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THE SYNTHESIS OF DEOXYTHALIDASTINE: A CONTRIBUTION TO THE STRUCTURE OF THE THALICTRUM ALKALOIDS

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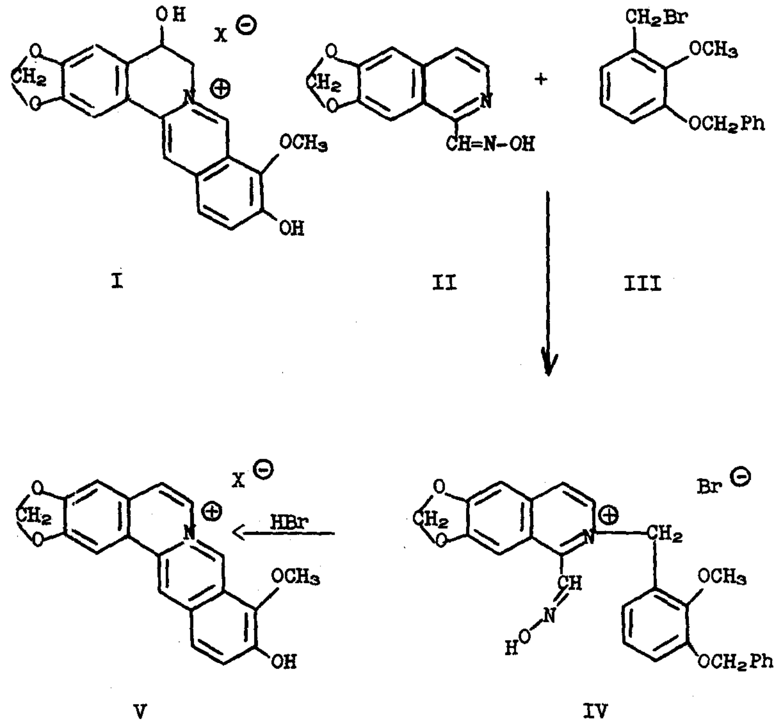
From the products of Thalictrum fendleri, Shamma and Dudock[1] have recently isolated the alkaloid thalidastine (I), a 5-hydroxylated protoberberine, in almost as large amounts as the accompanying berberine, and shown thalidastine chloride (I, X = Cl) to be readily dehydrated to the fully aromatic deoxythalidastine chloride (V, X = Cl). The availability of the necessary starting compounds has enabled us to synthesise deoxythalidastine quite simply by a route developed earlier[2,3]. Thus the oxime (II) of 6,7-methylenedioxyisoquinoline-1-carboxaldehyde[3] was quaternized in dimethylformamide at 100° with 3-benzyloxy-2-methoxybenzyl bromide (III)[2]. The product, presumably IV, was not isolated but cyclized directly by heating with 48% hydrobromic acid for 10 minutes at 100°. Simultaneous



debenzylation occurred and the product, deoxythalidastine bromide (V, X = Br) crystallized in 68% overall yield, m.p. >400°. Recrystallization was carried out from methanol (large volume) or trifluoroacetic acid. λ_{max}^{EtoH}, mμ(log ε) 247 (4.55), 271 (4.50), 278 (4.50), 308 (4.39), 349 (4.35), 463 (3.95). The identity of the material so prepared with that obtained from natural thalidastine[4] is clearly apparent from infrared, electronic and n.m.r. spectra obtained by us and from TLC experiments performed by Professor Shamma's group.

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4. We are indebted to Professor M. Shamma for supplying us with a sample of deoxythalidastine and for carrying out TLC comparisons of his product with ours.