STRUCTURE OF THALFINE AND THALFININE

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An account has been given previously of the isolation from the roots of Thalictrum foetidum L. of two new alkaloids: thalfine $C_{38}H_{36}N_2O_8$ (I) and thalfinine $C_{39}H_{42}N_2O_8$ (II) [1]. In this paper the results of a study of their structures are given.

The UV spectrum of base I has two absorption maxima, at 260 and 348 mμ. Absorption at 1562 cm^{-1} in the UV spectrum shows the presence of an isoquinoline ring in the molecule of thalfine [2]. Two repetitions of the Hofmann degradation of thalfine dimethiodide gave trimethylamine, but the reaction product contained nitrogen. Consequently, one half of the molecule of thalfine has the isoquinoline structure.

Thalfine dimethiodide was reduced with zinc in 20% H_2SO_4. The reaction product, N-methyltetrahydrothalfine methiodide, was treated with ethanolamine [3]. The N-methyltetrahydrothalfine formed had one absorption maximum in the UV spectrum at 283 mμ, which is characteristic for the benzyl tetrahydroisoquinoline bases, but its IR spectrum (in chloroform) was identical with that of thalfinine (II).

When thalfine was oxidized with potassium permanganate in acetone, an acid with mp 290° C was obtained which, on methylation with diazomethane, formed an ester with mp 91–92° C which was identified as the dimethyl ester of 2-methoxy-(diphenyl oxide)-5, 4'-dicarboxylic acid from a mixed melting point and mass spectra.

The formation of this acid showed that thalfine belongs to the bisbenzylisoquinoline bases and makes it possible to establish the position of one ether bridge and one methoxyl group in the molecule and shows that the remaining substituents are present in the isoquinoline and tetrahydroisoquinoline parts of the molecule.

When thalfine was cleaved with sodium in liquid ammonia, two products were obtained: laudanidine, and O-methylarmepavine, formed from the tetrahydroisoquinoline moiety of the molecule. The results of a study of the cleavage products enabled the positions of the three methoxyl groups in the one half of the molecule and those of the ethylenedioxy and of the one methoxyl group in the isoquinoline ring of the other half to be established.

Alkaloid	$N-CH_3$*		$O-CH_3$				O_2CH_2		H_{arom}
	2	2′	6	7	5′	4″	6′	7′	8
Thalfine	7.80	—	6.50	6.60	6.39	6.24	3.96	—	4.07
Thalfinine	7.70	7.46	6.57	6.64	6.34	6.20	4.20	—	4.08

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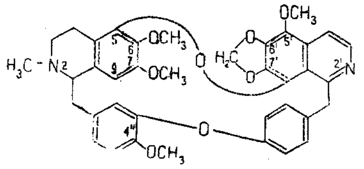
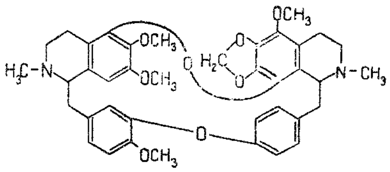
*τ scale.

On the basis of an assignment of the signals of the N-methyl, methoxyl, and methylenedioxy groups and also of the aromatic proton in position 8 [4] (table), the structure I is proposed as the most probable for thalfine, and II for thalfinine.



I



II

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