

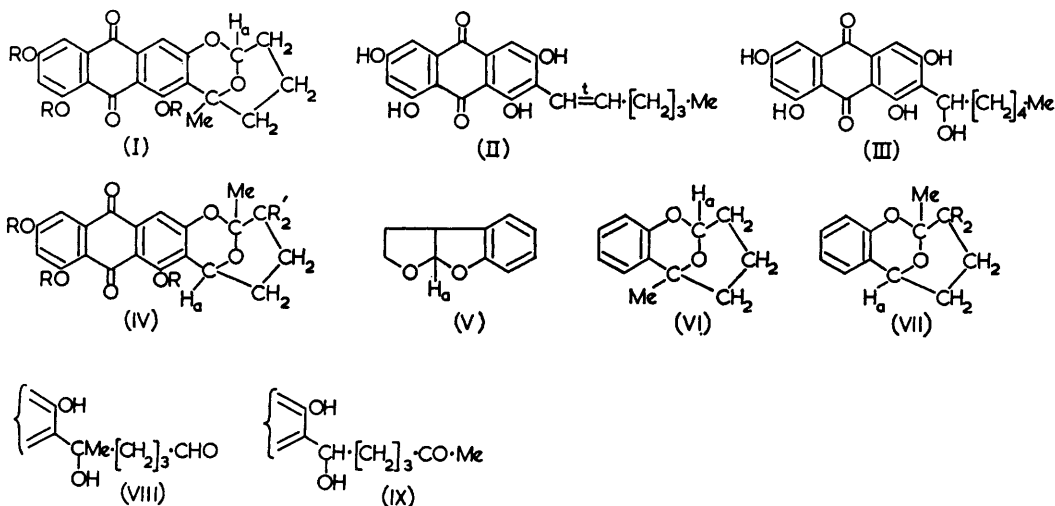
A Revised Structure for Averufin

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AN unusual feature of structure (I; R=H) suggested for averufin, a metabolite of *Aspergillus versicolor* (Vuillemin) Tiraboschi, arises from its suggested biogenetic origin.¹ The molecule was postulated as being derived from eight acetate residues and one molecule of acetoacetaldehyde by appropriate transformations.¹ Averythrin² (II), and averantin³ (III) are also derivatives of a

The resonance, a deformed triplet at τ 4.5, in the n.m.r. spectrum of averufin tri-*O*-methyl ether (I; R=Me) was interpreted¹ as being due to a proton, H_a, situated in the β -position to two oxygen atoms. The position of the resonance might be thought to be at a somewhat high field for a proton in such an environment. In the furanoid systems aflatoxin B₂,⁵ aflatoxin G₂,⁵



1,3,6,8-tetraoxygenated-2-alkylanthraquinone and are metabolites of *A. versicolor*. The two latter compounds probably originate biogenetically from a linear β -polyketo-acid, and since all three pigments are produced by genotypically similar fungi, and possess six carbon atom side chains it has been proposed⁴ that averufin has the alternative ketal structure (IV; R=R'=H), derived biogenetically from a linear β -polyketo-chain.

dihydrosterigmatocystin,⁶ and *O*-methylaversin,⁶ which each contain the partial structure (V), the similarly located proton H_a resonates in the range τ 3.48—3.78.

Consequently, we have synthesised⁷ the model benzo-1,3-dioxans (VI) and (VII; R=H), related respectively to the possible structures (I; R=H) and (IV; R=R'=H) for averufin. From the position of the resonances of the protons designated

H_a in (VI) τ 4.49, and (VII; R=H) τ 4.92 these data appear to support the original assignment of structure (I; R=H) for averufin.

However, since averufin is either a cyclic acetal (I; R=H), or a cyclic ketal (IV; R=R'=H) it should be possible to determine unequivocally the correct structure by deuteration experiments in acidic media. Under these conditions the acetal (I; R=H) would be in equilibrium with the hydroxy-aldehyde (VIII), and the ketal (IV; R=R'=H) with the hydroxy-ketone (IX). Using a slight modification of the conditions of Seibl and Gäumann,⁸ tri-*O*-methylaverufin incorporated chiefly

two atoms of deuterium. Careful examination of the n.m.r. and mass spectra of this compound showed it to be mainly the dideutero-compound (IV; R=Me, R'=D). In a parallel experiment conducted under identical conditions, similar incorporation was obtained with model ketal (VII; R=H) which gave mainly the dideutero-compound (VII; R=D). However, the model acetal (VI) incorporated no deuterium under these conditions.

We regard this evidence as proof of structure (IV; R=R'=H) for averufin.

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