HAPLAMIDINE – A NEW ALKALOID FROM Haplophyllum latifolium

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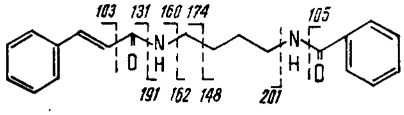
Continuing a study of the alkaloids of Haplophyllum latifolium, we have investigated the epigeal part of the plant collected by K. Taidzhanov in the flowering–incipient fruit-bearing phase on May 26, 1975, in the Alchamaidan area (Fergana range, Baubasta mountains, KirgSSR). The evaporated methanolic extract from 7 kg of the plant was distributed between chloroform and 10% sulfuric acid. The acid solution contained no alkaloids. The chloroform solution was shaken with 4% alkali, and the neutral fraction remaining in the chloroform, after distillation of the solvent, was chromatographed on alumina, and then on silica gel. The first ethereal eluates yielded haplamine [1], and the last gave a new alkaloid which we have called haplamidine (I).

Haplamidine is a white crystalline substance with the composition $C_{20}H_{22}N_2O_2$, mp 139-140°C (ethanol) possessing no basic properties and sparingly soluble in organic solvents and insoluble in water and dilute acids and alkalis. λ_{max} 218, 224, 274 nm (log ε 4.36, 4.37, 4.19). The IR spectrum of (I) shows absorption bands at (cm^{-1}) 3320, 1630 (NH–CO) and 1581, 1542, 771, and 725 (monosubstituted benzene ring), resembling those in the spectrum of haplamine.

The NMR spectrum of (I) (CF_3COOH, τ scale) shows signals at (ppm) 1.65 (broadened signal, 2 × NH), 2.45 and 3.58 (doublets, 1 H each, J = 16 Hz, CH=CH), 2.67-2.90 (multiplet, $2 \times C_6H_5$), 6.61 and 8.44 (broadened signals, 4 H each, $> N-(CH_2)_4-N <$). All the signals with the exception of the doublets at 2.45 and 3.58 ppm, the chemical shifts and coupling constants of which are typical for trans-olefinic protons conjugated with a carbonyl group [3] are also present in the spectrum of haplamine [1]. This permits the assumption that haplamidine has the structure of N-benzoyl-N'-cinnamoyltetramethylenediamine (I):



I

The mass spectrum of (I) has the peaks of the following ions: m/e (%): 322 (33, M^+), 201 (80, M–121), 191 (17, M–131), 175 (69, M–147), 174 (80, M–148), 162 (17, M–160), 160 (11, M–162), 148 (20, M–174), 146 (11, M–176), 131 (100, M–191), 105 (57, M–217), 103 (26, M–219), 77 (9). The intense fragments with m/e 131 and 103 are characteristic for compounds having a cinnamoyl residue [3]. The presence of two NH groups is confirmed by the displacement of the peak of the molecular ion by two mass units when haplamidine is deuterated. Consequently, the mass spectrum of haplamidine is in good agreement with structure (I).

Thus, the epigeal part of H. latifolium collected in the KirgSSR does not contain the furanoquinoline alkaloids characteristic of this plant [1, 2].

From the epigeal part of the plant (KazSSR) containing haplamine [1], we also isolated haplamidine (0.001% on the weight of the dry plant).

Amides are found in plants of the family Rutaceae [4], but among representatives of the genus Haplophyllum they have been hitherto detected only in H. latifolium.

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LITERATURE CITED

1. E. F. Nesmelova, I. A. Bessonova, and S. Yu. Yunusov, Khim. Prirodn. Soedin., 289 (1977).
2. E. F. Nesmelova, I. A. Bessonova, and S. Yu. Yunusov, Khim. Prirodn. Soedin., 666 (1975).
3. G. Englert, K. Klings, R. Hamet, E. Schlitler, and W. Vetter, Helv. Chim. Acta, 56, 474 (1973).
4. P. G. Waterman, Biochem. Syst. and Ecol., 3, 149 (1975); R. Hegnauer, Chemotuxonomie der Pflanzen, Birkhäuser Verlag, Basel-Stuttgart, Vol. 6 (1973), p. 188.

NEW ALKALOIDS OF Corydalis ledebouriana

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Continuing the separation of the combined alkaloids of the epigeal part of Corydalis ledebouriana collected in the Tashkent oblast [1], we have isolated two new bases (I) and (II).

Base (I), with mp 219-220°C (methanol + chloroform), $[\alpha]_D \pm 0°$ has the composition $C_{21}H_{23}O_6N$. The IR spectrum of (I) shows absorption bands at (cm^{-1}) 3540, 3520 (hydroxy group), 1515 (aromatic ring), and 1040, 930, and 920 (methylenedioxy group). The mass spectrum of (I) contains the peaks of ions with m/e 385 (M^+), 370, 367, 352, 338, 324, 308, and 206. According to its NMR spectrum, base (I) contains a N-methyl group, two methoxy groups, and a methylenedioxy group (see below). The spectral characteristics are identical with those of d-raddeanine [2]. To confirm this, we reduced dl-raddeanone (III) [2], which we isolated from the same plant (shown to be identical with an authentic sample by Prof. T. Kametani, Japan), with sodium tetrahydroborate and obtained dihydroraddeanone with mp 218-219°C, $[\alpha]_D \pm 0°C$, a direct comparison of which with (I) showed their identitiy. Thus, base (I) is dl-raddeanine.

Base (II) with mp 140-141°C, $[\alpha]_D +114°$ (c 0.28; methanol), which we have called ledebouridine, has the composition $C_{20}H_{21}O_6N$, mol. wt. 371 (mass spectrometrically). The IR spectrum of (II) has absorption bands at (cm^{-1}) 3540, 3430 (OH), 1600, 1500 (aromatic ring), and 1030 and 920 (CH_2O_2). The NMR spectrum of (II) (see below) shows the signals of N-methyl, methoxy, and methylenedioxy groups. The mass spectrum contains, in addition to the peak of the molecular, peaks of ions with m/e 356, 353, 338, 324, 308, 294, 192, 190, 177. The facts given show that ledebouridine belongs to the group of spirobenzylisoquinoline alkaloids containing two hydroxy groups in the five-membered ring [2-4].

The PMR spectra were taken on a JNM-4H-100/100 MHz instrument with HMDS as internal standard. Below we give the chemical shifts (δ scale, CDC-$_3$):

	d-Raddeanine [2]	dl-Raddeanine (I)	O-Methylledebouridine	Ledebouridine (II)
C_1—H	6,16	6,11	6,12	6,19
C_4—H	6,55	6,61	6,61	6,59
C_{10}—H	6.76 (d, 8 Hz)	6.76 (d, 8 Hz)	6.76 (d, 8 Hz)	6.77
C_{11}—H	6,80	6,88	6,86	6,77
C_{14}—H	5,42	5,39	5,36	5,33
C_9—H	5,21	5,19	5,15	5,11
C_2—OCH_3	3,40	3,35	3,35	—
C_3—OCH_3	3,81	3,78	3,78	3,75
N—CH_3	2,60	2,56	2,55	2,50
CH_2O_2	5,97	5,94	5,91	5,91

The presence in the mass spectrum of (II) of the peak of an ion with m/e 192 shows that in the isoquinoline part of the molecule of the base there is a methoxy group and a hydroxy group. The methylation of ledebouridine with diazomethane gave O-methylledebouridine with mp 204-205°C (acetone), $[\alpha]_D +107°$ (c 0.18;

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