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PHOTO-OXYGENATION OF CAROTENOIDS. I.
THE FORMATION OF DIHYDROACTINIDIOLIDE AND β-IONONE FROM β-CAROTENE

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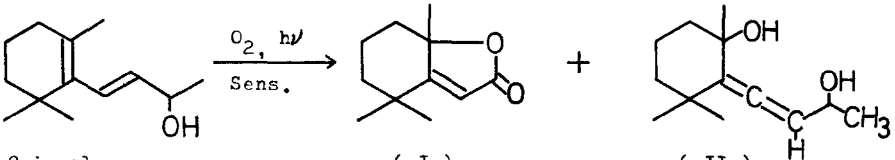
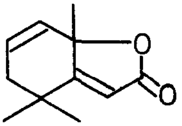
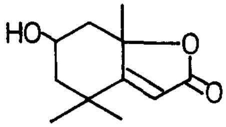
In previous paper[1] we demonstrated the photosensitized oxygenation of β-ionol to dihydroactinidiolide (I) and allenic alcohol (II) as a model for the biosynthesis of C_{11}- and C_{13}-oxygenated compounds. The recent isolation of actinidiolide (III)[2], dihydroactinidiolide (I)[2,3] and loliolide (IV)[4] from several species of plants, the isolation of allenic ketone (V)[5] from insect and the natural occurrence of oxygenated carotenoids[6] which appears to involve photo-oxygenation in their formation from β-carotene led us to the postulation that carotenoids are the sole precursor for these C_{11}- and C_{13}-oxygenated compounds.



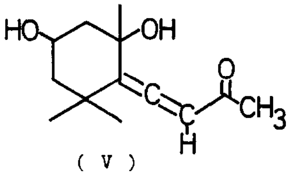
β-ionol (I) (II)



(III)



(IV)



(V)

Exhaustive oxygenation of β-carotene was carried out in different conditions; under irradiation with or without sensitizer[7]. When the solution of β-carotene in benzene and methanol was oxygenated under irradiation by 30W-fluorescent lamp in the presence of catalytic amounts of alkali and rose bengal initial dark brown color changed after 48 hours to faint red which indicates the absence of β-carotene.

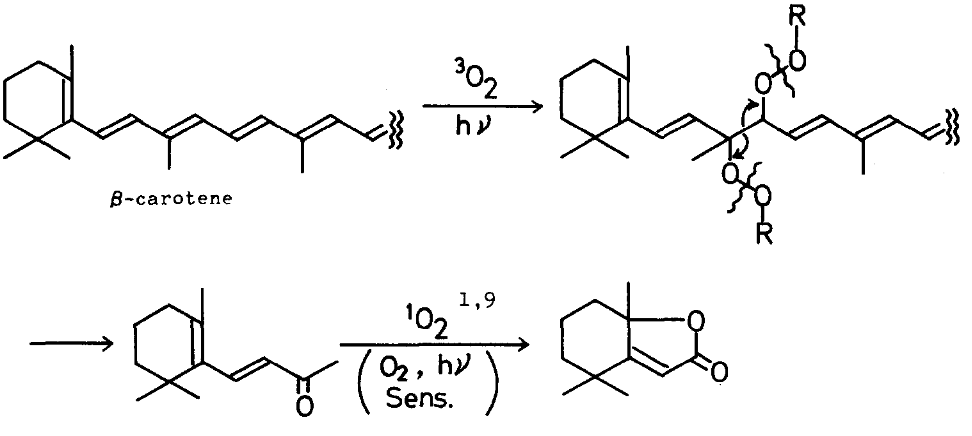
After evapolation of solvent, the residue was steam distilled. From the distillate dihydroactinidiolide (I) was isolated as main product. In this case small amounts of β-ionone[8], 6-hydroxy-2,2,6-trimethylcyclohexanone (VI) and an unknown lactone were isolated. The identities of these compounds with authentic specimens were provided by the comparison of their IR, NMR and mass spectra.

When the photo-oxygenation of β-carotene was carried out without sensitizer the composition of oxidation product was parallel except that β-ionone was main product and dihydroactinidiolide was minor.

As a control, oxygenation of β-carotene was carried out in the dark in which case the brown color was almost remained unchanged even after 10 days. Although the total yield of oxidation products was quite low in the dark, the relative yield of each oxidation product was parallel to that under irradiation without sensitizer.

From these findings it is most likely that triplet oxygen reacts with β-carotene biradicals whose formation are greately enhanced by light absorption.

One of the possible mechanisms for the oxygenation of β-carotene to β-ionone and dihydroactinidiolide is as follows.



β-carotene

β-ionone

(I)

The details on the mechanisms of photo-oxygenation of β-carotene will be discussed elswhere.

These results and our previous observations[1] strongly suggest that $C_{11}$and C_{13}-oxygenated compounds are produced from carotenoids in vivo by the mechanism analogous to photo-oxygenation and further lead to the postulation that abscisic acid is an oxidized metabolite derived from carotenoid.

The results of photo-oxygenation of zeaxanthin and other carotenoids will be forthcoming.

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