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THE STRUCTURE OF VINCARICINE

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By separating the weakly basic fraction of the total alkaloids of the epigeal part of Vinca erecta Rgl. et Schmalh [1] on a column of alumina, we have isolated a base $C_{21}H_{24}N_2O_4$ with mp 187°-189° C (methanol, acetone), $[\alpha]_D^{22}$ 0 ± ± 5° (c 0.6; chloroform); R_f 0.89 [1-butanol-acetic acid-water (20 : 1 : 20)], R_f 0.19, TLC on silica gel [ethyl acetate-methanol (9 : 1)]. The IR spectrum of the substance shows absorption bands at 3180 cm^{-1} (NH), 1750 cm^{-1} (ester carbonyl group), and 770 cm^{-1} (1, 2, 3-trisubstituted benzene ring).

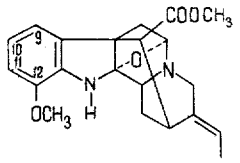
UV spectrum: λ_{max} 236, 308 mμ (log ε 3.85, 3.48) (ethanol), which is characteristic for indoline alkaloids. When the IR spectrum of the base was recorded in concentrated perchloric acid solution, a shift of the absorption bands to the region of longer wavelengths was observed λ_{max} 255, 343 mμ (log ε 3.97, 4.02). Consequently, the molecule of the alkaloid contains a chromophoric system similar to that in the alkaloids picroline and picrinine [2, 3].

Spectral characteristics and elementary analysis showed that the base corresponds to the following developed formula: $C_{18}H_{17}$(=NH) (=N-) ($COOCH_3$)(OCH_3)·(-O-). This alkaloid proved to be new and we have called it vincaricine.

The mass spectrum of vincaricine has peaks of ions with m/e 368 (M^+) (70%), 350 ($M-H_2O$)$^+$ (100%), 309 ($M-COOCH_3$)$^+$ (20%), 337 ($M-OCH_3$)$^+$ (18%), 291 ($M-COOCH_3+H_2O$)$^+$ (24%), 269 (90%). The last ion corresponds to a peak with m/e 239 in the mass spectrum of picroline and picrinine [2, 3].

The NMR spectrum of vincaricine has signals of an ethylidine group at δ = 1.45 ppm and at 5.36 ppm. A three-proton singlet at δ = 3.62 ppm is given to a methoxy group in position 12; the methoxyl of an ester group appears at δ = 3.67 ppm (singlet) and aromatic protons at δ = 6.53-6.69 ppm. The values of the chemical shifts of the aromatic and methoxyl protons agree with those given in the literature for pyrifoline [4].

On the basis of the data given above, the following structure is proposed for vincaricine:



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MASS-SPECTROMETRIC STUDY OF THE STRUCTURE OF FUGAPAVINE AND HEXAHYDROFUGAPAVINE

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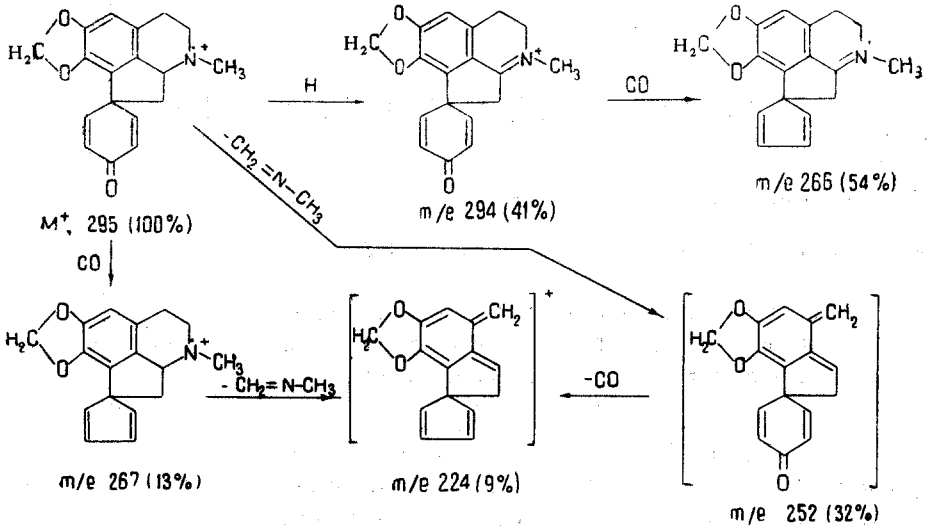
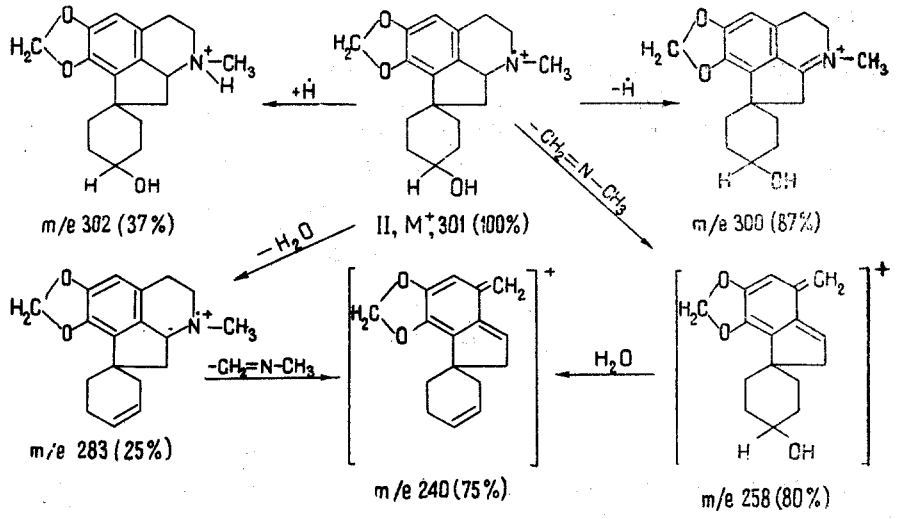
We have studied the mass-spectrometric properties of fugapavine (mecambrine) (I) [1-4] and hexahydrofugapavine (II) [1].

In the mass spectrum of fugapavine there are fairly strong peaks for M −1, M −29, and M −43, and also a peak with m/e 267. The fragment (M −29) is apparently formed as a result of the expulsion of −CO from the fragment with m/e 294, while the peak of the ion M −28 is formed directly from the molecular ion with the elimination of carbon monoxide.

In the fragmentation of the ion with m/e 267 due to the loss of a methyleneimine group, the peak of an ion with m/e 224 is obtained. Decomposition of fugapavine by the third route possibly takes place as a result of the loss of a methyleneimine group (M −43) by the molecular ion with the formation of a fragment with m/e 252. Subsequent fragmentation begins with the expulsion of carbon monoxide, giving a fragment with m/e 224, which is also formed by the second route of decomposition.



The presence of a hydroxy group in hexahydrofugapavine (II) and the hydrogenation of the diene system possibly increases the stabilization of the molecular ion; the peak of the ion M+1 (37%) appears. The ion M −1 amounts to 87% of the maximum, while in the case of fugapavine the figure is 42%. The spectrum also has peaks for M −18, M −43, and M −61. These fragments are formed by the successive elimination of H_2O and CH_2=N−CH_3, or conversely, the stabilization of the ions taking place with the lengthening and rearrangement of the system of conjugated double bonds.



Thus, the mass spectrometric fragmentation of fugapavine and hexahydrofugapavine takes place in the same way as the fragmentation of aporphine and proaporphine alkaloids [5–7].

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THE ALKALOIDS OF THALICTRUM SIMPLEX. THE STRUCTURE OF THALICTRICINE

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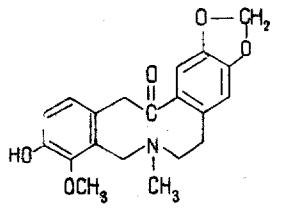
We have continued our study of the alkaloids of the roots of T. simplex L. [1]. The chloroform fraction of the mixture of bases was treated with acetone. The soluble part was chromatographed on a column of alumina, and from fractions 5-6 of the chloroform eluate were isolated golden orange crystals with mp 263°-265° C, identical with thalicmidine [2].

The phenolic fraction of the ethereal part of the mixed bases was dissolved in methanol, and white prismatic crystals of an optically inactive base $C_{20}H_{21}NO_5$ with mp 261°-263° C (methanol) were obtained. The base is sparingly soluble in all organic solvents and in water; it dissolves in aqueous alkali and contains N-methyl, methoxy, and methylenedioxy groups. Its IR spectrum has absorption bands at 3640 cm^{-1} (OH), 2900, 1240, 1130 (OCH_3), 2860 ($N-CH_3$), 1640 (C=O), 1040, 930, (O_2CH_2), 1615, 1580, and 1505 cm^{-1} (stretching vibrations of an aromatic ring). UV spectrum: λ_{max} 288 mμ (log ε 3.95).

The substance obtained proved to be new, and we have called it thalictricine.

The mass spectrum of the alkaloid (MKh-1303 instrument, 40V, 0.4 mA, 135° C) has peaks with m/e 335 (M^+), 269, 207, 206 (the principal peak), 192, and 150. The features of the mass spectrum of the base agree with the data given for alkaloids of the cryptopine type [3].

These properties of thalictricine show that it belongs to the alkaloids of the cryptopine type. The methylation of thalictricine with an ethereal solution of diazomethane gave a base with mp 164°-165° C (acetone), the UV, IR, and NMR spectra of which were identical with those of β-allocryptopine [1]. Since the properties of thalictricine differ from those of hunnemanine [4], the only possible structure remaining for it is as follows:



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