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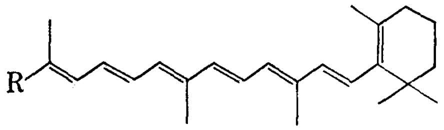
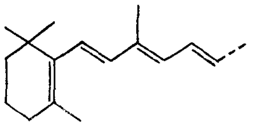
Photosensitized Oxygenation of All-*trans* β-Carotene

Recent reports on the exhaustive photosensitized oxygenation of β-ionol and of β-carotene[1] prompted us to report our results. We now report the formation of new C_{40}-carotenoids, *viz.*, an allenic, an acetylenic, and a cross-conjugated carotenoids along with a hydroxymutatochrome, from all-*trans* β-carotene (I).

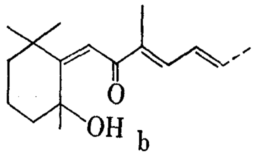
Photosensitized oxygenation[2] of all-*trans* I in the presence of chlorophyll, followed by basic alumina treatment, afforded complicated chromatograms on a lime column. In addition to the *cis*-isomers, 5,6-monoepoxide, and possibly 5,8-furanoid oxide of I, four new carotenoids A—D (in order of decreasing adsorption) were isolated from the less adsorbed portion of the column. The pigment A, $C_{40}H_{56}O_2$ (M^+ 568), exhibited λ_{max} (hexane) 475 (sh.), 450, and 424 (sh.) mμ, λ_{max} (MeOH) 458 mμ, ν (CS_2) 2.74, 6.01 μ, τ ($CDCl_3$) 8.96 (6H), 8.73 (9H), 8.27 (3H), 8.02 (9H), and 7.72 (3H), *m/e* (200°) 568 (M^+), 550, 416 (base), and 324 (base $-C_7H_8$), and partition ratio[3] 75:25 (not affected by alkali). The results of chemical reactions[4] of the parent as well as the reduced pigment were consistent with a cross-conjugated ketone structure (II) deduced from the spectral data. The pigment B, $C_{40}H_{56}O_2$ (M^+ 568), mp 155° (benzene–MeOH), gave similar ultraviolet, infrared, and nuclear magnetic resonance spectral characteristics[5] as all-*trans* mutatochrome (III). However, its partition ratio (94:6), reaction behaviours,[4] and mass spectra (*m/e* (200°) 568 (M^+), 552, 472 (M^+-16-80), 460 (M^+-16-C_7H_8), 336, 205, and 165 (base)) strongly supported a *tert*-hydroxylated III structure (IV). The pigment C, $C_{40}H_{56}O_2$ (M^+ 568), mp 80° (acetone–H_2O), indicated λ_{max} (hexane) 455 (sh.), 431, and 405



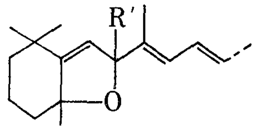
I: R=a IV: R=d
II: R=b V: R=e
III: R=c VI: R=f



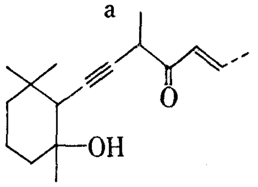
a



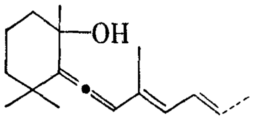
b



c (R'=H)
d (R'=OH)



e



f

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[1] S. Isoe, S.B. Hyeon, H. Ichikawa, S. Katsumura, and T. Sakan, *Tetrahedron Letters*, **1968**, 5561; S. Isoe, S.B. Hyeon, and T. Sakan, *ibid.*, **1969**, 279. They obtained dihydroactinidiolide and an allenic C_{13}-alcohol from β-ionol, and dihydroactinidiolide, β-ionone and 6-hydroxy-2,2,6-trimethylcyclohexanone from β-carotene.

[2] Oxygen was bubbled through the benzene–EtOH solution under irradiation with a 250W spot light and cooling with a fan.

[3] Distributed between petroleum ether and 95% MeOH.

[4] Throughout the experiments, reduction with $NaBH_4$, silylation, HCl–$CHCl_3$ treatment, conc. HCl reaction, isomerization with iodine, allylic methyl ether formation, and acetylation were conducted on each parent pigment as well as corresponding reduction product.

[5] K. Tsukida and L. Zechmeister, *Arch. Biochem. Biophys.*, **74**, 408 (1958); N. Suzuki, *Chem. Pharm. Bull.* (Tokyo), **9**, 257 (1961); K. Tsukida, S. Yamane, and M. Yokota, *J. Vitaminology*, **14**, 95 (1968); K. Tsukida and M. Yokota, *Vitamins*, **38**, 135 (1968).

(sh.) mμ, λ_{max} (MeOH) 450 mμ, ν (CS_2 and CCl_4) 2.74, 4.20, 4.43, and 6.02 μ, τ ($CDCl_3$) 8.98 (9H), 8.75 (6H), 8.29 (3H), 8.07 (3H), 8.02 (6H), and 7.79 (3H), *m/e* (200°) 568 (M^+), 414, 406, 390 (base), 347, and 314. In addition to these spectral data, partition and reaction behaviours[4] suggested formula V for this new carotenoid. The pigment D, $C_{40}H_{56}O$ (M^+ 552), mp 135° (benzene–MeOH), exhibited an ultraviolet spectrum and an isomerization pattern after iodine treatment indistinguishable from those of all-*trans* I. However, the major product produced from D after iodine catalysis was clearly separated from the latter on a lime column. Mass spectrum (300°) gave a stable molecular ion peak at *m/e* 552 (base) together with 506, 460 (M^+-C_7H_8), 446 (M^+-C_8H_{10}) and 414. A *tert*-hydroxyl and an allenic groups were also demonstrated by NMR (τ 8.19 (3H) in $CDCl_3$), IR (2.94, 5.10, and 5.18 μ in CS_2) and chemical reactions.[4] The data presented above revealed the structure of this compound as formula VI.

To our knowledge this is the first case in which photosensitized oxygenation has yielded both 6,7- and 7,8-dehydro derivatives of C_{40} carotenoid *in vitro* and may give a good model for biosynthesis of allenic carotenoids abundant in nature.

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