

BIOGENETIC TYPE SYNTHESIS OF GRASSHOPPER KETONE AND LOLIOLIDE  
AND A POSSIBLE BIOGENESIS OF ALLENIC CAROTENOIDS\* 1)

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In previous paper<sup>2)</sup> we demonstrated the photosensitized oxygenation of  $\beta$ -ionol to dihydroactinidiolide (I) and allenic alcohol (II) as a model for the biogenesis of the possible metabolites<sup>3)</sup> of carotenoids. We developed this reaction for the synthesis of grasshopper ketone<sup>4)</sup>, an allenic ketodiol isolated from defensive secretions of a sort of large flightless grasshopper, Romalea microptera, and loliolide, a minute constituents of Lolium perenne<sup>5)</sup>, Digitalis purpurea<sup>6)</sup> and Menyanthes trifoliata<sup>7)</sup>.

Hydroboration of 3,4-dehydro  $\beta$ -ionol acetate followed by treatment with alkaline hydrogen peroxide and hydrolysis yielded 3-hydroxy- $\beta$ -ionol (III), IR 3320, 1650, 1150, 1050 $\text{cm}^{-1}$ ; UV  $\lambda_{\text{max}}$ (EtOH) 234 $\mu\text{m}$ ; NMR(CDCl<sub>3</sub>) 8.95(6H,s), 8.65(3H,d,J=6cps), 8.30(3H,s), 7.15(OH), 6.1(1H,m), 5.7(1H,m), 4.1-4.4(2H,m). Photosensitized oxygenation of 3-hydroxy- $\beta$ -ionol (III) in methanol in the presence of minute amounts of rose bengal and alkali yielded dl-loliolide (IV)<sup>8)</sup>, m.p.143.5-144 $^{\circ}$ , IR(CHCl<sub>3</sub>) 3600, 3420, 1735, 1625 $\text{cm}^{-1}$ ; MS m/e 196 M<sup>+</sup>(C<sub>11</sub>H<sub>16</sub>O<sub>3</sub>); NMR (Table I), dl-isololiolide (V)<sup>9)</sup>, IR(oil) 3440, 1740, 1635 $\text{cm}^{-1}$ ; MS m/e 196 M<sup>+</sup>(C<sub>11</sub>H<sub>16</sub>O<sub>3</sub>); NMR (Table I) and allenic triol (VI), IR 3330, 1955 $\text{cm}^{-1}$ .

Table I

The NMR Spectra of dl-Loliolide(IV) and dl-Isololiolide(V) ( $\tau$  value in CDCl<sub>3</sub>)

(IV) 8.72(3H,s), 8.52(3H,s), 8.22(3H,s), 7.10(OH), 5.70(1H,m), 4.32(1H,s)

(V) 8.74(3H,s), 8.70(3H,s), 8.42(3H,s), 6.65(OH), 5.85(1H,m), 4.27(1H,s)

Selective oxidation of crude allenic triol (VI) with active manganese dioxide in acetone gave allenic ketodiol, IR 3400, 1940, 1670 $\text{cm}^{-1}$ ; UV  $\lambda_{\text{max}}$ (EtOH) 234 $\mu\text{m}$ ; MS m/e 224 M<sup>+</sup>(C<sub>13</sub>H<sub>20</sub>O<sub>3</sub>), whose stereochemistry was assigned as (VII)<sup>10)</sup> based on its NMR spectrum in which each chemical shift of three methyl on the ring is comparable to that of natural ketone (VIII) (Table II) and the reaction mechanism of singlet oxygen oxidation<sup>11)</sup>.

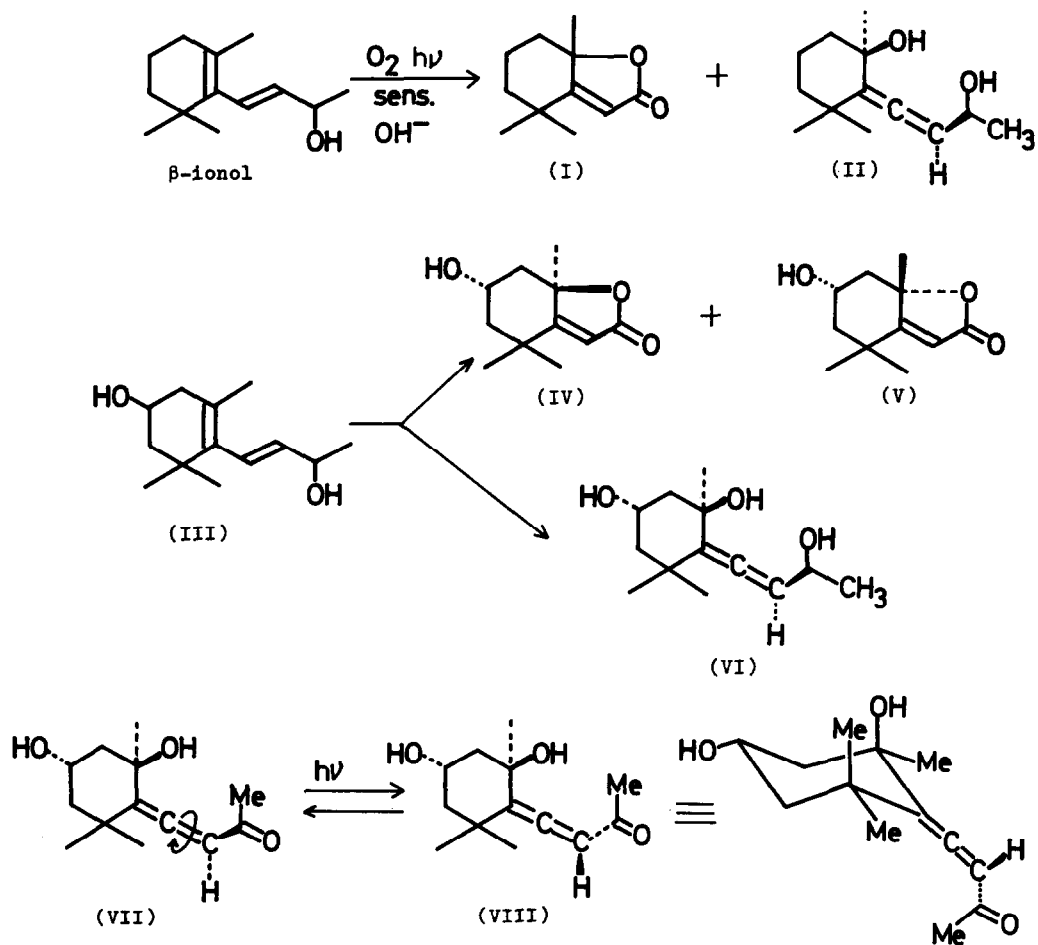


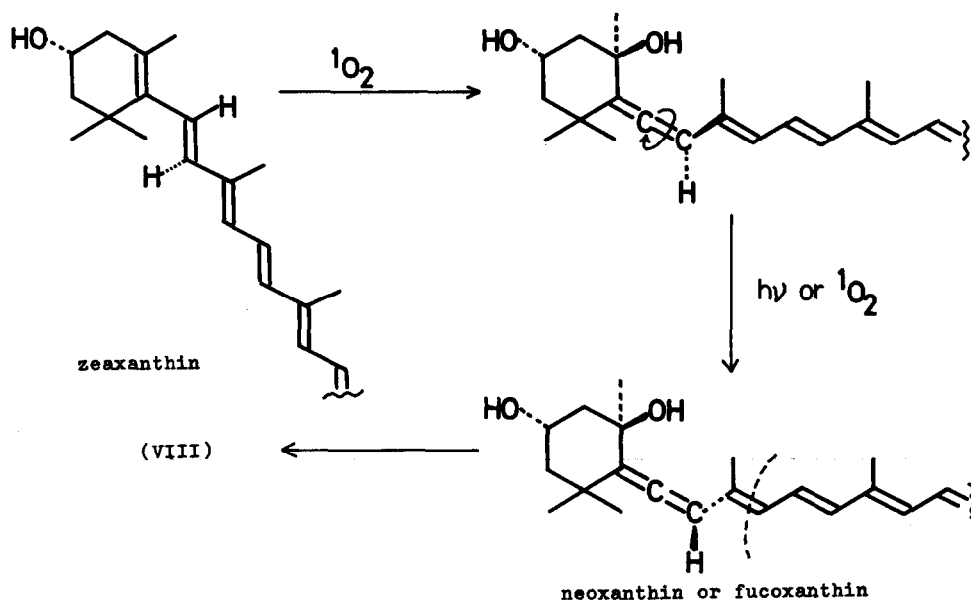
Table II The NMR Spectra of Allenic ketodiols(VII), Photoequilibrium mixture and dl-Grasshopper ketone(VIII) ( $\tau$  value in  $CDCl_3$ )

(VII)	Photoequilibrium mixture	(VIII)
8.88(3H,s)	8.88, 8.84	8.84(3H,s)
8.60(3H,s)	8.57- 8.62	8.64(3H,s)
8.57(3H,s)		8.58(3H,s)
*7.72(3H,s)	7.72, 7.83	*7.83(3H,s)
5.75(1H,m)	5.70- 5.75	5.71(1H,m)
*4.00(1H,s)	4.00, 4.17	*4.17(1H,s)

As allenic ketodiols thus obtained was isomeric with respect to allenic double bond with natural grasshopper ketone (VIII)<sup>12)</sup>, we next attempted the photoisomerization of allenic double bond. When the ethanolic solution of allenic ketodiols (VII) was irradiated with high pressure mercury lamp through pyrex glass filter under nitrogen atmosphere 50-50 per cent photoequilibrium between (VII) and (VIII) was set up after 30 minutes. This was followed by NMR in which the marked shift of each signal of allenic hydrogen and methyl of acetyl was observed as indicated in Table II. This is the first case which the stereomutation of allenic double bond was attained.

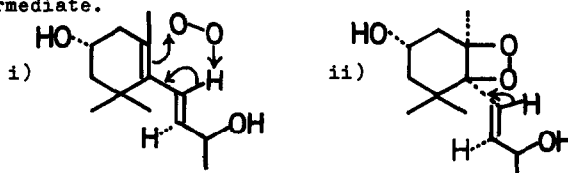
The allenic ketodiols of natural stereochemistry was thus obtained from  $\beta$ -ionone by the sequence of reactions involving photosensitized oxygenation and photostereomutation.

As we previously suggested<sup>2),13)</sup>, the same reaction may involve in the biosynthesis of fucoxanthin and neoxanthin, the abundant allenic carotenoids in nature, in which the easy stereomutation be expected by visible light or singlet oxygen<sup>14)</sup> as shown below.



\* This paper is dedicated to Emeritus Professor Munio Kotake in commemoration of his 77th birthday.

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