

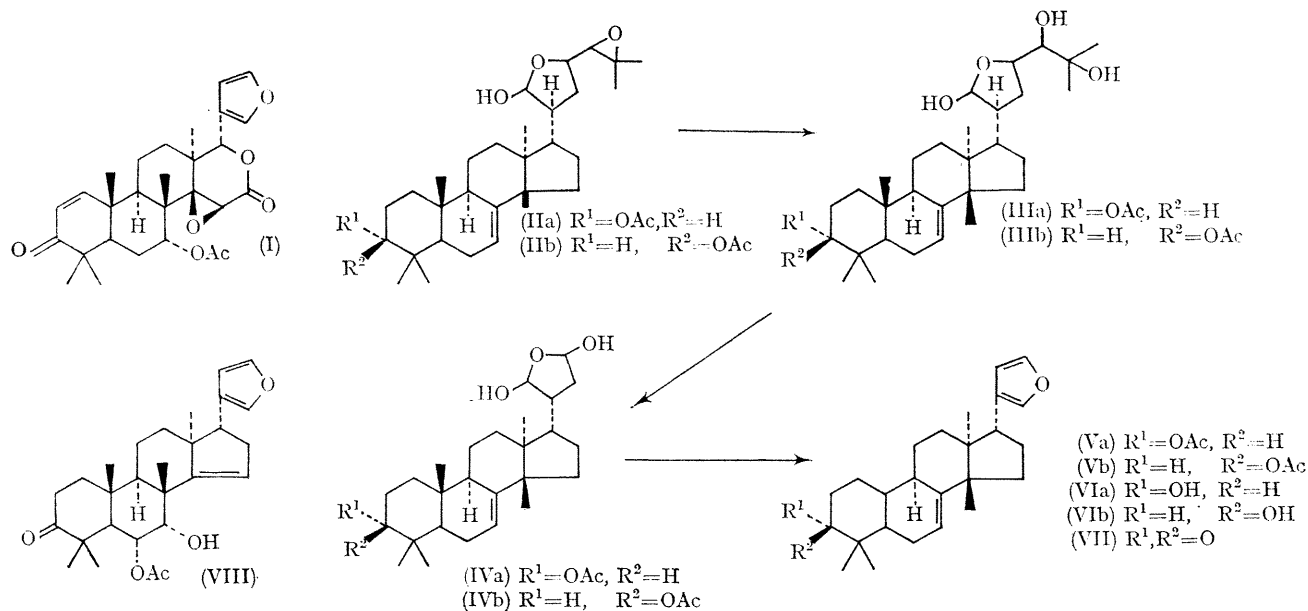
## The Synthesis of Possible Intermediates in the Biogenesis of Tetranortriterpenes by the Conversion of the Side-chain of Turraeanthin into a $\beta$ -Substituted Furan

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It has been suggested<sup>1</sup> that (VIa) might be a key compound in the biosynthesis of the tetranortriterpenes such as gedunin (I)<sup>2</sup> found in the *Meliaceae* and *Rutaceae* families. Turraeanthin (IIb) appeared to be a suitable starting

material for the synthesis of the corresponding  $3\beta$ -isomer (VIb), as has now been established by the conversion of the side-chain of turraeanthin into a  $\beta$ -substituted furan by a two-stage synthesis in high yield.



Treatment of turraeanthin (IIb) with sodium metaperiodate in aqueous dioxan containing a trace of perchloric acid gave a product which was mainly the labile cyclic hemiacetal (IVb). Treatment of this with toluene-*p*-sulphonic acid in benzene using a water separator gave the  $\beta$ -substituted furan (Vb), m.p. 185—187°,  $[\alpha]_D - 1^\circ$ , with the expected spectral properties.

For this investigation further quantities of turraeanthin from *Turraeanthus africanus* were isolated and from the particular sample of timber used, which differed from that used in the original isolation, the corresponding 3 $\alpha$ -isomer (IIa),<sup>†</sup> m.p. 206—208°,  $[\alpha]_D - 45^\circ$ , and the glycols<sup>3</sup> (IIIa) and (IIIb) were also isolated. From the 3 $\alpha$ -isomer (IIa) a parallel reaction sequence gave the  $\beta$ -substituted furan

(Va), m.p. 170—170.5°,  $[\alpha]_D - 35^\circ$ . Hydrolysis of the two acetates (Va) and (Vb) gave the corresponding alcohols (VIa), m.p. 173—175°,  $[\alpha]_D - 16^\circ$ , and (VIb), m.p. 163—165°,  $[\alpha]_D - 7^\circ$ , respectively. Sarett oxidation of the alcohols gave the ketone (VII), m.p. 112—113°,  $[\alpha]_D - 47^\circ$ . So far these  $\beta$ -substituted furans have not been isolated from natural sources but their natural occurrence is probable. These results together with those reported<sup>1</sup> earlier on the rearrangement of the 7 $\alpha$ ,8 $\alpha$ -epoxide of methyl 3 $\alpha$ -acetoxytirucall-7-en-21-oate to a 7 $\alpha$ -hydroxyapo-derivative open up a possible route, which is now being investigated, to the tetracarbocyclic tetranortriterpenes of which meldenin (VIII)<sup>4</sup> is one of the simplest examples.

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<sup>†</sup> It is possible that the 3 $\alpha$ -acetate (IIa) is identical with aphanamixin, (A Chatterjee and A. B. Kundu, *Tetrahedron Letters*, 1967, 1471) m.p. 232—234°,  $[\alpha]_D - 45^\circ$ . This has been formulated as the 21-epimer of turraeanthin, partly on the basis of a comparison of its lactone with the lactone obtained from a sample believed to be turraeanthin supplied to Dr. A. Chatterjee by Professor C. W. L. Bevan in 1965. At that time the co-occurrence of both turraeanthin and its 3 $\alpha$ -epimer in varying proportion in some samples of *Turraeanthus africanus* had not been appreciated and it now appears likely that the sample supplied to Dr. Chatterjee contained a substantial proportion of the 3 $\alpha$ -epimer.

<sup>1</sup> G. P. Cotterrell, T. G. Halsall, and M. J. Wriglesworth, *Chem. Comm.*, 1967, 1121.

<sup>2</sup> A. Akisanya, C. W. L. Bevan, T. G. Halsall, J. W. Powell, and D. A. H. Taylor, *J. Chem. Soc.*, 1961, 3705; S. A. Sutherland, G. A. Sim, and J. M. Robertson, *Proc. Chem. Soc.*, 1962, 222.

<sup>3</sup> J. G. St. C. Buchanan, P. P. Croughan, and T. G. Halsall, to be published.

<sup>4</sup> J. D. Connolly, K. L. Handa, and R. McCrindle, *Tetrahedron Letters*, 1968, 437.