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NOVEL PHOTOCHEMICAL CONVERSION OF CHALCONES TO FLAVANONOLS

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Chalcones are the important key intermediates for the biogenesis of naturally occurring oxygen heterocycles particularly the flavonoids. They can be conveniently converted to the flavonoids of different oxygenation level by chemical as well as enzymatic methods[1]. Very recently Pelter et al., using labelled chalcone precursors, have shown that flavanonols arise from chalcones in plants[2]. They ruled out the possibility of a flavonoid intermediate with central heterocyclic ring having a 2,3-double bond and also the involvement of a 4'-hydroxyl in the biogenesis of flavanonols. Further, no conclusive evidence could be obtained for the origin of oxygenation in the 3-position, i.e., whether it comes from water or from molecular oxygen[3].

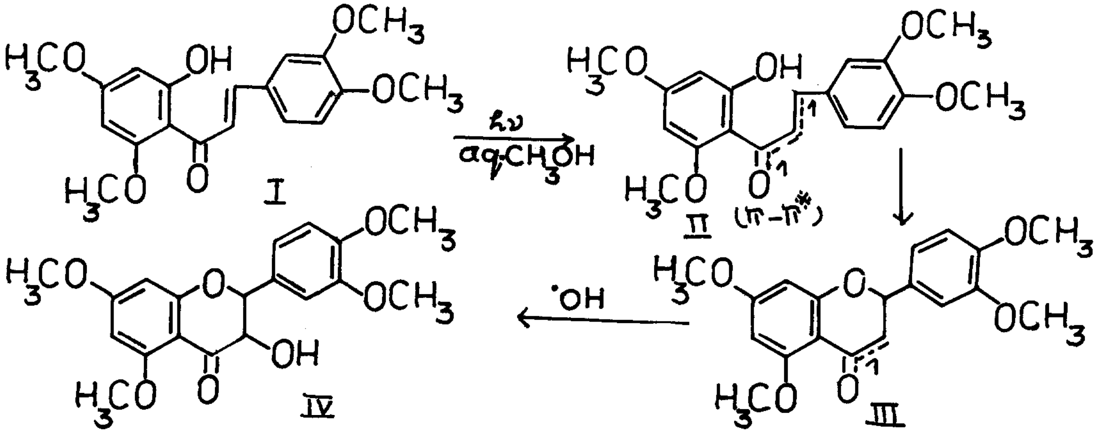
Taking dye sensitized photochemical oxidation by visible light as a simulation of the chlorophyll sensitized photochemical processes occurring in plants, it has been possible to convert chalcones to flavanonols and to throw some light on the nature of the reaction. In the present work, 2'-hydroxy-4',6',3,4-tetramethoxy chalcone was subjected to irradiation with visible light in presence of methylene blue as sensitiser when 5,7,3',4'-tetramethoxy flavanonol was obtained. This photochemical conversion is also the first report of one step transformation of chalcones to flavanonols.

A solution of 2'-hydroxy-4',6',3,4-tetramethoxychalcone (I) (50 mg) in 4% aqueous methanol (50 ml) containing a catalytic amount of methylene blue (5 mg) was irradiated with 100 watt tungsten flood lamp for 48 hr. The loss of solvent due to evaporation was replenished by the addition of a fresh lot of solvent. The reaction mixture was worked up by distilling off methanol under reduced pressure and extracting the residual mass with ethyl acetate. The ethyl acetate extract was subjected to column and preparative thin layer chromatography (silica gel) when a light yellow compound m.p. 168-9°, λ_{max}^{MeOH} 285; with $AlCl_3$, 310; with $AlCl_3$+HCl, 285 nm; ν_{max}^{KBr} 3500, 1660 cm^{-1}; NMR($CDCl_3$, δ): 4.1(3H, s, $OC\underline{H}_3$), 4.18(9H, s, 3 $OC\underline{H}_3$), 4.7(1H, d, J=14 Hz, $\underline{H}_2$), 5.3(1H, d, J=14 Hz, $\underline{H}_3$), 6.5(1H, s, $Ar\underline{H}_8$), 7.4(2,5',6', 3H, m, $Ar\underline{H}$), 7.65(1H, s, $Ar\underline{H}_6$) was obtained. It was identified to be 5,7,3',4'-

tetramethoxydihydroflavonol(IV) by comparison with a synthetic sample.

As methylene blue is known to be a free radical generator, it can be visualized that the above reaction probably proceeds by a diradical (II) formed through the excitation of α, β -unsaturated carbonyl group of the chalcone by n- π^* and π - π^* transitions, the latter being more predominant[4].

The radical nature of the reaction was confirmed by its inhibition on addition of quinol, a well known radical quencher. The diradical II undergoes an intramolecular radical abstraction from 2'-hydroxyl to yield (III) which may then yield the flavanonol either by radical-water molecule collison or by combination with the hydroxyl radical formed by the photolysis of aqueous methanol.



When the reaction was repeated in non-aqueous solvents such as benzene, benzene-methanol mixtures and absolute methanol, no flavanonol could be detected in the reaction mixture even after prolonged irradiation. However, on addition of small amounts of water (~5%, v/v) the reaction yielded the flavanonol. This suggests that the source of 3-hydroxyl in the flavanonol formation is probably water. As the chalcone studied contained no hydroxyl in the B-ring, the flavanonol formation supports the view[2] that 4'-hydroxyl is not involved in its biogenesis.

Further work on the mechanism of the reaction is in progress.

References

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