The Meliacins (Limonoids). Partial Synthesis of Mexicanolide

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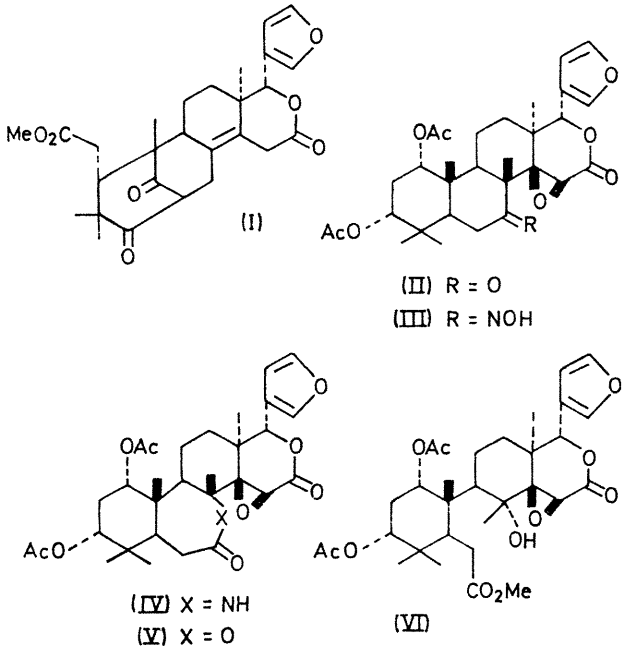
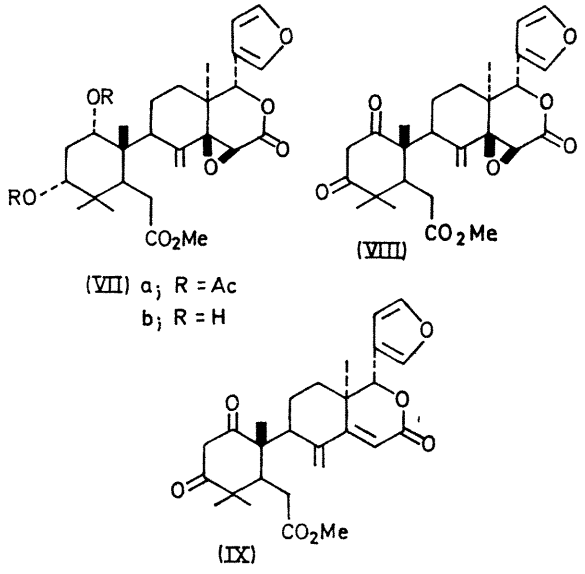
Summary The product of Beckmann rearrangement of the oxime of 7-deacetoxy-7-oxokhivorin on treatment with nitrous acid affords an ε-lactone which we have converted into mexicanolide.

A RECENT publication[1] on a partial synthesis of mexicanolide (I) prompts us to report our own work on the same subject especially in view of the large significant differences between the m.p.s. observed by us and those reported by Connolly *et al.* for several compounds for which the same structures are claimed.† In our synthesis ring B of the meliacin was cleaved by a different route involving Beckmann rearrangement of the oxime of 7-deacetoxy-7-oxokhivorin (II). The oxime (III), m.p. 168—170°, on treatment with thionyl chloride gave the lactam (IV), m.p. 230°, which reacted with sodium nitrite[2] in cold AcOH–Ac_2O to afford the ε-lactone (V), m.p. 315—317°. When set aside for 1 h in dilute methanolic KOH the lactone ring opened to give a hydroxy-acid, characterised as the methyl ester (VI), m.p. 283—284°, which was dehydrated with thionyl chloride in pyridine (1 h) to the unsaturated ester (VIIa), m.p. 195—196°, δ 5·07 and 5·40 ($C=CH_2$) p.p.m. Hydrolysis with cold dilute methanolic KOH afforded the dihydroxy-compound (VIIb) obtained as a micro-crystalline powder. This was oxidised with Jones reagent to the β-diketone (VIII), m.p. 195—196°, λ_{max} 258 (ε 14,000) (MeOH) and 285 nm (16,000) (alkaline MeOH). Reduction of (VIII) with chromium(II) chloride gave the diene (IX), m.p. 230°, which when treated with $NaHCO_3$ cyclised to mexicanolide, m.p. 225°, identical (m.p., mixed m.p., i.r., and t.l.c.) with the natural product[3-5] from *Cedrela odorata*.





Solvolytic cleavage of ring B of khivorin has also been achieved by treatment of 7-deacetoxy-14,15-deoxy-7-oxokhivorin with $KOBu^t$ in Me_2SO.

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† We obtained satisfactory microanalyses for all new compounds.

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