

PHOTO-OXYGENATION OF CAROTENOIDS. II. THE ABSOLUTE CONFIGURATION OF LOLIOLIDE AND DIHYDROACTINIDIOLIDE*.

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We have previously shown that photo-oxygenation of β -carotene yields dihydroactinidiolide (VI), β -ionone (IX) and 2-hydroxy-2,6,6-trimethylcyclohexanone (I)¹.

We now wish to report further studies on the photo-oxygenation of β -carotene, vitamin A acetate and zeaxanthin as well as the stereochemical correlation of loliolide and dihydroactinidiolide with zeaxanthin.

Exhaustive photo-oxygenation of β -carotene in benzene in the presence of trace of water yielded in addition to aforementioned three compounds geronic acid (III), IR(liq.) 1700 cm^{-1} ; NMR(CCl_4) δ 1,17(6H,s), 2,06(3H,s), and desoxy-xanthoxin (XI), IR(liq.) 1655, 1630, 1205, 1120, 975 cm^{-1} ; UV λ_{max} (EtOH) 283nm; MS 234(M^+). Parallel results were also obtained with vitamin A acetate.

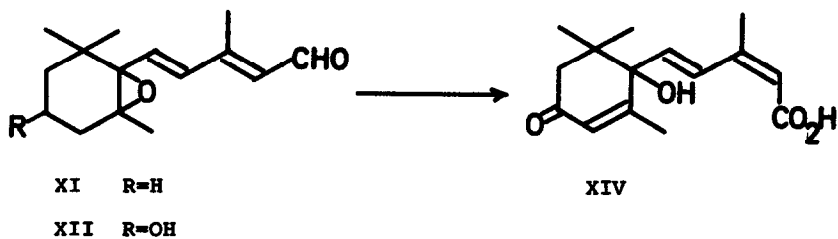
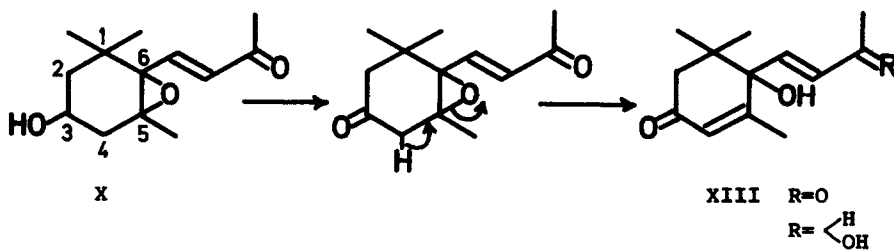
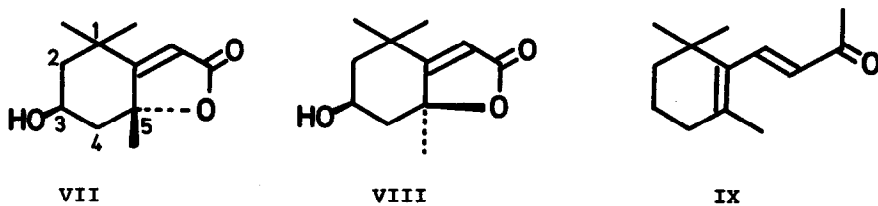
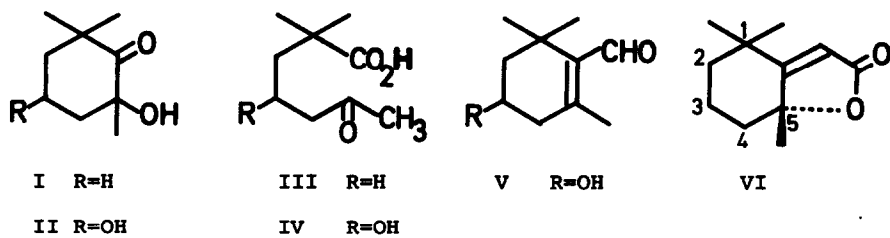
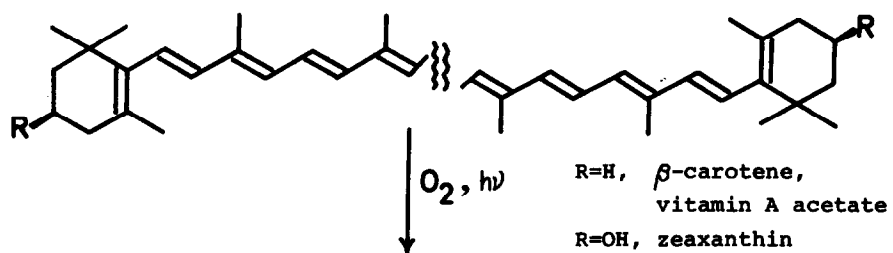
Exhaustive photo-oxygenation of zeaxanthin yielded 2,4-dihydroxy-2,6,6-trimethylcyclohexanone (II), [its acetate, IR(liq.) 1730, 1370, 1240, 1030 cm^{-1} ; NMR(CCl_4) δ 1,26(6H,s), 1,47(3H,s), 2,02(6H,s), 5,00(1H,m)], hydroxy geronic acid (IV), [its lactone, m.p. 38-39 $^{\circ}$; IR(nujol) 1765, 1718 cm^{-1} ; NMR(CCl_4) δ 1,30(3H,s), 1,32(3H,s), 2,20(3H,s)], 3-hydroxy- β -cyclocitral (V), [its acetate, $[\alpha]_{\text{D}}^{16}$ -63 $^{\circ}$; IR(liq.) 1745, 1680, 1620, 1370, 1240, 1030 cm^{-1} ; UV λ_{max} (EtOH) 246nm; NMR(CCl_4) δ 1,17(3H,s), 1,32(3H,s), 1,83(3H,s), 2,02(3H,s)], loliolide (VII), [m.p. 151,5-153 $^{\circ}$; $[\alpha]_{\text{D}}^{15}$ -97,2 $^{\circ}$ (CHCl_3), its acetate, $[\alpha]_{\text{D}}^{15}$ -65,2 $^{\circ}$ (CHCl_3); NMR(CCl_4) δ 1,28(3H,s), 1,37(3H,s), 1,66(3H,s), 2,04(3H,s), 5,10(1H,m), 5,65(1H,s)], iso-lololide (VIII), [$[\alpha]_{\text{D}}^{15}$ +80,6 $^{\circ}$ (CHCl_3); its acetate, $[\alpha]_{\text{D}}^{15}$ +47,5 $^{\circ}$; NMR(CCl_4) δ 1,29(3H,s), 1,31(3H,s), 1,65(3H,s), 1,97(3H,s), 5,05(1H,m), 5,65(1H,s)], and 3-hydroxy-5,6-epoxy- β -ionone (X), [its acetate, m.p. 126-127 $^{\circ}$; $[\alpha]_{\text{D}}^{15}$ -77,5 $^{\circ}$; IR(nujol) 1733, 1680, 1630, 1370, 1240, 1030 cm^{-1} ; NMR(CCl_4) δ 0,98(3H,s), 1,15(3H,s), 1,20(3H,s),

1,94(3H,s), 2.20(3H,s), 4,80(1H,m), 6,20(1H,d,J=16Hz), 6,90(1H,d,J=16Hz)] .

The value of the specific rotation of loliolide(VII) obtained by photo-oxygenation of natural zeaxanthin, m.p.202-204°; $UV\lambda_{max}(CHCl_3)$ 493, 462, 429nm, (from *Physalis alkekengi* var *Francheti*) was completely identical with that of natural loliolide, $[\alpha]_D^{20} -100,5^{\circ}$ ²⁾. Thus the absolute configuration of (-)-loliolide was correlated with 3R,3'R-zeaxanthin³⁾ and was assigned as 3S,5R-configuration. This suggests that loliolide is derived from zeaxanthin or violaxanthin.

Dehydration of hydroxy group of (-)-loliolide with phosphoryl chloride in pyridine followed by hydrogenation over palladium charcoal yielded (-)-dihydroactinidiolide(VI), $[\alpha]_D^{18} -86,3^{\circ}(CHCl_3)$ ⁴⁾. Thus (-)-dihydroactinidiolide was assigned as 5R-configuration.

The formation of 3-hydroxy-5,6-epoxy- β -ionone(X) from zeaxanthin coupled with the formation of desoxy-xanthoxin(XI) from β -carotene suggests that vomifoliol(XIII)⁵⁾, xanthoxin(XII)⁶⁾ and abscisic acid(XIV)⁷⁾ are derived from carotenoids(zeaxanthin or violaxanthin) by the mechanism indicated in figure. These results together with Taylor's results⁶⁾ that oxidation of violaxanthin yields loliolide, 3-hydroxy-5,6-epoxy- β -ionone and xanthoxin, which leads to natural (+)-abscisic acid, suggest that absolute configuration of abscisic acid assigned previously by Cornforth et al⁸⁾ should be revised as R(+)-abscisic acid and also establish the stereochemistry of violaxanthin in which 3-hydroxyl is trans to the 5,6-epoxide³⁾.



References

- * Part of this paper was presented at 13th symposium on the chemistry of natural products, Sapporo, 1969, (Symposium papers p.107) and 14th symposium on the chemistry of terpenes, essential oils and aromatics, Kitami, 1970, (Symposium papers p.16).
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