

## Partial Synthesis of Mexicanolide from 7-Oxo-7-deacetoxykhivorin

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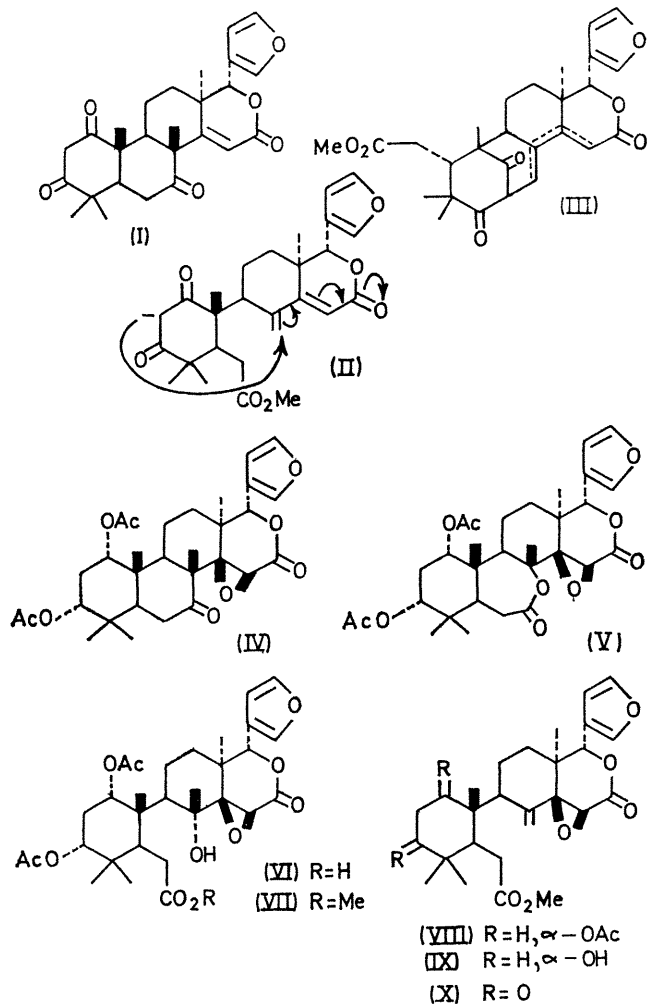
**Summary** 7-Oxo-7-deacetoxykhivorin has been transformed into the diene-lactone (XI), a postulated biogenetic precursor of the bicyclonanolide group of tetranortriterpenoids, which when treated with very mild base readily undergoes intramolecular Michael addition to give mexicanolide (XII).

It has been suggested<sup>1</sup> that the bicyclo[3,3,1]nonane ring

system, found in the bicyclonanolide group of tetranortriterpenoids, arises from an intact skeletal type (I) by cleavage of ring B followed by Michael addition of a carbanion at C-2 to the diene-lactone system (II) to give (III). We now report a partial synthesis of mexicanolide<sup>2,3</sup> (XII) from 7-oxo-7-deacetoxykhivorin (IV) by a route which mirrors *in vitro* the above biogenetic reactions.

7-Oxo-7-deacetoxykhivorin (IV) was oxidised under

Baeyer-Villiger conditions with  $\text{AcO}_2\text{H}$  to the  $\epsilon$ -lactone (V)



m.p.  $308^\circ$ . In mild base the  $\epsilon$ -lactone ring opened to give the hydroxy-acid (VI) whose methyl ester (VII) m.p.  $259$ – $266^\circ$  [ $\nu_{\text{max}}$  ( $\text{CHCl}_3$ )  $3590\text{ cm}^{-1}$ ] was converted into the *exo*-methylene derivative (VIII) m.p.  $197$ – $199^\circ$  [n.m.r.  $\delta$  5.06, 5.4 ( $\text{CH}_2 <$ )] in good yield with thionyl chloride. Mild alkaline hydrolysis of the acetate groups of (VIII) yielded the corresponding diol (IX) as a gum which was oxidised with Jones' reagent to the  $\beta$ -diketone (X) m.p.  $177$ – $181^\circ$  [ $\lambda_{\text{max}}$  261 nm ( $\epsilon$  9300); n.m.r.  $\delta$  3.89 (s) C-2 methylene]. The epoxide ring of (X) was readily removed with chromium(II) chloride to give the desired diene-lactone precursor (XI) m.p.  $172$ – $176^\circ$  [ $\lambda_{\text{max}}$  262 nm ( $\epsilon$  9000)]. When stirred in chloroform in the presence of a few drops of aqueous sodium bicarbonate (XI) underwent ready intramolecular cyclisation (see II) to mexicanolide (XII), m.p.  $221$ – $226^\circ$ , identical in all respects to the natural material.

A similar transformation of 7-oxo-7-deacetoxykhivorin (IV) into methyl angolensate (XIII) has been reported.<sup>4</sup>

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