and 2.03 (6 H, $OCOCH_3$); doublets at 1.01 (3 H, 27-CH_3), 1.08 (3 H, $-CH-CH_3$ of a side chain SC), 5.14 (H, H−C−O-acyl); triplets at 0.83 (3 H, $-CH_2-CH_3$ SC), 4.95 (H, H−C−O-acyl); and a multiplet at 5.74 (H, H−C−O-acyl). The NMR spectrum of (III) showed singlets at (ppm) 0.94 (3 H, 19-CH_3), 1.12 (3 H, 21-CH_3), 1.88 (3 H, $-CH=C-CH_3$ SC), 2.00 (3 H, $OCOCH_3$); doublets at 1.00 (3 H, 27-CH_3), 1.07 (3 H, $-CH-CH_3$ SC), 1.26 (3 H, $-C=CH-CH_3$ SC); a triplet at 0.82 (3 H, $-CH_2-CH_3$ SC); a quartet at 5.71 ppm (H, olefinic proton); and a multiplet at 5.04 ppm (3 H, H−C−O-acyl).

From the sparingly soluble metaphosphate fraction of the combined alkaloids by chromatography on a column of silica gel and elution with acetone–benzene (4 : 8) we isolated an alkaloid with mp 212-213°C, $C_{27}H_{43}NO$ (IV), identified as solandine (IR and mass spectra, mp) [7].

The benzene-soluble fraction of the combined alkaloids [1] was also separated by means of an acetate buffer at pH 4.0 into eight fractions. Treatment of the third and fourth fractions with chloroform led to the separation of a base with mp 237-239°C, $[\alpha]_D$ −23.07, $C_{33}H_{53}NO_6$ (V). The IR spectrum had ν_{max} (cm^{-1}) 3400 (OH), 1660 (double bond), and 1010-1110 (OH). The mass spectrum contained as the main peaks those of ions with m/e 150 (100%), 204, 380, 397, 544 (M − 15), and 559 (M^+). The peaks of ions with m/e 150 and 204 are characteristic for alkaloids of the solanidine group [8]. In actual fact, the hydrolysis of (V) liberated an aglycone identical with an authentic sample of solanidine (IR spectrum, mp) [7] and galactose (paper chromatography). Consequently, the alkaloid (V) is the known glycoalkaloid γ-solanine [9], and this is the first time it has been obtained from the genus Veratrum.

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