

THE STRUCTURE AND STEREOCHEMISTRY OF RAUJEMIDINE

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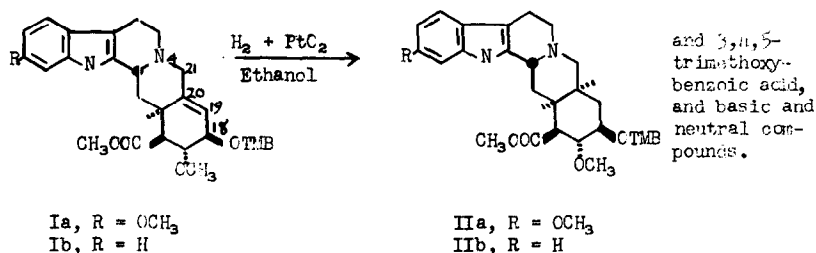
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The study of the chemistry of the indole alkaloid raujemidine, obtained from *Rauwolfia canescens*, has been handicapped by the relatively small amounts of this base available. It was originally isolated by CIBA chemists who noted that the compound had u.v. and i.r. spectra very close to those of reserpine (IIa), and that the elemental analysis indicated it could be an isomer of reserpine.² It was later observed that raujemidine quaternizes very rapidly with methyl iodide, the pseudo first order rate of quaternization being $3 \times 10^{-2} \text{ sec.}^{-1}$, so that the N_b atom had to be sterically unhindered.³

This fast rate of methiodide formation made a comparison of raujemidine with the recently elucidated deserpideine (Ib)⁴ imperative, since the latter alkaloid exhibits the same fast rate as raujemidine. In complete analogy with deserpideine, the nmr spectrum of raujemidine was found to exhibit absorption at 5.6 ppm. which could be due to a C-19 vinylic absorption superimposed on that of a C-18 hydrogen.⁴

As was the case with deserpideine (Ib), catalytic hydrogenation of 354 mg. of raujemidine (Ia) which had been freshly recrystallized from



methanol over Adams catalyst in ethanol solution was found to give a mixture of products resulting from both hydrogenation and allylic hydrolysis, so that the crude product exhibited at least ten spots on a silica gel thin layer plate. The mixture was, therefore, separated into a basic, a neutral, and an acidic fraction. The acidic component, obtained in about 45% yield, was characterized as 3,4,5-trimethoxybenzoic acid, as indicated by its melting point, mixture melting point and i.r. spectrum.

The basic fraction, weighing 239 mg., was submitted to preparative scale thin layer chromatography using Adsorbosil-1 and 90 CHCl₃:6 EtOH:4 acetone as the solvent system. The band that had the same R_f factor as authentic reserpine, which was spotted on the sides of the plate, was scraped off and washed with methanol to give 25 mg. of a slightly yellow crystalline compound which was recrystallized from methanol. The recrystallized material was shown to be reserpine (IIa) by m.p. and mixture m.p. with an authentic sample. Furthermore, the i.r. and n.m.r. spectra of this basic, crystalline, hydrogenation product and authentic reserpine were also practically identical. The yield of reserpine from the hydrogenation was about 8%.

The neutral material from the catalytic reduction exhibited no carbonyl absorption between 5.5 and 6 μ but possessed a peak at 6.12 μ characteristic of substituted lactams. This result again parallels the formation of lactams from deserpideine via cleavage of the allylic 21-4 bond.⁴

Raujemidine (Ia) must, therefore, analyze for C₃₃H₃₈O₉N₂ and corresponds to 19-dehydroreserpine. It is thus the second member of the 19-dehydroyohimbinoic alkaloids to be characterized. A complete study of the products of the catalytic hydrogenation of raujemidine is now in progress.

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References

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