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PHOTOOXYGENATION OF 2',4,4'-TRIHYDROXYCHALCONE: IDENTITY WITH PRODUCTS FROM ENZYMIC OXIDATION

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Key Word Index—Dioxetanes; chalcones; photooxygenation.

Abstract—The dioxetane derivative of 2',4,4'-trihydroxychalcone, previously known as a product from peroxidase-catalysed oxidation, has now been detected in the dye-sensitized photooxygenation of the same chalcone and shown to be accountable for the host of other products formed.

Previous study [1, 2] on the peroxidase-catalysed oxidation of 2',4,4'-trihydroxychalcone (1) has led to the identification of a host of products, including 4',7-dihydroxyflavonol, 4',7-dihydroxyflavanonol, the quinol vinyl ether (5) (OC), the stereoisomeric coumaranone (6) (Y1/Y2) and stereoisomeric forms of the initial enzymic product (EP) for which the dioxetane structure 2 was proposed [1, 2]. Dioxetanes are known products of reaction of electron-rich double bonds with singlet oxygen [3–5]. Chawla and Chakrabarty [6] have recently studied the dye-sensitized photooxygenation of a number of chalcones and have identified flavonols and/or carbonyl and acid fragments as reaction products, with the latter being presumed degradation products of dioxetane intermediates. We now report on the identity of the products formed in the dye-sensitized photooxygenation of 2',4,4'-trihydroxychalcone.

The reaction was carried out under conditions similar to those used by Chawla and Chakrabarty [6]. The products obtained were analysed by TLC and HPLC and compared with those from the enzymic reaction analysed in a similar manner. Products from the photochemical reaction thus identified were *p*-hydroxybenzaldehyde, 2,4-dihydroxybenzoic acid and the EP isomers 2, Y1/Y2 (6), OC (5), 4',7-dihydroxyflavonol and 4',7-dihydroxyflavanonol. The overall extent of the reaction was about 10%, with *p*-hydroxybenzaldehyde, 2,4-dihydroxybenzoic acid and Y1/Y2 (6) constituting the major products.

The range of products formed from the photochemical reaction can thus be seen to be analogous to that from the enzyme-catalysed reaction previously studied [1, 2]. The detection of the EP compound under the conditions used in the photochemical reaction in this work is significant, in accord with it being the expected product having the previously assigned dioxetane structure. As in the enzyme-catalysed reaction, the other products of the photooxygenation reaction can be accounted for as artefacts of this labile initial product.

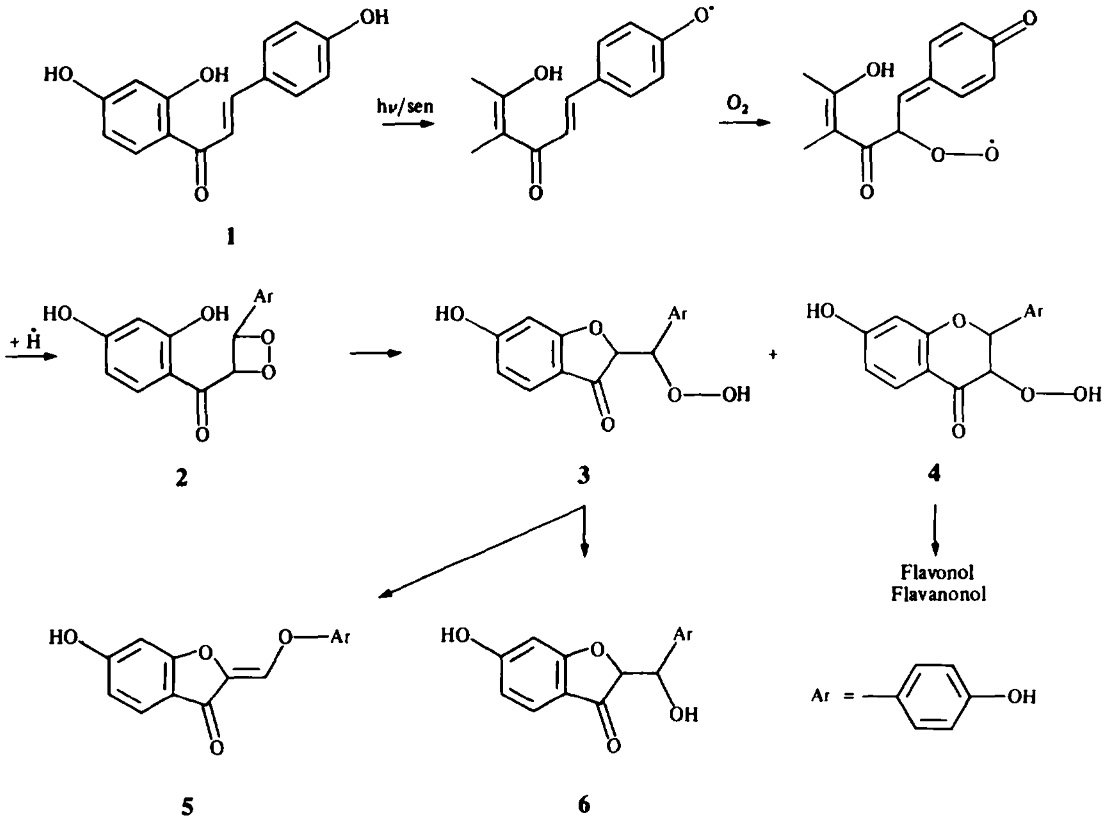
It should be noted that the dioxetane product from the photochemical reaction reported here was also detected in the form of the various stereochemical isomers. As in the enzymic reaction [7], this non-stereospecific formation can be rationalized in terms of a stepwise mechanism involving initial formation of a phenoxy radical [8, 9], with subsequent addition of oxygen as shown in Scheme 1. Intramolecular nucleophilic displacement by *o*-hydroxyl, at either the α- or β-carbon of the dioxetane moiety, would give the hydroperoxide tautomers 3 or 4 as possible intermediate species. Subsequent O–O cleavage in these, with or without concomitant reduction [3, 10], would account for the series of five- and six-membered heterocyclic compounds found as end products in the reaction. The scheme presented here differs from that of Chawla and Chakrabarty [6] in that concerted addition of singlet oxygen to chalcone is not involved. Another example of probable dioxetane formation from an allylic hydroperoxide has recently been reported by Chan *et al.* [11].

EXPERIMENTAL

Photooxygenation. A soln of the chalcone (40 mg) in MeOH (100 ml) containing methylene blue (10^{-5} M) was cooled in an ice bath and irradiated with a 1000 W incandescent lamp (Philips NK17/Z), with air being continuously passed through the soln. After 4 hr, the mixture was evaporated *in vacuo* and the residue was partitoned in H_2O (20 ml) and Et_2O (2 × 40 ml). The Et_2O extract was evaporated and taken up in MeOH (400 μl) as a stock soln for chromatography. The aq. mother liquor after acidification to pH 2 was further extracted with EtOAc (2 × 20 ml) to give a stock soln in MeOH (200 μl) of the acidic components. Reactions have also been carried out at room temp. for a shorter period (2 hr) with qualitatively similar results being obtained.

Enzymic oxidation. Peroxidase-catalysed oxygenation of the chalcone was carried out as previously described [1, 2]. Stock solns of products in MeOH were either analysed immediately (when the presence of the EP compounds was maximal) or after storage (1 hr at 50° or at −20° for longer periods) when inevitably transformation products predominate.

Identification of products. Products from the enzymic reaction were analysed by 2D TLC on cellulose powder sheets (C_6H_6–HOAc–H_2O, 125:72:3; 5% HOAc) and by HPLC on 5 μ RP-18 columns (13 cm × 4.6 mm) (40% MeOH, 1 ml/min).



Scheme 1.

Peaks were identified from their UV spectral data and by correlation with the previously known chromatographic behaviour of the individual components on 2D PC. Identities of products from the photochemical reaction were established by direct chromatographic comparison with the enzymic reaction products, and from UV spectral data.

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