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THE SYNTHESIS OF ACTINIDIOLIDE, DIHYDROACTINIDIOLIDE AND ACTINIDOL

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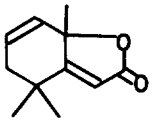
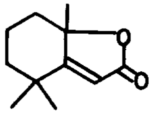
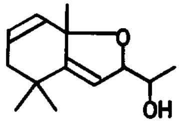
In previous paper$^{1)}$ we reported the structure of actinidiolide (I), dihydroactinidiolide (II) and actinidol (III), the odd terpenes from <u>Actinidia</u> <u>polygama</u> Miq..



(I)



(II)



(III)

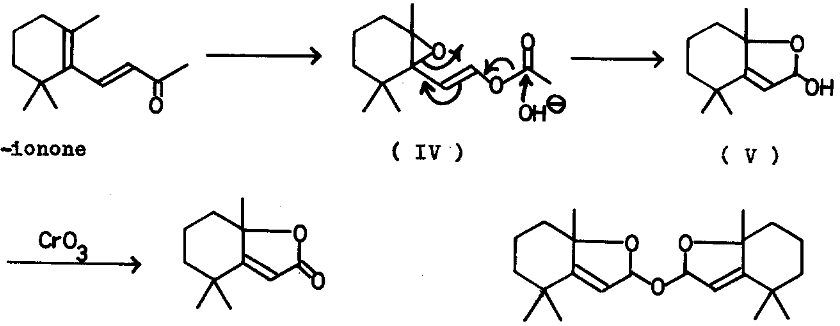
Recently, much attention has been devoted to dihydroactinidiolide because of its isolation from several species of plants$^{2)}$ as one of principles of tea aroma.

We herein report the biogenetic type synthesis of actinidiolide, dihydroactinidiolide and actinidol and the formation of allenic compound from β-ionol by photosensitized oxygenation.

Although the synthesis of dihydroactinidiolide has already been reported by Sakan et al.$^{1)}$, Mousseron-Canet el al.$^{3)}$ and Demole et al.$^{4)}$ we have developed two alternative synthetic routes to dihydroactinidiolide.

Oxidation of β-ionone with two moles of perbenzoic acid gives an epoxy-enolacetate (IV)(UV: end absorption; IR: $\nu_{C=O}$1760cm^{-1}, ν_{C-O}1220cm^{-1}, $\nu_{C=C}$1670cm^{-1}; NMR: 0.94 (3H,s), 1.02 (3H,s), 1.16 (3H,s), 2.07 (3H,s), 5.45 (1H,d,J=12cps) and 7.01ppm (1H,d,J=12cps)) in almost quantitative yield. Alkaline hydrolysis of (IV) gives a hemiacetal (V) (IR: ν_{OH}3350, ν_{C-O}1000, 1070, $\nu_{C=C}$1650cm^{-1}) which is oxidized to dihydroactinidiolide (II) with chromic anhydride in good yield. When the alkaline hydrolysis of (IV) was carried out in the aeration dihydroactinidiolide was directly obtained. In this case a small amount of hemiacetal-dimer (VI) (m.p.138-139°; IR: $\nu_{C=C}$1650, ν_{C-O}975, 995cm^{-1}; NMR: 1.15 (6H,s), 1.20 (6H,s), 1.44 (6H,s), 5.40 (2H,d,J=2cps) and 5.85ppm (2H,d,J=2cps)) was also formed.

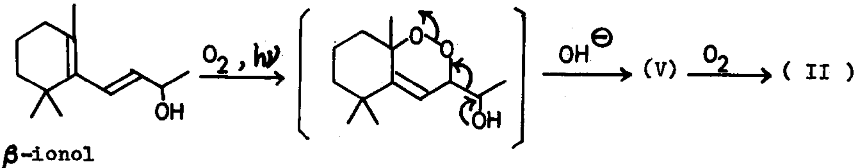
Dimer (VI) was converted to dihydroactinidiolide by the oxidation with chromic acid.



β-ionone (IV) (V)

(II) (VI)

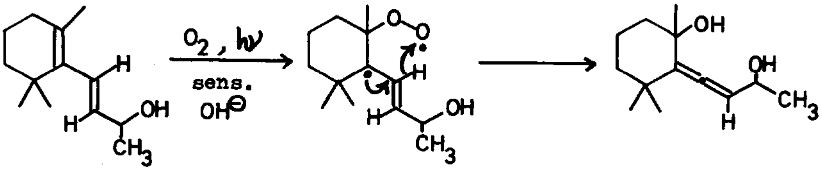
Dihydroactinidiolide, m.p.42-43°, thus obtained has same elegant tea aroma as natural specimen. Dihydroactinidiolide was also synthesized by the another route which based on the hypothetical biogenesis of dihydroactinidiolide described previously[1]. Photosensitized oxygenation of β-ionol in the presence of catalytic amounts of alkali yielded (II) as major product by the mechanism illustrated below.



β-ionol

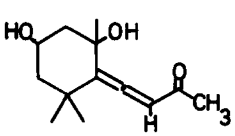
One of the minor products was a crystalline compound whose elemental analysis agreed most closely with $C_{13}H_{22}O_2$. Allenic structure (VII) was assigned for this compound by the spectroscopic data (IR: $\nu_{C=C=C}$ 1955, ν_{OH} 3200 cm^{-1}; IR of acetate: $\nu_{C=C=C}$ 1955, ν_{OH} 3450, $\nu_{C=O}$ 1725 cm^{-1}; NMR of acetate: 1.10 (3H,s), 1.33 (3H,s), 1.36 (3H,s) 1.45 (3H,d,J=6cps), 2.1 (3H,s), 5.35 (2H,m) and 3.15 (1H,OH)).

The formation of (VII) from β-ionol is explained by the following mechanism.

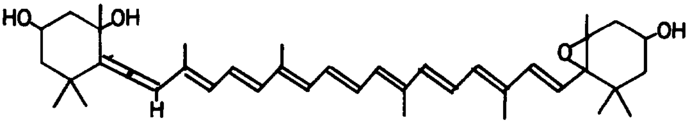


β- ionol (VII)

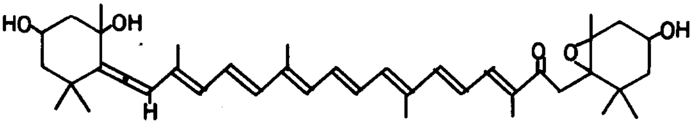
This is the first case which diene gives allene by photosensitized oxygenation. Most recently, Meinwald et al.[5] reported the isolation of allenic ketone (VIII) from grass hopper Romalea microptera as one of defensive secretions. The structure of (VIII) is quite similar to that of (VII). While the recently characterized carotenoid pigments foliaxanthin (neoxanthin)(IX)[6] and fucoxanthin (X)[7] are the another examples which possess close analogies for structure (VII).



(VIII)



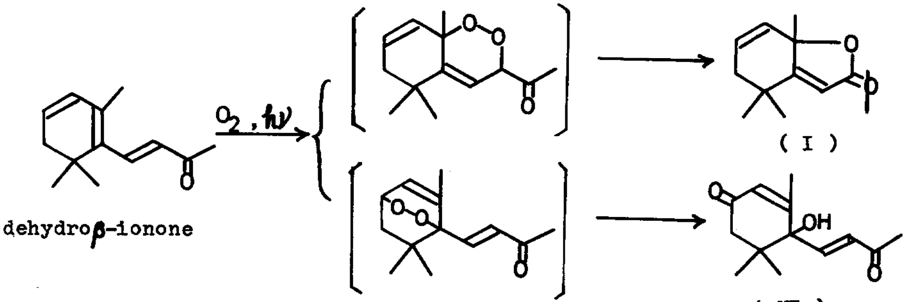
(IX)



(X)

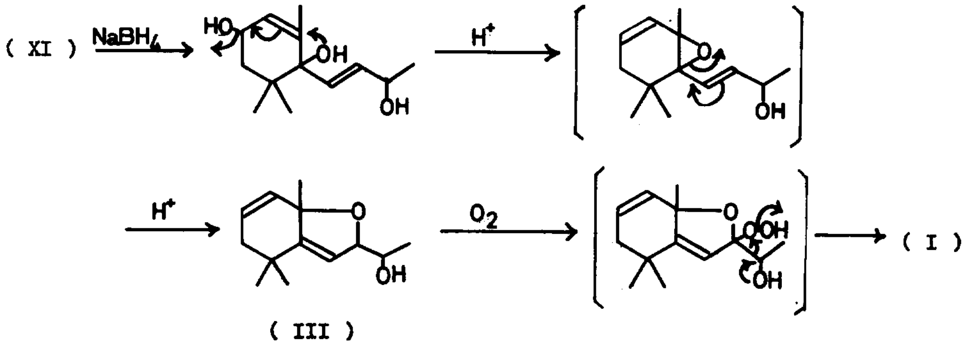
It appears most likely that these naturally occurring allenes are produced from the polyene precursor by photosensitized oxygenation of terminal double bond.

We next attempted the biogenetic type synthesis of actinidiolide and actinidol. Photosensitized oxygenation of dehydro β-ionone, followed by the column chromatography of a reaction product afforded the actinidiolide (I) (m.p.40-41.5°) as a minor product. The major product was hydroxydiketone (XI), (m.p.108-109°), whose structure was assigned by its spectroscopic data (UV: λ_{max}^{EtOH} 242m (ε=21900); IR: ν_{OH} 3480, $\nu_{C=O}$ 1670, $\nu_{C=C}$ 1630cm^{-1}, NMR: 1.04 (3H,s), 1.11 (3H,s), 1.95 (3H,d,J=1.5cps), 2.35 (3H,s), 2.5 (2H,d,J=3cps), 3.26 (1H,OH), 6.1 (1H,d,J=1.5cps), 6.6 (1H,d,J=16cps), and 7.1ppm (1H,d,J=16cps)). The formation of (I) and (XI) from dehydroβ-ionone is illustrated as follows.



(XI)

Reduction of hydroxydiketone (XI) with sodium borohydride, followed by treatment with dilute sulfuric acid affords a mixture of ether soluble compounds, from which actinidiolide and actinidol were isolated by gas-liquid chromatography. Both compounds thus isolated were identified respectively with natural specimens by the comparison of their IR spectra.



The significance of photosensitized oxygenation in the biosynthesis of C-11 and C-13 terpenes and oxygenated carotenoids was demonstrated.

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