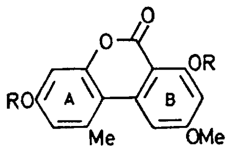
Selective Chromic Acid Oxidation of Alternariol Trimethyl Ether; *X*-Ray Crystal Structure of the Major Product

By Mark F. C. Ladd and David C. Povey
(*Department of Chemical Physics*)
and Robert Thomas*
(*Department of Chemistry, University of Surrey, Guildford, Surrey*)

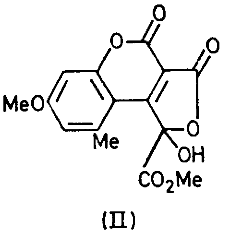
Summary The structure (II) of a chromic acid oxidation product of the diphenyl derivative alternariol trimethyl ether (Ia) has been elucidated by *X*-ray crystallographic analysis; a possible intermediate (III) has also been characterised as a product of this reaction.

Alternariol trimethyl ether, $C_{17}H_{16}O_5$ (Ia)[1], has been found to undergo an exothermic reaction with CrO_3 in glacial acetic acid. The major product (II) crystallised from aqueous acetic acid (*ca.* 25% yield) as pale yellow plates, $C_{15}H_{12}O_8$, m.p. 240° (decomp.); n.m.r. analysis [$(CD_3)_2SO$] indicated the retention of one *C*-methyl group [τ 7·46 (3H, s)], 2 OMe groups [τ 6·06 and 6·16 (each 3H, s)], and two *meta*-coupled aromatic protons [τ 2·95 and 3·07 (each 1H, d, *J* 2·7 Hz)]; one D_2O-exchangeable proton appeared at τ 0·16 br (1H, s). Titration with cold aqueous alkali showed an indefinite end-point, but on heating 3 equiv were consumed. These data are consistent with structure (II), which was established by *X*-ray crystallographic analysis.

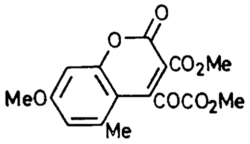
Crystals of (II) separate from ethanol as pale yellow, monoclinic parallelepipeds: $P2_1/c$, $a = 10·748(3)$, $b = 9·644(7)$, $c = 13·845(7)$ Å, $\beta = 104·59(3)°$, $Z = 4$ (2 are D and 2 are L). Intensities of 1350 reflections with $\sin\theta/\lambda \leqslant 0·5$ were measured on a Siemens diffractometer (A.E.D.) with Cu-K_α radiation (λ 1·5418 Å); of these, 200 were reckoned unobserved. The structure (*cf.* Figure) was solved by the symbolic-addition procedure using the



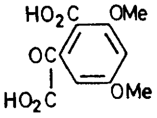
(Ia) R=Me
(Ib) R=H



(II)

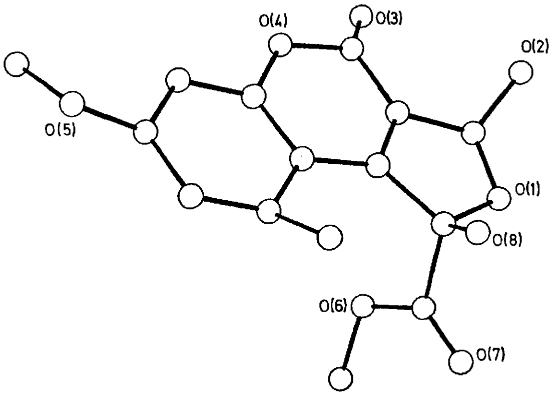


(III)



(IV)

program MULTAN[2], and refined by full-matrix least-squares methods to a current R value of 0·07. The molecular ring conformation is planar to within 0·2 Å. A *hydrogen bond* (2·74 Å) exists between the OH group and the CO group of the 5-membered ring of an adjacent molecule. This bonding links the molecules in chains, thereby contributing to the relatively high m.p. of these crystals.



Figure

The mother liquors from which (II) was isolated, also yielded (8%) a yellow crystalline product (III), $C_{16}H_{14}O_8$, m.p. 164—165° (decomp.); τ ($CDCl_3$) τ 7·79 (3H, s, CMe), 6·03, 6·12, and 6·13 (each 3H, s, OMe), and 3·25 and 3·34 (each 1H, d, J 3·0 Hz, *meta*-coupled ArH). These data are consistent with the structure (III), which suggests that it may be formed as an intermediate in the conversion of (Ia) into (II).

The required selective oxidative loss of a single carbon atom from ring B of the substituted diphenyl (Ia) appears to constitute a novel addition to the various known types of oxidations of alkyl aryl ethers.[3] The formation of this α-keto-ester (III) contrasts with that of the α-keto-acid (IV), which is a product of the oxidative cleavage of ring A of (Ia) with alkaline permanganate.[1] Selective oxidations of ring A of the *Alternaria tenuis* metabolite alternariol methyl ether (Ib)[4] including ring fission are also apparent in the biosynthetic derivation of its co-metabolites dehydroaltenusin[5] and altenuic acid II.[6]

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