ALKALOIDS OF Veratrum lobelianum

R. Shakirov and S. Yu. Yunusov

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In preceding communications [1, 2] we have described results of an investigation of the alkaloids of the epigeal part of V. lobelianum. From the hypogeal part of this plant by chloroform extraction we have obtained 1.01% of combined ethereal and 0.8% of combined chloroformic bases (on the weight of the dry raw material). We treated the combined ethereal bases with benzene. Precipitate A that deposited was separated on a column of alumina (activity grade II). Elution was performed with benzene and with chloroform. The chloroform eluate yielded a base (I) with mp 203-205°C (from benzene), $[\alpha]_D$ +9.98° (chloroform), R_f 0.41 in system 1 [acetone–benzene (2:1)] on TLC in silica gel. Alkaloid (I) forms salts: hydrochloride with mp 215-216°C, hydrobromide with mp 212-213°C, picrate with mp 187-189°C, thiocyanate with mp 220-222°C. IR spectrum, cm^{-1}: 3360 (OH), 2935, 1465 ($-CH_3$ and $-CH_2-$), 1742, 1250 (ester C=O). The alkaline hydrolysis of (I) gave an amino acid with mp 222-225°C $[\alpha]_D$ +19.06° (10% acetic acid), $C_{27}H_{43}O_8N$ [6], α-methylbutyric acid with R_f 0.54 (a marker was obtained by the saponification of visnadin, kindly given to us by G. K. Nikonov), and α-hydroxy-α-methylbutyric acid with R_f 0.33. The latter was detected by paper chromatography [3].

The facts given above confirm that compound (I) is germerine [4-6].

The last fraction of the chloroform eluate yielded a base (II) with the composition $C_{32}H_{51}O_9N$, mp 157-159°C (from benzene), $[\alpha]_D$ +8.02° (chloroform), R_f 0.35 (1).

The benzene-soluble fraction of the total material, after the removal of the precipitate A, was separated by partition between benzene and an acetate buffer with pH 4.0 into eight fractions. From the second fraction alkaloid (III) crystallized with mp 259-261°C (from acetone), $[\alpha]_D$ −38.79° (chloroform), R_f 0.38 in system 2 [butyl acetate–chloroform–ethanol (1:2:3)]. IR spectrum, cm^{-1}: 3470 (OH), 2945, 1440 ($-CH_3$ and $-CH_2-$), 1711, 1277 (ester C=O), 1605, 1520 (aromatic ring). The UV spectrum (λ_{max} 220, 263, 294 nm) was identical with that of veratroylzygadenine [6, 7].

When (III) was saponified, the acid fraction yielded a substance with mp 177-179°C identified as veratric acid from its IR spectrum and a mixed melting point, and the alkaline fraction yielded an amino alcohol with mp 166-170°C. The melting point of this amino alcohol corresponded to that of pseudozygadenine [6]. Consequently, (III) is veratroylzygadenine. When the mother liquor from (III) was treated with acetone, crystals of substance (IV) with the composition $C_{27}H_{39}O_3N$ precipitated with mp 243-245°C (from methanol), $[\alpha]_D$ −150.7° (ethanol), this substance being identical with jervine from its IR spectrum [8, 9] and a mixed melting point.

The fifth and sixth fractions, by treatment with acetone, gave a base (V) with mp 220-221°C (from acetone) $[\alpha]_D$ −173.17° (chloroform), R_f 0.82, and veralosinine (VI) [1].

The combined chloroformic alkaloids were treated with a mixture of acetone and methanol to give alkaloid (VII) with mp 275-277°C (from methanol), $[\alpha]_D$ −54.11° (10% acetic acid).

The mother liquor from (VII) was separated according to basicities into five fractions. Fraction 1 yielded a base (VIII) with mp 278-280°C (from methanol), $[\alpha]_D$ −100.98° (ethanol–chloroform), R_f 0.39, IR spectrum, cm^{-1}: 3535, 3300 (OH, NH) 2930, 1450 ($-CH_3$ and $-CH_2-$), 1700, 1635 ($O{=}C-C{=}C-$), 1145-1000 (broad absorption band characteristic for glycoalkaloids). Its UV spectrum (λ_{max} 253, 361 nm) was similar to that of jervine [9]. The hydrolysis products of (VIII) were shown by paper chromatography to contain D-glucose and jervine [2, 8].

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From what has been said it follows that (VIII) is a glycoalkaloid of jervine – pseudojervine [8].

Thus, of the total bases of the hypogeal part of V. lobelianum we have isolated the following known alkaloids – germerine, veratroylzygadenine jervine, and pseudojervine – and, as new alkaloids, veralosinine and three bases – (II), (V), and (VII) – the study of which is continuing.

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