ALKALOIDS OF *Fumaria vaillantii*

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From *Fumaria vaillantii*, collected in the Tashkent province, 18 alkaloids have been isolated of which N-methyladlumine with mp 198-199°C, $[\alpha]_D - 45°$ (c 0.5; methanol) has proved to be new. Its structure has been established on the basis of spectral characteristics and a direct comparison with *l*-adlumine methiodide.

Continuing a study of the total alkaloids of *Fumaria vaillantii* [1, 2] collected in the Tashkent province in the period of flowering and incipient budding, from the nonphenolic fraction we have isolated protopine, bicuculline, d-α-hydrastine, adlumidine, adlumine, stylopine, fumariline, ledecorine, styropine methohydroxide, and adlumidiceine, and from the phenolic fraction cheilanthifoline, parfumine, coclaurine, recticuline, isoboldine, norjuziphine, and scoulerine. All the alkaloids have been identified by comparison with authentic samples [1-4], and fumaridine and adlumidiceine by comparing properties and spectral characteristics with literature information [5, 6].

From the quaternary fraction a new optically active base with mp 198-199°C has been isolated in the form of the iodide. Its UV spectrum has three maxima at 240, 292, and 330 nm (log ε 4.46, 4.04, 3.14). In its IR spectrum there are absorption bands at (cm^{-1}) 915, 1035 (CH_2O_2), 1490, 1510 (aromatic ring) and 1775 (CO). The NMR spectrum, taken in trifluoroacetic acid, shows signals in the form of three-proton singlets at 2.85, 3.11, 3.21, and 3.50 ppm, one-proton doublets at 4.41 and 5.09 ppm (J = 8 Hz), and a broad singlet at 5.69 ppm corresponding to four protons. In the 6.44 ppm region there is a one-proton doublet (J = 8 Hz). Another pair of doublets is overlapped by the signals of the protons of the methylenedioxy group, which appear at 5.69 ppm. There is a one-proton singlet at 6.48 ppm.

The spectral characteristics given above permit the assumption that the base belongs to the quaternary phthalide-isoquinoline alkaloids. A direct comparison with *l*-adlumine methiodide showed their identity. Thus, our base is N-methyladlumine.

EXPERIMENTAL

For chromatography we used type KSK silica gel. IR spectra were taken on a UR-20 instrument (tablets with KBr), and NMR spectra in $CDCl_3$ and CF_3COOH on a JEOL instrument with HMDS as standard, its signal being taken as 0 (δ scale); mass spectra were recorded on an MKh-1303 instrument.

Isolation and Separation of the Total Alkaloids. The air-dry comminuted plant (23 kg) was extracted with methanol. After the solvent had been distilled off, the residual extract was dissolved in 10% H_2SO_4. The acid solution was washed with ether and was made alkaline with 25% ammonia, and the alkaloids were extracted with ether and chloroform. After the solvents had been distilled off, 48.74 g of combined ether-extracted and 22.0 g of combined chloroform-extracted alkaloids were obtained. The ether-soluble material was separated into ether-extracted phenolic (5.34 g), chloroform-extracted phenolic (1.60 g), and nonphenolic fractions. From the combined nonphenolic material by treatment with methanol 6.0 g of protopine, 2.0 g of d-α-hydrastine, and 3.20 g of a mixture of crystals consisting of bicuculline. adlumidine, and adlumine were obtained. The mother liquor (30.6 g) was chromatographed on a column containing silica gel (1 : 30). Benzene and benzene—ethanol mixtures in various proportions were used as eluents. The benzene eluates yielded 0.01 g of stylopine and 0.34 g of d-α-hydrastine. The fractions eluted by a 98 : 2 mixture gave 0.75 g of fumariline, and a 94 : 6 mixture yielded 0.03 g of adlumidine, 0.01 g of adlumine, and 0.57 g of bicuculline, From the fractions eluted by a 92 : 8 mixture were isolated 0.17 g of ledecorine, and by a 4 : 1 mixture of 0.06 g of stylopine methohydroxide and 1.50 g of adlumidiceine.

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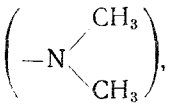
The combined ether-soluble phenolic material was chromatographed on a column containing silica gel (1 : 30). The alkaloids were eluted with chloroform and with a mixture of chloroform and ethanol. The chloroform fraction yielded 0.05 g of cheilanthifoline and 0.2 g of scoulerine. The fractions eluted with the 98 : 2 mixture gave 0.45 g of parfumine and 0.45 g of norjuziphine, and the 92 : 8 mixture gave 0.01 g of isoboldine and 0.02 g of coclaurine. From the fractions eluted by the 4 : 1 mixture, 0.15 g of reticuline was isolated.

The remaining alkaline solution was acidified with sulfuric acid and was treated with a saturated solution of potassium iodide, and the iodides of the quaternary alkaloids were extracted with chloroform. The chloroform solution was filtered and the residue (after the elimination of the solvent), was treated with methanol. This gave 0.14 g of N-methyladlumine.

Fumariline, mp 137-138°C, $[\alpha]_D$ + 66° (c 0.1; ethanol). UV spectrum: λ_{max} 235, 260, 295, 355 nm (log ε 4.17, 3.94, 3.72, 3.76). IR spectrum (cm^{-1}): 940, 1040 (CH_2O_2), 1710 (CO). Mass spectrum: m/z 351 (M^+), 336, 322 (100%), 308, 293, 264, 175, 135. NMR spectrum, ppm: 2.36 (N—CH_3), 2.60-3.55 (6H), 5.85 and 6.17 (2 CH_2O_2), 6.21 and 6.58 (singlet, 1 H each), and 6.89 and 7.15 (J = 8 Hz, doublets, 1 H each).

Adlumidiceine, mp 209-210°C. IR spectrum, cm^{-1}: 920, 1050 (CH_2O_2), 1610, 1505 (Ar), 1700 (CO). Mass spectrum: m/z 399 (M^+), 381, 336, 58 (100%). PMR spectrum, ppm: 2.67 (), 2.90-3.64 (6 H), 5.47 and 5.70 (2 CH_2O_2), 6.15 and 6.30 (singlets, 1 H each).

N-Methyladlumine, mp. 198-199°C, $[\alpha]_D$ − 45° (c 0.5; methanol).

SUMMARY

From the combined alkaloids of *Fumaria vaillantii* 18 bases have been isolated, of which N-methyladlumine has proved to be new, and its structure has been established.

This is the first time that cheilanthifoline, coclaurine, reticuline, isoboldine, ledecorine, adlumidiceine, norjuziphine, and styropine methohydroxide have been isolated from the genus *Fumaria*, and the first time that stylopine and fumariline have been isolated from this particular species of plant.

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