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ALKALOIDS OF THE ROOTS OF THALICTRUM FOETIDUM

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From the roots of Th. foetidum L. we have previously isolated 0.3% of combined alkaloids, 0.1% of which consists of quaternary bases [1] and 0.2% of tertiary bases. The tertiary bases have been separated into phenolic and nonphenolic fractions, and two new alkaloids have been obtained. When the nonphenolic fraction was treated with ethanol, prismatic crystals of a base (I) with mp 141°–142° C (decomp.), $[\alpha]_D^{15}$ +69° (c 1.0; ethanol) deposited. The homogeneity of the base (I) was confirmed by TLC on a nonfixed layer of alumina in the chloroform–ethyl acetate (1 : 1) system.

UV spectrum in ethanol: λ_{max} 260, 348, mμ (log ε 4.58, 3.86); IR spectrum: 920, 1030, 1050, cm^{-1} (CH_2O_2).

In the NMR spectrum of (I) taken on a JNM-100/100 MHz instrument in deuterochloroform (τ-scale) signals are observed for the protons of a N-methyl group at 7.80, for four methoxy groups at 6.60, 6.50, 6.39, and 6.24, and for a methylenedioxy group at 4.07 ppm. mol. wt. 648 (mass spectrometry).

The data given above and the elementary analysis enable us to establish for the base (I) the composition $C_{38}H_{36}O_8N_2$ and the developed formula $C_{32}H_{19}N(N-CH_3)(OCH_3)_4(CH_2O_2)(-O-)_2$. We have called the base thalfine.

The mother liquor after the isolation of thalfine was chromatographed on alumina. The benzene fractions (16–30) showed two spots, one of which corresponded to thalfine. Treatment with ethanol isolated thalfine, and from the mother liquor needle-like crystals of a perchlorate were obtained with mp 234°–235° C (decomp.), $[\alpha]_D^{21}$ +135° [c 1.16; ethanol–water (2 : 1)]. The hydrochloride formed prisms with mp 223°–226° C (decomp., water). Decomposition of the perchlorate gave an amorphous base (II) with mp 117°–118° C, $[\alpha]_D^{16}$ +115° (c 0.95, ethanol). UV spectrum in ethanol: λ_{max} 282 mμ (log ε 3.76). IR spectrum: 3600–3300 cm^{-1} (hydroxy group), 1030, 920 cm^{-1} (methylenedioxy group).

The NMR spectrum of the base (II) showed signals for protons of two N-methyl groups at 7.70 and 7.46 ppm, of four methoxy groups at 6.66, 6.57, 6.34, and 6.20 ppm, and of a methylenedioxy group at 4.20 ppm.

On the basis of the above data and its elementary analysis, substance (II) has the composition $C_{39}H_{44}O_8N_2$ and the developed formula $C_{32}H_{24}(N-CH_3)_2(OCH_3)_4(CH_2O_2)(OH)\cdot(-O-)$. We have called the base II thalfinine.

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THE STRUCTURE OF ERVINCININE

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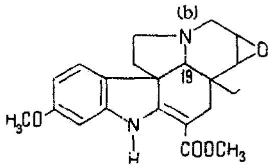
Continuing our investigation of the alkaloids of the epigeal part of Vinca erecta Rgl. et Schmalh., we have isolated vincaridine and a new base—ervincinine [1, 2]. A comparison of the UV, IR, NMR, and mass spectra, and some of the chemical properties of vincaridine and picrinine has established the identity of these substances [3].

Ervincinine has the composition $C_{22}H_{26}O_4N_2$, mol. wt. 382 (by mass spectrometry), mp 247°–248° C (decomp.) from methanol), $[\alpha]_D^{22}$ −80.5° (c 0.39; chloroform). UV spectrum: λ_{max} (ethanol) 250, 330 mμ (log ε 4.08, 4.18), which is characteristic for α-methyleneindoline alkaloids. IR spectrum: 3265 cm^{-1} (NH—), 1685 cm^{-1} (ester carbonyl group conjugated with a double bond), and 840 cm^{-1} (1, 2, 4-trisubstituted benzene ring).

The reduction of ervincinine with zinc in methanolic sulfuric acid gave dihydroervincinine $C_{22}H_{28}O_4N_2$, mol. wt. 384 (by mass spectrometry), mp 206.5°–207.5° C (ether). UV spectrum: λ_{max} (ethanol), 245, 304 mμ (log ε 4.06, 4.02), which is characteristic of indoline bases.

The NMR spectrum of ervinicinine exhibited signals of an ethyl group (δ = 0.61 ppm), of the six protons of two methoxy groups (δ = 3.71 ppm, singlet), of three aromatic protons (δ = 6.34–7.01 ppm), and of an NH group (δ = 8.89 ppm, singlet). The mass spectrum of ervincinine is very similar to that of lochnerinine [4], differing only by the low intensity of the peaks with m/e 138 and 108. The IR spectra of the base lacks a band in the 2700–2800 cm^{-1} region, showing cis-orientation of the hydrogen in relation to the unshared pair of electrons of the nitrogen atom N(b).

On the basis of the data presented, a structure is proposed for ervincinine which differs from that of lochnerinine by the configuration of the hydrogen at C_{19}.



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STRUCTURE AND CONFIGURATION OF PETILIDINE

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From the acetonic mother liquors from petilinine [1] we have isolated a new alkaloid, petilidine (I), with mp 265°-266° C (acetone–methanol (2:1)), $[\alpha]_D$ −15.5° (c 1.2; methanol), composition $C_{27}H_{45}O_2N$, mol. wt. 415 (mass spectrum). In a thin layer of Al_2O_3 and $CaSO_4$ (9 : 1), R_f 0.19 in the chloroform–benzene–methanol (10 : 5 : 0.5) system. The alkaloid forms a hydrochloride with mp 273°-274° C and a hydrobromide with mp 310°–312° C. IR spectrum of peptilidine: ν_{max} 3300, 1055 (−OH), 2950–2860, 1450 ($-CH_3$), 2750 cm^{-1} (trans-quinolizidine). A mixture of petilidine with petilinine melted at 235°–246° C.

Chemical Shifts, τ

Substance	(S), 3H, C–19 CH_3	(D), 3H, C–21 CH_3	(D), 3H, C–27 CH_3	(S) 6H, 2 $COOCH_3$	(M) 2H, 2 HCO $COCH_3$
(I)	9.29	9.23	9.23	—	—
(II)	9.21	9.23	9.23	8.04	5.42
(III)	9.13	9.22	9.22	—	—

The action of acetic anhydride on petilidine in pyridine forms the difficultly crystallizing diacetylpetilidine (II). In a thin layer of Al_2O_3 and $CaSO_4$ (9 : 1), R_f = 0.82 in the butyl acetate–petroleum ether–methanol (20 : 20 : 5) system. IR spectrum: ν_{max} 1730, 1245, 1030 cm^{-1}. The NMR spectrum exhibited a 6-proton singlet at 8.04 τ. Oxidation of the alkaloid with chromic acid gave a diketone with mp 226°–228° C (III) (ν_{max} 1708 cm^{-1}), identical with petilininedione. Reduction of the latter by the Huang-Minlon method led to an oxygen-free base which was identical with desdioxotetra-