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BIOLOGICALLY PATTERNED SENSITIZED PHOTOOXYGENATION OF CHALCONES

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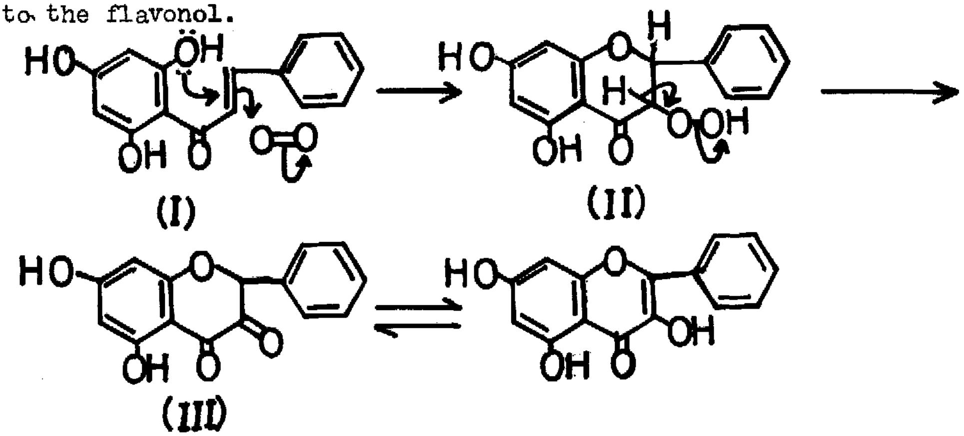
The similarity between dioxygenase-catalysed biological oxidations and sensitized photooxygenations has been well demonstrated in a number of reactions of singlet oxygen particularly with oxygen heterocycles as substrates and it has been established that photooxygenation in the presence of sensitizers can act as non-enzymatic models for dioxygenases[1,2].

Our attention was directed to the biological oxidations of chalcones to their flavonoid derivatives which are known to occur together in the plant kingdom. Chemically and enzymatically chalcones can be converted to the corresponding flavanones and flavonols[3,4], and biogenetically also the chalcones are considered to be the precursors[5]. It was of interest to see whether singlet oxygen could play a part in such oxygenations (or hydroxylations) as the plants contain well known photosensitizers such as chlorophyll. As a first step towards this objective photosensitizers like methylene blue and rose bengal have been used for simulation of natural conditions.

As most of the naturally occurring oxygen heterocycles have phloroglucinol pattern, 2',4',6'-trihydroxychalcone was considered to be the most convenient non-enzymatic model. Its methanolic solution containing catalytic amounts of methylene blue was irradiated with a 100W tungsten lamp and air was bubbled through the solution for six hours. The reaction mixture was worked up according to the procedure of Matsuura _et al._[6] and the product purified by silica gel chromatography. A light yellow compound, m.p. 219-28 (λ_{max}^{MeOH} 240, 268, 360; with $AlCl_3$, 273, 337, 414; with NaOAc, 275, 328, 388 nm) was obtained which was identified as 5,7-dihydroxy flavonol by comparison with an authentic sample[7].

In order to confirm the participation of singlet molecular oxygen the reaction was repeated in the absence of a sensitizer when no reaction took place and the starting material was recovered unchanged. In the presence of rose bengal, lesser yield of the flavonol was observed due to decreased concentration of $^1\Delta_g$ state of oxygen and the formation of the $^1\Sigma_g$ state which leads to the formation of side products[8].

The formation of the flavonol can be envisaged by the mechanism depicted below. Initial reaction of $^1O_2$ and the chalcone could lead to α-keto hydroperoxide (II) which dehydrates to the diketone (III) followed by tautomerization to the flavonol.



The possibility of the commonly envisaged dioxetane intermediate was ruled out because it would decompose to benzaldehyde and 2,4,6-trihydroxy benzoyl formic acid which could not be detected in the reaction mixture[9]. Further work on the mechanism of the reaction is in progress.

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