# Carotenoids and Related Compounds. Part XXIX.[1] Stereochemistry and Synthesis of the Allenic End Group. Absolute Configuration of Zeaxanthin

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Three of the four racemates of the allenic ketone. 4-(2.4-dihydroxy-2.6.6-trimethylcyclohexylidene)but-3-en-2-one. have been synthesised and their configurations determined. Except for optical activity, one of these racemates is identical with the allenic ketone from the grasshopper *Romalea microptera*. and its mono- (secondary) acetate with a degradation product of fucoxanthin. The latter has been converted into an optically active allenic ketone identical with that from grasshoppers. The absolute configuration of the product was established by X-ray crystallographic analysis of its p-bromobenzoate.

These results reveal that zeaxanthin (3,3'-dihydroxy-β-carotene) has the 3R,3'R-configuration.

THE allene (1), apo-9'-fucoxanthinone,‡ was a key fragment in the oxidative degradations used in the determination of the structure of fucoxanthin (3).[2-4] An allenic ketone with the gross structure (2) was subsequently

(1) R = Ac
(2) R = H

(3) X = a, Y = b
(5) X = e, Y = c

(4) X = Y = d

a

b: R = Ac
c: R = H

d

e
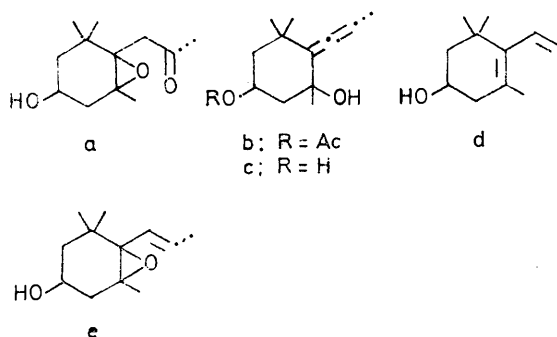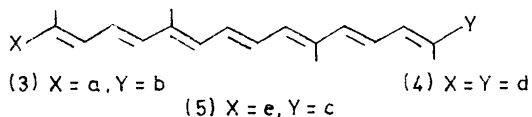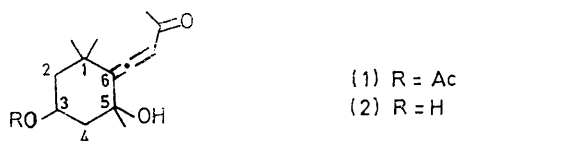
isolated from ant-repellant secretions of the large flightless grasshopper, *Romalea microptera*.[5] In this paper we describe the synthesis of the racemates of these allenic ketones; also studies which establish their absolute configuration and, indirectly, that of zeaxanthin (4) and

related carotenoids (for preliminary communications see refs. 6—9).

Treatment of the enyne diacetate (8)[1] with monoperphthalic acid gave, as expected, two epoxides (*ca.* 1 : 2) which were separated by chromatography on silica gel. The minor, more strongly adsorbed isomer was assigned the *trans*-configuration (9) by analogy with the minor product from the epoxidation of (6) under similar conditions, which is known to be the *trans*-isomer (7).[3,10] Reduction of (9) with lithium aluminium hydride below 20° gave the acetylenic diol (10) which, on treatment with the same reagent in boiling tetrahydrofuran, gave the crystalline allenic triol (14). Selective oxidation of the latter with manganese dioxide in acetone then gave the racemate of the allenic ketone (17), m.p. 111°.

The reduction of the acetylenic diol (10) to the allenic triol (14) resembles the formation of α-hydroxy-allenes on treatment of 1,4-dihydroxyacetylenes[11,12] (and their monotetrahydropyranyloxy-derivatives[13]) with lithium aluminium hydride; the preparation of the 5-deoxy-analogue (27) of the grasshopper ketone, reported in the Experimental section, includes an example of this reaction. With (10) an organoaluminium intermediate of the type (13) is probably involved, and it was therefore predicted that in the final product (17) the tertiary hydroxy-group at C-5 would be *trans* to both the other oxygen functions. This expectation was proved conclusively by an X-ray crystallographic analysis of the p-bromobenzoate (18) of the product.[7] Thus the reaction of lithium aluminium hydride with the acetylene (10) results in insertion of a hydrogen atom at the position α to the propargylic hydroxy-group, and *cis* to the departing propargylic oxygen substituent. This

[1] Part XXVIII, D. E. Loeber, S. W. Russell, T. P. Toube, B. C. L. Weedon, and J. Diment, *J. Chem. Soc. (C),* 1971, 404.

[2] R. Bonnett, A. K. Mallams, J. L. Tee, B. C. L. Weedon, and A. McCormick, *Chem. Comm.,* 1966, 515.

[3] R. Bonnett, A. K. Mallams, A. A. Spark, J. L. Tee, B. C. L. Weedon, and A. McCormick, *J. Chem. Soc. (C),* 1969, 429.

[4] A. Jensen, *Acta Chem. Scand.,* 1966, **20,** 1728.

[5] J. Meinwald, K. Erickson, M. Hartshorn, Y. C. Meinwald, and T. Eisner, *Tetrahedron Letters,* 1968, 2959.

[6] S. W. Russell and B. C. L. Weedon, *Chem. Comm.,* 1969, 85.

[7] T. E. De Ville, M. B. Hursthouse, S. W. Russell, and B. C. L. Weedon, *Chem. Comm.,* 1969, 754.

[8] T. E. De Ville, M. B. Hursthouse, S. W. Russell, and B. C. L. Weedon, *Chem. Comm.,* 1969, 1311.

[9] T. E. De Ville, J. Hora, M. B. Hursthouse, T. P. Toube, and B. C. L. Weedon, *Chem. Comm.,* 1970, 1231.

[10] L. Bartlett, W. Klyne, W. P. Mose, P. M. Scopes, G. Galasko, A. K. Mallams, B. C. L. Weedon, J. Szabolcs, and Gy. Tóth, *J. Chem. Soc. (C),* 1969, 2527.

[11] T. Miki and Y. Hora, *Pharm. Bull. (Japan),* 1956, **4,** 89.

[12] B. C. L. Weedon, in ' Carotenoids,' ed. O. Isler, Birkhäuser Verlag, Basel and Stuttgart, 1971, ch. 5.

[13] J. S. Cowie, P. D. Landor, and S. R. Landor, *Chem. Comm.,* 1969, 541.

differs from the *trans*-stereochemistry proposed for S_N2' attack by a hydride donor on other propargylic systems.[14]

The *cis*-acetoxy-epoxide (11) yielded an isomeric allenic ketone when submitted to the same sequence of
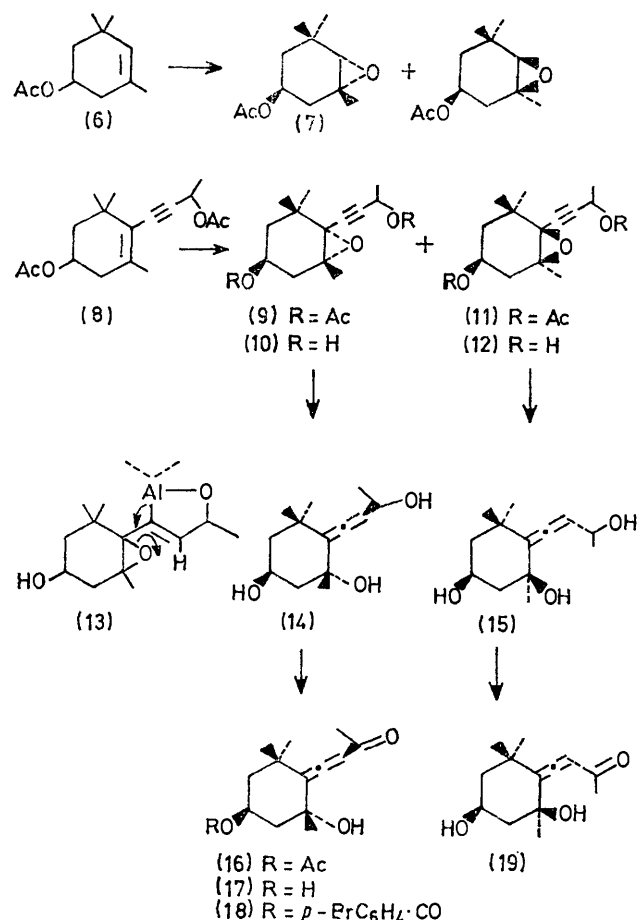

reactions as its epimer (9). If we assume that the reduction of the acetylenic intermediate (12) parallels that of (10) in the previous series, then the resulting ketone (19) has the stereochemistry shown in which the two hydroxy-groups are *cis* to one another.

Photosensitised oxidation of β-ionol (20) and of a number of related compounds is reported to give, among other products, allenic hydroperoxides which yield the corresponding allenic alcohols [*e.g.* (22)] on reduction.[15-17] This suggested a route to one of the racemates of the allenic ketone (2) in which the tertiary hydroxy-group at C-5 is *cis* to the acetyl group at C-8. Oxidation of 7-*trans*-3-hydroxy-β-ionol (21)[1] photochemically in the presence of Rose Bengal as sensitizer, reduction of the resulting crude hydroperoxides with sodium borohydride to give the allenic triols (23), and selective oxidation of the latter with manganese dioxide furnished

[14] W. T. Borden and E. J. Corey, *Tetrahedron Letters*, 1969, 313.
[15] S. Isoe, S. B. Hyeon, H. Ichikawa, S. Katsumura, and T. Sakan, *Tetrahedron Letters*, 1968, 5561.

the allenic ketone (24), m.p. 152°. The stereochemistry of the product was established by X-ray crystallographic analysis of its p-bromobenzoate (25).[9] This confirms the stereochemistry predicted for the allenes formed by singlet oxygen attack on β-ionol and related compounds. It is also interesting that in the present example the only allenic product detected was that in which the hydroxy-groups at C-3 and C-5 are *trans* to one another. Evidently attack of singlet oxygen on 3-hydroxy-β-ionol (23) occurs mainly (if not exclusively) *trans* to the hydroxy-group at C-3. This contrasts with the attack on related cyclohexenols and their acetates, such as (8), by peroxy-acids, which occurs preferentially *cis* to the oxygen function at C-3.

The mass spectra of the 3,5-dihydroxyallenes [*e.g.* (14), (17), and (24)] included an abundant ion resulting from the loss of 101 mass units from the molecular ion. This
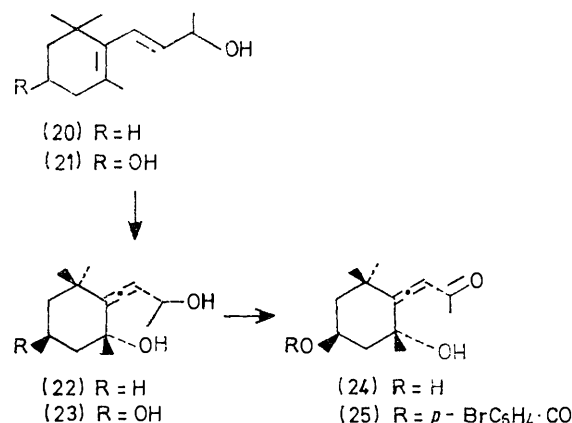
characteristic fragmentation corresponds to the loss of 143 mass units previously noted from the acetoxyallene (1).[3]

Principal n.m.r. bands of allenic ketones [a,b]

	1-Me's	5-Me	9-Me	3-H	8-H	OAc
Apo-9'-fucoxanthi-none (16‡)	1·15, 1·42	1·42	2·17	5·39(m)	5·84	2·03
	[1·15, 1·41	1·41	2·15	5·39(m)	5·75	1·97]
Racemate (16)	1·16, 1·43	1·43	2·18	5·39(m)	5·84	2·03
	[1·15, 1·41	1·41	2·14	5·38(m)	5·74	1·97]
Grasshopper ketone (17‡) [c]	1·16, 1·36	1·40	2·15	4·28(m)	5·80	
Grasshopper ketone (17‡) [d]	1·16, 1·39	1·43	2·17	4·30(m)		
Racemate (17)	1·15, 1·37	1·42	2·17	4·29(m)	5·83	
	[1·13, 1·37	1·38	2·13		5·67]	
Racemate (19)	1·20, 1·45	1·45	2·18	4·23(m)	5·93	
	[1·22, 1·29	1·44	2·13	4·04(m)	5·78]	
Racemate (24)	1·12, 1·40	1·42	2·25	3·73(m)	5·97	
	[1·11, 1·37	1·45	2·20	3·86(m)	5·80]	
Ketone (27)	1·06, 1·41	1·03	2·18	4·23(m)	5·84	
		(d, J 6·5)			(d, J 3·5)	
Diketone (28)	1·20, 1·20	1·14	2·19		5·98	
		(d, J 6·5)			(d, J 3·5)	

[a] Spectra (δ values; J in Hz) were determined at 100 MHz for dilute solutions in [²H]chloroform (unless stated otherwise), using tetramethylsilane as an internal reference. Unless indicated to the contrary, bands were singlets. When three singlets were observed for the methyl groups attached to the ring, the band at lowest field has been arbitrarily assigned to the 5-Me. [b] Data in square brackets for solutions in [²H₆]acetone. [c] Data from Meinwald *et al.*[5] [d] Semisynthetic, from fucoxanthin.

The three isomeric allenic ketones (17), (19), and (24) had similar u.v. and i.r. light absorption properties, but their n.m.r. spectra contained features (Table) which

[16] M. Mousseron-Canet, J.-P. Dalle, and J.-C. Mani, *Tetrahedron Letters*, 1968, 6037.
[17] C. S. Foote and M. Brenner, *Tetrahedron Letters*, 1968, 6041.

provide a convenient means of detecting differences in relative configuration between C-5 and either C-3 or C-8. The n.m.r. data reported for the optically active allenic ketone (m.p. 128°) from *R. microptera* clearly indicate that it has the same relative configuration as the racemate (17) and not, as at one time proposed,[18] that of the racemate (24). In mixed thin-layer chromatograms (for which we are indebted to Dr. L. B. Hendry) no separation was observed between the natural ketone and our synthetic racemate (17).

Treatment of the racemate (17) with acetic anhydride in pyridine gave a monoacetate (16) with n.m.r. signals (in both [²H]chloroform and [²H₆]acetone) identical with those of the optically active degradation product of fucoxanthin (3). Furthermore the synthetic and 'natural' acetates did not separate on mixed thin-layer chromatography. The allenic end group of fucoxanthin must therefore have the same relative configuration as the racemate (16).

Though there were some grounds for believing that structure (16 ‡) also represents the absolute configuration of the allenic ketone (1) from fucoxanthin,[3,10] independent proof of this key assignment was sought. Reduction of the allenic ketone (1) with lithium aluminium hydride gave the allenic triol (14 ‡). The latter, on selective oxidation with manganese dioxide, gave the optically active allenic ketone (17 ‡), which was converted into the *p*-bromobenzoate (18 ‡). An X-ray crystallographic analysis [8] of this derivative established its absolute configuration as 3S,5R,6R. The c.d. curve of a small sample of the natural grasshopper ketone (kindly supplied by Professor J. Meinwald and Dr. L. B. Hendry) was qualitatively identical with that of the allenic ketone (17 ‡) prepared from fucoxanthin. Thus the natural grasshopper ketone must have the 3S,5R,6R-configuration (17 ‡).

Since the methods used to prepare (18 ‡) from fucoxanthin were such as to preserve stereochemistry, the allenic end group in this major carotenoid, and in neoxanthin (5) which has been correlated with it,[19] must also have the 3S,5R,6R-configuration. The suggestion[5,6] that the grasshopper *R. microptera* produces the allenic ketone (17 ‡) by degradation of neoxanthin, a constituent

It has previously been established that the chirality at C-3' in fucoxanthin (3), and at the corresponding position in neoxanthin (5), is identical with that at C-3 and C-3' in zeaxanthin (4).[3,10,19] The latter xanthophyll can therefore be assigned the 3R,3'R-configuration with end groups of structure (26 ‡).[8] These, and stereochemical correlations with various other carotenoids, are discussed fully elsewhere.[8,12]

Following our synthesis of the racemate (17), an alternative route to this compound was reported.[18] Though this product was originally thought to have the relative configuration (24), its n.m.r. properties, and the results of direct comparisons with ours (by Dr. L. B. Hendry), show that the two racemates are identical. Our route, with minor modifications, has been repeated by Mori using a partially resolved starting material;[20] comparison of the c.d. properties of the product with those that we obtained for the fucoxanthin degradation product (17 ‡) indicates that his final allenic ketone has an optical purity of 63%. Our photosensitised oxidation of 3-hydroxy-β-ionol, and the conversion of the product into the racemic allenic ketone (24), have also been repeated.[21]

It has been suggested that the biosynthesis of the allenic carotenoids, fucoxanthin and neoxanthin, may involve a photochemical oxidation of zeaxanthin (4) or a related carotenoid, by a process formally analogous to that observed *in vitro* with β-ionol and similar compounds.[15-17] In this connection we note a recent claim that photochemical oxidation of β-carotene [dehydroxy-(4)] using chlorophyll as photosensitiser gives a mixture of products which includes a C_{40} allene.[22]

After it had been shown [9] that the relative configuration about the allene group in (24) is the opposite of that in the common natural allenic carotenoids, it was further suggested [21] that the latter are the results of stereomutation of isomeric allenes formed initially. In support of this view it was reported that irradiation of (24) with a high-pressure mercury lamp gives a product which, on the basis of its n.m.r. spectrum, appears to be an equilibrium mixture (1:1) of (24) and (17). Other mechanisms have been proposed for the postulated conversion of zeaxanthin into allenic carotenoids which would lead to the correct allenic stereochemistry directly.[3,7,23,24]

EXPERIMENTAL

Apart from the photochemical oxidation, all operations were carried out in an inert atmosphere. Light petroleum refers to the fractions of b.p. 60—80°, unless stated otherwise. M.p.s were determined for samples in evacuated capillary tubes and are corrected.

(26)   (27) X = H,OH
            (28) X = O

of all green leaves and hence of the insect's diet, is therefore consistent with the present stereochemical findings.

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‡ Formula numbers marked ‡ in the text signify the enantiomer shown; elsewhere numbers referring to formulae which indicate relative configuration are intended to imply the racemates of these structures.

[18] J. Meinwald and L. Hendry, *Tetrahedron Letters*, 1969, 1657.
[19] L. Cholnoky, K. Györgyfy, A. Rónai, J. Szabolcs, Gy. Tóth, G. Galasko, A. K. Mallams, E. S. Waight, and B. C. L. Weedon, *J. Chem. Soc. (C)*, 1969, 1256.

[20] K. Mori, *Tetrahedron Letters*, 1973, 723.
[21] S. Isoe, S. Katsumura, S. B. Hyeon, and T. Sakan, *Tetrahedron Letters*, 1971, 1089.
[22] K. Tsukida, S.-C. Chô, and M. Yokota, *Chem. and Pharm. Bull. (Japan)*, 1969, 17, 1755.
[23] B. H. Davies, S. Matthews, and J. T. O. Kirk, *Phytochem.*, 1970, 9, 797.
[24] B. C. L. Weedon, *Rev. Pure Appl. Chem.* 1970, 20, 51.

Except where indicated to the contrary, i.r. spectra were determined for solutions in chloroform (selected bands only are quoted), and n.m.r. spectra for solutions in [²H]chloroform at 100 MHz. Mass spectra were determined on an A.E.I. MS 902 instrument; selected lines only are quoted.

cis- and *trans-2-Acetoxy-4-(4-acetoxy-1,2-epoxy-2,6,6-trimethylcyclohexyl)but-3-yne* [(11) *and* (9)].—Ethereal monoperphthalic acid (10 ml; 2 g atom active oxygen) was added to a cooled solution of 2-acetoxy-4-(4-acetoxy-2,6,6-trimethylcyclohex-1-enyl)but-3-yne [1] (1·6 g) in ether (10 ml). The mixture was kept at 5° for 48 h, afterwards at 20° for 24 h, then poured into an excess of aqueous sodium hydrogen carbonate. The crude product was extracted with ether, and the extracts were washed, dried, and evaporated. Chromatography of the residual oil on a column of silica gel (containing 18% water), using benzene as eluant, gave the diacetoxy-epoxide as a mixture of isomers (1·0 g), b.p. (air bath) 135—140° at 0·05 mmHg; $\nu_{max.}$ (film) 2220 and 1740 cm^{-1}; *m/e* 308 (<1%, $M^{+\cdot}$; $C_{17}H_{24}O_5$), 292 (<1, $M - 16$), and 248 (7, $M - 60$).

Further chromatography on the same adsorbent [gradient elution with light petroleum (b.p. 40—60°) and benzene, and subsequently with benzene and ether] gave (i) the less polar *cis-acetoxy-epoxide* (11) (650 mg), δ (60 MHz) 1·16 (3H, s), 1·21 (3H, s), 1·45 (3H, s), 1·49 (3H, d, *J* 7 Hz), 2·00 (3H, s), 2·07 (3H, s), 4·87 (1H, m), and 5·84 (1H, q, *J* 7 Hz); *m/e* 308 ($M^{+\cdot}$); and (ii) the more polar *trans-acetoxy-epoxide* (9) (350 mg), δ (60 MHz) 1·13 (3H, s), 1·24 (3H, s), 1·49 (3H, s), 1·50 (3H, d, *J* 7 Hz), 2·01 (3H, s), 2·07 (3H, s), 4·90 (1H, m), and 5·49 (1H, q, *J* 7 Hz); *m/e* 308 ($M^{+\cdot}$).

N.m.r. analysis revealed *ca.* 7% contamination of each isomer with the other.

cis- and *trans-4-(1,2-Epoxy-4-hydroxy-2,6,6-trimethylcyclohexyl)but-3-yn-2-ol* [(12) *and* (10)].—(i) Lithium aluminium hydride (60 mg) in ether (10 ml) was added slowly to a cold ($-50°$) solution of the *trans*-acetoxy-epoxide (9) (300 mg) in ether (15 ml). The mixture was allowed to warm to 20°, excess of aqueous potassium sodium tartrate (20%) was added, the aqueous layer was saturated with salt, the product was extracted with ether, and the extracts were dried and evaporated. Preparative t.l.c. of the crude product on Kieselgel H (38% acetone in light petroleum as eluant) yielded the *trans-epoxy-diol* (10) (170 mg); $\nu_{max.}$ 3615 and 2240 cm^{-1}; δ (60 MHz) 1·11 (3H, s), 1·25 (3H, s), 1·47 (3H, d, *J* 6·5 Hz), 1·50 (3H, s), 3·83 (1H, m), and 4·59 (1H, q, *J* 6·5 Hz); *m/e* 224 (46%, $M^{+\cdot}$, $C_{13}H_{20}O_3$), 208 (5, $M - 16$), 206 (13, $M - 18$), and 191 (5, $M - 18 - 15$).

(ii) Similar treatment of the *cis*-epoxy-diacetate (600 mg) with lithium aluminium hydride (120 mg) yielded the *cis-epoxy-diol* (12) (340 mg); $\nu_{max.}$ 3612 and 2240 cm^{-1}; δ (60 MHz) 1·18 (3H, s), 1·45 (3H, d, *J* 6·5 Hz), 1·48 (3H, s), 3·81 (1H, m), and 4·57 (1H, q, *J* 6·5 Hz); *m/e* 224 ($M^{+\cdot}$).

4-(trans-2,4-Dihydroxy-2,6,6-trimethylcyclohexylidene)but-3-en-2-ol (14).—Lithium aluminium hydride (150 mg) was added to the *trans*-epoxy-diol (10) (150 mg) in tetrahydrofuran (30 ml), and the mixture was boiled under reflux for 6 h and then cooled. The excess of reagent was decomposed by addition of aqueous potassium sodium tartrate (20%), the aqueous layer was saturated with salt, and the mixture was extracted thoroughly with ethyl acetate. The extracts were dried and evaporated. Crystallisation of the residual oil (150 mg) from ethyl acetate–light petroleum gave the *allenic triol* (30 mg) as needles, m.p. 163—164°; $\nu_{max.}$ (KBr) 3340 and 1955 cm^{-1}; δ ([²H₆]acetone) 1·04 (3H, s), 1·20 (3H, d, *J* 5·5 Hz); singlet on secondary irradiation at 4·20), 1·28 (3H, s), 1·30 (3H, s), 3·64 (1H, m), 4·20 (1H, dq, *J* 5·5 and 6 Hz), and 5·26 (1H, d, *J* 5·5 Hz; singlet on secondary irradiation at 4·20); *m/e* 226·157 (1%, $M^{+\cdot}$; $C_{13}H_{22}O_3$ requires 226·157), 208 (35, $M - 18$), 190 (2, $M - 18 - 18$), 125 (40, $M - 101$), and 107 (38, $M - 101 - 18$).

Racemate (17) of (3R)-4-[(2R,4S)-2,4-Dihydroxy-2,6,6-trimethylcyclohexylidene]but-3-en-2-one.—A solution of the preceding crystalline allenic triol (23 mg) in acetone (5 ml) was shaken with manganese dioxide (130 mg) at 20°. The reaction was monitored by t.l.c., and after 5 h was judged to be complete. The mixture was filtered, and the filtrate was evaporated. Crystallisation of the residual oil from ethyl acetate–light petroleum (b.p. 40—60°) gave the racemic *allenic ketone* (18 mg) as plates, m.p. 110—111°; $\lambda_{max.}$ (EtOH) 233 nm (ε 13,100); $\nu_{max.}$ 3600, 1946, and 1678 cm^{-1}; δ, see Table; *m/e* 224·142 (7%, $M^{+\cdot}$; $C_{13}H_{20}O_3$ requires 224·141), 209 (22, $M - 15$), 191 (4, $M - 15 - 18$), 163 (20, $M - 18 - 43$), and 123 (31, $M - 101$).

The allenic ketone (4·7 mg) in pyridine (1 ml) was treated at 0° with *p*-bromobenzoyl chloride (8 mg) in pyridine (1 ml) for 16 h. Water (2 ml) was added, and the mixture was stirred for 30 min and then evaporated. Thin-layer chromatography of the residue on Kieselgel HF$_{254}$ (25% acetone in light petroleum as eluant), isolation of the main band, and crystallisation from ethanol gave the *p*-bromobenzoate as monoclinic crystals. After *X*-ray crystallographic analysis [7] the recovered derivative had m.p. *ca.* 192°.

Racemate (16) of (3R)-4-[(2R,4S)-4-Acetoxy-2-hydroxy-2,6,6-trimethylcyclohexylidene]but-3-en-2-one.—Acetic anhydride (0·5 ml) was added dropwise to a solution of the preceding dihydroxy-allenic ketone (6·0 mg) in dry pyridine (3 ml), and the mixture was stirred for 15 h. Ether was added and the solution was washed with water, dried, and evaporated. Thin-layer chromatography of the residue on Kieselgel HF$_{254}$ (25% acetone in light petroleum as eluant) gave the racemic *acetate* (6·0 mg) as an oil; δ, see Table; *m/e* 266·152 (5%, $M^{+\cdot}$; $C_{15}H_{22}O_4$ requires 266·152), 251 (10, $M - 15$), 206 (18, $M - 60$), 191 (37, $M - 60 - 15$), 163 (43, $M - 60 - 43$), and 123 (100, $M - 143$). No separation was observed in mixed thin-layer chromatograms of the synthetic racemate and the optically active degradation product of fucoxanthin [3] on Kieselgel HF$_{254}$ with any of the following solvent systems: 25% acetone in light petroleum; acetone–dichloromethane–light petroleum (3 : 20 : 10) 4% ethanol in chloroform; and 30% ethyl acetate in benzene.

Racemate (19) of (3S)-4-[(2S,4S)-2,4-Dihydroxy-2,6,6-trimethylcyclohexylidene]but-3-en-2-one.—Lithium aluminium hydride (150 mg) was added to the *cis*-epoxy-diol (12) (150 mg) in tetrahydrofuran (30 ml), and the mixture was boiled under reflux for 6 h and then cooled. The mixture was decomposed and the allenic triol was isolated as described for the isomeric triol (14). The resulting oil in acetone (5 ml) was stirred with manganese dioxide (200 mg) until no further reaction was observed (3 days). Isolation of the product as in the isomeric series gave the racemic *allenic ketone* as an oil (20 mg); $\lambda_{max.}$ (EtOH) 231 nm; $\nu_{max.}$ 3595, 1943, and 1677 cm^{-1}; δ, see Table; *m/e* 224 ($M^{+\cdot}$, $C_{13}H_{20}O_3$).

Racemate (24) of (3S)-4-[(2R,4S)-2,4-Dihydroxy-2,6,6-trimethylcyclohexylidene]but-3-en-2-one.—A solution of 3-hydroxy-β-ionol [1] (885 mg) and Rose Bengal (50 mg) in methanol (100 ml) was irradiated (Osram Nitraphot 500 W bulb) at $-10°$ in a Pyrex flask while a slow stream of air was bubbled through the solution. When the optical absorbance at

231 nm had dropped to a third of its original value (4 h) the reaction was stopped. Sodium borohydride (1·0 g) was added and the mixture was stirred at 20° for 15 h, and then evaporated. The residue was extracted with ethyl acetate, and the extracts were washed with water, dried, and evaporated. Chromatography on silica gel (ethyl acetate as eluant) gave unchanged starting material (214 mg) and several products. One band yielded a mixture of allenic triols (12 mg); $\nu_{max.}$ (CHCl$_3$) 3600 and 1955 cm^{-1}. This mixture in acetone (10 ml) was stirred with manganese dioxide (25 mg) at 25° for 24 h. The mixture was filtered, and the filtrate was evaporated. Chromatography of the residue on silica gel [chloroform–ethyl acetate (1 : 1) as eluant] and crystallisation of the crude product (8 mg) from ethyl acetate–light petroleum gave the racemic *allenic ketone* (5·8 mg), m.p. 151—152°; $\nu_{max.}$ 3590, 1941, and 1670 cm^{-1}; δ, see Table; *m/e* 224·141 (18%, $M^{+\cdot}$; C$_{13}$H$_{20}$O$_3$ requires 224·141), 209 (30, $M - 15$), 206 (9, $M - 18$), 191 (24, $M - 15 - 18$), 188 (21, $M - 18 - 18$), 173 (55, $M - 18 - 18 - 15$), 123 (100, $M - 101$).

p-Bromobenzoyl chloride (5 mg) in pyridine (0·2 ml) was added to the allenic ketone (3·0 mg) in pyridine (0·1 ml). After 5 h water was added, and after a further 30 min the mixture was extracted with light petroleum. The extracts were washed thoroughly with water, dried, and evaporated. Thin-layer chromatography on Kieselgel H (10% acetone in light petroleum as eluant) and crystallisation of the product from ether–light petroleum, gave the *p*-bromobenzoate (2·7 mg), m.p. 172—173°. The crystals for *X*-ray crystallographic analysis [9] were grown from 95% ethanol and had the same m.p.

(3R)-4-[(2R,4S)-2,4-*Dihydroxy-2,6,6-trimethylcyclohexylidene*]*but-3-en-2-one* (17 ‡).—Lithium aluminium hydride (20 mg) was added to a solution of apo-9′-fucoxanthinone [3] (15 mg) in ether (5 ml) at −70°. After the mixture had warmed to 20° decomposition of the excess of reagent, and isolation of the product as described for the synthetic racemate, gave the crude allenic triol which in acetone (2 ml) was stirred with manganese dioxide (40 mg) for 6 h. The mixture was filtered and the filtrate was evaporated. Thin-layer chromatography of the residue on Kieselgel HF$_{254}$ (30% acetone in light petroleum as eluant) gave an oil (9 mg) which slowly crystallised. Recrystallisation from ethyl acetate–light petroleum gave the *allenic ketone* as plates, m.p. 124—126°; $\lambda_{max.}$ (EtOH) 233 nm (ε 12,000); $\nu_{max.}$ 3600, 1946, and 1679 cm^{-1}; δ, see Table; *m/e* 224

($M^{+\cdot}$), 209, 191, and 123 ($M - 101$); $\Delta\varepsilon_{211} - 1.83$, $\Delta\varepsilon_{229} + 2.98$, $\Delta\varepsilon_{255} - 3.43$. (A sample of authentic grasshopper ketone, though too small for accurate quantitative data to be obtained, gave a c.d. curve qualitatively identical with that of the semisynthetic sample.) The *p*-bromobenzoate, prepared as described for the racemate, formed monoclinic crystals, m.p. 172—173° [from ethyl acetate–light petroleum (b.p. 80—100°)], which were used for *X*-ray crystallographic analysis.[8]

4-(4-*Hydroxy-2,2,6-trimethylcyclohexylidene*)*but-3-en-2-ol*.—Lithium aluminium hydride (60 mg) was added to 4-(1,4-dihydroxy-2,2,6-trimethylcyclohexyl)but-3-yn-2-ol [1] (m.p. 120—122°; 180 mg) in ether (60 ml). The mixture was boiled under reflux for 8 h and then cooled. Isolation of the product in the usual way, chromatography, and crystallisation from ether–light petroleum (b.p. 40—60°), gave the *allenic diol* as needles (50 mg), m.p. 90—91°; $\nu_{max.}$ (KBr) 3320 and 1960 cm^{-1}; δ (60 MHz) 1·00 (3H, d, *J* 7 Hz), 1·05 (3H, s), 1·28 (3H, d, *J* 5·5 Hz), 1·34 (3H, s), 1·50—1·70 (5H, m), *ca.* 4·22 (2H, m), 5·40 (1H, dd, *J* 5 and 3 Hz); *m/e* 210 (<1%; $M^{+\cdot}$, C$_{13}$H$_{22}$O$_2$), 177 (44, $M - 18 - 15$), and 121 (100).

4-(4-*Hydroxy-2,2,6-trimethylcyclohexylidene*)*but-3-en-2-one* (27).—The preceding diol (29 mg) in acetone (5 ml) was stirred with manganese dioxide (100 mg) for 3 days. Isolation of the product in the usual way, and chromatography on Kieselgel HF$_{254}$ (30% acetone in light petroleum as eluant) gave (i) the *allenic hydroxy-ketone* (27) (16 mg); $\lambda_{max.}$ (EtOH) 230 nm; $\nu_{max.}$ (CCl$_4$) 3630, 1942, and 1681 cm^{-1}; δ 1·03 (3H, d, *J* 6·5 Hz), 1·06 (3H, s), 1·41 (3H, s), 2·18 (3H, s), 4·23 (1H, m), and 5·84 (1H, d, *J* 3·5 Hz); *m/e* 208·147 ($M^{+\cdot}$; C$_{13}$H$_{20}$O$_2$ requires 208·146); and (ii) 4-(2,2,6-*trimethyl-4-oxocyclohexylidene*)*but-3-en-2-one* (28) (8 mg); $\lambda_{max.}$ (EtOH) 226 nm; $\nu_{max.}$ (CCl$_4$) 1948, 1723, and 1683 cm^{-1}; δ 1·14 (3H, d, *J* 6·5 Hz), 1·20 (6H, s), 2·19 (3H, s), 2·10—2·40 (5H, m), and 5·98 (1H, d, *J* 3·5 Hz); *m/e* 206·131 ($M^{+\cdot}$; C$_{13}$H$_{18}$O$_2$ requires 206·131).