The Structure of Cercosporin, a Naturally Occurring Quinone

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Summary The structure suggested for cercosporin, a naturally occurring dihydroxy-perylenequinone, is unusual in having a methylenedioxy-group present in a seven-membered ring bridging a biphenyl system.

THE bright red pigment, cercosporin (I), produced by the mould *Cercosporina Kikuchii Matsumoto et Tomoyasu* (responsible for the pathogen of the Purple Speck disease of Japanese soy beans), was first investigated by Kuyama and Tamura.[1] They made a detailed study of its properties and chemical transformation products. From its electronic and i.r. spectra, the green colour of its alkaline solution, and the formation of mellitic acid by nitric acid oxidation, it was concluded that cercosporin is derived from 4,9-dihydroxyperylene-3,10-quinone, but no detailed structure was suggested.

Because of our interest in natural perylenequinones[2] we have studied cercosporin.[3] We find, using high-resolution mass spectrometry, that the empirical formula of the pigment is $C_{29}H_{26}O_{10}$, rather than the C_{30} formula given by

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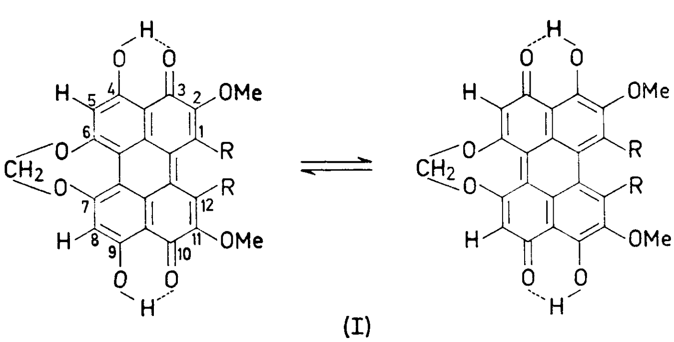
Kuyama.[1] The m.p. (271°) and i.r. spectrum of the compound are identical to those given by Kuyama, while the electronic spectrum (ethanol) shows additional weak absorptions at 325 and 564 nm. The electronic spectrum of the product of reductive acetylation is identical to that given by Kuyama and strongly resembles that of 3,4,9,10-tetra-acetoxyperylene and the corresponding product obtained from elsinochrome A.[4] The n.m.r. data and results of decoupling experiments are entirely consistent with structure (I). The extreme sharpness of the *peri*-hydroxy-group resonance at τ — 4·86 suggested a rapid tautomerism (commonly encountered in *peri*-hydroxyquinones of this type) between the two possible quinonoid forms of (I). The sharp and single resonances of the *peri*-hydroxy, the aromatic, the methylenedioxy, the methoxy, and side-chain hydroxy protons, integrating in the ratios 2:2:2:2:6:2 (τ — 4·86, 2·94, 4·24, 5·79, and 8·42) are consistent only with a symmetrical arrangement of the substituents on the parent ring system. A methyl doublet (J 6 Hz) and an ABX-type multiplet, both representing six protons, appear at τ 9·37 and 6·7, respectively, and represent the side-chain protons. The assignment of the methoxy-groups at C-2 and C-11, rather than at C-5 and C-8, is based upon the position of their n.m.r. resonance, which is comparable to the one of the corresponding groups in the spectrum of elsinochrome A.[4] Moreover, the methoxy-resonance fails to undergo an appreciable solvent shift, $\Delta(CDCl_3,C_6D_6)$, which is compatible with the position of the methoxy-groups on the parent ring system.[5] The position of the side-chains at C-1 and C-12 is evident from the results of zinc dust distillation of (I),[1] which yielded a hydrocarbon with an electronic absorption spectrum closely resembling that of benzo[*g,h,i*]perylene.



(I)

R=CH2CHOHMe

A detailed further investigation of (I), especially of the isomerization to isocercosporin, and of other transformations that have been described,[1] is planned as a co-operative effort in our respective laboratories.

The structure suggested for (I) is unusual: the methylenedioxy-group, although common in other types of natural compounds, has only been encountered in three quinones so far (one of them[2] the perylenequinone elsinochrome D), and in the arrangement present in (I), *i.e.* in a seven-membered ring bridging a biphenyl system, it appears to be unprecedented in nature, as far as we know.

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[5] R. J. J. Ch. Lousberg, L. Paolillo, H. Kon, U. Weiss, and C. A. Salemink, *J. Chem. Soc.* (*C*), 1970, 2154.