Carotenoids and Related Compounds. Part 38.[1] Synthesis of (3*RS*,3'*RS*)-Alloxanthin and Other Acetylenes

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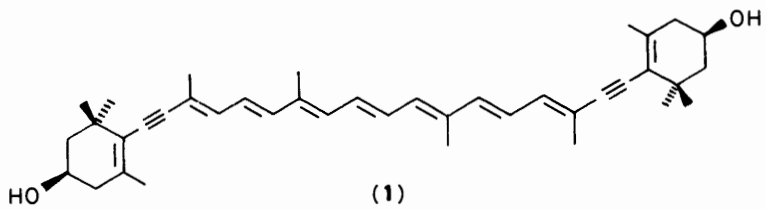
The all-*trans*, 9-*cis*, and 9,9'-di-*cis* forms of (3*RS*,3'*RS*)-alloxanthin have been synthesised, also the 9-*cis*-isomer of (3*RS*,6'*RS*)-crocoxanthin. Perhydrogenation of alloxanthin gives a product with the same optical properties as perhydrozeaxanthin. These results confirm the formulation of alloxanthin as (3*R*,3'*R*)-7,8,7',8'-tetradehydro-β,β-carotene-3,3'-diol, of diatoxanthin as (3*R*,3'*R*)-7,8-didehydro-β,β-carotene-3,3'-diol, of crocoxanthin as an enantiomer (probably 3*R*) of (6'*R*)-7,8-didehydro-β,ε-caroten-3-ol, of monadoxanthin as an all-*trans*-isomer of 7,8-didehydro-β,ε-carotene-3,3'-diol, and of pectenolone as an all-*trans*-isomer of 3,3'-dihydroxy -7',8'-didehydro-β,β-caroten-4-one. Carotenoid isomers with the *cis*-configuration about the acyclic double bond adjacent to an acetylenic linkage in either the 7- or 7'-position were shown to be thermodynamically more stable than the all-*trans*-forms.

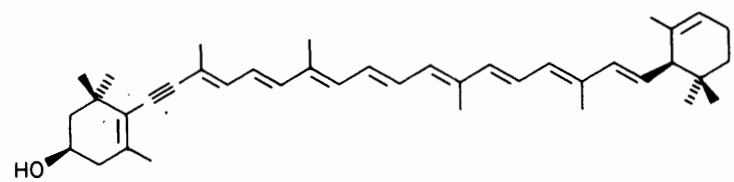
Alloxanthin, crocoxanthin, and monadoxanthin were isolated from flagellates of the algal class Cryptophyceae,[2,3] and provided the first examples of natural acetylenic carotenoids.[4] Alloxanthin was subsequently shown[5] to be identical with pectenoxanthin from the scallop *Pecten maximus*,[6,7] with cynthiaxanthin from the tunicate, *Halocynthia papillosa*,[6–8] and with a carotenoid present in the edible mussel, *Mytilus edulis*, and the California sea mussel, *M. californianus*.[5]

Alloxanthin was formulated as the 7,7'-diacetylenic analogue‡ of zeaxanthin (**8**), largely on the basis of its n.m.r. and mass spectra.[4] The i.r. absorption due to the carbon–carbon triple bond stretching frequency was surprisingly weak, presumably owing to the nature of the substitution. Its perhydro-derivative (see Experimental section) exhibited similar optical rotation to that of perhydro-zeaxanthin, indicating the 3*R*,3'*R* configuration (**1**).[9,10]

Crocoxanthin, monadoxanthin, and pectenolone (a minor pigment from *P. maximus* and *H. papillosa*[5]) were similarly formulated as the mono-acetylenic analogues (**3**), (**4**), and (**5**) of α-cryptoxanthin (**9**), lutein (**10**), and adonixanthin (**11**), respectively.[4,5] Diatoxanthin, a common pigment of diatoms[11] and Chrysophyceae,[12,13] was formulated[4] as the mono-acetylenic analogue (**6**) of zeaxanthin (**8**), and assigned the 3*R*,3'*R* configuration (**7**) on the basis of o.r.d. studies.[9,10] The latter also



(**1**)



(**2**)

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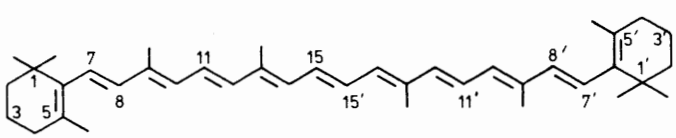
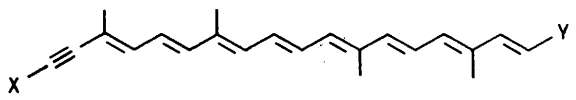
‡ See abstract for naming of acetylenic cartenoids according to the recommendations of the IUPAC–IUB Commission on Biochemical Nomenclature (*Pure Appl. Chem.*, 1975, **41**, 407). The positions in the molecule are numbered according to the same recommendations, as shown in (A). Other compounds are named and numbered according to normal conventions.



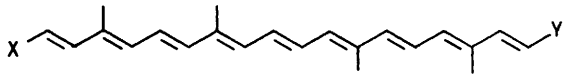
(A)

revealed that crocoxanthin has a 6'*R* configuration. It is probable on biogenetic grounds that the asymmetric centre at C-3 is *R*, and hence the absolute configuration (**2**) was proposed.[9] In this paper we give details of the studies undertaken to confirm these novel structures by synthesis of alloxanthin and crocoxanthin (for preliminary publications see refs. 14—16). The presence of the acetylenic bonds in alloxanthin has also been confirmed by ^{13}C n.m.r. spectrometry.[17] Several further examples of naturally occurring acetylenic carotenoids have been reported.[14,18–20]

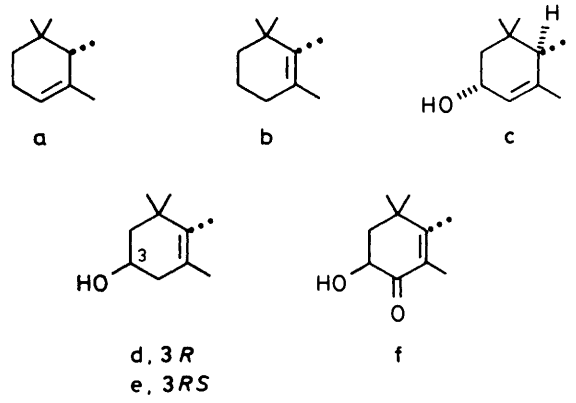
The cis-*Series.*—Reaction of the Grignard or lithium derivative of 2-*cis*-3-methylpent-2-en-4-yn-1-ol (**12**),[21] a key intermediate in the manufacture of vitamin A, with the ketone (**14**), prepared from isophorone,[22] readily gave the diol (**16**); since it



(3) X = e, Y = a
(4) X = e, Y = c
(5) X = e, Y = f
(6) X = Y = e
(7) X = Y = d



(8) X = Y = d
(9) X = d, Y = a
(10) X = d, Y = c
(11) X = e, Y = f



a b c

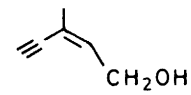
d, 3*R*
e, 3*RS*

f

···· represents point of attachment

is probable that its formation involved attack by the acetylene on the less hindered side of the carbonyl group in the preferred conformation of (**14**), the product was assigned the (relative) stereochemistry shown in (**16**). Treatment with dilute acid gave the dihydroxy-ketone (**17**). Reduction of the latter with sodium borohydride then yielded the crystalline triol (**18**); assuming attack by the hydride on the less hindered side of the ketone in the preferred conformation, the product was assigned the relative configuration shown in (**18**). The same product was obtained on mild reduction of the ketone (**17**) with lithium aluminium hydride. Under vigorous conditions reduction of the triple bond also occurred to give the diene triol (**15**).

Acetylation of the triol (**18**) with acetic anhydride in pyridine produced the hydroxy-diacetate (**19**), but in boiling acetic acid



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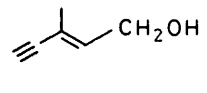

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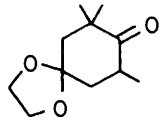

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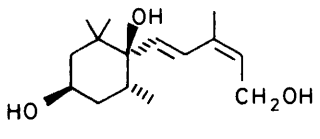


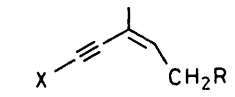
(15)

acetylation was accompanied by dehydration of the tertiary hydroxy function with formation of the enynene diacetate (**20**). This, on hydrolysis, gave the diol (**21**).

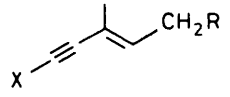
On treatment of (**16**), (**18**), and (**21**) with triphenylphosphonium bromide, each was converted into the corresponding Wittig salt, (**22**), (**23**), and (**24**) respectively. *X*-Ray crystallographic analysis of the last salt confirmed the 2-*cis*-configuration.[23]

The Wittig salt (**22**) reacted with the triene-dial (**33**)[24] to give the 9-*cis*-12′-apo-carotenal (**34**), but further reaction to give (**38**) occurred slowly and in low yield (the relative reactivity of the triene-dial and apo-carotenals is discussed later). This approach was not pursued further.

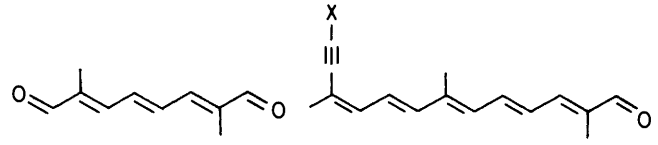
The Wittig salt (**23**) reacted with the triene-dial (**33**) to give a mixture of the corresponding 9-*cis*-12′-apo-carotenal (**35**) and



(16) X = g, R = OH
(17) X = h, R = OH
(18) X = i, R = OH
(19) X = j, R = OAc
(20) X = k, R = OAc
(21) X = e, R = OH
(22) X = g, R = PPh_3Br
(23) X = i, R = PPh_3Br
(24) X = e, R = PPh_3Br

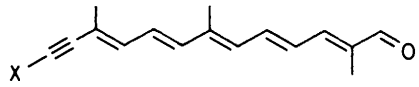


(25) X = g, R = OH
(26) X = h, R = OH
(27) X = i, R = OH
(28) X = j, R = OAc
(29) X = k, R = OAc
(30) X = e, R = OH
(31) X = k, R = PPh_3Br
(32) X = e, R = PPh_3Br

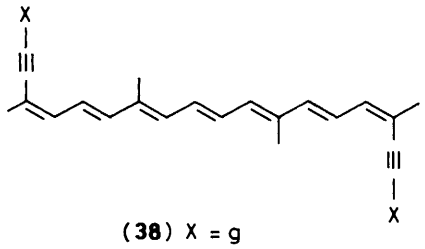


(33)

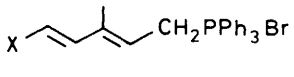
(34) X = g
(35) X = i
(36) X = e



(37) X = e



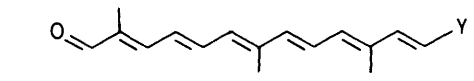
(38) X = g
(39) X = i
(40) X = k
(41) X = e



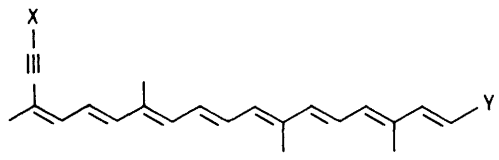
(42) X = a

the 9,9′-di-*cis*-tetraol (**39**). The latter, with acetic anhydride, yielded the dihydroxy-diacetate which, on treatment with phosphorus oxychloride, furnished the required 9,9′-di-*cis*-diacetate (**40**), albeit in low overall yield. Reaction of (**35**) with the Wittig salt (**42**)[25] led to the diol (**44**) which was similarly converted into the 9-*cis*-acetate (**45**).

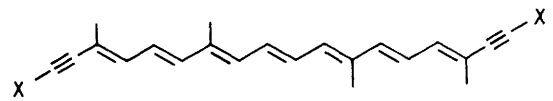
Condensation of the Wittig salt (**24**) with the triene-dial (**33**) furnished the expected 9-*cis*-12′-apo-carotenal (**36**). This, on further reaction with the same Wittig reagent yielded the required 9,9′-di-*cis*-diacetylenic diol (**41**), which exhibited visible light absorption maxima at wavelengths 10—12 nm shorter than those of natural (all-*trans*) alloxanthin, as would be expected for a carotenoid with two unhindered *cis*-bonds.[10,26] Reaction of the Wittig salt (**24**) with the 12′-apo-ε-carotenal (**43**)[25] similarly gave the 9-*cis*-isomer of (3*RS*,6′*RS*)-crocoxanthin (**48**).



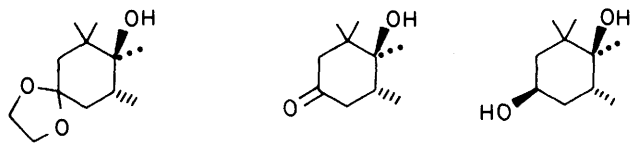
(**43**) Y = a



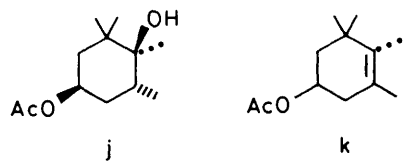
(**44**) X = i, Y = a
(**45**) X = k, Y = a
(**46**) X = i, Y = b
(**47**) X = k, Y = b
(**48**) X = e, Y = a



(**49**) X = e



g h i



j k

Stereomutation.—It is well known from the classical studies of the Zechmeister school that irradiation of a solution of a carotenoid, in the presence of iodine, yields an equilibrium mixture of geometrical isomers in which the all-*trans*-form normally predominates.[26] When submitted to this procedure, the synthetic mono- and di-acetylenic carotenoids described above yielded a mixture consisting mainly of the starting material; none of the all-*trans*-isomers could be detected. When natural (all-*trans*) crocoxanthin and alloxanthin were similarly treated, mixtures of geometrical isomers were obtained identical (apart from optical configuration) with those from the respective synthetic mono- and di-*cis*-compounds.[14,15] The latter are therefore the most stable forms thermodynamically.*

An explanation of the difference between the polyenes and their acetylenic analogues is suggested[14] by the *X*-ray crystallographic studies on β-carotene and related compounds.[27] These reveal some steric interference between the hydrogen atom at C-11 and the side chain methyls at C-9 and C-13. Though this would be relieved by the adoption of a 9-*cis*-configuration, the advantage would be outweighed by the introduction of steric interactions between the hydrogen atoms at C-8 and C-11. There is no such drawback to the adoption of a 9-*cis*-configuration with the 7-mono- and 7,7′-di-acetylenic analogues.[14]

Our findings on the stereomutation of alloxanthin have been confirmed and extended by Antia *et al.*,[28] and by Liaaen-Jensen *et al.*[29] The former group reported that the major isomer produced, and which we have shown by the synthesis described above to be the 9,9′-di-*cis*-form, is identical with manixanthin, a carotenoid isolated from a bleached autolysed culture of the marine cryptomonad *Chroomonas salina*.

The trans-*Series.*—Though the synthesis of the *cis*-isomers provided the desired confirmation of the structures assigned to the new class of acetylenic carotenoids, the synthesis of the all-*trans*-forms was explored further.[16]

A Grignard reaction of 2-*trans*-3-methylpent-2-en-4-yn-1-ol (**13**)[21] with the ketone (**14**) gave the required 2-*trans*-diol (**25**) which, on hydrolysis, yielded the corresponding dihydroxy-ketone (**26**). Reduction with sodium borohydride furnished a crystalline triol (**27**) which was assigned the (relative) configuration shown for the reasons discussed for the 2-*cis*-isomer. Reaction of the 2-*trans*-triol (**27**) with hot acetic anhydride, as described in the *cis*-series, was accompanied by stereomutation about the acyclic double bond and produced the 2-*cis*-diacetate (**20**). However, reaction with cold acetic anhydride in pyridine at 20 °C yielded the 2-*trans*-hydroxy-diacetate (**28**) which, on treatment with phosphorus oxychloride in the same solvent, was slowly converted into the required 2-*trans*-diacetate (**29**). Mild hydrolysis then gave the diol (**30**). Both (**29**) and (**30**) reacted with triphenylphosphonium bromide to give the corresponding Wittig salts, (**31**) and (**32**) respectively.

The diol (**30**) and its precursors exhibited u.v. light absorption at wavelengths which were only slightly (1—2 nm) longer than those of the corresponding 2-*cis*-isomers. However isomeric compounds in the two series were readily distinguished by their n.m.r. spectra. In the *trans*-series the signals due to the olefinic proton at C-2 were found at lower fields than the corresponding signals in the *cis*-series, whereas the signals due to the methylene protons at C-1 were at higher fields in the 2-*trans*- than in the 2-*cis*-compounds (Table 1).

Reaction of the triene-dial (**33**) with the phosphorane prepared by treating the Wittig salt (**32**) with sodium methoxide in methanol readily gave the all-*trans*-12′-apo-β-carotenal (**37**) which exhibited a light absorption maximum at a wavelength 4 nm longer than that of the 9-*cis*-isomer (**36**). Further reaction proved more difficult to achieve. Similar differences in reactivity were encountered in the *cis*-series. These differences were not unexpected since the carbonyl group in the apo-carotenals is deactivated by conjugation with the polyene chain, whereas nucleophilic attack on one of the carbonyl groups in the triene-dial (**33**) is facilitated by the electron withdrawing properties of the other. Reaction of (**37**) with the same phosphorane occurred slowly, even at 40 °C, and was accompanied by extensive stereomutation to give a product consisting mainly of the thermodynamically stable 9,9′-di-*cis*-isomer (**41**). Reaction of

* Further exceptions have since been observed with in-chain substituted carotenoids (S. Liaaen-Jensen, *Pure Appl. Chem.*, 1969, **20**, 421).

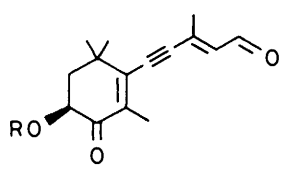
Table 1. Principal ^{1}H n.m.r. bands (δ values) for C_{15}-intermediates, and their derivatives[a]

Compound	1-Me_2 (2′-Me_2)	5-Me (6′-Me)	9-Me (3-Me)	10-H (2-H)	11-H_2 (1-H_2)	Other bands
cis-Series						
(**16**)	1.12, 1.13	1.06 (d, *J* 6.5)	1.87 (m, *J* 1)	5.85 (tm, *J* 7, 1.5)	4.27 (dm, *J* 7, 1)	1.20—1.80 (4H, m, 2- and 4-H_2), 2.00—2.40 (1 H, m, 5-H), 2.80 (1 H, br m[b]), 3.02 (1 H, br m[b]), 3.89 (4 H, m, $-OCH_2CH_2O-$)
(**17**)	0.99, 1.22	1.16 (d, *J* 7)	1.90 (d, *J* 1.5)	5.91 (tm, *J* 7, 1.5)	4.20 (d, *J* 6.5)	2.08 (1 H, dd, *J* 14, 1.5, 2-H, equatorial), 2.30 (3 H, br m, 4-H_2 and 5-H), 2.67 (1 H, d, *J* 14, 2-H, axial), 3.43 (br s[b])
(**17**)-Acetate	0.99, 1.22	1.16 (d, *J* 7)	1.93 (d, *J* 1.5)	5.88 (t, *J* 7)	4.76 (d, *J* 7)	2.03 (3 H, s, OAc), 2.31—3.18 (2 H, m), 2.31 (2 H, s), 2.91 (1 H, s[b])
(**18**)[c]	1.10, 1.23	1.05 (d, *J* 6.5)	1.86	5.85 (tm, *J* 7, 1.5)	4.29 (dm, *J* 7, 1)	1.40—1.80 (3 H, m), 2.00—2.20 (2 H, m), 3.43 (1 H, br s[b]), 3.80 (1 H, s[b]), 3.95 (1 H, s[b]), 3.95 (1 H, m, 3-H)
(**19**)	1.12, 1.15	1.09 (d, *J* 6.5)	1.92 (d, *J* 1.5)	5.79 (t, *J* 7)	4.73 (d, *J* 7)	2.05 (6 H, s, both OAc), 1.75 (3 H, m), 2.28 (2 H, m), 4.95 (1 H, m)
(**20**)	1.18, 1.20	1.90[d] (d, *J* 1.5)	1.94[d] (d, *J* 7, 1.5)	5·74 (tq, *J* 7, 1.5)	4.75 (d, *J* 7)	2.02 (3 H, s, OAc), 2.04 (3 H, s, OAc), 5.00 (1 H, m, 3-H)
(**21**)	1.14, 1.19	1.90[d] (3, *J* 2)	1.92[d] (d, *J* 1.5)	5.81 (tm, *J* 7, 1.5)	4.34 (dm, *J* 7, 1)	1.74 (2 H, br[b]), 3.73—4.10 (1 H, m, 3-H)
trans-Series						
(**25**) [*trans*-(**16**)]	1.12, 1.12	1.06 (d, *J* 7)	1.83 (d, *J* 1)	5.97 (tm, *J* 6.5)	4.20 (d, *J* 6.5)	1.20—2.20 (5 H, m, 2-H_2, 4-H_2, and 5-H), 2.28 (2 H, s[b]), 3.90 (4 H, m, $-OCH_2CH_2O-$)
(**26**), Dimethyl acetal	1.12, 1.27	1.06 (d, *J* 7)	1.83	5.97 (tm, *J* 7, 1.5)	4.21 (dm, *J* 7)	2.40 (2 H, br[b]), 1.40—2.9 (5 H, m, 2-H_2, 4-H_2, and 5-H), 3.17 (6 H, s, both OMe)
(**26**) [*trans*-(**17**)]	1.00, 1.21	1.15 (d, *J* 6)	1.85	6.03 (tm, *J* 7, 1.5)	4.24 (dm, *J* 7, 1.5)	1.60 (2 H, br[b]), 2.07 (1 H, dd, *J* 15, 1.5, 2-H, equatorial), 2.30 (3 H, m, 4-H_2 and 5-H), 2.67 (1 H, d, *J* 15, 2-H, axial)
(**26**), Mono-acetate	0.99, 1.20	1.17 (d, *J* 7)	1.89 (d, *J* 1.5)	5.95 (t, *J* 7)	4.65 (d, *J* 7)	2.06 (3 H, s, OAc), 2.29 (2 H, m), 2.57—2.81 (2 H, m) 2.91 (1 H, s[b])
(**27**) [*trans*-(**18**)][c]	1.08, 1.22	1.05 (d, *J* 6.5)	1.80 (m)	5.90 (tm, *J* 6.5, 1.5)	4.15 (dm, *J* 6.5, 1)	1.30—2.50 (5 H, m), 2.95 (2 H, br[b]), 3.81 (1 H, br[b]), 3.95 (1 H, m, 3-H)
(**28**) [*trans*-(**19**)]	1.12, 1.15	1.08 (d, *J* 6.5)	1.88	5.90 (tm, *J* 7.5, 2)	4.64 (dm, *J* 7.5)	1.30—2.50 (5 H, m), 2.03 (3 H, s, OAc), 2.06 (3 H, s, OAc), 4.95 (1 H, m, 3-H)
(**29**) [*trans*-(**20**)]	1.17, 1.19	1.89[d] (m)	1.92[d] (d, *J* 1.5)	5.89 (tq, *J* 7, 1.5)	4.65 (dm, *J* 7)	1.40—2.70 (4 H, m, 2-H_2 and 4-H_2), 2.03 (3 H, s, OAc), 2.06 (3 H, s, OAc), 5.03 (1 H, m, 3-H)
(**30**) [*trans*-(**21**)][c]	1.12, 1.16	1.87	1.87	5.92 (t, *J* 6)	4.19 (d, *J* 6)	2.77 (2 H, br s[b])

[a] For ease of comparison, carotenoid numbering (see footnote ‡ on p. 2147) is used in this Table. The numbering given in parentheses at the head of the columns corresponds to the conventional numbering used in the Experimental section for the cyclohexyl intermediates with a C_{15}-carbon skeleton; standard conventions require a different numbering of the ring positions in the related compounds with a cyclohexenyl end group (20, 21, 24, and 29—32). All bands had the expected relative intensities and, unless indicated to the contrary, were observed as singlets. [b] Band due to hydroxy proton(s); removed after shaking the solution of the sample with deuterium oxide. [c] In [$^2H_6$]acetone. [d] The assignment of pairs of signals marked [d] for any one compound is arbitrary, and the two assignments may need to be exchanged.

(**37**) with the more reactive phosphorane derived from the Wittig salt (**42**)[25] occurred at 20 °C, but was again accompanied by extensive stereomutation to give a mixture of the *trans* and *cis* isomers of (3*RS*,6′*RS*)-crocoxanthin [(**3**) and (**48**)]. These results pointed to the need to use a condensation procedure applicable at low temperatures.

Reaction of the triene-dial (**33**) with an excess of the Wittig salt (**31**), in the presence of potassium hydroxide in propan-2-ol at −30 °C, gave a mixture of all-*trans*-(3*RS*,3′*RS*)-alloxanthin (**49**) and its 9-mono-*cis*-isomer which was separated by thin layer chromatography (t.l.c.). The all-*trans*-product had light absorption, n.m.r., and mass spectral properties in good agreement with those of the natural alloxanthin, from which it did not separate on mixed thin layer chromatography. Independently Yamaguchi *et al.*[30] have used a low temperature Wittig condensation to synthesise the all-*trans*-isomers of two naturally occurring acetylenic carotenoids with aromatic end groups, though the yields were low as in the present studies. In the synthesis of the 4,4′-diketo-derivative of alloxanthin, a component of asterinic acid, Bernhard *et al.*[31] found that analogous Wittig condensations, even at −70 °C, gave only the thermodynamically more stable *cis*-isomers. However, these difficulties



(**50**)

Table 2. Principal ^{1}H n.m.r. bands (δ values) of carotenoids and 12′-apo-carotenals[a]

Compound	1-Me$_2$	5-Me	9-Me	13-Me	13′-Me	9′-Me	5′-Me	1′-Me$_2$	Other bands
(**34**)	1.18, 1.18	1.05 (d, *J* 7)	1.88	2.00	2.00				3.90 (4 H, m, –OCH$_2$CHO–), 9.50 (1 H, s, CHO)
(**38**)	1.18, 1.25	1.02 (d, *J* 6)	1.92	1.97	1.97	1.92	1.02 (d, *J* 6)	1.25, 1.18	
(**35**)	1.18, 1.26	1.11 (d, *J* 7)	1.88	2.00	2.00				1.70 (1 H, br), 2.46 (2 H, s[b]), 9.44 (1 H, s, CHO)
(**39**)	1.20, 1.25	1.05 (d, *J* 7)	1.95	1.95	1.95	1.95	1.05 (d, *J* 7)	1.25, 1.20	
(**39**)-Diacetate	1.20, 1.25	1.05 (d, *J* 6)	1.95	1.95	1.95	1.95	1.05 (d, *J* 6)	1.25, 1.20	2.02 (6 H, s, both OAc)
(**44**)	1.16, 1.25	1.11 (d, *J* 7)	1.95	1.95	1.95	1.95	1.59	0.90, 0.83	
(**46**)	1.20, 1.25	0.98 (d, *J* 7)	1.95	1.95	1.95	1.95	1.73	1.05, 1.05	
(**46**)-Acetate	1.20, 1.25	0.98 (d, *J* 7)	1.95	1.95	1.95	1.95	1.73	1.05, 1.05	2.05 (3 H, s, OAc)
(**45**)	1.20, 1.25	1.94	1.98	1.98	1.98	1.98	1.55	0.89, 0.81	2.05 (3 H, s, OAc)
(**47**)	1.20, 1.25	1.92	1.95	1.94	1.94	1.95	1.70	1.05, 1.05	
(**48**)	1.19, 1.24	1.92	1.96	1.96	1.96	1.92	1.58	0.92, 0.83	
(**36**)	1.18, 1.24	1.88	1.96	1.98	2.00				1.66 (1 H, br), 2.34 (2 H, d, *J* 7), 9.44 (1 H, s, CHO)
(**37**)	1.18, 1.18	1.88	1.95	2.00	2.00				9.46 (1 H, s, CHO)
(**41**)	1.17, 1.24	1.94	1.98	1.94	1.94	1.98	1.94	1.24, 1.17	
(**40**)	1.20, 1.25	1.92	1.99	1.94	1.94	1.99	1.92	1.25, 1.20	
9-*cis*-(**49**)	1.18, 1.25	1.94	1.99	1.94	1.94	1.99	1.92	1.20, 1.14	1.52 (2 H, s[b])
(**49**)	1.15, 1.20	1.91	1.99	1.94	1.94	1.99	1.95	1.20, 1.15	1.50 (2 H, s[b])
Natural acetylenes									
Alloxanthin (**1**)[4]	1.14, 1.19	1.90	1.99	1.94	1.94	1.99	1.90	1.19, 1.14	1.50 (2 H, s[b]), 2.29 (4 H, d, *J* 7)
Crocoxanthin (**2**)	1.14, 1.19	1.92	1.99	1.95	1.95	1.92	1.60	0.91, 0.83	
Monadoxanthin (**4**)	1.14, 1.19	1.91	1.99	1.95	1.95	1.91	1.62	0.85, 1.00	
Diatoxanthin (**7**)	1.16, 1.21	1.91	1.99	1.96	1.96	1.96	1.74	1.09, 1.09	1.52 (2 H, s[b])
Pectenolone (**5**)-acetate	1.18, 1.20	1.89	1.97	1.97	1.97	1.97	1.89	1.33, 1.26	2.01 (3 H, s, OAc), 2.16 (3 H, s, OAc)
Related polyenes									
Zeaxanthin (**8**)[9]	1.08, 1.08	1.74	1.97	1.97	1.97	1.97	1.74	1.08, 1.08	
Lutein (**10**)[9]	1.07, 1.07	1.72	1.96	1.96	1.96	1.90	1.62	0.84, 0.99	
Calthaxanthin[c]	1.07, 1.07	1.73	1.96	1.96	1.96	1.90	1.64	0.85, 0.94	
α-Cryptoxanthin (**9**)[d]	1.07, 1.07	1.74	1.97	1.97	1.97	1.91	1.58	0.90, 0.82	1.54 (2 H, s[b])
Astaxanthin diacetate[5]	1.21, 1.34	1.89	1.98	1.98	1.98	1.98	1.89	1.34, 1.21	2.17 (6 H, s, both OAc)

[a] All bands had the expected relative intensities and, unless indicated to the contrary, were observed as singlets. The assignment of the bands due to methyl groups on sp^2 hybridised carbon atoms, and which differ by only 5 p.p.m. or less, is arbitrary. [b] Band due to hydroxy proton(s); removed after shaking the solution of the sample with deuterium oxide. [c] Opictally inactive synthetic product differing from lutein in the relative configuration of the ε-end group.[19] [d] D. E. Loeber, S. W. Russell, T. P. Toube, B. C. L. Weedon, and J. Diment, *J. Chem Soc. C*, 1971, 404.

were overcome by condensing the keto-aldehyde (**50**), in which the reactivity of the aldehyde group is enhanced by conjugation with the carbonyl function, with the appropriate bis-Wittig salt; this gave the desired all-*trans*-isomer in 18% yield.

Related Acetylenic Carotenoids.—The n.m.r. spectra of crocoxanthin, monadoxanthin, diatoxanthin, and pectenolone (as its diacetate) all contained a set of bands identical with those associated with the end groups in alloxanthin (Table 2). The nature of the other end group in each of the four unsymmetrical carotenoids was revealed by comparison with the n.m.r. spectra of non-acetylenic carotenoids of known structure.[4,5] With monadoxanthin, the relevant n.m.r. bands resemble those of the ε-end group in lutein (**10**), rather than those associated with the corresponding end group in the 3′-epimer. It is therefore concluded that in monadoxanthin the 3′-hydroxy group is *cis* to the hydrogen atom at C-6′, as in lutein (**10**).[16,32,33]

It is interesting to note that the visible light absorption maxima with each of the five all-*trans*-acetylenic carotenoids under discussion occur at wavelengths very similar to, or slightly longer than, those of the corresponding bands of their ethylenic counterparts (Table 3). Normally substitution of an acetylenic linkage for a carbon–carbon disubstituted double bond results in a marked shift in the light absorption maxima to shorter wavelengths (a difference of 22 nm is observed between zeaxanthin and its 15,15′-acetylenic analogue[22]). However, in zeaxanthin and related compounds steric hindrance between the ring methyl groups and the hydrogen atoms at C-8 and C-8′ results in structures in which the π-orbitals of the ring double bonds are not fully co-planar with those of the acyclic portions of the polyene chain. Consequently zeaxanthin absorbs at lower wavelengths than would be expected purely on the basis of the number of double bonds in the chromophore. In alloxanthin there are no hydrogen atoms at C-8 and C-8′, and therefore the chromophore can adopt a planar conformation. The hypsochromic effect of substituting a triple for a double bond in the 7- and 7′-positions is thus offset by the bathochromic effect due to the relief of steric hindrance.[14]

Table 3. Visible light absorption maxima of acetylenic carotenoids, and their ethylenic analogues

Compound	Solvent	$\lambda_{max.}$(nm)	$\Delta\lambda$[a]
Alloxanthin (**1**)[3]	Hexane	480, 451	0
Diatoxanthin (**6**)[3]	Hexane	479, 450	−1
Zeaxanthin (**8**)[22]	Light petroleum	480, 452	
15′,15′-Didehydrozeaxanthin[22]	Light petroleum	458, 430	−22
Crocoxanthin (**2**)[3]	Hexane	475, 445, 422	0
α-Cryptoxanthin (**9**)[b]	Hexane	475, 445, 422	
Monadoxanthin (**4**)[3]	Hexane	475, 445, 422	+1
Lutein (10)[3]	Hexane	474, 445, 420	
Pectenolone (**5**)-diacetate[5]	Ethanol	463	−2
Adonixanthin (**11**)-esters[c]	Ethanol	465	
3-Hydroxy-β,β-caroten-4-one[d]	Ethanol	460	
3-Hydroxy-β,β-caroten-4-one[d]	Light petroleum	457	
3-Hydroxy-15,15′-didehydro-β,β-caroten-4-one[d]	Light petroleum	434	−23

[a] Difference (nm) between longest wavelength maximum of the acetylenic carotenoid and its ethylenic analogue. [b] L. Cholnoky, J. Szabolcs, and E. Nagy, *Ann. Chem. (Warsaw)*, 1958, **616**, 207. [c] H. Kleinig and K. Egger, *Phytochemistry*, 1967, **6**, 611. [d] R. D. G. Cooper, J. B. Davis, A. P. Leftwick, C. Price, and B. C. L. Weedon, *J. Chem. Soc., Perkin Trans. 1*, 1975, 2195.

Experimental

Unless indicated to the contrary, the following general points apply:

All operations involving polyenes or acetylenes were carried out in an atmosphere of nitrogen. With acetylenes in the *trans*-series exposure to bright light was avoided.

Solutions were dried over anhydrous sodium or magnesium sulphate, or by addition of benzene and azeotropic distillation. Solvents were evaporated under reduced pressure. Light petroleum refers to the fraction, b.p. 60—80 °C. Ether refers to diethyl ether.

Alumina for chromatography was graded according to Brockmann and Schodder.[34] Thin layer chromatograms (t.l.c.) were performed on Kieselgel with the eluants indicated in parentheses.

N.m.r. spectra were determined at 60 or 100 MHz on dilute solutions in deuteriochloroform using tetramethylsilane as an internal reference. The results (given mainly in Tables 1 and 2) are quoted in δ values; doublets are indicated by d, triplets by t, multiplets by m, and broad bands by br. Coupling constants (J) are given in Hz. Selected bands only are cited for mass spectra and i.r. light absorption spectra. The media for u.v., visible, and i.r. light absorption spectra are indicated in parentheses.

Melting points were determined in evacuated capillary tubes and are uncorrected.

The Natural Acetylenic Carotenoids.—Samples kindly supplied by Dr. D. J. Chapman,[3,4] or extracted from *Pecten maximus*,[5,6] had the following characteristics.

Alloxanthin (**1**) crystallised from acetone–light petroleum as red needles, m.p. 189—190 °C; $\lambda_{max.}$(benzene) 495 and 464 nm (ε 107 000 and 122 000); $\lambda_{max.}$(ethanol) 483 and 454 nm; $\lambda_{max.}$(hexane) 480 and 451 nm; $\nu_{max.}$($CHCl_3$) 3 610, 3 460, 2 167w, 1 612, 1 600, 1 045, 1 022, and 965 cm^{-1}; δ, see Table 2; o.r.d., see ref. 9; m/z 564.398 ($M^{+\cdot}$ 50%. Calc. for $C_{40}H_{52}O_2$ m/z 564.397), 549 (M − 15, 1), 546 (M − 18, 1), 531 (M − 18 − 15, <1), 472 (M − 92, <1), 119 (14), 105 (18), 91 (25), and 41 (100). The *diacetate* (of a sample extracted from *Pecten maximus*) crystallised from acetone–light petroleum as red prisms, m.p. 154—156 °C; $\lambda_{max.}$(benzene) 493 and 462 nm; $\nu_{max.}$($CHCl_3$) 2 180w, 1 728, 1 600, 1 024, and 966 cm^{-1}; m/z 648.420 ($M^{+\cdot}$, $C_{44}H_{56}O_4$ requires m/z 648.418).

Crocoxanthin (**2**) crystallised from benzene–methanol as red needles, m.p. 163—165 °C; $\lambda_{max.}$(benzene) 488, 458, and 432 nm; $\lambda_{max.}$(ethanol) 477 and 447 nm; $\lambda_{max.}$(hexane) 475, 445, and 422 nm; $\nu_{max.}$(CCl_4) 3 623, 2 169vw, 1 046, 1 026, and 962 cm^{-1}; δ, see Table 2; o.r.d., see ref. 9; m/z 550.421 ($M^{+\cdot}$, 100%. Calc. for $C_{40}H_{54}O$ m/z 550.417), 535 (M − 15, 2), 532 (M − 18, 1), 517 (M − 15 − 18, <1), 494 (M − 56, <1; m^* 444, $494^2/550$ = 444), 479 (<1), 458 (M − 92, 2), 444 (M − 106, <1), 119 (17), 105 (21), and 91 (26).

Monadoxanthin (**4**) crystallised from acetone–light petroleum as red needles, m.p. 167—168 °C; $\lambda_{max.}$(benzene) 487 and 456 nm; $\lambda_{max.}$(ethanol) 477, 447, and 424 nm; $\lambda_{max.}$(hexane) 475, 445, and 422 nm; $\nu_{max.}$(KBr disc) 3 380, 2 167vw, 1 048, 1 025, and 958 cm^{-1}; δ, see Table 2; o.r.d., see ref. 9; m/z 566.411 ($M^{+\cdot}$, 100%. Calc. for $C_{40}H_{54}O_2$ m/z 566.412), 548 (M − 18, 17), 533 (M − 18 − 15, 2), 530 (M − 18 − 18, <1), 474 (M − 92, 4), 460 (M − 106, 2), 119 (34), 105 (42), and 91 (56).

Diatoxanthin (**7**) crystallised from acetone–light petroleum as red needles, m.p. 201 °C; $\lambda_{max.}$(benzene) 492 and 463 nm; $\lambda_{max.}$(ethanol) 480 and 452 nm; $\lambda_{max.}$(hexane) 479 and 450 nm; $\nu_{max.}$(KBr disc) 3 400, 2 170vw, 1 620, 1 043, 1 025, and 960 cm^{-1}; δ, see Table 2; o.r.d., see ref. 9; m/z 566.412 ($M^{+\cdot}$, 4%. Calc. for $C_{40}H_{54}O_2$ m/z 566.412), 548 (M − 18, 1), 474 (M − 92, <1), 460 (M − 106, <1), 119 (15), 105 (18), and 91 (22).

Pectenolone (**5**) was isolated from *Pecten maximus* as the diacetate[5] which had $\lambda_{max.}$(benzene) 470 nm; $\lambda_{max.}$(ethanol) 463 nm; $\nu_{max.}$($CHCl_3$), 2 175w, 1 730, 1 674, 1 037, and 967 cm^{-1}; δ, see Table 2; m/z 664 ($M^{+\cdot}$) and 604.394 (M − 60. Calc. for $C_{44}H_{56}O_5$ m/z 604.392). The product formed on treatment with potassium borohydride had $\lambda_{max.}$(ethanol) 478 and 451 nm. The product from a similar reduction of astaxanthin diacetate had $\lambda_{max.}$(ethanol) 473 and 448 nm.

Perhydrogenation.—(i) Natural zeaxanthin (**8**) (10 mg) in glacial acetic acid (50 ml) was shaken with platinum oxide (5 mg) in an atmosphere of hydrogen for 48 h. Removal of catalyst and solvent, and preparative t.l.c. (20% acetone in light petroleum), gave perhydro-zeaxanthin (8 mg) as a colourless oil; $\nu_{max.}$($CHCl_3$) 3 623 cm^{-1}; δ, 0.89 (12 H, s), 0.94 (18 H, d, J 7), 1.22 (36 H, br), and *ca.* 1.4 (10 H, br); m/z 590.601 ($M^{+\cdot}$, $C_{40}H_{78}O_2$ requires m/z 590.600) and 572.586 (M − 18, $C_{40}H_{76}O$ requires m/z 572.592); [α] −9.3° at 589 nm, −9.3° at 578 nm, −10.7° at 546 nm, −17.1° at 436 nm, and −26.0° at 365 nm; the bis-(trimethylsilyl) ether had m/z 734 ($M^{+\cdot}$, $C_{46}H_{94}O_2Si_2$ requires m/z 734).

(ii) Similar hydrogenation of natural alloxanthin (**1**) (5 mg) gave an oil; $\nu_{max.}$(CCl_4) 3 623 cm^{-1}; δ, identical with that reported under (i); m/z 590.601 ($M^{+\cdot}$) and 572.590 (M − 18); [α] −9.8° at 589 nm, −10.4° at 578 nm, −11.6° at 546 nm, −12.7° at 436 nm, and −27.1° at 365 nm; the bis(trimethylsilyl) ether had m/z 734.

The two perhydro-derivatives did not separate on mixed t.l.c. (20% acetone in light petroleum).

2-cis-5-(4′,4′-Ethylenedioxy-1′-hydroxy-2′,2′,6′-trimethylcyclohexyl)-3-methylpent-2-en-4-yn-1-ol (**16**).—(i) A solution of *2-cis*-3-methylpent-2-en-4-yn-1-ol (**12**)[21] (2.9 g) in dichloromethane (30 ml) was added dropwise to one of ethylmagnesium bromide (from 1.5 g of magnesium and 6.5 g of ethyl bromide) in ether (100 ml) at 20 °C. The mixture was warmed for 10 min, and stirred for a further 1 h. 4,4-Ethylenedioxy-2,2,6-trimethylcyclohexanone (**14**)[22] (4.0 g) in dichloromethane (30 ml) was added over 30 min. The mixture was stirred under reflux for 12 h and then cooled. The Grignard complex was decomposed by adding saturated aqueous ammonium chloride. After the mixture had been stirred for 30 min, the product was isolated with ether and purified by column chromatography on silica gel (graded elution with acetone in light petroleum) to give the *diol*

(5.0 g) as a pale yellow viscous oil, n_D^{20} 1.5174; $\lambda_{max.}$(ethanol) 228 nm (ε 12 000); $\nu_{max.}$(liquid film) 3 410, 2 980, 2 880, 2 210vw, 1 630, 1 150, 1 090, 830, 770, and 720 cm^{-1}; δ, see Table 1; *m/z* 294 ($M^{+\cdot}$, $C_{17}H_{26}O_4$ requires *m/z* 294, 1%), 276 (*M* − 18, 14.5), 263 (*M* − 31, 2.5), 129 (65), 127 (26), 120 (40), 113 (100), 91 (10), 87 (50), 86 (40), 43 (35), 42 (13), and 41 (35) (Found: C, 68.9; H, 9.1. $C_{17}H_{26}O_4$ requires C, 69.4; H, 8.9%).

(ii) 2-*cis*-3-Methylpent-2-en-4-yn-1-ol (**12**) (12.0 g) was added to lithamide (from 4.2 g of lithium) in liquid ammonia (250 ml). Simultaneously ether was added and the ammonia allowed to evaporate. After the mixture had been stirred for 1 h, 4,4-ethylenedioxy-2,2,6-trimethylcyclohexanone (**14**) (5.0 g) in ether (15 ml) was added dropwise. The mixture was stirred for 16 h at 20 °C and then poured into cold (0 °C) saturated aqueous ammonium chloride. Isolation of the product with ether, and chromatography on a column of Grade IV alumina (ether–light petroleum) gave the diol (3.5 g). Its u.v. and i.r. light absorption properties, and n.m.r. spectrum, were identical with those of the sample from (i), from which it did not separate on mixed t.l.c. (25% acetone in light petroleum).

2-cis-5-(1′-*Hydroxy*-2′,2′,6′-*trimethyl*-4′-*oxocyclohexyl*)-3-*methylpent*-2-*en*-4-*yn*-1-*ol* (**17**).—A solution of the preceding diol (**16**) (4.0 g) in acetone (50 ml) was added to 0.75M-sulphuric acid (50 ml). After the mixture had been stirred at 20 °C for 2 h, a slight excess of saturated aqueous sodium hydrogen carbonate was added, and the product was isolated with ether. Chromatography on a column of silica gel (acetone–benzene) gave the *dihydroxy-ketone* as a pale yellow viscous liquid (2.7 g), n_D^{20} 1.5062; $\lambda_{max.}$(ethanol) 228 nm (ε 12 500); $\nu_{max.}$(liquid film) 3 400, 2 970, 2 880, 2 210vw, 1 700, 1 630, 1 100, 1 070, 1 030, 850, and 780 cm^{-1}; δ, see Table 1; *m/z* 250 ($M^{+\cdot}$, $C_{15}H_{22}O_3$ requires *m/z* 250, 35%), 232 (*M* − 18, 6; *m** 215.5, $232^2/250$ = 215.3), 219 (*M* − 31, 4), 217 (5), 179 (40), 165 (75), 148 (41), 139 (34), 123 (26), 120 (30), 106 (100), 91 (43), 79 (21), 77 (37), 69 (30), and 41 (100) (Found: C, 71.7; H, 8.7. $C_{15}H_{22}O_3$ requires C, 72.0; H, 8.9%).

When hydrolysis of the dioxolane grouping was effected with boiling aqueous acetic acid, in the presence of sodium acetate, the main product was 2-cis-1-*acetoxy*-5-(1′-*hydroxy*-2′,2′-6′-*trimethyl*-4′-*oxocyclohexyl*)-3-*methylpent*-2-*en*-4-*yne* which crystallised from ether as needles, m.p. 100 °C; $\lambda_{max.}$(ethanol) 228 nm (ε 14 000); $\nu_{max.}$(CCl_4) 3 600, 3 500, 2 980, 2 890, 1 740, 1 720, 1 640, 1 073, and 1 035 cm^{-1}; δ, see Table 1 (Found: C, 69.5; H, 8.1. $C_{17}H_{24}O_4$ requires C, 69.8; H, 8.3%). The same acetate was obtained quantitatively on reaction of the dihydroxyketone (**17**) with acetic anhydride in pyridine at 20 °C.

2-cis-5-(1′,4′-*Dihydroxy*-2′,2′,6′-*trimethylcyclohexyl*)-3-*methylpent*-2-*en*-4-*yn*-1-*ol* (**18**).—Sodium borohydride (200 mg) in water (1 ml) was added slowly to a stirred solution of the preceding dihydroxy-ketone (**17**) (1.5 g) in methanol (10 ml), and the reaction monitored by t.l.c. (25% acetone in light petroleum). When the reaction was complete (2 h), the excess of sodium borohydride was decomposed by the addition of water. Isolation of the product with ether and crystallisation from acetone–light petroleum gave the *triol* (1.0 g) as a colourless solid, m.p. 152 °C; $\lambda_{max.}$(ethanol) 228 nm (ε 13 000); $\nu_{max.}$(Nujol) 3 360, 2 960, 2 850, 2 230vw, 1 635, 1 060, 1 035, 1 020, 1 005, 930, 840, 790, and 720 cm^{-1}; δ, see Table 1; *m/z* 252 ($M^{+\cdot}$, $C_{15}H_{25}O_3$ requires *m/z* 252, 1%), 234 (*M* − 18, 13), 221 (*M* − 31, 1.5), 219 (3), 216 (1), 179 (16), 165 (21), 148 (100), 122 (5), and 41 (50) (Found: C, 70.8; H, 9.4. $C_{15}H_{24}O_3$ requires C, 71.4; H, 9.6%).

The same triol was obtained on reduction of the dihydroxy-ketone (**17**) or its mono-acetate with lithium aluminium hydride in ether at 20 °C.

Reaction of the triol (100 mg) with acetic anhydride in pyridine, isolation of the product in the usual way, and crystallisation from ether–light petroleum, gave the hydroxy-diacetate (**19**), m.p. 101 °C; $\lambda_{max.}$(ethanol) 228 nm (ε 13 000); $\nu_{max.}$(CCl_4) 3 500, 2 940, 1 730, 1 630, 1 065, 1 025, and 970 cm^{-1}; δ, see Table 1.

2-cis-5-(1′,4′-*Dihydroxy*-2′,2′,6′-*trimethylcyclohexyl*)-3-*methylpenta*-2,4-*dien*-1-*ol* (**15**) (*with* **W. J. S. Lockley** *and* **T. P. Toube**).—A suspension of lithium aluminium hydride (300 mg) in tetrahydrofuran (10 ml) was added slowly to a solution of the enyne triol (**18**) (1.2 g) in the same solvent (20 ml). The mixture was boiled under reflux for 20 h, and then cooled. The excess of hydride was decomposed by cautiously adding saturated aqueous sodium potassium tartrate, and the product was isolated with ether. Chromatography on silica gel (graded elution with acetone in light petroleum) gave the 2-cis,4-trans-*diene-triol* (**15**) (300 mg) as a colourless glass, $\lambda_{max.}$(ethanol) 238 nm (ε 12 000); $\nu_{max.}$(film) 3 400, 2 940, 1 650, 1 610, 1 210, 910, and 880 cm^{-1}; δ 0.82 (3 H, s, 2′-Me), 0.83 (3 H, d, *J* 7, 6′-Me), 1.12 (2 H, m, 3′-H_2 or 5′-H_2), 1.25 (3 H, s, 2′-Me), 1.68 (2 H, m, 3′-H_2 or 5′-H_2), 1.88 (3 H, m, *J* 1.5, 3-Me), 2.10 (3 H, br, removed on shaking with D_2O, hydroxy protons), 4.07 (1 H, m, 4′-H), 4.29 (2 H, dm, J_1 7, J_2 1, 1-H_2), 5.54 (1 H, tm, J_1 7, J_2 1.5, 2-H), 5.86 (1 H, d, *J* 16, 4-H), and 6.69 (1 H, d, *J* 16, 5-H); *m/z* 254 ($M^{+\cdot}$, $C_{15}H_{26}O_3$ requires *m/z* 254, 4%) 236 (*M* − 18, 5), 223 (<0.5), 218 (<0.5), 150 (22), 123 (20), 101 (50), 81 (40), 71 (27), 69 (26), 59 (68), 58 (70), 55 (37), and 41 (100).

Treatment with acetic anhydride in pyridine yielded the di-acetate, which crystallised from ether–light petroleum as colourless needles, m.p. 130 °C; $\lambda_{max.}$(ethanol) 237 nm (ε 12 000); $\nu_{max.}$(CCl_4) 2 960, 2 880, 1 730, 1 460, 1 015, and 980 cm^{-1}; δ 0.82 (3 H, s), 0.83 (3 H, d, *J* 7), 1.20 (3 H, s), 1.62 (1 H, br, removed on shaking with D_2O), 1.77 (2 H, m), 1.90 (3 H, d, *J* 1.5), 2.06 (6 H, s), 4.75 (2 H, d, *J* 7), 5.05 (1 H, m), 5.50 (1 H, t, *J* 7), 5.92 (1 H, d, *J* 16), and 6.73 (1 H, d, *J* 16); *m/z* 338 ($M^{+\cdot}$, $C_{19}H_{30}O_5$ requires *m/z* 338, 5%), 320 (1), 278 (*M* − 60, 33), 260 (*M* − 60 − 18, 2), 236 (5), 218 (*M* − 60 − 60, 33), 200 (5), and 43 (100).

Oxidation of the diene-triol (**15**) in acetone with manganese dioxide gave the corresponding dihydroxy-aldehyde which crystallised from ether–light petroleum as colourless needles, m.p. 105 °C; $\lambda_{max.}$(ethanol) 283 nm (ε 13 000); $\nu_{max.}$($CHCl_3$) 3 600, 3 000, 2 950, 1 655, 1 630, 1 125, 1 030, and 980 cm^{-1}; δ 0.84 (3 H, d, *J* 7), 0.86 (3 H, s), 1.11 (3 H, s), 1.26 (2 H, m), 1.60 (3 H, m), 2.08 (3 H, d, *J* 1.5), 4.05 (1 H, br, removed on shaking with D_2O), 5.85 (1 H, d, *J* 8), 6.38 (1 H, d, *J* 15), 7.34 (1 H, d, *J* 15), and 10.22 (1 H, d, *J* 8, CHO).

2-cis-1-*Acetoxy*-5-(4′-*acetoxy*-2′,6′,6′-*trimethylcyclohex*-1′-*enyl*)-3-*methylpent*-2-*en*-4-*yne* (**20**).—A mixture of the preceding enyne triol (**18**) (140 mg), acetic anhydride (2 ml), and glacial acetic acid (3 ml) was boiled under reflux for 14 h and then cooled and poured into saturated aqueous sodium hydrogen carbonate. Isolation of the product with ether, and preparative t.l.c. (7% acetone in light petroleum) gave the *diacetate* (120 mg) as a pale yellow viscous oil, n_D^{20} 1.5161; $\lambda_{max.}$(ethanol) 283 and 271 nm (ε 13 000 and 16 500); $\nu_{max.}$(liquid film) 2 970, 2 870, 2 190w, 1 740, 1 619, 1 030, and 975 cm^{-1}; δ, see Table 1; *m/z* 318 ($M^{+\cdot}$, $C_{19}H_{26}O_4$ requires *m/z* 318, <0.5%), 259 (8), 258 (*M* − 60, 40), 243 (1), 216 (3), 215 (2.5), 199 (6.5), 198 (6.5), 183 (35; *m** 169.0, $183^2/198$ = 169.1), 91 (11), and 43 (100) (Found: C, 71.9; H, 7.6. $C_{19}H_{26}O_4$ requires C, 71.7 and H, 8.2%).

Reduction of the dihydroxy-ketone (**17**) (12.0 g) with sodium borohydride (1.2 g) in ethanol (150 ml) yielded the crude triol (**18**) (10.0 g). A portion (7.5 g) was treated with acetic anhydride and acetic acid as described above. Isolation of the crude product, and chromatography in a column of silica gel (graded elution with light petroleum–ether) gave the required diacetate (5.8 g).

2-cis-5-(4′-*Hydroxy*-2′,6′,6′-*trimethylcyclohex*-1′-*enyl*)-3-*methylpent*-2-*en*-4-*yn*-1-*ol* (**21**).—The preceding diacetate (**20**) (4.8 g) in methanol (20 ml) was added to a stirred solution of potassium hydroxide (2.5 g) in methanol (20 ml), and the reaction was monitored by t.l.c. Hydrolysis was complete after 90 min. The reaction mixture was poured into water, the solution was saturated with sodium chloride, and the product (4.1 g) was isolated with ether. Crystallisation from light petroleum–ether gave the diol, m.p. 94—96 °C; $\lambda_{max.}$(ethanol) 284 and 270 nm (ε 12 000 and 15 000); δ, see Table 1; *m/z* 234 ($M^{+\cdot}$, $C_{15}H_{22}O_2$ requires *m/z* 234, 100%), 216 (*M* − 18, 1), 203 (*M* − 31, 7), 202 (40), 184 (9), 174 (26), 160 (24), 148 (26), 146 (25), 132 (29), 120 (26), 106 (37), 92 (50), and 78 (40).

2-cis-5-(4′-*Hydroxy*-2′,6′,6′-*trimethylcyclohex*-1′-*enyl*)-3-*methylpent*-2-*en*-4-*yn*-1-*yltriphenylphosphonium Bromide* (**24**).—A solution of the preceding crystalline diol (**21**) (936 mg) and triphenylphosphonium bromide (1.37 g) in methanol (50 ml) was kept at 20 °C for 5 days. The solution was then evaporated (rotary evaporator) at 20 °C and the residue was extracted thoroughly with ether. The ether insoluble Wittig salt (1.46 g) was used in synthesis without further purification. One batch, after crystallisation three times from dichloromethane–ether, had m.p. 118—126 °C, and was used for *X*-ray crystallographic analysis.[23]

Evaporation of the ethereal extracts of the crude product, and preparative t.l.c. (light petroleum–ether) gave 2-*cis*-5-(4′-hydroxy-2′,6′,6′-trimethylcyclohex-1′-enyl)-1-methoxy-3-methylpent-2-en-4-yne (280 mg).

9-cis-3-*Hydroxy*-7,8-*didehydro*-12′-*apo*-β-*caroten*-12′-*al* (**36**).—Sodium methoxide (from 3 mg of sodium) in methanol was added to the preceding Wittig salt (**24**) (56 mg) in methanol (10 ml). After 15 min, all-*trans*-2,7-dimethylocta2,4,6-triene-1,8-dial (**33**)[24] (18 mg) in methanol (2 ml) was added, and the mixture was stirred under reflux for 14 h. The mixture was then cooled and poured into water. Isolation of the product with ether, and preparative t.l.c. (20% acetone in light petroleum) gave the C_{25}-aldehyde as an orange solid (22 mg), $\lambda_{max.}$(benzene) 416 nm; $\nu_{max.}$(CCl_4) 3 620, 3 500, 2 930, 2 210w, 1 680, 1 615, 1 582, 1 462, 1 412, 1 385, 1 362, 1 190, 1 055, and 975 cm^{-1}; δ, see Table 2; *m/z* 364 (($M^{+\cdot}$, $C_{25}H_{32}O_2$ requires *m/z* 364).

9-cis-9′-cis-7,8,7′,8′-*Tetradehydro*-β,β-*carotene*-3,3′-*diol*. (3RS,3′RS)-*Manixanthin* (**41**).—Sodium methoxide (from 5 mg of sodium) in methanol was added to the preceding Wittig salt (**24**) (100 mg) in methanol (20 ml). After 15 min, the preceding C_{25}-aldehyde (**36**) (15 mg) in methanol (4 ml) was added. The mixture was stirred under reflux for 14 h, then cooled and poured into water. Isolation of the product with ether, and preparative t.l.c. (30% acetone in light petroleum) gave the diacetylenic diol (18 mg) which crystallised from acetone–light petroleum as orange needles, m.p. 204—206 °C; $\lambda_{max.}$(benzene) 480, 452, and 427 nm (ε 90 500, 102 000, and 70 000); $\lambda_{max.}$(ethanol) 466, 439, and 346 nm; $\nu_{max.}$($CHCl_3$) 3 600, 3 450, 2 905, 2 860, 2 170w, 1 600w, 1 035, 1 020, and 963 cm^{-1}; δ, see Table 2; *m/z* 564 ($M^{+\cdot}$, $C_{40}H_{52}O_2$ requires *m/z* 564).

Stereomutation.—A solution of the synthetic diacetylenic diol (**41**) (2 mg) in benzene (50 ml), containing a trace of iodine, was irradiated (tungsten filament lamp) for 75 min. The solution was then washed with aqueous sodium thiosulphate and water, dried, and evaporated. The residual equilibrium mixture of geometrical isomers had $\lambda_{max.}$(ethanol) 468, 440, and 347 nm. Chromatography on Schleicher and Schull filter paper no. 287 (Kieselguhr impregnated) (10% acetone in light petroleum) revealed three isomers: (i) neo U (*ca.* 55%), $\lambda_{max.}$(ethanol) 467, 439, and 347 nm; (ii) neo A (*ca.* 40%), $\lambda_{max.}$ 464, 439, and 347 nm; and (iii) neo B (*ca.* 5%), $\lambda_{max.}$ 468, 440, and 347 nm. Similar stereomutation of natural (all-*trans*) alloxanthin gave a mixture of three stereoisomers in the same proportions, and with the same light absorption and chromatographic properties. There was no separation of the corresponding isomers in the two sets on mixed paper chromatography. There was no separation between the neo U isomer and the synthetic 9,9′-di-*cis* isomer on mixed paper chromatography. No all-*trans* isomer was detected in either equilibrium mixture.

9-cis-7,8-*Didehydro*-β,ε-*caroten*-3-*ol* (**48**).—Sodium methoxide (from 2.5 mg of sodium) in methanol was added to the preceding Wittig salt (**24**) (50 mg) in methanol (20 ml). After 15 min, a solution of 12′-apo-ε-caroten-12′-al (**43**)[25] (8 mg) in methanol (4 ml) was added. The mixture was stirred under reflux for 14 h, then cooled and poured into water. Isolation of the product with ether, and preparative t.l.c. (20% acetone in light petroleum) gave the 9-cis-*acetylenic carotenol* (10 mg) as an orange solid, $\lambda_{max.}$(benzene) 479, 450, and 426 nm; $\lambda_{max.}$(ethanol) 469, 440, 417, 339, and 326 nm; $\nu_{max.}$($CHCl_3$) 3 610, 3 460, 2 960, 2 920, 2 860, 2 170w, 1 610, 1 040, 1 020, and 963 cm^{-1}; δ, see Table 2; *m/z* 550.414 (($M^{+\cdot}$, $C_{40}H_{54}O$ requires *m/z* 550.417).

Stereomutation of the synthetic product, as described above for the diacetylenic analogue, gave an equilibrium mixture, $\lambda_{max.}$(ethanol) 468, 439, 418, 339, and 327 nm. Paper chromatography as before (10% acetone in light petroleum) revealed two isomers: (i) neo U (*ca.* 60%), $\lambda_{max.}$(ethanol) 470, 441, 418, 340, and 328 nm, and (ii) neo A (*ca.* 40%), $\lambda_{max.}$(ethanol) 465, 437, 417, 339, and 326 nm. Similar stereomutation of natural (all-*trans*) croxoxanthin gave a mixture of two isomers in the same proportions, and with the same light absorption properties and chromatographic properties. There was no separation of the corresponding isomers in the two sets on mixed paper chromatography. There was no separation between the neo U isomer and the synthetic 9-*cis*-carotenol on mixed paper chromatography.

9-cis-3,6-*Dihydroxy*-7,8-*didehydro*-5,6-*dihydro*-12′-*apo*-β-*caroten*-12′-*al* (**35**).—A solution of the triol (**18**) (1.8 g) and triphenylphosphonium bromide (2.43 g) in methanol (25 ml) was kept at 20 °C for 60 h. Evaporation of the solvent, and trituration of the residue with ether gave the dihydroxy Wittig salt (**23**) (2.9 g) which was used without further purification.

Sodium methoxide (from 60 mg of sodium) in methanol (5 ml) was added to the dihydroxy Wittig salt (1.0 g) in methanol (10 ml). After 15 min, all-*trans*-2,7-dimethylocta-2,4,6-triene-1,8-dial (**33**)[24] (400 mg) in methanol (10 ml) was added. The mixture was stirred under reflux for 1 h, then cooled and poured into water. Isolation of the product with ether, and preparative t.l.c. (25% acetone in light petroleum) gave: (i) the C_{25}-aldehyde as an orange solid (314 mg), m.p. 206—210 °C; $\lambda_{max.}$(benzene) 402 nm; $\nu_{max.}$(CCl_4) 3 620, 3 500, 2 930, 2 210, 1 680, 1 615, 1 055, and 975 cm^{-1}; δ, see Table 2; *m/z* 382 ($M^{+\cdot}$, $C_{25}H_{34}O_3$ requires *m/z* 382), and (ii) the 9,9′-di-*cis*-tetraol (**39**) (343 mg) described below.

9-cis-9′-cis-7,8,7′,8′-*Tetradehydro*-5,6,5′,6′-*tetrahydro*-β,β-*carotene*-3,6,3′,6′-*tetraol* (**39**).—A solution of the preceding C_{25}-aldehyde (**35**) (40 mg) in methanol (10 ml) was added slowly to the phosphorane prepared from the preceding dihydroxy Wittig salt (**23**) (220 mg) in methanol (10 ml). The mixture was stirred under reflux, and then cooled. Isolation of the product, as in the previous experiment, gave the *tetraol* which crystallised from acetone–light petroleum as red needles (25 mg), $\lambda_{max.}$(benzene) 461, 433, and 411 nm; $\lambda_{max.}$(light petroleum) 448, 420, and 400 nm; $\nu_{max.}$($CHCl_3$) 3 600, 3 440, 2 910, 2 860, 2 170, 1 600, 1 030,

1 070, and 970 cm^{-1}; δ, see Table 2; *m/z* 600.418 ($M^{+\cdot}$, $C_{40}H_{56}O_4$ requires *m/z* 600.418).

9-cis-9′-cis-3,3′-*Diacetoxy*-7,8,7′,8′-*tetradehydro*-β,β-*carotene* (**40**) (*with* **J. Hora**).—Acetic anhydride (1 ml) was added to a solution of the preceding tetraol (**39**) (20 mg) in pyridine (5 ml). The mixture was kept for 14 h and then poured into water. Isolation of the product with ether, and preparative t.l.c. (30% acetone in light petroleum) gave the dihydroxy-diacetate (18 mg) as a red gum; $\lambda_{max.}$(benzene) 461, 433, and 411 nm; $\lambda_{max.}$(light petroleum) 448, 420, and 400 nm; δ, see Table 2.

Phosphorus oxychloride (25 mg) was added to the dihydroxy-diacetate (18 mg) in pyridine (0.5 ml). After 14 h, the mixture was cooled to −25 °C and crushed ice was added. Isolation of the product with ether, and chromatography on silica gel (benzene) gave the diacetate (4 mg) as a red viscous oil, $\lambda_{max.}$(benzene) 481, 453, and 430 nm; $\lambda_{max.}$(light petroleum) 466, 438, and 418 nm; δ, see Table 2; *m/z* 684 ($M^{+\cdot}$, $C_{44}H_{60}O_6$ requires *m/z* 684).

9-cis-7,8-*Didehydro*-5,6-*dihydro*-β,ε-*carotene*-3,6-*diol* (**44**).—Sodium methoxide (from 6 mg of sodium) in methanol was added to 5-(2′,2′,6′-trimethylcyclohex-5′-enyl)-3-methylpenta-2,4-dien-1-yltriphenylphosphonium bromide (**42**)[25] (440 mg) in methanol (20 ml). After 30 min, the C_{25}-aldehyde (**35**) (80 mg) in methanol (10 ml) was added. The mixture was stirred and warmed for 14 h, then cooled and poured into water. Isolation of the product with ether, and preparative t.l.c. (25% acetone in light petroleum) gave the *diol* (77 mg) as a red gum, $\lambda_{max.}$(benzene) 470, 442, and 422 nm; $\lambda_{max.}$(light petroleum) 461, 443, and 418 nm; $\nu_{max.}$(KBr disc) 3 400, 3 010, 2 960, 2 910, 2 860, 2 170, 1 620, 1 170, 1 120, 1 050, 1 025, and 960 cm^{-1}; δ, see Table 2; *m/z* 568.427 ($M^{+\cdot}$, $C_{40}H_{56}O_2$ requires *m/z* 568.428).

9-cis-3-*Acetoxy*-7,8-*didehydro*-β,ε-*carotene* (**45**) (*with* **J. Hora**).—Acetic anhydride (1 ml) was added to a solution of the preceding diol (**44**) (20 mg) in pyridine (5 ml). After 14 h the mixture was poured into water. Isolation of the product with ether, and preparative t.l.c. (20% acetone in light petroleum) gave the hydroxy-acetate (19 mg), $\lambda_{max.}$(benzene) 461, 443, and 418 nm; $\lambda_{max.}$(light petroleum) 457, 428, and 406 nm. The product in pyridine (0.5 ml) was treated with phosphorus oxychloride (25 mg). After 14 h, the mixture was cooled to −25 °C and then poured onto crushed ice. Isolation of the product with ether, and chromatography on silica gel (benzene) gave the acetate as a red viscous oil, $\lambda_{max.}$(benzene) 481, 453, and 432 nm; $\lambda_{max.}$(light petroleum) 468, 439, and 419 nm; δ, see Table 2.

9-cis-7,8-*Didehydro*-5,6-*dihydro*-β,β-*carotene*-3,6-*diol* (**46**).—Sodium methoxide (from 6 mg of sodium) in methanol was added to the preceding dihydroxy Wittig salt (**23**) (680 mg) in methanol. The mixture was warmed for 15 min, then 12′-apo-β-caroten-12′-al (150 mg) in methanol (10 ml) was added. The mixture was stirred under reflux and the reaction monitored by t.l.c. After 4 h, the mixture was cooled and poured into water. Isolation of the product with ether, and preparative t.l.c. (25% acetone in light petroleum) gave the *diol* (142 mg) as an orange solid, $\lambda_{max.}$(benzene) 451 nm; $\nu_{max.}$ 3 400, 3 010, 2 960, 2 910, 2 860, 2 170, 1 620, 1 170, 1 120, 1 050, 1 025, and 960 cm^{-1}; δ, see Table 2; *m/z* 568.429 ($M^{+\cdot}$, $C_{40}H_{56}O_2$ requires *m/z* 568.428).

9-cis-3-*Acetoxy*-7,8-*didehydro*-β,β-*carotene* (**47**) (*with* **J. Hora**).—Acetic anhydride (0.5 ml) was added to the preceding diol (**46**) (12 mg) in pyridine (4 ml). After 14 h the mixture was poured into water. Isolation of the product with ether, and preparative t.l.c. on Kieselgel (20% acetone in light petroleum) gave the hydroxy-acetate (11 mg) as a red gum, $\lambda_{max.}$(benzene) 451 nm; $\lambda_{max.}$(light petroleum) 431 nm; δ, see Table 2. The product (11 mg) in pyridine (0.5 ml) was treated with phosphorus oxychloride (25 mg). After 14 h, the mixture was cooled to −25 °C and crushed ice was added. Isolation of the product with ether, and chromatography on silica gel (benzene) gave the acetate (4 mg) as a red gum, $\lambda_{max.}$(benzene) 483, 456, and 434 nm; $\lambda_{max.}$(light petroleum) 468, 441, and 419 nm; δ, see Table 2.

9-cis-3,3-*Ethylenedioxy*-7,8-*didehydro*-5,6-*dihydro*-6-*hydroxy*-12′-*apo*-β-*caroten*-12′-*al* (**34**).—A solution of the diol (**16**) (250 mg) and triphenylphosphonium bromide (295 mg) in methanol (25 ml) was kept at 20 °C for 60 h. Evaporation of the solvent and trituration of the residue with ether gave the Wittig salt (**22**) (500 mg) which was used without further purification.

Sodium methoxide (from 3 mg of sodium) in methanol was added to a solution of the Wittig salt (60 mg) in methanol (10 ml). After 15 min, all-*trans*-2,7-dimethylocta-2,4,6-triene-1,8-dial (**33**) (20 mg) was added. The mixture was stirred under reflux for 3 h, then cooled and poured into water. Isolation of the product with ether, and preparative t.l.c. (25% acetone in light petroleum) gave the apo-carotenal (35 mg); $\lambda_{max.}$(benzene) 402 nm; $\nu_{max.}$($CHCl_3$) 3 620, 3 500, 2 930, 2 210w, 1 680, 1 615, 1 582, 1 460, 1 410, 1 390, 1 360, 1 190, 1 055, and 975 cm^{-1}; δ, see Table 2.

Further reaction of the apo-carotenal with the Wittig reagent occurred slowly giving, after 7 days, 30% of (**38**), $\lambda_{max.}$(benzene) 464 and 437 nm; $\nu_{max.}$($CHCl_3$) 3 430, 2 960, 2 910, 2 880, 2 190, 1 650, 1 550, 1 440, 1 350, 1 320, 1 090, 1 050, and 970 cm^{-1}; δ, see Table 2.

2-trans-5-(4′,4′-*Ethylenedioxy*-1′-*hydroxy*-2′,2′,6′-*trimethylcyclohexyl*)-3-*methylpent*-2-*en*-4-*yn*-1-*ol* (**25**).—A Grignard reaction between 4,4-ethylenedioxy-2,2,6-trimethylcyclohexanone (**14**) (4.0 g) and 2-*trans*-3-methylpent-2-en-4-yn-1-ol (**13**) (2.9 g), as described above with the 2-*cis* isomer, and purification of the crude product first by chromatography on a column of alumina (Grade III) (ethyl acetate–benzene), and then by crystallisation from ether–light petroleum, gave the diol (2.4 g), m.p. 111 °C; $\lambda_{max.}$(ethanol) 230 nm (ε 14 000); $\nu_{max.}$(Nujol) 3 360, 2 900, 970, 760, and 720 cm^{-1}; δ, see Table 1; *m/z* 294 ($M^{+\cdot}$, $C_{17}H_{26}O_4$ requires *m/z* 294, 1.5%), 276 (*M* − 18, 1), 263 (*M* − 31, 1), 129 (100), 127 (19), 120 (26), 113 (55), 91 (19), 87 (50), 86 (25), 53 (15), 43 (40), 42 (20), 41 (55), and 31 (9).

2-trans-5-(1′-*Hydroxy*-2′,2′,6′-*trimethyl*-4′-*oxocyclohexyl*)-3-*methylpent*-2-*en*-4-*yn*-1-*ol* (**26**).—Hydrolysis of the preceding diol (**25**) (2.4 g), as described for the 2-*cis* isomer, and chromatography of the crude product on a column of alumina (Grade III) (ethyl acetate–benzene), gave the dihydroxy-ketone as a viscous oil (2.0 g), n_D^{20} 1.5097; $\lambda_{max.}$(ethanol) 230 nm (ε 12 500); $\nu_{max.}$(liquid film) 3 400, 2 970, 2 880, 2 200w, 1 720, 1 630, 1 075, and 930 cm^{-1}; δ, see Table 1; *m/z* 250 ($M^{+\cdot}$, $C_{15}H_{22}O_3$ requires *m/z* 250, 75%), 232 (*M* − 18, 2; *m** 215.5, $232^2/250 = 215.3$), 219 (*M* − 31, 15), 179 (46), 165 (40), 152 (60), 148 (80), 139 (43), 123 (32), 106 (45), 91 (42), 77 (35), 69 (43), 55 (45), and 41 (100).

Hydrolysis of the ethylenedioxy-compound with boiling aqueous acetic acid in the presence of sodium acetate gave a mixture which was separated by preparative t.l.c. (acetone–light petroleum) to give the above dihydroxy-ketone (29%) and the corresponding mono-acetate (31%), n_D^{21} 1.5133; $\lambda_{max.}$(ethanol) 230 nm (ε 14 500); $\nu_{max.}$(liquid film) 3 500, 2 970, 2 890, 2 230w, 1 740, 1 720, 1 642, 1 480, 1 385, 1 370, 1 240, 1 078, 1 039, and 970 cm^{-1}; δ, see Table 1.

2-trans-5-(1′,4′-*Dihydroxy*-2′,2′,6′-*trimethylcyclohexyl*)-3-*methylpent*-2-*en*-4-*yn*-1-*ol* (**27**).—The preceding dihydroxy-

ketone (**26**) (1.8 g), in methanol (20 ml), was treated with sodium borohydride (273 mg) in water (2 ml) in the manner described for the 2-*cis* isomer. Isolation of the crude product in the usual way, preparative t.l.c. (acetone–light petroleum), and crystallisation of the major fraction from acetone–light petroleum, gave the triol (1.2 g), m.p. 156 °C; $\lambda_{max.}$(ethanol) 230 nm (ε 13 500); $\nu_{max.}$(Nujol) 3 340, 2 980, 2 840, 1 640, 1 070, 1 040, 1 000, 975, 940, 850, 820, and 805 cm^{-1}; δ, see Table 1; *m/z* 252 ($M^{+\cdot}$, $C_{15}H_{24}O_3$ requires *m/z* 252, 20%), 234 (*M* − 18, 20), 221 (*M* − 31, 4), 216 (*M* − 18 − 18, 6), 203 (8), 178 (19), 166 (85), 152 (40), 148 (70), 96 (20), 95 (20), 93 (20), 91 (40), 79 (30), 77 (30), 71 (19), 69 (30), 67 (30), 65 (20), 55 (50), 53 (30), 43 (75), and 41 (100).

Isolation of the minor product from the t.l.c., and crystallisation from acetone–light petroleum, gave the dimethyl acetal (0.2 g) of the main product. The acetal had m.p. 186 °C; $\nu_{max.}$ 3 320, 3 160, 2 900, 1 635, 1 070, 1 040, 1 005, and 940 cm^{-1}; δ, see Table 1; *m/z* 296 ($M^{+\cdot}$, $C_{17}H_{30}O_4$ requires *m/z* 296, 0.7%), 278 (*M* − 18, 2), 265 (*M* − 31, 8), 264 (9), 247 (13), 240 (24), 131 (41), 129 (21), 115 (100), 91 (15), 89 (32), 88 (17), 73 (18), 55 (19), 43 (48), and 41 (41).

2-trans-5-(4′-*Acetoxy*-1′-*hydroxy*-2′,2′,6′-*trimethylcyclohexyl*)-1-*acetoxy*-3-*methylpent*-2-*en*-4-*yne* (**28**).—Acetic anhydride (1.8 ml) was added slowly to a solution of the preceding triol (**27**) (350 mg) in pyridine (2 ml). The mixture was stirred at 20 °C for 24 h, and then poured into water. Isolation of the product with ether, and chromatography on a column of silica gel (benzene) gave the hydroxy-diacetate (250 mg) as an oil, $\lambda_{max.}$(ethanol) 230 nm; $\nu_{max.}$(liquid film) 3 500, 2 960, 2 940, 2 880, 2 210, 1 730, 1 630, 1 030, 995, and 970 cm^{-1}; δ, see Table 1; *m/z* 336 ($M^{+\cdot}$, $C_{19}H_{28}O_5$ requires *m/z* 336, <0.5%), 321 (*M* − 15, <0.5), 318 (*M* − 18, <0.5), 276 (*M* − 60, 23), 261 (0.8), 233 (1.5), 216 (*M* − 60 − 60, 10; *m** 169.0, $216^2/276$ = 169.0), 160 (27), 134 (11), 106 (23), 91 (7), and 43 (100).

2-trans-1-*Acetoxy*-5-(4′-*acetoxy*-2′,6′,6′-*trimethylcyclohex*-1′-*enyl*)-3-*methylpent*-2-*en*-4-*yne* (**29**).—Phosphorus oxychloride (1.8 ml) was added slowly to a stirred solution of the preceding hydroxy-diacetate (**28**) (1.1 g) in pyridine (16 ml), and the mixture was stirred in the dark at 20 °C for 5 days. The mixture was then cooled, and the excess of oxychloride was decomposed by the cautious addition of ice. Isolation of the product with ether, and preparative t.l.c. (20% acetone in light petroleum) gave recovered starting material (700 mg), and the diacetate as an oil (220 mg), $\lambda_{max.}$(ethanol) 270 nm; $\nu_{max.}$(liquid film) 2960, 2925, 2 860, 2 185, 1 730, 1 615, 1 030, 970, 910, and 760 cm^{-1}; δ, see Table 1; *m/z* 318 (*M*′, $C_{19}H_{26}O_4$ requires *m/z* 318, 3%), 276 (*M* − 42, 2), 258 (*M* − 60, 100), 243 (3), 234 (1), 216 (6.5), 215 (4.5), 201 (6), 200 (4), 198 (*M* − 60 − 60, 12), 183 (70), and 43 (70).

Treatment of the 2-*trans*-triol (**27**) with hot acetic anhydride, as described for the 2-*cis*-triol (**18**), gave (60%) the 2-*cis*-diacetate; it exhibited the same u.v. and i.r. light absorption properties, and n.m.r. characteristics, as those reported above for the authentic 2-*cis*-diacetate (**19**).

Hydrolysis of the 2-*trans*-diacetate with potassium hydroxide in methanol gave (85%) the corresponding diol (**30**), $\lambda_{max.}$(ethanol) 283 and 271 nm; δ, see Table 1. A sample was crystallised from dichloromethane–light petroleum and had m.p. 94—97 °C, depressed by over 20 °C on admixture with the 2-*cis*-diol (**21**), m.p. 94—96 °C.

9-trans-3-*Hydroxy*-7,8-*didehydro*-12′-*apo*-β-*caroten*-12′-*al* (**37**).—A solution of the preceding 2-*trans*-diol (**30**) (100 mg) and triphenylphosphonium bromide (100 mg) in methanol (10 ml) was stirred at 20 °C for 60 h, and then evaporated. Trituration of the residue with ether gave the Wittig salt (**32**) (150 mg) which was used without further purification.

Sodium methoxide (from 6 mg of sodium) in methanol (5 ml) was added to the Wittig salt (150 mg) in methanol (15 ml). After the mixture had been stirred for 15 min, all-*trans*-2,7-dimethylocta-2,4,6-triene-1,8-dial (**33**) (30 mg) was added. The mixture was stirred at 20 °C for 7 h and then poured into water. Isolation of the product with ether, and chromatography on alumina, gave the *apo*-β-*carotenal* (34 mg) as an orange solid, $\lambda_{max.}$(ethanol) 418 nm; $\lambda_{max.}$(benzene) 420 nm; δ, see Table 2; *m/z* 364.240 ($M^{+\cdot}$, $C_{25}H_{32}O_2$ requires *m/z* 364.240).

Further reaction with the same Wittig salt in methanol at 40 °C gave small amounts of the C_{40}-carotenoid as a mixture of isomers, $\lambda_{max.}$(benzene) 470 and 452 nm. The light absorption maxima indicated that this mixture consisted mainly of the 9,9′-di-*cis* isomer.

Treatment of the apo-β-carotenal with an excess of 2-*trans*-5-(2′,2′,6′-trimethylcyclohex-5′-enyl)-3-methylpenta-2,4-dien-1-yltriphenylphosphonium bromide (**42**)[25] in the presence of methanolic sodium methoxide at 20 °C gave (*ca.* 30%) a mixture of isomers of optically inactive crocoxanthin, $\lambda_{max.}$(ethanol) 470, 452, and 420 nm. The light absorption maxima indicates that it consisted mainly of the 9-*cis*-isomers. A partial separation was achieved by t.l.c. on zinc carbonate [light petroleum–benzene–acetone (50:40:10)] and separation of the main band into two halves. The more strongly adsorbed half had $\lambda_{max.}$(ethanol) 477 and 444 nm and did not separate on mixed t.l.c. from an authentic sample of natural all-*trans*-crocoxanthin.

7,8,7′,8′-*Tetradehydro*-β,β-*carotene*-3,3′-*diol*: (3RS,3′RS)-*Alloxanthin* (**49**).—A solution of the diacetate (**29**) (170 mg) and triphenylphosphonium bromide (180 mg) in methanol (10 ml) was stirred at 20 °C in the dark for 60 h. Evaporation of the solvent, and trituration of the residue with ether, gave the Wittig salt (**31**) (220 mg), m.p. 86—90 °C (with decomposition), which was used without further purification.

A suspension of the Wittig salt (210 mg, 3.5 mol) in propan-2-ol (7 ml) was added to a stirred suspension of 2,7-dimethylocta-2,4,6-triene-1,8-dial (**33**) (16 mg, 1 mol) in the same solvent (5 ml) at −30 °C. Potassium hydroxide (22 mg, 4.0 mol), dissolved in the minimum quantity of water, was added over 3 min. The mixture was stirred at −30 °C for 6 h, allowed to warm to 20 °C, and then poured into water. Isolation of the product with ether, and preparative t.l.c. [acetone–light petroleum (30:70)] gave the mixture of C_{40}-pigments which was separated into two components by t.l.c. on magnesium carbonate [acetone–light petroleum (15:85)]. The more polar component (2.5 mg), after chromatography on a column of silica gel (gradient elution with acetone in benzene), and crystallisation from acetone–light petroleum, gave (3RS,3′RS)-9-cis-*alloxanthin* (2 mg) as red needles, m.p. 104 °C; $\lambda_{max.}$(ethanol) 474, 446, and 347 nm (*cis*-peak); $\lambda_{max.}$(benzene) 486, 456, and 352 nm (*cis*-peak) (ε_{456} 66 000); $\nu_{max.}$(KBr disc) 3 250, 1 555, 1 440, 1 025, 960, and 830 cm^{-1}; δ, see Table 2; *m/z* 564.395 ($M^{+\cdot}$, $C_{40}H_{52}O_2$ requires *m/z* 564.397, 55%), 549 (5), 546 (*M* − 18, 4), 531 (2), 472 (*M* − 92, 14), 457 (4), 406 (4), 282 (6), 119 (17), 105 (23), 92 (7), and 91 (100).

Chromatography of the less polar component on a column of silica gel (6% acetone in benzene), and crystallisation from acetone–light petroleum, gave (3RS,3′RS)-*alloxanthin* (2 mg) as orange needles, m.p. 186 °C; $\lambda_{max.}$(ethanol) 481 and 452 nm; $\lambda_{max.}$(benzene) 492 and 462 nm (ε_{462} 131 000); $\nu_{max.}$(KBr disc) 3 350, 2 170vw, 1 560, 1 450, 1 050, 1 020, 960, and 950 cm^{-1}; δ, see Table 2; *m/z* 564.396 ($M^{+\cdot}$, $C_{40}H_{52}O_2$ requires *m/z* 564.397, 11%), 549 (1), 546 (*M* − 18, <0.5), 528 (*M* − 18 − 18, <0.5), 472 (*M* − 92, 4), 457 (1), 406 (3), 105 (12), 92 (75), and 91 (100). The synthetic product did not separate from natural alloxanthin on mixed t.l.c. on either Kieselgel H [acetone–light

petroleum (30:70)] or magnesium carbonate [acetone–light petroleum (15:85)].

In a similar condensation using only 2.6 mol of the Wittig salt, the mixture of C_{40}-pigments consisted predominantly (*ca.* 80%) of (3*RS*,3′*RS*)-9-*cis*-alloxanthin.

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