

## The Synthesis of the Simplest Meliacins (Limonoids) from Tetranortirucallane Triterpenoids containing a $\beta$ -Substituted Furyl Side-chain

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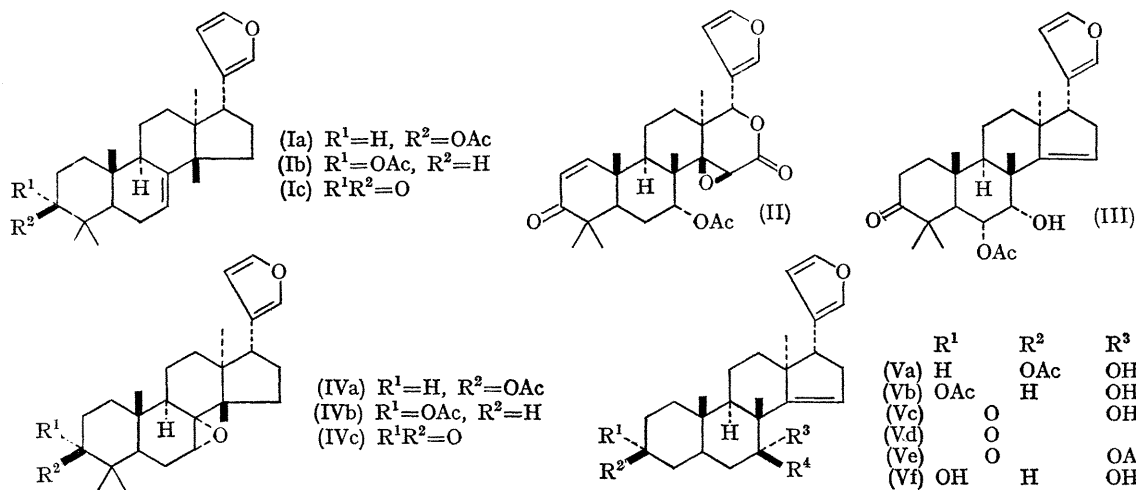
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RECENTLY<sup>1</sup> the preparation of the tetranortriterpenoid  $\beta$ -substituted furans (Ia), (Ib), and (Ic) was described. The possible role of these compounds in the biosynthesis of the tetranortriterpenes of the meliacin (limonoid) group such as gedunin (II)<sup>2</sup> and meldenin (III)<sup>3</sup> found in the *Meliaceae* and *Rutaceae* families has already been discussed and it has been suggested<sup>4</sup> that the carbon skeleton of the compounds of this group, which are all oxygenated at C-7, could arise by the formation of the  $7\alpha,8\alpha$ -epoxide of a compound such as (Ia) followed by rearrangement to a  $7\alpha$ -hydroxy- $\Delta^{14}$ -apo-derivative. Such transformations have now been carried out in satisfactory yield [76% overall in the best case

starting from compound (Ic)] to give the simplest members of the meliacin group.

The  $3\beta$ -acetate (Ia) with monoperphthalic acid in dry ether at  $-3^\circ$  for 21 hr. yielded the  $7\alpha,8\alpha$ -epoxide (IVa),<sup>†</sup> m.p.  $199-201^\circ$ ,  $[\alpha]_D -31^\circ$ , which rearranged with boron trifluoride etherate to give the apo-compound (Va), m.p.  $182-184^\circ$ ,  $[\alpha]_D +26^\circ$ , which is one of the simplest meliacins. Similarly the  $3\alpha$ -acetate (Ib) and the ketone-3 (Ic) gave the corresponding epoxides (IVb), m.p.  $162.5-164.5^\circ$ ,  $[\alpha]_D -76^\circ$  and (IVc), m.p.  $161-163^\circ$ ,  $[\alpha]_D -88^\circ$ , which were rearranged to give the meliacins (Vb), m.p.  $193-194^\circ$ ,  $[\alpha]_D -76^\circ$ , and (Vc), m.p.  $175-177^\circ$ ,  $[\alpha]_D -12^\circ$ . The

<sup>†</sup> All compounds gave satisfactory elemental analyses and possessed the expected spectral properties.



keto-alcohol (Vc) was converted into the diketone (Vd), m.p. 158—159°,  $[\alpha]_D -92^\circ$ , and into its acetate (Ve), m.p. 152—154°,  $[\alpha]_D -16^\circ$ . Hydrolysis of the 3 $\alpha$ -acetate (Vb)

gave the 3 $\alpha,7\alpha$ -diol (Vf), m.p. 237.5—239,  $[\alpha]_D -49^\circ$ , which can be regarded as the simplest of all the meliacins.

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