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STRUCTURE OF THALICSIMIDINE

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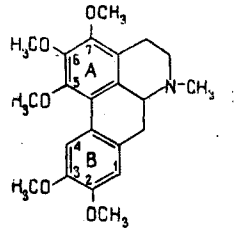
We have previously reported the isolation of an aporphine base from the roots of Thalictrum simplex L. [1]. The base proved to be new, and we called it thalicsimidine. It contains a N-methyl and five methoxy groups. The molecular weight determined by mass spectroscopy is 385. The fragmentation of the base (the mass spectra were taken on a MKh-1303 mass spectrometer at an energy of the ionizing electrons of 34 eV with an ionizing current of 150 μa, at 130° C) agrees with the data published for aporphines [2]. The mass spectrum of thalicsimidine has peaks of ions with m/e 385 (M^+), 384 $(M-1)^+$, 370 $(M-CH_3)^+$, 354 $(M-OCH_3)^+$, 342 $(M-CH_2=N-CH_3)^+$. The last ion, by losing a methyl group, gives an ion with m/e 327, the loss of one methoxyl leads to an ion with m/e 311, and the loss of two methoxyls to an ion m/e 280. However, the peaks with m/e 152 and 165 found in the spectra of three aporphine bases [2] are not present in the spectrum of thalicsimidine. The strongest peaks are those with m/e 57, 56, 55, and 43. Since the specific rotation of the base is less than 100°, the substituents in ring B must be located at C-2 and C-3 [3].



I

By analogy with other penta-substituted aporphines, we propose for thalicsimidine the structure I.

The NMR spectra of the base (taken by M. R. Yagudaev on a JNM-4H-100/100 MHz instrument in deuterochloroform) confirm the structure that we have proposed [4]. In the region of aromatic protons there are two one-proton singlets at δ 6.70 and 7.89, the latter relating to the hydrogen at C-4. The protons of N-methyl group appear in the form of a 3-proton singlet at δ 2.47. The methoxy groups give four peaks at δ 3.88 (C-7), 3.85 (two OCH_3, at C-2 and C-3), 3.82 (C-6), and 3.64 (C-5).

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ALKALOIDS OF PEDICULARIS OLGAE

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Continuing our investigation of the alkaloids of P. olgae [1,2], by chromatographing the ethereal fraction of the combined alkaloids on alumina (eluant: benzene–chloroform (2:1)], we have isolated a crystalline base with mp 188–189° C (ethanol), R_f 0.77 [1-butanol–water–acetic acid (20:20:1) system], $[\alpha]_D^{25}$ +61.5° (c 0.95; ethanol), $C_{10}H_{11}NO$,

mol. wt. 161 (mass spectrometry).

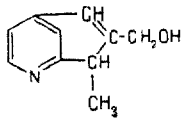
The UV spectrum is characteristic for pyridine bases: λ_{max} (in chloroform) 265 mμ.

The IR spectrum of the alkaloid has absorption bands at 3200 cm^{-1} (hydroxy group), 2960 ($C-CH_3$ group), 1950 (pyridine ring), and 810–890 cm^{-1} (2, 3, 4-trisubstituted benzene ring).

This alkaloid has proved to be new and has been called pediculine. The catalytic hydrogenation of pediculine forms a dihydro derivative.

The mass spectrum of pediculine has a strong molecular ion with m/e 161 (100%), which is characteristic for pyridine bases, and the peaks of ions with m/e 146, 117, and 91.

The ion with m/e 146 is formed from the molecular ion by the splitting off of a methyl group, the ion with m/e 117 from the ion with m/e 146 by the splitting off of a formyl radical and the ion with m/e 91 from the ion with m/e 117 by the elimination of a CH=CH group. The following structure is considered probable for pediculine:



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THE STRUCTURE OF ALBERTINE

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Albertine, isolated from the epigeal part of Leontice Albertii is an optically active $[\alpha]_D$ −101°) ditertiary monoacid crystalline base (mp 161° C) with the composition $C_{15}H_{22}O_2N_2$ [1]. Its IR spectrum has absorption bands due to the presence of a lactam carbonyl group (1655 cm^{-1}), a double bond (1675 cm^{-1}), a trans-quinolizidine system (2795, 2760 cm^{-1}), and a hydroxy group (3300 cm^{-1}). The UV spectrum is characteristic for the $-C=C-N-C=O$ chromophore (λ_{max} 244 mμ, log ε 4.2). The base forms an o-tosyl ester with mp 155–156° C. The catalytic hydrogenation of albertine in acetic acid over platinum at 70–80° C forms dihydroalbertine with mp 170° C. Reduction of the alkaloid with lithium aluminum hydride leads to the deoxy base, which gives a diperchlorate having mp 190° C. Reduction of the latter with lithium aluminum hydride or borohydride and also catalytic hydrogenation give a saturated dihydro base ($C_{15}H_{26}ON_2$) with mp 214° C, the IR spectrum of which has no absorption band between 1700 and 1600 cm^{-1}, the absorption band of the active hydrogen being somewhat displaced (3150 cm^{-1}). It has been established by a study of the mass spectra of deoxydihydroalbertine and matridine and a comparison of them with the spectrum of hydroxysparteine [2] that albertine has the heterocyclic skeleton of matridine with a hydroxyl present in ring D.

When the alkaloid was heated with phosphorus pentoxide at 200–210° C (5 hr), anhydroalbertine was formed with mp 163–164° C, $[\alpha]_D$ −90°, which was identical with sophoramine [3]. The NMR spectrum of albertine lacks the signal of an olefinic proton. Consequently, the double bond is located at C_7-C_{11}. The displacement of the absorption bands of the hydroxy group in the IR spectra of deoxyalbertine and deoxydihydroalbertine excludes the location of the hydroxyl at C_{14}, and it is probably attached to C_{13}.

Thus, albertine corresponds to the structure 13-hydroxy-$\Delta^{7,11}$-dehydromatrine and it is the first representative of the matrine alkaloids with a substituent in ring D.