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STRUCTURES OF XANTHOPHANIC AND GLAUCOPHANIC ACID

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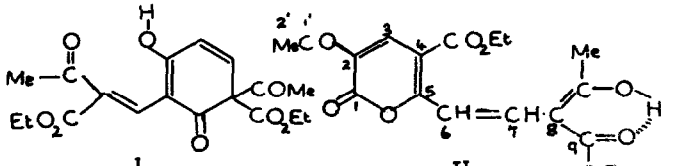
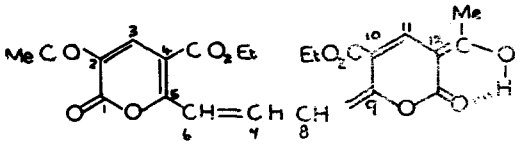
Diethyl xanthophanic acid (yellow) and diethyl glaucophanic acid (black) form when ethyl ethoxymethyleneacetoacetate and ethyl sodioacetoacetate are heated together.[1] Diethyl xanthophanic acid has received implausible quinonoid formulations,[2,3] but Fiest[4] has suggested a more acceptable structure (I). Structure (II) is now proposed with (III) for the hitherto unformulated diethyl glaucophanic acid. Other esters may be prepared analogously; they are novel pyrone-oxonols.



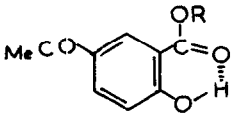
I II



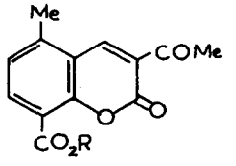
III

Diethyl xanthophanic acid $C_{18}H_{20}O_8$ (mass spectral mol.wt. 364) is monobasic, $\lambda_{max.}$ (ethanol; deteriorates) 298, 440 and 520 mμ (ε 13,250,

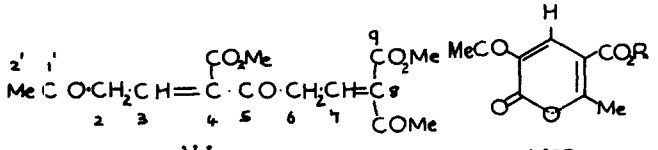
22,600 and 3,950), $\nu_{max.}$ ($CHCl_3$) 1743 (pyrone), 1713 (4-ester), 1681 (2-acetyl), 1643, 1582-1574 (•C:C• and chelated system) $cm.^{-1}$ Assignments in the n.m.r. spectrum are τ7•58, 7•35 (2-acetyl and 8-enolised acetyl methyls), 2•21, 1•98, quartet J, 15c/s (6,7-olefin hydrogens), 1•31 (3-hydrogen) and 4•51 (chelated enolic hydrogen). When heated with water, dimethyl xanthophanic acid gives methyl acetoacetate, the acetyl ester (IV, R=Me) and the coumarin (V, R=Me), the structure of which rests on spectral information and degradation to 2,6-cresotaldehyde. The three compounds are derived from the decarboxylation product (VI), the first two by 7,8-retroaldol followed by 2,7-aldol condensation and the third by 1',6-aldol and pyrone formation. On pyrolysis the α-pyrone (VII, R=Me or Et) is formed in small yield from dimethyl or diethyl xanthophanic acid. The xanthophanic acids apparently arise by Michael addition of sodioacetoacetate to ethoxymethylene acetoacetate followed by elimination to give diacetyl glutaconic ester. Michael addition of the latter to ethoxymethylene acetoacetate then gives (VIII) which cyclises to the pyrone (II).



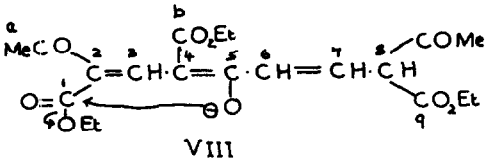
IV



V

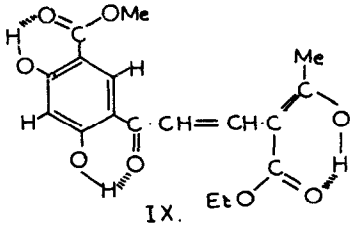


VI VII

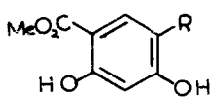


VIII

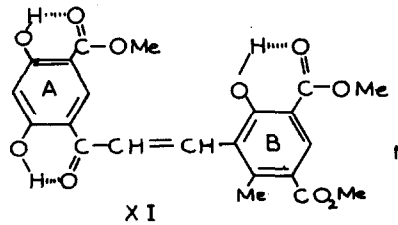
With magnesium methoxide, diethyl xanthophanic acid gives a methyl ethyl ester $C_{17}H_{18}O_8$, $\lambda_{max.}$ (ethanol) 252, 352 and 430 mμ (22,700; 18,100 and 1,950), $\nu_{max.}$ 1674 (chelated ester) $cm.^{-1}$, τ1·54, 3·5 (6 and 3 aryl hydrogens), near 2·2 and 2·3 (quartet; 2',3'-hydrogens), -1·31 and -4·58 (three chelated hydroxyls), 7·61 (enolised acetyl methyl). This is formulated as (IX) since when ozonised it gives the methyl ester (X, R=CO·CHO), degraded by periodate and alkali to 4,6-dihydroxyisophthalic acid. Pyrolysis gives (X, R=COMe). The ultraviolet spectrum of the 2',3'-dihydroester from (IX) closely simulates that of methyl resacetophenone carboxylate. Formation of the compound (IX) results from methoxide ion opening of the pyrone (II), followed by formal Claisen condensation [cf. a-b on (VIII)]. Diethyl glaucophanic acid with magnesium methoxide gives a product formulated as (XI), on spectral evidence relating to it and its triacetate, and on ozonolysis to give (X, R=COCHO) and (XII, R=CHO). On pyrolysis the compound (XI) gives (X, R=COMe) plus the expected dimethyl-4-methyl-6-hydroxyisophthalate (XII, R=H).



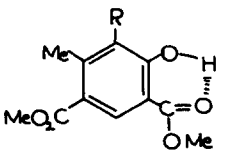
IX.



X

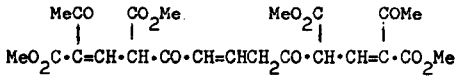


XI



XII

Diethyl glaucophanic acid $C_{23}H_{22}O_{10}$ (mass spectral mol.wt. 458) is monobasic, a stronger acid than the xanthophanic acid, and forms blue solutions, $\lambda_{max.}$ (ethanol; deteriorates) 242, 260, 290, 330, 385, 425, 515 and 672 mμ (ε 7,900; 6,850; 4,400; 5,200; 7,350; 6,500; 8,400 and 133,500), $\nu_{max.}$ ($CHCl_3$) 1743 (pyrone), 1712 (ester), 1684 (acetyl) and 1598, 1579, 1541 and 1524 (double bonds and chelate system) $cm.^{-1}$, τ2·97, 2·37, 1·75 (ABC system J 11c/s and 15c/s; 6,7,8, hydrogens), 1·24 and 2·26 (3 and 11 hydrogens), 7·30 and 7·62 (2 and 12 acetyls). On the basis of this and the nature of the "rearrangement" product (XI), a structure (III) is proposed for diethyl glaucophanic acid. In agreement, the pyrone (VII, R=Me or Et) is formed when dimethyl or diethylglaucophanic acid is pyrolysed, whilst boiling the latter with water gives the acetyl ester (IV) but no acetoacetic ester. On this basis the glaucophanic acids may be envisaged as arising from double pyrone formation from the ester (XIII): this ester can be dissected into two diacetylglutaconic residues linked through a one carbon fragment. The product (XI) obtained in the magnesium methoxide reaction is derived formally from Claisen cyclisation at one end and aldol condensation at the other end of the chain. The symmetry of the anion from (III) accords with the enhanced acidity of the glaucophanic acids.



(XIII)

Acknowledgment:

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