ALKALOIDS OF *Merendera trigina*

STRUCTURE OF TRIGAMINE

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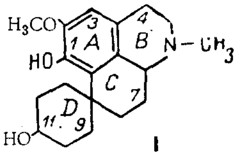
Merendera trigina (Adams) Woron. belongs to the little-studied species of plants of the family Liliancese. The presence of colchicine and of other, unidentified compounds in it has been shown by chromatographic methods [1-3]. We have studied the alkaloids of the epigeal and hypogeal parts of this plant collected in the foothills of the Alagyaz (ArmSSR). Methanolic extraction yielded 0.18% of weak bases and 0.05% of strong bases, which were separated into alkali-soluble and alkali-insoluble fractions. In the mixture of weak alkali-insoluble bases, colchicine and β-lumicolchicine were identified chromatographically, and in the mixture of alkali-soluble bases colchiceine, 2-demethylcolchiceine, and 2-demethylcolchicine.

The strong-base fraction from the plant consisted of compounds without a tropolone ring. Its alkali-soluble fraction consisted mainly of a compound with R_f 0.40, and the alkali-insoluble fraction of a compound with R_f 0.47 [PC on Filtrak No. 1 paper; n-butanol–5% acetic acid (50 :50)], and these were chromatographed on alumina. The substances were eluted from the adsorbent with chloroform and were crystallized from acetone.

An alkaloid with the composition $C_{21}H_{25}O_5N$, mp 230-231°C, $[\alpha]_D$ + 90° (c 1.0; chloroform), R_f 0.40 was identified by its UV, IR, PMR, and mass spectra as S-fluoramultine [4]. A base with the composition $C_{19}H_{27}O_3N$, mp 169-170°C, $[\alpha]_D - 7°$ (c 1.0; chloroform), R_f 0.7 differed from known compounds in its physical constants and spectral characteristics. It has been called trigamine (I). In its UV spectrum there are absorption maxima at 216 and 287 nm and in its IR spectrum characteristic bands at (cm^{-1}) 3400-3200 (OH), 1600 (arom. $-C=C-$), and 1480 ($-CH_2-$). The PMR spectrum (in $CDCl_3$) shows the signal of an aromatic methoxy group (three-proton singlet at 3.75 ppm), a N-methyl group (three-proton singlet at 2.34 ppm), and one proton of a benzene ring (one-proton singlet at 6.48 ppm). The mass spectrum of (I) has peaks of the main ions with m/e 317 (M^+, 49%), M–1 (100%), 300, 274, 256, 244, 228, 205, 202, which are characteristic for various derivatives of tetrahydroisoquinoline [5, 6].

The spectral characteristics presented permit trigamine to be assigned to compounds of the homoproaporphine series and the structure of 1,11-dihydroxy-2-methoxyhexahydrohomoproaporphine (I) to be proposed for it:



I

The position of the methoxy group at C_2 in (I) is confirmed by the results of a study of the intramolecular nuclear Overhauser effect relative to the C_3 proton. The location of a secondary alcoholic hydroxy group at C_{11} of ring D agrees with literature information for compounds of similar structure [7].

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SYNTHESIS OF DEOXYPEGANINE AND ITS ANALOGS BY THE AMIDOMETHYLATION OF ACETANILIDE WITH N-(HYDROXYMETHYL)LACTAMS

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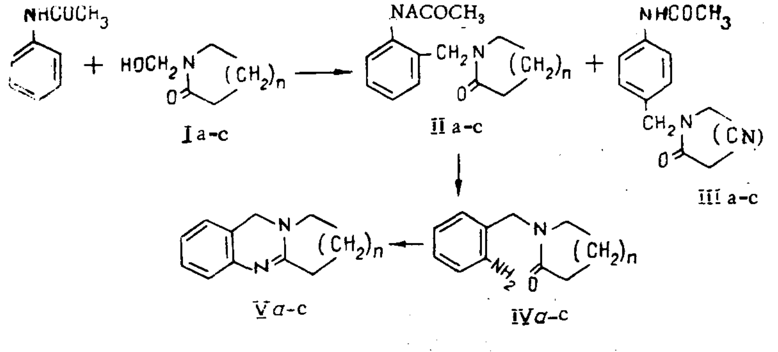
Continuing investigations on the synthesis of deoxypeganine derivatives [1, 2], we have performed the reactions of acetanilide and of p-methoxyacetanilide with N-(hydroxymethyl)lactams. By the reaction of acetanilide with N-(hydroxymethyl)pyrrolidone (Ia), N-(hydroxymethyl)piperidone (Ib), and N-(hydroxymethyl)caprolactam (Ic) in concentrated sulfuric acid at 70°C, we obtained a mixture of the o- and p-acetylaminobenzyl derivatives of pyrrolidone (IIa) and (IIIa), of piperidone (IIb) and (IIIb), and of caprolactam (IIc) and (III)c, respectively.

Performance of the reaction at room temperature led to the formation only of substance (III). The hydrolysis of (II) in an acid medium gave the corresponding o-aminobenzyl derivatives of pyrrolidone (IVa), of piperidone (IVb), and of caprolactam (IVc). The latter, on being treated with water-abstracting agents, cyclized to form 2,3-trimethylene-, 2,3-tetramethylene-, and 2,3-pentamethylene-3,4-dihydroquinazolines (Va, b, and c, respectively). In its physicochemical properties, (Va) was completely identical with deoxypeganine [1, 3]. Substance (Vb) was identical with an alkaloid isolated from the plant Mackilaya [4] and proved to belong to a new class of quinazoline alkaloids. Compound (Vc) has been obtained previously by a multistage method from 1-(o-aminobenzyl)hexamethyleneimine [5]. The reaction of p-methoxyacetanilide with (Ia) at 20°C formed (5-acetylamino-2-methoxybenzyl)pyrrolidone (VI). Its structure was shown by its PMR spectrum, which contained the signals of protons in the following regions: (ppm): 2.0 (the protons of two methyl groups); 2.3, 3.2, and 3.7, (the protons of three methylene groups) 4.4 (aminomethylene group); and 7.1 and 7.3 ppm (protons of an aromatic ring).



Throughout a: $n = 1$: b: $n = 2$: c: $n = 3$

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