

REDUCTIVE METHYLATION OF METHOXYNAPHTHOIC ACIDS AND
ELABORATION TO THE RING A SYSTEM OF THE GIBBERELLINS

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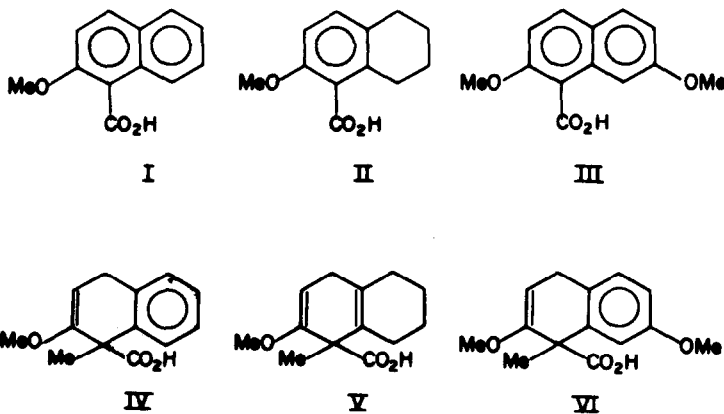
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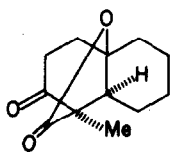
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In the course of exploring routes to compounds containing the methyl hydroxy-lactone system present in ring A of most of the gibberellins we have found that the carboxylated ring of certain methoxy-1-naphthoic acids and -tetrahydronaphthoic acids can be selectively reduced by sodium in liquid ammonia in the absence of a proton donor, and that the resulting dicarbanion can then be methylated *in situ* with methyl iodide to give the corresponding 1,4-dihydro-1-methylnaphthoic acid.

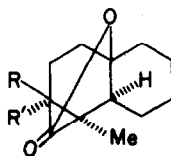
Thus, acids (I), (II)¹ and (III)² gave in high yield the corresponding products (IV), m.p. 146°, (V), m.p. 150°, and (VI), m.p. 127.5-128° respectively.



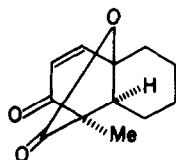
Treatment of acid (V) with sulphuric acid in chloroform under controlled conditions led directly to the keto-lactone (VII), m.p. $59-60^{\circ}$, $\nu_{\text{max}}^{\text{chlf.}}$ 1740 and 1790 cm^{-1} . Reduction of this with sodium borohydride gave mainly the equatorial hydrogen-bonded hydroxy-lactone (VIIIa), m.p. $88.5-89^{\circ}$, $\nu_{\text{max}}^{\text{CCl}_4}$ 3580, 3450 and 1775 cm^{-1} , while Meerwein-Ponndorf reduction gave a mixture of the latter and its epimer (VIIIb), m.p. $110.5-111^{\circ}$, $\nu_{\text{max}}^{\text{CCl}_4}$ 3625, 3490 and 1775 cm^{-1} . Bromination - dehydrobromination of ketone (VII) gave the unsaturated



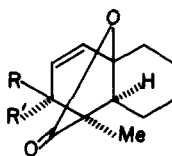
VII



VIIIa R=OH, R'=H
 VIIIb R=H, R'=OH



IX



Xa R=OH, R'=H
 Xb R=H, R'=OH

keto-lactone (IX), m.p. 72-73°, $\nu_{\text{max}}^{\text{chlf.}}$ 1780, 1695 and 1618 cm^{-1} . Its Meerwein - Ponndorf reduction gave a mixture of the two unsaturated hydroxy-lactones (Xa), m.p. 116.5-119°, $\nu_{\text{max}}^{\text{CCl}_4}$ 3570, 3470, 1770 and 1640 cm^{-1} , and (Xb), m.p. 95.5-96°, $\nu_{\text{max}}^{\text{CCl}_4}$ 3620, 3470, 1780 and 1650 cm^{-1} .

Acid treatment of compound (Xa) under conditions similar to those giving gibberic acid from gibberellic acid³⁾ led to the formation of 5,6,7,8-tetrahydro-1-methylnaphthalene, identified by its n.m.r. and u.v. spectrum.

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