The Crystal Structure of (±)-Dehydroaltenusin

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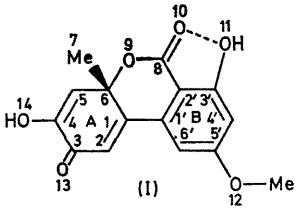
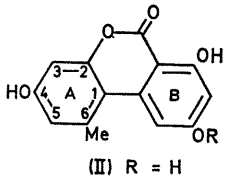
Summary The crystal structure of (±)-dehydroaltenusin, $C_{15}H_{12}O_6$, has been determined by direct *X*-ray crystallographic analysis.

(±)-DEHYDROALTENUSIN, $C_{15}H_{12}O_6$ (I), is one of a series of related phenolic compounds which has been isolated from extracts of the mould *Alternaria tenuis*.[1] The only two members of this series which have previously been fully characterised structurally are the dibenzo-α-pyrone, alternariol,[2] $C_{14}H_{10}O_5$ (II), and its monomethyl ether[3] (III). A further *A. tenuis* metabolite is altenusin,[1] $C_{15}H_{14}O_6$, which is readily interconvertible with dehydroaltenusin by easy oxidation ($FeCl_3$) and reduction ($Na_2S_2O_4$).

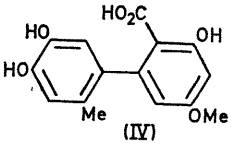


Previous studies[3] indicated that dehydroaltenusin was a lactone derivative of a monomethyl ether of a substituted β-resorcylic acid, and that this portion of its structure was identical to ring B of (III). This conclusion is supported by the n.m.r. spectrum ($CDCl_3$) which shows one aromatic methoxy-group at τ 6·10 (s, 3H) and two *meta*-coupled protons at τ 3·37 and 3·26 (d, 1H each, *J* 2·3 Hz). The remainder of the molecule contains a ketonic function,[1] together with an olefinic C-methyl group (τ 8·29, s, 3H) and two uncoupled olefinic protons (τ 3·30 and 3·72, s, 1H each). However, no unique structure could be assigned on the basis of these data and the previously reported analyses of various derivatives, including a triacetylation product,[1] $C_{21}H_{18}O_6$, which no longer shows the ketonic reactivity of the starting material. Insufficient dehydroaltenusin was available for further detailed chemical studies; however, recrystallisation from ethanol afforded crystals suitable for an *X*-ray crystallographic examination.

Crystals of dehydroaltenusin are yellow, monoclinic blocks, $P2_1/n$, $a = 8{\cdot}759$, $b = 14{\cdot}064$, $c = 10{\cdot}768$ Å, $\beta = 101{\cdot}29°$, 4 mols/cell (2 are D and 2 are L). Intensities of 2514 reflections were measured on a Siemens diffractometer with Cu–K_α radiation (to θ *ca.* 71°) and of these, 101 were reckoned unobserved. The structure was solved by the symbolic-addition procedure and refined to a current *R* value of 0·045. The molecular configuration is largely planar [(I) corresponds to one enantiomer] and contains an intramolecular hydrogen bond of 2·590 Å, which appears to have induced some strain in the lactone ring as indicated by the long C(6) to O(9) bond of 1·477(2) Å. This would be consistent with a ready cleavage of the bond during reduction of (I) with $Na_2S_2O_4$ to form altenusin, which is consequently provisionally formulated as (IV). A fairly weak intermolecular hydrogen bond (2·99 Å) between O(12) of one molecule and O(14) of another is essentially coplanar with the substituted phenoxymethyl fragment (ring B), thereby indicating the sp^2 character of O(12).

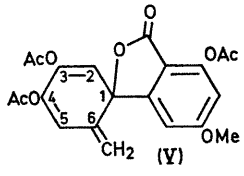


(II) R = H
(III) R = Me



(IV)

The cross-conjugated dienone–resorcylic acid structure (I) simply rationalises the known chemical and spectroscopic properties of dehydroaltenusin, which could rearrange on acetylation to form the previously mentioned triacetyl derivative, the n.m.r. and i.r. spectra of which are consistent with (V). Structure (IV), provisionally assigned to altenusin, also accommodates the reported formation of tetramethylaltenusin,[1] $C_{19}H_{22}O_6$, although other properties[4] including its behaviour on acetylation and dehydration require further examination.



(V)

The structural smilarity of (I) and (III) is indicative either of their biosynthetic derivation from a common polyketide precursor, or of a sequential relationship,[3,5] such as (II) → (III) → (IV) → (I), requiring the intermediate conversion of the substituted resorcinol ring A in (III) into the corresponding catechol (IV).

A recent publication[6] proposes an identical structure for altenusin (IV) and also a structure for dehydroaltenusin, which, however, differs from (I).

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[2] H. Raistrick, C. E. Stickings, and R. Thomas, *Biochem. J.*, 1953, **55**, 421.
[3] R. Thomas, *Biochem. J.*, 1961, **80**, 234.
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[5] R. Thomas, *Biochem. J.*, 1961, **78**, 748.
[6] R. G. Coombe, J. J. Jacobs and T. R. Watson, *Austral. J. Chem.*, 1970, **23**, 2343.