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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).

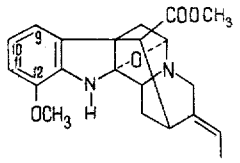
UV spectrum: λ_{max} 236, 308 mμ (log ε 3.85, 3.48) (ethanol), which is characteristic for indoline alkaloids. When the IR spectrum of the base was recorded in concentrated perchloric acid solution, a shift of the absorption bands to the region of longer wavelengths was observed λ_{max} 255, 343 mμ (log 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].