# Carotenoids and Related Compounds. Part XXXII.[1] Synthesis of Astaxanthin, Phoenicoxanthin, Hydroxyechinenone, and the Corresponding Diosphenols †

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Autoxidation of 4-oxo-carotenoids in the presence of potassium t-butoxide gives the corresponding diosphenols (3,4-didehydro-3-hydroxy-4-ones). These on reduction with potassium borohydride give the 3,4-dihydroxy-compounds which, on carefully controlled oxidation, yield the 3-hydroxy-4-ones.

Astaxanthin (3,3'-dihydroxy-β,β-carotene-4,4'-dione), phoenicoxanthin (3-hydroxy-β,β-carotene-4,4'-dione), and hydroxyechinenone (3-hydroxy-β,β-caroten-4-one) have been synthesised in this way from canthaxanthin (β,β-carotene-4,4'-dione), echinenone (β,β-caroten-4-one), and their 15,15'-acetylenic analogues.

ASTAXANTHIN † (1) is a red pigment found in many crustacea, such as the common lobster (*Homarus gammarus*),[2,3] in salmon (*Salmo salar*),[4] in the feathers of flamingos (*e.g. Phoenicopterus ruber*),[5] and in numerous other organisms.[3,6] It is also the prosthetic group in many carotenoproteins, of which large numbers have been reported, mainly in invertebrates, and which range in colour from colourless to bright blue.[7] Diesters with palmitic acid or other fatty acids are also common, *e.g.* in the skin of the common goldfish (*Carassius auratus*) [8] and trout (*Salmo trutta*).[9]

Several other carotenoids with the α-ketol end group (d) of astaxanthin have been reported.[10] These include phoenicoxanthin in the flamingo,[5] adonirubin in the red flowers of *Adonis annua*,[11,12] both of which have been formulated as (2), and another pigment in *A. annua* regarded as hydroxyechinenone (3).[11,12] The latter pigment has also been reported in *Daphnia magna* [13] and, as an ester, in the brine shrimp *Artemia salinas*.[14]

Carotenoids with the α-ketol end group (d) undergo autoxidation, especially under basic conditions, to give the corresponding diosphenols (b).[15] This occurs particularly readily with astaxanthin to give astacene (4), the familiar red pigment from boiled lobsters and crabs.[3,15] Astacene and related diosphenols have been obtained from many sources,[3,10] but it is arguable whether they are genuine natural products rather than artefacts formed by autoxidation of the α-ketols during isolation.

At the lower oxidation level, several 3,4-dihydroxy-carotenoids have been reported. These include the 3,4-diol (5),[16] a related triol [possibly (6)],[17] and crustaxanthin which accompanies astaxanthin in the crustacean *Arctodiaptomus salinus* and which has been formulated as the tetraol (7).[18] These α-glycols are conceivably intermediates in the biosynthesis of the α-ketols, or may arise from them by reduction.

In this paper we describe the first total syntheses of carotenoids with end groups of the three types discussed above (for preliminary accounts see refs. 19—21). Canthaxanthin (8), echinenone (9), and their 15,15'-didehydro-analogues [(8') and (9')] have been prepared by a number of routes [22] and were therefore chosen as convenient starting materials. Since they can be formed under strongly basic conditions without appreciable decomposition,[23] attention was directed to their autoxidation using the conditions developed by Barton *et al.*[24,25] for the conversion of unconjugated ketones into the corresponding diosphenols.

When a solution of canthaxanthin in t-butyl alcohol containing potassium t-butoxide was shaken in oxygen, astacene (4) was produced in yields of up to 90%. It

† The common trivial names of carotenoids are used throughout this paper, but are defined in the Experimental section according to the Nomenclature of Carotenoids (rules approved 1974) (I.U.P.A.C.–I.U.B., *Pure Appl. Chem.*, in the press).

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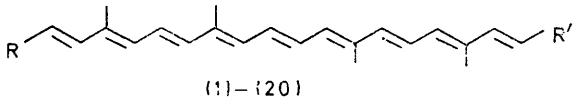
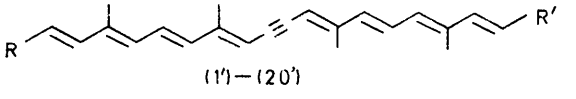
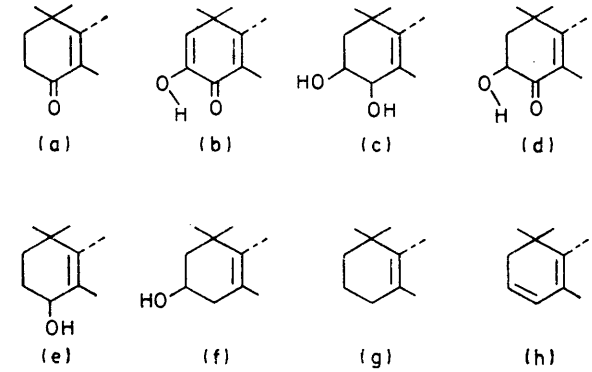
was identical with a sample derived from lobsters. From the products of incomplete autoxidation of canthaxanthin (8) the intermediate diosphenol (10) was isolated. Our synthetic material was compared directly ($\lambda_{max.}$; t.l.c. before and after borohydride reduction) with phoeniconone by Professor D. L. Fox,[5] with dehydroadonirubin by Dr. K. Egger,[12] and with a pigment from *Chlorococcum* algae by Dr. F.-C. Czygan.[26] Identity was reported in all three cases, thus confirming the structures assigned to these pigments of natural origin and to phoenicoxanthin (adonirubin).




(1)–(20)




(1')–(20')




(a) (b) (c) (d)

(e) (f) (g) (h)

| | R | R′ | | R | R′ | | R | R′ |
|---|---|---|---|---|---|---|---|---|
| (1) or (1′) | (d) | (d) | (8) or (8′) | (a) | (a) | (15) or (15′) | (c) | (e) |
| (2) or (2′) | (d) | (a) | (9) or (9′) | (a) | (g) | (16) or (16′) | (h) | (h) |
| (3) or (3′) | (d) | (g) | (10) or (10′) | (b) | (a) | (17) or (17′) | (f) | (f) |
| (4) or (4′) | (b) | (b) | (11) or (11′) | (b) | (g) | (18) or (18′) | (f) | (g) |
| (5) or (5′) | (c) | (g) | (12) or (12′) | (b) | (e) | (19) or (19′) | (d) | (e) |
| (6) or (6′) | (c) | (e) | (13) or (13′) | (a) | (e) | (20) or (20′) | (c) | (d) |
| (7) or (7′) | (c) | (c) | (14) or (14′) | (e) | (e) | | | |

Autoxidation of echinenone (9) gave the diosphenol (11) in 80% yield. Its i.r. and n.m.r. properties indicate that, like the related compounds studied, it exists predominantly in the enolic form. As a result of its pseudoacidic properties it is tenaciously adsorbed on alumina. In this respect it differs markedly from euglenanone, a minor pigment in the alga *Euglena gracilis*, to which this structure (or that of the tautomeric α-diketone) had been tentatively assigned.[27] Direct t.l.c. comparison with a sample kindly supplied by Professor N. I. Krinsky confirmed the need for a revision of the structure of euglenanone. However direct comparison (t.l.c. in several systems) by Dr. K. Egger of our synthetic (11) with a pigment from *Adonis annua* [11,12] showed the two to be identical.

A pigment from the alga *Protosiphon botryoides* has been formulated as the 4′-hydroxy-diosphenol (12).[28] This structure was conveniently synthesised by reaction of the diosphenol (11) with *N*-bromosuccinimide in the presence of acetic acid, and hydrolysis of the acetate thus formed. Direct autoxidation of 4′-hydroxy-echinenone (13) gave only poor yields of (12) owing to simultaneous oxidation to canthaxanthin and its derivatives.

Autoxidation of the 15,15′-didehydro-analogues [(8′) and (9′)] of canthaxanthin and echinenone furnished the acetylenic diosphenols (4′) and (11′), respectively in >90% yield. The 4′-methoxy-derivative of (9′) was similarly converted into the corresponding diosphenol. Catalytic hydrogenation of the acetylenes (4′) and (11′) over palladium yielded the 15-*cis*-carotenoids, which readily underwent stereomutation to give astacene and (11), respectively.

Reaction of the diosphenols with acetic anhydride gave the corresponding enol acetates. These are less strongly adsorbed than the parent diosphenols and are therefore more easily purified. On hydrolysis the diosphenols are regenerated.

Though the diosphenols exist predominantly in the enol form, they react with *o*-phenylenediamine to give the expected phenazine derivatives,[29] and with hydroxylamine under appropriate conditions to give the furazans.

Reduction of the diosphenols with potassium borohydride, gave the corresponding mono- or bis-α-glycols as mixtures of stereoisomers. Bodea *et al.*[30] reported that the mixture of tetraols (7) formed by borohydride reduction of ' natural ' astacene (4) could be separated by chromatography on magnesium carbonate into four fractions, the least polar of which resembled natural crustaxanthin. However, some other workers have been unable to repeat this separation.[31-33]

In the isolation of products with the 4-hydroxy-end group (e) it is important to avoid treatment with dilute acids in the presence of alcohols. As observed by Zechmeister *et al.*[34] with isozeaxanthin (14), and confirmed in the present studies with the acetylenic analogue (14′), and the triols (15) and (15′), this leads to rapid formation of the corresponding alkoxy-compounds. The acetylenic triol (15′) was also obtained in good yield by treatment of the diacetate of (5) with *N*-bromosuccinimide in the presence of acetic acid, and hydrolysis of the triacetate thus formed.

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Many polyene allylic alcohols on treatment with hydrogen chloride in chloroform undergo dehydration with extension of the chromophore.[35] The reaction is known to be complex with both isozeaxanthin (14)[34] and the mixture of tetraols (7),[30] but the acetylenic analogue (14′) of isozeaxanthin was dehydrated normally to give (16′). The reaction was therefore examined with the acetylenic α-glycols. The tetraol (7′) formed a mixture of ketones from which, after reduction with lithium aluminium hydride, 15,15′-didehydrozeaxanthin (17′) was isolated in low overall yield. The diol (5′) was similarly converted into 15,15′-didehydrocryptoxanthin (18′). Since the partial hydrogenation of (17′) and (18′) and the stereomutation of the products have previously been reported,[36,37] these transformations constitute new formal syntheses of zeaxanthin (17) and cryptoxanthin (18).

Selective oxidation of the synthetic α-glycols to the required α-ketols proved difficult. Though the 4- and 4′-hydroxy-groups are allylic, and might be expected to be oxidised readily, the resulting products are, as mentioned earlier, rapidly oxidised further to the diosphenols. In model studies with the acetylenic diol (5′) only traces of the required product (3′) were obtained with nickel peroxide and manganese dioxide, and with dichlorodicyano-*p*-benzoquinone the yields were variable and did not exceed 6%. Oppenauer oxidation of (5′) under carefully controlled conditions gave (3′) in 45% yield (15% conversion). The glycol (5) similarly gave hydroxyechinenone (3) in 35% yield (10% conversion). On autoxidation it yielded the diosphenol (11).

None of the required α-ketol (2′) could be detected on oxidation of the acetylenic triol (6′) with nickel peroxide, dichlorodicyano-*p*-benzoquinone, or the Oppenauer reagent, or on irradiation in the presence of *p*-chloranil

Principal n.m.r. bands (60 MHz; dilute solutions in $CDCl_3$)

| Diosphenols | C-1 Me's | C-5 Me | C-9 Me | C-13 Me | C-13′ Me | C-9′ Me | C-5′ Me | C-1′ Me's | Other |
|---|---|---|---|---|---|---|---|---|---|
| (4) | 1.30 | 2.10 | 2.02 | 2.02 | 2.02 | 2.02 | 2.10 | 1.30 | 6.06 (C-2 and C-2′ H) |
| (4′) | 1.30 | 2.08 | 2.05 | 2.12 | 2.12 | 2.05 | 2.08 | 1.30 | |
| (10) | 1.29 | 2.08 | 1.99 | 1.99 | 1.99 | 1.99 | 1.87 | 1.19 | |
| (10′) | 1.29 | 2.09 | 2.02 | 2.12 | 2.12 | 2.02 | 1.87 | 1.19 | |
| (11) | 1.30 | 2.08 | 1.98 | 1.98 | 1.98 | 1.98 | 1.72 | 1.02 | |
| (11′) | 1.29 | 2.08 | 2.04 | 2.12 | 2.12 | 1.99 | 1.72 | 1.03 | |
| (12) | 1.30 | 2.10 | 2.01 | 1.98 | 1.98 | 1.98 | 1.84 | 1.03, 1.06 | |
| 4′-Methoxy-(11′) | 1.28 | 2.10 | 2.02 | 2.07 | 2.07 | 1.96 | 1.78 | 1.01 | 3.37 (OMe) |
| Enol acetates | | | | | | | | | |
| (4) | 1.35 | 2.04 | 2.04 | 2.02 | 2.02 | 2.04 | 2.04 | 1.35 | 2.29 (OAc) |
| (4′) | 1.35 | 2.03 | 2.03 | 2.12 | 2.12 | 2.03 | 2.03 | 1.35 | 2.25 (OAc) |
| (10) | 1.33 | 2.02 | 1.98 | 1.98 | 1.98 | 1.98 | 1.87 | 1.19 | 2.27 (OAc) |
| (10′) | 1.35 | 2.04 | 2.04 | 2.13 | 2.13 | 2.04 | 1.87 | 1.19 | 2.28 (OAc) |
| (11) | 1.31 | 1.97 | 1.94 | 1.94 | 1.94 | 1.94 | 1.68 | 1.02 | 2.23 (OAc) |
| (11′) | 1.34 | 1.99 [a] | 2.03 [a] | 2.11 | 2.11 | 2.03 [a] | 1.70 | 1.01 | 2.28 (OAc) |
| 3-Hydroxy-4-ketones | | | | | | | | | |
| (1) | 1.20, 1.31 | 1.94 | 1.98 | 1.98 | 1.98 | 1.98 | 1.94 | 1.20, 1.31 | |
| (2) | 1.20, 1.30 | 1.93 | 1.97 | 1.97 | 1.97 | 1.97 | 1.82 | 1.18 | |
| (3) | 1.23, 1.32 | 1.95 | 1.99 | 1.99 | 1.99 | 1.99 | 1.73 | 1.04 | |
| (3′) | 1.21, 1.32 | 1.94 | 1.99 | 2.11 | 2.11 | 1.99 | 1.71 | 1.03 | |
| 4′-Methoxy-(3′) | 1.21, 1.31 | 1.92 | 1.98 | 2.10 | 2.10 | 1.98 | 1.78 | 1.03 | 3.39 (OMe) |
| Others | | | | | | | | | |
| (14) | 1.02, 1.04 | 1.84 | 1.97 | 1.97 | 1.97 | 1.97 | 1.84 | 1.02, 1.04 | |
| (14′) | 1.02 | 1.80 | 1.95 | 2.06 | 2.06 | 1.95 | 1.80 | 1.02 | |
| (13) | 1.02, 1.04 | 1.84 | 1.97 | 1.97 | 1.97 | 1.97 | 1.87 | 1.19 | |
| (13′) | 1.01, 1.04 | 1.82 | 1.97 | 2.09 | 2.09 | 1.97 | 1.85 | 1.17 | |
| (13′) Methyl ether | 1.17 | 1.85 | 1.96 | 2.10 | 2.10 | 1.96 | 1.78 | 1.01 | 3.37 (OMe) |
| (17) | 1.07 | 1.73 | 1.97 | 1.97 | 1.97 | 1.97 | 1.73 | 1.07 | |
| (17′) | 1.07 | 1.71 | 1.96 | 2.08 | 2.08 | 1.96 | 1.71 | 1.07 | |
| (18′) | 1.07 | 1.70 | 1.97 | 2.08 | 2.08 | 1.97 | 1.70 | 1.01 | |
| (14′) Dimethyl ether | 1.03 | 1.75 | 1.97 | 2.10 | 2.10 | 1.97 | 1.75 | 1.03 | 3.37 (OMe) |
| (16′) | 1.04 | 1.86 | 1.98 | 2.10 | 2.10 | 1.98 | 1.86 | 1.04 | *ca.* 2.05 (C-2 and C-2′ H's) |

[a] Assignment of these bands is arbitrary.

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[36] O. Isler, H. Lindlar, M. Montavon, R. Rüegg, G. Saucy, and P. Zeller, *Helv. Chim. Acta*, 1957, **40**, 456.

[37] O. Isler, H. Lindlar, M. Montavon, R. Rüegg, G. Saucy, and P. Zeller, *Helv. Chim. Acta*, 1956, **39**, 2041.

and iodine.[38] Use of manganese dioxide gave traces of the required product, and by further oxidation of the intermediate (19) with dichlorodicyano-*p*-benzoquinone the α-ketol (2′) was obtained in *ca.* 2% overall yield. A similar two-step oxidation of the triol (6) gave phoenicoxanthin (2); it did not separate on mixed t.l.c. with an authentic sample isolated from the wing feathers of *Phoenicopterus ruber*, and on autoxidation gave the diosphenol (10).

Though it is reported that allylic oxidation of the tetraols (7) cannot be achieved with nickel peroxide, or by the *p*-chloranil and iodine method,[39] treatment with dichlorodicyano-*p*-benzoquinone, and isolation of the product after 15 min, gave astaxanthin (1) in *ca.* 2% yield. The acetylenic tetraols (7′) similarly gave 15,15′-didehydroastaxanthin (1′) which, on partial hydrogenation of the triple bond and stereomutation of the initial product, also gave astaxanthin. The synthetic products were compared directly with astaxanthin from the lobster *Homarus gammarus*, and from the sea water crayfish *Jasus lalandei*. The diacetate was also compared with an authentic sample. For additional confirmation a sample of synthetic astaxanthin was sent to Dr. P. F. Zagalsky who showed that, like natural astaxanthin,[40] it combined with the appropriate apoprotein to give the blue carotenoprotein, α-crustacyanin. Recently Hodler *et al.*[41] have reported that oxidation of the tetraols (7) with chromium trioxide on graphite gives the oxo-triol, idoxanthin (20).

The characteristic n.m.r. bands of most of the compounds reported above are summarised in the Table. With the diosphenol end group (b) a band due to the protons of the geminal methyl groups is found near δ 1.30, and another due to the C-5 methyl protons in the range δ 2.08—2.10. In the corresponding enol acetates these bands are shifted to positions near δ 1.35 and 2.03, respectively. The two geminal methyl groups in the astaxanthin type end group (d) experience different shielding from one another and are associated with separate signals near δ 1.21 and 1.32; the C-5 methyl has a band near δ 1.94.

The mass spectra of the diosphenols and their acetates, and of the α-ketols, are discussed elsewhere.[42-44]

## EXPERIMENTAL

Unless indicated to the contrary, n.m.r. spectra were determined at 60 MHz for dilute solutions in deuteriochloroform, and i.r. spectra for solutions in chloroform. Selected bands only are quoted for n.m.r., i.r., and mass spectra.

Apart from the autoxidation experiments, polyenes were handled in an inert atmosphere, usually nitrogen, without exposure to bright light. Solutions were evaporated under reduced pressure.

M.p.s were determined for samples in evacuated capillary tubes and are corrected. T.l.c. was normally performed on Kieselgel H (Merck); eluants are indicated in parentheses. Light petroleum refers to the fraction of b.p. 60—80°.

*Astacene* (*3,3′-Dihydroxy-2,3,2′,3′-tetradehydro-β,β-carotene-4,4′-dione*) (4).—A solution of canthaxanthin (β,β-carotene-4,4′-dione) (1.0 g) in benzene (15 ml) was added to one of potassium t-butoxide in t-butyl alcohol (1.40N; 130 ml), and the mixture was shaken at 20 °C in oxygen for 30 h. Water (200 ml) was added, followed by 0.5N-hydrochloric acid (800 ml), and the product was extracted with chloroform (300 ml). The extract was washed with saturated aqueous sodium hydrogen carbonate (3 × 300 ml) and then with water (2 × 300 ml). Benzene (50 ml) was added and the solution was evaporated under reduced pressure. Crystallisation of the residue from chloroform–ethanol (1 : 5) gave astacene (540 mg) as deep purple leaflets, m.p. 232—233°; $\lambda_{max.}$ (pyridine) 498 nm ($10^{-3}\varepsilon$ 100); $\lambda_{max.}$ ($CS_2$) 513 nm; $\lambda_{max.}$ (hexane) 477 nm; $\lambda_{max.}$ (EtOH) 483 nm; $\lambda_{max.}$ (KOH–EtOH) 478 nm; $\nu_{max.}$ ($CHCl_3$) 3 410br (ε *ca.* 90), 1 610 (1 200), 1 550, 1 327, and 969 (895) $cm^{-1}$; $\nu_{max.}$ ($CCl_4$) 3 410 (sharp; ε *ca.* 125) $cm^{-1}$; δ see Table; *m/e* 592 ($M^{+\cdot}$) (Found: O, 10.8, 10.85. Calc. for $C_{40}H_{48}O_4$: O, 10.8%). In other experiments yields of up to 90% were obtained.

The product did not separate from authentic astacene (derived from lobsters) in mixed chromatograms on sucrose [benzene–light petroleum (1 : 4) as eluant]. The spectral properties of the ' natural ' and synthetic samples were in good agreement, and there was no depression in m.p. on admixture.

Acetic anhydride (0.043 ml) was added to astacene (68 mg) in pyridine (2 ml) and the mixture was kept at 25 °C for 24 h. Methanol (0.02 ml) was added to decompose the excess of anhydride, and then water (1.0 ml). The mixture was kept at 0 °C for 24 h, and the product was then collected and washed with 50% aqueous pyridine. Crystallisation from chloroform–ethanol (1 : 5) gave astacene diacetate (27 mg), m.p. 232—233° (decomp.); $\lambda_{max.}$ (pyridine) 497 nm ($10^{-3}\varepsilon$ 109); $\lambda_{max.}$ (EtOH) 474 nm; $\nu_{max.}$ ($CHCl_3$) 1 756 (ε 530), 1 639 (1 150), 1 555, and 972 $cm^{-1}$; δ see Table; *m/e* 676 ($M^{+\cdot}$, $C_{44}H_{52}O_6$). The i.r. spectrum was in good agreement with that of an authentic specimen. For the naturally derived diacetate, Kuhn *et al.*[45] give m.p. 235° (decomp.).

A solution of astacene (125 mg) and (freshly purified) *o*-phenylenediamine (157 mg) in glacial acetic acid (10 ml) was heated in the dark at 100 °C for 90 min and then cooled. Water (200 ml) was added and the product was extracted with chloroform (40 ml). The extract was washed successively with N-hydrochloric acid, saturated aqueous sodium hydrogen carbonate, and water. Benzene (50 ml) was added and the solution then evaporated under reduced pressure. Chromatography of the residue on alumina (grade IV) with benzene–light petroleum as eluant, collection of the main purple-red band, evaporation, and crystallisation of the residue (39 mg) from chloroform–

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ethanol (1 : 1) gave the bisphenazine derivative as purple needles (21 mg), m.p. 231°; $\lambda_{max.}$ (pyridine) 503 nm ($10^{-3}\varepsilon$ 140); $\lambda_{max.}$ ($CS_2$) 517 nm; $\nu_{max.}$ ($CHCl_3$) 1 550, 1 391, and 969 (ε 800) $cm^{-1}$ (Found: N, 7.6. Calc. for $C_{52}H_{56}N_4$: N, 7.6%). The product did not separate in a mixed chromatogram from an authentic sample which had an identical i.r. spectrum. For the naturally derived material Kuhn *et al.*[46] give m.p. 224—225°, $\lambda_{max.}$ ($CS_2$) 515 nm.

A mixture of astacene (500 mg), hydroxylamine hydrochloride (800 mg), and pyridine (20 ml) was boiled under reflux for 2 h, then cooled and poured into water. The product was isolated with chloroform and crystallised from dichloromethane–methanol to give the *difurazan* (420 mg) as prisms, m.p. 221°; $\lambda_{max.}$ ($CHCl_3$) 472 nm ($10^{-3}\varepsilon$ 91); $\nu_{max.}$ (KBr) 3 400 and 960 $cm^{-1}$; δ (pyridine) 1.15 (12 H, s), 2.02 (12 H, s), 2.28 (6 H, s), and 2.96 (4 H, s) (Found: $M^{+\cdot}$ 616.372. $C_{40}H_{48}N_4O_2$ requires *M*, 616.378).

15,15′-*Didehydroastacene* (4′).—A mixture of 15,15′-didehydrocanthaxanthin (1.2 g) in benzene (25 ml), and potassium t-butoxide in t-butyl alcohol (1.3N; 170 ml) was shaken in oxygen. After the initial uptake of oxygen had subsided (1 min), the reaction was allowed to continue until 2 mol. equiv. had been absorbed; t.l.c. then showed the absence of didehydrocanthaxanthin. Water (300 ml) was added, followed by 0.5N-hydrochloric acid (950 ml) and chloroform (300 ml). The chloroform extract was washed well with saturated sodium hydrogen carbonate solution and then with water. Removal of the solvents under reduced pressure gave a red solid (1.19 g, 95%), m.p. 196—200°. Recrystallisation from benzene–ethanol gave 15,15′-*didehydroastacene* as plates, m.p. 200—201°; $\lambda_{max.}$ ($C_6H_6$) 460 nm ($10^{-3}\varepsilon$ 90); $\lambda_{max.}$ (pyridine) 466 nm ($10^{-3}\varepsilon$ 90); $\lambda_{max.}$ ($CHCl_3$) 460 nm; $\nu_{max.}$ 3 423, 2 146, 1 618 (ε 1 180), 1 565, 970, and 957 $cm^{-1}$; δ see Table; *m/e* 590 ($M^{+\cdot}$) (Found: C, 81.5; H, 7.9; O, 11.0. $C_{40}H_{46}O_4$ requires C, 81.3; H, 7.85, O, 10.8%). The *diacetate* crystallised from benzene–light petroleum as red plates, m.p. 219—221°; $\lambda_{max.}$ (pyridine) 460 nm ($10^{-3}\varepsilon$ 94.4); $\nu_{max.}$ 2 018, 1 760, 1 650, 1 610, and 985 $cm^{-1}$; δ see Table; *m/e* 674 ($M^{+\cdot}$) (Found: C, 78.0; H, 7.5; O, 14.75. $C_{44}H_{52}O_6$ requires C, 78.3; H, 7.5; O, 14.3%).

15-cis-*Astacene*.—15,15′-Didehydroastacene (52.4 mg) in ethyl acetate (5 ml) containing a trace of quinoline was shaken in the dark under hydrogen in the presence of Lindlar catalyst (80 mg). The reaction ceased after 1.1 mol. equiv. of hydrogen had been absorbed. The catalyst and solvent were removed, and the residue was crystallised from chloroform–ethanol to give 15-*cis*-astacene (45 mg), m.p. 156°; $\lambda_{max.}$ (pyridine) 487 and 401 nm ($10^{-3}\varepsilon$ 59.1 and 33.7); $\nu_{max.}$ 3 410, 1 708, and 1 617 $cm^{-1}$; $\nu_{max.}$ ($CS_2$) 1 064, 971, and 784 $cm^{-1}$.

A solution of 15-*cis*-astacene (40 mg) in benzene (1 l) containing a trace of iodine was exposed to light (100 W bulb) for 4 h, until the peak at λ 401 nm had disappeared. The solution was washed with aqueous sodium thiosulphate, and then with water. The solvent was evaporated off, and the residue was crystallised from chloroform–ethanol giving astacene (35 mg), m.p. 233°; $\lambda_{max.}$ (pyridine) 498 nm. The m.p. of the product was undepressed on admixture with an authentic sample from which it did not separate on reverse-phase t.l.c. (90% aqueous acetone as eluant).

*Phoeniconone* (3-*Hydroxy*-2,3-*didehydro*-β,β-*carotene*-4,4′-*dione*) (10).—A solution of canthaxanthin (1.4 g) in benzene (200 ml) was added to potassium t-butoxide (15 g) in t-butyl alcohol (600 ml) and the mixture was shaken in oxygen. The reaction was monitored by t.l.c. and was interrupted after 4 h when most of the canthaxanthin had reacted. The crude product was isolated in the usual way and dissolved in pyridine (120 ml). Acetic anhydride (5 ml) was added and the mixture kept at 15 °C for 15 h. Chloroform was added and the solution was washed with water and then evaporated. Preparative t.l.c. of the residual red gum on kieselgel plates (20% acetone–light petroleum), isolation of the product from the middle band, and crystallisation from methanol gave *phoeniconone acetate* (185 mg), m.p. 153—154°; $\lambda_{max.}$ ($CHCl_3$) 486 nm; $\lambda_{max.}$ ($C_6H_6$) 482 nm ($10^{-3}\varepsilon$ 105); $\nu_{max.}$ ($CHCl_3$) 1 755, 1 650, 1 615, and 975 $cm^{-1}$; δ see Table; *m/e* 620 ($M^{+\cdot}$, $C_{42}H_{52}O_4$).

Aqueous 5% sodium hydroxide (10 ml) was added to a solution of phoeniconone acetate (185 mg) in benzene (650 ml) and ethanol (1 350 ml), and the mixture was kept at 15 °C for 12 h. Benzene was added, and the solution was washed thoroughly with water. Evaporation, and crystallisation of the residue from chloroform–ethanol gave phoeniconone (170 mg) as purple needles, m.p. 210°; $\lambda_{max.}$ (pyridine) 490 nm; $\lambda_{max.}$ ($CHCl_3$) 487 nm; $\lambda_{max.}$ ($C_6H_6$) 485 nm ($10^{-3}\varepsilon$ 100); $\nu_{max.}$ 3 450, 1 685, 1 655, 1 625, and 975 $cm^{-1}$; δ see Table (Found: $M^{+\cdot}$, 578.375. Calc. for $C_{40}H_{50}O_3$: *M*, 578.376); *m/e* 486 (*M* − 92) and 472 (*M* − 106). The *phenazine derivative* had m.p. 194—196°; $\lambda_{max.}$ ($C_6H_6$) 498 nm ($10^{-3}\varepsilon$ 101); $\nu_{max.}$ 980 $cm^{-1}$ (Found: N, 4.35. $C_{46}H_{54}N_2O$ requires N, 4.3%).

15,15′-*Didehydrophoeniconone* (10′).—Autoxidation of 15,15′-didehydrocanthaxanthin (1.4 g) in benzene (200 ml) in the presence of potassium t-butoxide (10 g) in t-butyl alcohol (600 ml) as in the previous experiment, isolation of the crude product after acetylation, and crystallisation from methanol, gave the *acetate* (285 mg) as plates, m.p. 173—175°; $\lambda_{max.}$ ($C_6H_6$) 451 nm ($10^{-3}\varepsilon$ 85); $\nu_{max.}$ 2 170, 1 760, 1 650, 1 610, and 975 $cm^{-1}$; δ see Table; *m/e* 618 ($M^{+\cdot}$, $C_{42}H_{50}O_4$).

Hydrolysis of the acetate (280 mg) as in the previous experiment, and crystallisation from chloroform–ethanol, gave 15,15′-*didehydrophoeniconone* (267 mg) as needles, m.p. 186—187°; $\lambda_{max.}$ (pyridine) 457 nm ($10^{-3}\varepsilon$ 82.3); $\lambda_{max.}$ ($C_6H_6$) 454 nm ($10^{-3}\varepsilon$ 84); $\nu_{max.}$ 3 450, 2 170, 1 685, 1 655, 1 620, and 975 $cm^{-1}$; δ see Table (Found: $M^{+\cdot}$, 576.364. $C_{40}H_{48}O_3$ requires *M*, 576.360).

15-cis-*Phoeniconone Acetate*.—A solution of 15,15′-didehydrophoeniconone acetate (150 mg) in ethyl acetate (130 ml), containing a trace of quinoline, was shaken in hydrogen in the presence of Lindlar catalyst (150 mg) at 15 °C for 12 h. Removal of catalyst and solvent gave the 15-*cis*-polyene; $\lambda_{max.}$ ($CHCl_3$) 471 and 390 nm.

A solution of the *cis*-polyene in benzene (500 ml), containing a trace of iodine, was irradiated with a 100 W tungsten filament lamp for 2 h. The mixture was washed with aqueous sodium thiosulphate, then with water, and evaporated. Crystallisation of the residue from methanol gave phoeniconone acetate (130 mg), m.p. and mixed m.p. with the sample described earlier, 153—154°. The two samples had identical light absorption properties, and did not separate on mixed t.l.c.

3-*Hydroxy*-2,3-*didehydro*-β,β-*caroten*-4-*one* (11).—A mixture of echinenone (ββ-caroten-4-one) (500 mg) in benzene (80 ml) and potassium t-butoxide (4.0 g) in t-butyl alcohol (100 ml) was shaken in oxygen at 15 °C for 18 h, and then poured onto ice-cold 2N-hydrochloric acid. The product was extracted with benzene, and the extract was washed

[46] R. Kuhn, J. Stene, and N. A. Sørensen, *Ber.*, 1939, **72**, 1688.

with aqueous sodium hydrogen carbonate and then with water. Evaporation of this solution to a small volume and addition of a small amount of methanol gave the diosphenol (425 mg) as prisms, 173—174°; $\lambda_{max.}$ (pyridine) 486 nm ($10^{-3}\varepsilon$ 114); $\lambda_{max.}$ ($CHCl_3$) 487 nm; $\lambda_{max.}$ (petroleum) 469 nm; $\lambda_{max.}$ (MeOH) 472 nm; $\nu_{max.}$ 3 413, 1 618, and 970 $cm^{-1}$; δ see Table; *m/e* 564 ($M^{+\cdot}$) (Found: C, 84.95; H, 9.55; O, 5.95. $C_{40}H_{52}O_2$ requires C, 85.05; H, 9.3; O, 5.65%).

The *acetate* crystallised from chloroform–ethanol as rhombs, m.p. 176—177°; $\lambda_{max.}$ ($C_6H_6$) 477 nm ($10^{-3}\varepsilon$ 110); $\lambda_{max.}$ ($CHCl_3$) 482; $\lambda_{max.}$ (EtOH) 473 nm; $\nu_{max.}$ 1 758, 1 680, 1 650, 1 610, and 975 $cm^{-1}$; δ see Table (Found: $M^{+\cdot}$, 606.403. $C_{42}H_{54}O_3$ requires *M*, 606.407); *m/e* 564 (*M* − 42), 548, 518 (*M* − 92), 500 (*M* − 106), 476, and 458.

The *furazan* crystallised from acetone–light petroleum as prisms, m.p. 189—190°; $\lambda_{max.}$ ($CHCl_3$) 470 nm ($10^{-3}\varepsilon$ 101); $\nu_{max.}$ 970 $cm^{-1}$; δ 1.03 (6 H, s), 1.11 (6 H, s), 1.71 (3 H, s), 1.97br (15 H), and 2.76 (2 H, s); δ (pyridine) 1.10 (6 H, s), 1.14 (6 H, s), 1.79 (3 H, s), 2.07br (16 H), 2.25 (3 H, s), and 2.90 (2 H, s) (Found: $M^{+\cdot}$, 576.410. $C_{40}H_{52}N_2O$ requires *M*, 576.408).

3-*Hydroxy*-2,3,15,15′-*tetradehydro*-β,β-*caroten*-4-*one* (11′).—Autoxidation of 15,15′-didehydroechinenone (1.5 g), isolation of the product as in the previous experiment, and crystallisation from benzene–ethanol, gave the *diosphenol* (1.0 g) as purple red prisms, m.p. 155—156°; $\lambda_{max.}$ (pyridine) 461 nm ($10^{-3}\varepsilon$ 87.5); $\lambda_{max.}$ ($C_6H_6$) 454 nm; $\lambda_{max.}$ ($CHCl_3$) 455 nm; $\nu_{max.}$ 3 413, 2 169, 1 692, 1 621, 1 560, and 971 $cm^{-1}$; δ see Table; *m/e* 562 ($M^{+\cdot}$) (Found: C, 85.6; H, 9.0; O, 5.75. $C_{40}H_{50}O_2$ requires C, 85.35; H, 8.95; O, 5.7%).

The *acetate*, crystallised from chloroform–ethanol, had m.p. 115—116°; $\lambda_{max.}$ (pyridine) 453 nm; $\lambda_{max.}$ ($CHCl_3$) 448 nm; $\nu_{max.}$ 2 141, 1 755, 1 680, 1 645, 1 610, and 975 $cm^{-1}$; δ see Table; *m/e* 618 ($M^{+\cdot}$, $C_{42}H_{52}O_3$).

The *phenazine* derivative crystallised from chloroform–ethanol as red prisms, m.p. 146—147°; $\lambda_{max.}$ (pyridine) 469 nm ($10^{-3}\varepsilon$ 90); $\nu_{max.}$ 2 169, 1 070, and 971 $cm^{-1}$; δ 1.04, 1.21, 1.26, 1.73, 2.00, 2.08, 2.13, 2.38, and 3.10 (Found: C, 86.6; H, 8.8; N, 4.6. $C_{46}H_{54}N_2$ requires C, 87.0; H, 8.6; N, 4.4%).

A mixture of the diosphenol (200 mg), hydroxylamine hydrochloride (300 mg), and pyridine (50 ml) was boiled under reflux for 10 min. Isolation of the product in the usual way, preparative t.l.c. (20% acetone–light petroleum), and crystallisation from acetone–light petroleum gave the *mono-oxime* (110 mg) as needles, m.p. 192—193°; $\lambda_{max.}$ ($CHCl_3$) 457 nm ($10^{-3}\varepsilon$ 88); $\nu_{max.}$ (KBr) 3 220, 2 140, 1 657, 960, and 950 $cm^{-1}$; δ 1.02 (6 H, s), 1.22 (6 H, s), 1.70 (3 H, s), 1.97br (9 H), 2.09 (6 H, s), and 2.87 (2 H, s) (Found: $M^{+\cdot}$, 577.391. $C_{40}H_{51}NO_2$ requires *M*, 577.391).

15-cis-3-*Hydroxy*-2,3-*didehydro*-β,β-*caroten*-4-*one*.—A solution of the preceding acetylenic diosphenol (60 mg) in ethyl acetate (6 ml) containing a trace of quinoline was shaken in the dark in hydrogen in the presence of Lindlar catalyst (90 mg) until 1.1 mol. equiv. of hydrogen had been absorbed. Removal of catalyst and solvent, and crystallisation of the residue from benzene–methanol at −15 °C, gave the 15-*cis*-polyene (48 mg) as purple prisms, m.p. 132—133°; $\lambda_{max.}$ (pyridine) 481 and 375 nm ($10^{-3}\varepsilon$ 53.8 and 30.5); $\nu_{max.}$ 3 410, 1 617, and 1 555 $cm^{-1}$; $\nu_{max.}$ ($CS_2$) 1 063, 1 055, and 783 $cm^{-1}$.

A solution of the *cis*-polyene (110 mg) in benzene (1 l), containing a trace of iodine, was irradiated with a 100 W tungsten filament lamp for 2 h. Isolation of the product in the usual way, and crystallisation from benzene–light petroleum, gave 3-hydroxy-2,3-didehydro-β,β-caroten-4-one (100 mg), m.p. 173—174°, undepressed on admixture with the sample described above, from which it did not separate on mixed t.l.c.

3,4′-*Dihydroxy*-2,3-*didehydro*-β,β-*caroten*-4-*one* (12).—A solution of *N*-bromosuccinimide (21.5 mg) in (ethanol-free) chloroform (5 ml) and acetic acid (0.15 ml) was added to a stirred solution of 3-hydroxy-2,3-didehydro-β,β-caroten-4-one (50 mg) in (ethanol-free) chloroform, and the mixture was kept at −20 °C for 45 s. *N*-Ethylmorpholine (0.6 ml) was added and the mixture allowed to warm to 15 °C. Chloroform was added, and the solution was washed with water and then evaporated. Methanolic 15% potassium hydroxide was added to the residue, and the mixture was kept at 15 °C for 30 min. Chloroform was added, and the solution was washed successively with 2N-hydrochloric acid, aqueous sodium hydrogen carbonate, and water. Evaporation, preparative t.l.c. (30% acetone–light petroleum), and crystallisation from benzene–ethanol, gave 3,4′-*dihydroxy*-2,3-*didehydro*-β,β-*caroten*-4-*one* (20 mg) as needles, m.p. 149—150°; $\lambda_{max.}$ ($CHCl_3$) 476—480 nm; $\lambda_{max.}$ ($C_6H_6$) 484 nm ($10^{-3}\varepsilon$ 116); $\nu_{max.}$ ($CCl_4$) 3 420, 1 680, 1 625, 1 073, and 970 $cm^{-1}$; δ see Table (Found: $M^{+\cdot}$ 580.386. $C_{40}H_{52}O_3$ requires *M*, 580.391), *m/e* 562 (*M* − 18) and 546.

The same product, together with canthaxanthin and 3-hydroxy-3,4-didehydro-β,β-carotene-4,4′-dione, was obtained on autoxidation of 4′-hydroxy-β,β-caroten-4-one [47] in the usual way.

15,15′-*Didehydro*-β,β-*carotene*-4,4′-*diol* (14′).—Lithium aluminium hydride (900 mg) was added to a solution of 15,15′-didehydrocanthaxanthin (900 mg) in benzene (750 ml) and ether (750 ml), and the mixture was kept at 15 °C for 10 min. Methanol was added carefully to decompose the excess of hydride and the mixture was poured onto ice-cold 2N-hydrochloric acid. The product was isolated with benzene. Crystallisation from acetone–light petroleum gave the diol (520 mg) as needles, m.p. 186—199°; $\lambda_{max.}$ ($C_6H_6$) 465 and 439 ($10^{-3}\varepsilon$ 78 and 93.5); $\lambda_{max.}$ (petroleum) 452 and 427 nm; δ see Table [Isler *et al.*[48] give m.p. 188—190°; $\lambda_{max.}$ (petroleum) 458 and 430 nm]. 2N-Hydrochloric acid (2 ml) was added to a solution of the diol (30 mg) in chloroform (20 ml) and methanol (200 ml). After 1 h the product was isolated in the usual way giving the dimethyl ether (15 mg), which crystallised from light petroleum–methanol and had m.p. 157—160°; $\lambda_{max.}$ (light petroleum) 454 and 430 nm ($10^{-3}\varepsilon$ 83.7 and 101.4); $\nu_{max.}$ 970 $cm^{-1}$; δ see Table.

3,4,15,3′,4′,15′-*Hexadehydro*-β,β-*carotene* (16′).—A saturated solution of hydrogen chloride in (ethanol-free) chloroform (25 drops) was added to one of the 15,15′-didehydro-β,β-carotene-4,4′-diol (130 mg) in the same solvent (40 ml). After 1 h the solution was washed with saturated aqueous sodium hydrogen carbonate and then with water. Evaporation of the solvent, chromatography of the residue in benzene–light petroleum on alumina (grade IV), and crystallisation from ethanol–light petroleum gave the hydrocarbon (30 mg), m.p. 170—172°; $\lambda_{max.}$ (light petroleum) 449 nm ($10^{-3}\varepsilon$ 107.5); $\nu_{max.}$ 970 $cm^{-1}$; δ see

[47] S. Liaaen-Jensen, *Acta Chem. Scand.*, 1965, **19**, 1166.
[48] O. Isler, H. Lindlar, M. Montavon, R. Rüegg, and P. Zeller, *Helv. Chim. Acta*, 1956, **39**, 449.
[49] O. Isler, H. Lindlar, M. Montavon, R. Rüegg, and P. Zeller, *Helv. Chim. Acta*, 1956, **39**, 274.

Table [Isler *et al.*[49] give m.p. 165—167° (uncorr.); $\lambda_{max.}$ (petroleum) 449 nm].

*4-Hydroxy-15,15′-didehydro-β,β-caroten-4′-one* (13′).—*p*-Chloranil (1.5 g) was added to a solution of the 15,15′-didehydro-β,β-carotene-4,4′-diol (500 mg) in benzene (2.5 l) and ethanol (250 ml). Iodine (3 mg) in light petroleum (10 ml) was added and the mixture was irradiated with two 60 W tungsten filament lamps for 2.5 h;[47] t.l.c. then indicated that all the diol had reacted. The mixture was washed with aqueous sodium thiosulphate, then with water, and evaporated. The residue in benzene was added to a column of alumina (grade IV) and the chromatogram was developed with 0.2% methanol–benzene. Isolation of the main product, and crystallisation from acetone, gave the *hydroxy-ketone* (300 mg), m.p. 178—179°; $\lambda_{max.}$ ($C_6H_6$) 443 nm ($10^{-3}\varepsilon$ 92.5); $\nu_{max.}$ 3 550, 2 190, 1 658, 1 615, and 970 $cm^{-1}$; δ see Table (Found: $M^{+\cdot}$, 564.396. $C_{40}H_{56}O_2$ requires *M*, 564.397).

*4′-Methoxy-15,15′-didehydro-β,β-caroten-4-one.* 2N-Hydrochloric acid (10 drops) was added to a solution of the preceding hydroxy-ketone (300 mg) in chloroform (20 ml) and methanol (200 ml), and the mixture was kept at 15 °C for 5 min. Benzene was added and the mixture was washed with aqueous sodium hydrogen carbonate and then with water. Evaporation, and crystallisation of the residue from acetone gave the *methoxy-ketone* (250 mg), m.p. 153°; $\lambda_{max.}$ ($C_6H_6$) 443 nm ($10^{-3}\varepsilon$ 92); $\nu_{max.}$ 2 190, 1 658, 1 615, 1 095, and 975 $cm^{-1}$; δ see Table (Found: $M^{+\cdot}$ 578.411. $C_{41}H_{54}O_2$ requires *M*, 578.412).

*3-Hydroxy-4′-methoxy-2,3,15,15′-tetradehydro-β,β-caroten-4-one.*—Autoxidation of the preceding methoxy-ketone (100 mg) in benzene (20 ml) in the presence of potassium t-butoxide (1.5 g) in t-butyl alcohol (60 ml), isolation of the product, preparative t.l.c. (25% acetone–light petroleum), and crystallisation from acetone, gave the *methoxy-diosphenol* (85 mg) as prisms, m.p. 175—176°; $\lambda_{max.}$ ($CHCl_3$) 448 nm; $\lambda_{max.}$ (petroleum) 434 nm; $\lambda_{max.}$ ($C_6H_6$) 447 nm ($10^{-3}\varepsilon$ 90); $\nu_{max.}$ 2 190, 1 685, 1 623, 1 080, and 975 $cm^{-1}$; δ see Table (Found: $M^{+\cdot}$, 592.392. $C_{41}H_{52}O_3$ requires *M*, 592.390).

The *acetate* had $\lambda_{max.}$ ($CHCl_3$) 445 nm (Found: $M^{+\cdot}$, 634.404. $C_{43}H_{54}O_4$ requires *M*, 634.402); *m/e* 602 (*M* − 32), 592 (*M* − 42), and 560.

Reduction of the methoxy-diosphenol in chloroform–methanol with potassium borohydride gave the corresponding *4′-methoxy-15,15′-didehydro-β,β-carotene-3,4-diol*, m.p. 166°; $\lambda_{max.}$ ($CHCl_3$) 462 and 437 nm; $\nu_{max.}$ 3 500br, 2 190, 1 095, and 975 $cm^{-1}$; δ 1.02br (12 H), 1.78 (6 H, s), 1.96 (6 H, s), 2.09 (6 H, s), and 3.37 (3 H, s) (Found: $M^{+\cdot}$, 596.418. $C_{41}H_{56}O_3$ requires *M*, 596.423).

*15,15′-Didehydro-β,β-carotene-3,4-diol* (5′).—Potassium borohydride (250 mg) was added to a solution of 3-hydroxy-2,3,15,15′-tetradehydro-β,β-caroten-4-one (200 mg) in chloroform (4 ml) and ethanol (200 ml). The mixture was boiled under reflux for 2 h, then cooled and poured onto ice-cold 2N-hydrochloric acid. Isolation of the product with chloroform and crystallisation from chloroform–methanol gave the diol (95 mg) as plates, m.p. 180°; $\lambda_{max.}$ ($CHCl_3$) 440 nm; $\lambda_{max.}$ ($C_6H_6$) 463 and 440 nm; $\nu_{max.}$ ($CCl_4$) 3 610, 3 400, 2 150, and 970 $cm^{-1}$; δ 1.04 and 1.08 (12 H), 1.72 (3 H, s), 1.82 (3 H, s), 1.98 (6 H, s), and 2.12 (6 H, s).

Treatment of the diol (80 mg) in pyridine (16 ml) with acetic anhydride (0.8 ml) at 15 °C for 5 h gave the diacetate (50 mg), which crystallised from benzene–ethanol and had m.p. 150—151°; $\lambda_{max.}$ ($C_6H_6$) 463 and 400 nm ($10^{-3}\varepsilon$ 79.6 and 95.1); $\nu_{max.}$ ($CCl_4$) 2 170, 1 760, 1 250, and 970 $cm^{-1}$; δ 1.03 (6 H, s), 1.08 (3 H, s), 1.14 (3 H, s), 1.65 (3 H, s), 1.71 (3 H, s), 1.98—2.08br (9 H), and 2.11 (9H, s) (Found: $M^{+\cdot}$ 650.426. $C_{44}H_{58}O_4$ requires *M*, 650.433); *m/e* 590 (*M* − 60), 560 (*M* − 90), and 546 (*M* − 104).

*15,15′-Didehydro-β,β-caroten-3-ol* (18′).—A saturated solution of hydrogen chloride in (ethanol-free) chloroform (25 drops) was added to one of 15,15′-didehydro-β,β-carotene-3,4-diol (245 mg) in the same solvent (100 ml). The mixture was kept at 20 °C for 24 h, then washed successively with saturated sodium hydrogen carbonate and water, and evaporated. Rapid chromatography of the residue in benzene on alumina (grade IV), collection of the main band, and evaporation, gave a mixture of ketones. Lithium aluminium hydride (500 mg) was added to the ketones in ether (100 ml). After 10 min methanol was added to decompose the excess of hydride and the product was isolated in the usual way. Chromatography from benzene on alumina (grade IV) yielded 15,15′-didehydro-β,β-caroten-3-ol (16 mg) as orange needles, m.p. and mixed m.p. 162—164°; $\lambda_{max.}$ (petroleum) 458 and 431 nm ($10^{-3}\varepsilon$ 86 and 107.5); $\nu_{max.}$ 3 600, 2 170, and 980 $cm^{-1}$; δ see Table [Isler *et al.*[37] give m.p. 161—162.5° (uncorr.); $\lambda_{max.}$ (petroleum) 458 and 432 nm]. The product and an authentic sample did not separate on mixed t.l.c.

*3-Hydroxy-15,15′-didehydro-β,β-caroten-4-one* (3′).—(i) A mixture of the preceding diol (100 mg) and aluminium t-butoxide (120 mg) in dichloromethane (20 ml) and acetone (0.3 ml) was boiled under reflux for 72 h, then cooled and poured into ice-cold 2N-hydrochloric acid. The crude product was isolated with chloroform. Preparative t.l.c. (5% acetone–benzene) gave the starting diol (65 mg) and the *hydroxy-ketone* (16 mg), which crystallised from dichloromethane–light petroleum as prisms, m.p. 165—166°; $\lambda_{max.}$ ($C_6H_6$) 448 nm ($10^{-3}\varepsilon$ 85); $\lambda_{max.}$ ($CHCl_3$) 448 nm; $\lambda_{max.}$ (petroleum) 434 nm; $\nu_{max.}$ 3 510, 2 160, 1 662, 1 610, and 970 $cm^{-1}$; δ see Table (Found: $M^{+\cdot}$, 564,401. $C_{40}H_{52}O_2$ requires *M*, 564,397); *m/e* 549 (*M* − 15), 548 (*M* − 16), 474 (*M* − 90), and 460 (*M* − 104).

(ii) 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone (50 mg) in dioxan (10 ml) was added to 15,15′-didehydro-β,β-carotene-3,4-diol (50 mg) in dioxan (10 ml), and the mixture was kept at 20 °C for 15 h. Chloroform was added and the solution was washed with 2N-sodium hydroxide, and then with water. Evaporation and preparative t.l.c. gave the hydroxy-ketone (3 mg), identical with the sample prepared in (i).

(iii) Oxidation of the diol in acetone with manganese dioxide gave the required hydroxy-ketone in <10% yield. Oxidation of the diol in benzene-ether with nickel peroxide also gave some hydroxy-ketone.

*β,β-Carotene-3,4-diol* (5).—Reduction of 3-hydroxy-2,3-didehydro-β,β-caroten-4-one (250 mg) in chloroform (4 ml) and ethanol (200 ml) with potassium borohydride (275 mg), as described for the acetylenic analogue, and chromatography on alumina (0.5% methanol–benzene) gave the diol (140 mg). A sample (20 mg) was submitted to preparative t.l.c. (25% acetone–light petroleum). Isolation of the main fraction, and crystallisation from dichloromethane–light petroleum, gave an isomer (15 mg) of the *diol* as prisms, m.p. 169—170°; $\lambda_{max.}$ ($CHCl_3$) 457 nm; $\lambda_{max.}$ (EtOH) 475 and 450 nm; $\lambda_{max.}$ ($C_6H_6$) 491 and 463 nm ($10^{-3}\varepsilon$ 101.3 and 113.6); $\nu_{max.}$ 3 600 and 975 $cm^{-1}$; δ 1.04 and 1.08 (12 H), 1.72 (3 H, s), 1.82 (3 H, s), and 1.97 (12 H, s) (Found: $M^{+\cdot}$, 568.429. $C_{40}H_{56}O_2$ requires *M*, 568.428); *m/e* 550 (*M* − 18) and 534.

Treatment of the diol (mixture of isomers; 520 mg) in pyridine (100 ml) with acetic anhydride (5 ml) at 15 °C for 15 h, and crystallisation of the product from dichloromethane–methanol gave the *diacetate* (170 mg), m.p. 109—110°; $\lambda_{max.}$ ($CHCl_3$) 486 and 462 nm ($10^{-3}\varepsilon$ 86.1 and 102.5); $\nu_{max.}$ 1 730 and 975 $cm^{-1}$; δ 1.02 (6 H, s), 1.07 (3 H, s), 1.13 (3 H, s), 1.64 (3 H, s), 1.70 (3 H, s), 1.95 (12 H, s), 2.00 (3 H, s), and 2.07 (3 H, s) (Found: $M^{+\cdot}$, 652.452. $C_{44}H_{60}O_4$ requires $M$, 652.449); $m/e$ 610 ($M$ − 42), 592 ($M$ − 60), 560 ($M$ − 92), and 546 ($M$ − 106).

*Hydroxyechinenone* (3-*Hydroxy*-β,β-*caroten*-4-*one*) (3).—(i) Aluminium t-butoxide (150 mg) was added to a solution of β,β-carotene-3,4-diol (mixture of isomers; 100 mg) and acetone (0.3 ml) in dichloromethane (20 ml). The mixture was boiled under reflux for 48 h, then cooled and poured onto ice-cold 2N-hydrochloric acid. Isolation of the product with chloroform, and preparative t.l.c. (5% acetone–benzene) gave starting material (70 mg) and *hydroxyechinenone* (10 mg), which crystallised from acetone–light petroleum as prisms, m.p. 155—157°; $\lambda_{max.}$ (petroleum) 457 nm; $\lambda_{max.}$ (EtOH) 460 nm; $\lambda_{max.}$ ($CHCl_3$) 472 nm; $\lambda_{max.}$ ($C_6H_6$) 473 nm ($10^{-3}\varepsilon$ 107.3); $\nu_{max.}$ ($CCl_4$) 3 520, 1 665, 1 610, and 975 $cm^{-1}$; δ see Table (Found: $M^{+\cdot}$, 566.415. $C_{40}H_{54}O_2$ requires $M$, 556.412).

(ii) Oxidation of the diol (4 mg) in acetone (10 ml) with manganese dioxide (10 mg), and chromatography of the product, gave the hydroxy-ketone (0.2 mg), $\lambda_{max.}$ ($CHCl_3$) 472 nm; mixed t.l.c. with a sample from (i) revealed no separation.

(iii) Hydrogenation of the acetylenic analogue (1 mg) over the Lindlar catalyst gave the crude 15-*cis*-isomer, $\lambda_{max.}$ ($C_6H_6$) 464 and 360 nm. Iodine-catalysed stereomutation gave a product with $\lambda_{max.}$ and chromatographic properties identical with those of the sample from (i).

When kept in methanolic 15% potassium hydroxide and air for 12 h at 20 °C, hydroxyechinenone was converted into the corresponding diosphenol. The latter on acetylation yielded the acetate ($m/e$ 606.402) which did not separate from an authentic specimen on mixed t.l.c.

15,15′-*Didehydro*-β,β-*carotene*-3,4,4′-*triol* (15′).—(i) A solution of *N*-bromosuccinimide (4 mg) in (ethanol-free) chloroform (1 ml) and acetic acid (0.03 ml) was added to a solution of 3,4-diacetoxy-15,15′-didehydro-β,β-carotene (8 mg) in (ethanol-free) chloroform (1 ml), and the mixture was stirred at −20 °C for 2.5 min. *N*-Ethylmorphine (0.2 ml) was added and the mixture allowed to warm to 15 °C. Chloroform was added, and the solution washed with 0.1N-hydrochloric acid, and then with water. The solution was evaporated and the residual gum was dissolved in methanolic 15% potassium hydroxide (1.5 ml); this solution was kept at 15 °C for 30 min, diluted with chloroform, and then washed thoroughly with water. Evaporation, and preparative t.l.c. (30% acetone–light petroleum), gave the *triol* (5 mg), which crystallised from acetone–light petroleum and had m.p. 156—157°; $\lambda_{max.}$ ($CHCl_3$) 434 nm ($10^{-3}\varepsilon$ 89.6); $\nu_{max.}$ 3 600, 3 470, 2 200, and 975 $cm^{-1}$; δ (pyridine) 1.11 (6 H, s), 1.18 (6 H, s), 2.03 (6 H, s), 2.15 (3 H, s), 2.20 (3 H, s), and 2.24 (6 H, s) (Found: $M^{+\cdot}$, 582.408. $C_{40}H_{54}O_3$ requires $M$, 582.407); $m/e$ 564 ($M$ − 18), 546 ($M$ − 18 − 18), 530, and 528.

(ii) Potassium borohydride (2 mg) was added to a solution of 3-acetoxy-2,3,15,15′-tetradehydro-β,β-caroten-4-one (2 mg) in chloroform–ethanol (1 : 50; 5 ml). The mixture was boiled under reflux for 30 min, and then cooled and poured onto ice-cold water. Isolation of the product with chloroform, and preparative t.l.c., gave the triol (1 mg), $\lambda_{max.}$ ($CHCl_3$) 433 nm. It was identified by mixed t.l.c. with the product from (i).

(iii) Substitution of 3-hydroxy-3,4,15,15′-tetradehydro-β,β-caroten-4-one (2 mg) for the acetate in the preceding experiment gave the same triol (1 mg), $\lambda_{max.}$ ($CHCl_3$) 434 nm, identified by mixed t.l.c. with the product from (i).

(iv) The crude reaction mixture from a similar reduction of 3-hydroxy-2,3,15,15′-tetradehydro-β,β-caroten-4-one (50 mg) in chloroform (1 ml) and ethanol (50 ml), with potassium borohydride (70 mg), was poured onto ice cold 2N-hydrochloric acid. Isolation of the products in the usual way gave the triol (5 mg) [identified by mixed m.p. and mixed t.l.c. with a sample from (i)] and 4′-*ethoxy*-15,15′-*didehydro*-β,β-*carotene*-3,4-*diol* (20 mg), which crystallised from acetone–light petroleum as needles, m.p. 158—160°; $\lambda_{max.}$ ($C_6H_6$) 464 and 438 nm ($10^{-3}\varepsilon$ 72 and 85); $\nu_{max.}$ ($CCl_4$) 3 640, 3 400, 2 150, and 972 $cm^{-1}$; δ 1.01 (3 H, s), 1.04 (3 H, s), 1.08 (6 H, s), 1.23 (3 H, t, $J$ 7 Hz), 1.79 (6 H, s), 1.97 (6 H, s), 2.11 (6 H, s), and 3.5—4br (2 H) (Found: $M^{+\cdot}$ 610.431. $C_{42}H_{58}O_3$ requires $M$, 610.438); $m/e$ 592 [$M$ − 18; $m^*$ 575 ($592^2/610 = 574.5$)], 564 [$M$ − 46; $m^*$ 521 ($564^2/610 = 521.5$)], and 546 [$M$ − 18 − 46; $m^*$ 503 ($546^2/592 = 503.6$)].

3-*Hydroxy*-15,15′-*didehydro*-β,β-*carotene*-4,4′-*dione* (2′).—A solution of 15,15′-didehydro-β,β-carotene-3,4,4′-triol (100 mg) in acetone (100 ml) was shaken with manganese dioxide (200 mg) at 15 °C for 5 min. The solution was filtered and the solid was washed with methanol. The filtrate and washings were combined and evaporated. Preparative t.l.c. (25% acetone–light petroleum) of the residue gave, in order of increasing polarity: (i) 3-*hydroxy*-4′-*methoxy*-15,15′-*didehydro*-β,β-*caroten*-4-*one* (6.8 mg), m.p. 114—115°; $\lambda_{max.}$ ($CHCl_3$) 443 nm; $\nu_{max.}$ 3 350, 2 170, 1 660, 1 610, and 975 $cm^{-1}$; δ see Table (Found: $M^{+\cdot}$, 594.410. $C_{41}H_{54}O_3$ requires $M$, 594.407); $m/e$ 562 ($M$ − 32); (ii) traces of the required hydroxy-dione: (iii) 3,4′-dihydroxy-15,15′-didehydro-β,β-caroten-4-one (5 mg), $\lambda_{max.}$ ($CHCl_3$) 443 nm; (iv) 4′-methoxy-15,15′-didehydro-β,β-carotene-3,4-diol (11 mg), m.p. 165—167° (from acetone); $\lambda_{max.}$ ($CHCl_3$) 462 and 437 nm ($10^{-3}\varepsilon$ 77.8 and 96.4); $\nu_{max.}$ 3 650, 3 480, 2 180, 1 095, and 975 $cm^{-1}$; δ 1.02—1.07br (12 H), 1.79 (6 H, s), 1.96 (6 H, s), 2.09 (6 H, s), and 3.38 (3 H, s), identified by mixed m.p. and mixed t.l.c. with the sample prepared by reduction of the corresponding methoxy-diosphenol; (v) the starting triol (20 mg).

The above 3,4′-dihydroxy-4-one (5 mg) in dioxan (10 ml) was oxidised further with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (5 mg) at 15 °C for 15 h. Chloroform was added to the mixture, and the solution was washed with 2N-sodium hydroxide, and then with water. Evaporation, and t.l.c. (20% acetone–light petroleum) of the residue gave 3-*hydroxy*-15,15′-*didehydro*-β,β-*carotene*-4,4′-*dione* (2 mg) as a gum; $\lambda_{max.}$ ($CHCl_3$) 453 nm; $\nu_{max.}$ 3 500, 2 170, 1 660, 1 610, and 970 $cm^{-1}$ (Found: $M^{+\cdot}$, 578.379. $C_{40}H_{50}O_3$ requires $M$, 578.376); $m/e$ 488 ($M$ − 90) and 474 ($M$ − 104).

4′-*Ethoxy*-β,β-*carotene*-3,4-*diol*.—(i) Potassium borohydride (75 mg) was added to a solution of 3-hydroxy-3,4-didehydro-β,β-carotene-4,4′-dione (50 mg) in chloroform (1 ml) and ethanol (50 ml). The mixture was boiled under reflux for 1 h, then cooled and poured onto ice-cold 2N-hydrochloric acid. Isolation of the product with chloroform, and t.l.c., gave the *ethoxy-diol* (10 mg), $\lambda_{max.}$ ($C_6H_6$) 462 and 486infl nm; $\nu_{max.}$ 3 600, 1 065, and 975 $cm^{-1}$; δ 1.01 (3 H, s), 1.04 (3 H, s), 1.07 (6 H, s), 1.81 (6 H, s),

and 1.97 (12 H, s) (Found: $M^{+\cdot}$, 612.456. $C_{42}H_{60}O_3$ requires $M$, 612.454); *m/e* 594 ($M$ − 18), 566 ($M$ − 46), 548 ($M$ − 64), and 520 ($M$ − 92).

(ii) Similar reduction of 3,4′-dihydroxy-2,3,15,15′-tetradehydro-β,β-caroten-4-one gave a product with the same $\lambda_{max.}$ and t.l.c. properties as that described in (i).

β,β-*Carotene*-3,4,4′-*triol* (15).—(i) Potassium borohydride (130 mg) was added to a solution of 3-acetoxy-2,3-didehydro-β,β-carotene-4,4′-dione (130 mg) in ethanol (150 ml). The mixture was boiled under reflux for 30 min, then cooled and poured onto ice-cold water. The mixture was extracted with ether, and the extracts were washed with water and evaporated. Crystallisation of the residue from acetone gave the triol (100 mg) as needles, m.p. 174—175°; $\lambda_{max.}$ ($CHCl_3$) 487 and 460 nm ($10^{-3}\varepsilon$ 86.8 and 99); $\nu_{max.}$ 3 440 and 970 $cm^{-1}$; δ (pyridine) 1.10 (6 H, s), 1.17 (6 H, s), 2.01 (12 H, s), and 2.14 (6 H, s).

(ii) Similar reduction of 3-hydroxy-2,3-didehydro-β,β-carotene-4,4′-dione (5 mg) gave the same product (4 mg), identified by mixed m.p. and mixed t.l.c.

*Phoenicoxanthin* (3-*Hydroxy*-β,β-*carotene*-4,4′-*dione*) (2).—Manganese dioxide (200 mg) was added to a solution of β,β-carotene-3,4,4′-triol (100 mg) in acetone (100 ml) and the mixture was stirred at 15 °C for 12 h and then filtered. The filtrate was evaporated and the residue submitted to preparative t.l.c. (25% acetone–light petroleum). The less polar fraction gave phoenicoxanthin (1 mg). The more polar fraction (4 mg), regarded as 3,4′-dihydroxy-β,β-caroten-4-one, was dissolved in dioxan (10 ml), 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (4 mg) was added, and the mixture was kept at 15 °C for 15 min. Benzene was added, and the solution was washed with 2N-sodium hydroxide, then with water, and evaporated. Preparative t.l.c. on kieselgel (20% acetone–light petroleum) gave *phoenicoxanthin* (2 mg) as a red gum. It did not separate in mixed t.l.c. from the sample mentioned above and had $\lambda_{max.}$ ($C_6H_6$) 478 nm; $\lambda_{max.}$ (EtOH) 464 nm; $\lambda_{max.}$ (hexane) 460 nm; $\lambda_{max.}$ ($CHCl_3$) 480 nm; $\nu_{max.}$ 3 600, 3 480, 1 653, 1 595, and 967 $cm^{-1}$; δ see Table (Found: $M^{+\cdot}$, 580.388. $C_{40}H_{52}O_3$ requires $M$, 580.391); *m/e* 564 ($M$ − 16), 488 ($M$ − 92), and 474 ($M$ − 106).

The $\lambda_{max.}$ and $\nu_{max.}$ of the synthetic product were in good agreement with those of a natural sample isolated [5] from the pink wing feathers of *Phoenicopterus ruber* (kindly supplied by Miss J. Cooper, Zoological Gardens, Regents Park). The natural and synthetic samples did not separate in mixed t.l.c. on kieselgel (20% acetone–light petroleum or 10% ethyl acetate–benzene), Micro-Cel (same two eluants), or alumina (25% acetone–light petroleum).

A small sample of synthetic phoenicoxanthin was dissolved in methanolic 15% potassium hydroxide, and the solution was kept in air for 12 h. The product, isolated in the usual way, was shown by $\lambda_{max.}$ and mixed t.l.c. to be phoeniconone. Further confirmation was obtained by conversion into the enol acetate, which was again identified by $\lambda_{max.}$ and mixed t.l.c. with an authentic sample.

15,15′-*Didehydro*-β,β-*carotene*-3,4,3′,4′-*tetraol* (7′).—Potassium borohydride (700 mg) was added to a solution of 15,15′-didehydroastacene (360 mg) in benzene (80 ml) and ethanol (720 ml). The mixture was boiled under reflux for 3 h, then cooled and poured onto ice-cold 2N-hydrochloric acid (200 ml). The product was extracted with chloroform–ethanol (1 : 1), and the extract was washed with aqueous sodium hydrogen carbonate and then aqueous ethanol (1 : 1). The solution was concentrated, and the solid which separated was collected giving the *tetraol* (126 mg), $\lambda_{max.}$ ($CHCl_3$) 467 and 442 nm; *m/e* 598 ($M^{+\cdot}$, $C_{40}H_{54}O_4$).

15,15′-*Didehydro*-β,β-*carotene*-3,3′-*diol* (17′).—A saturated solution of hydrogen chloride in (ethanol-free) chloroform (2 ml) was added to one of 15,15′-didehydro-β,β-carotene-3,3′,4,4′-tetraol (2.0 g) in the same solvent (1 l). The mixture was kept at 20 °C for 24 h, then washed successively with saturated aqueous sodium hydrogen carbonate and water, and evaporated. Chromatography of the residue in benzene on a short column (4 in) of alumina (grade IV), elution of the main band with benzene–ethyl acetate (3 : 1), and evaporation, gave a mixture of ketones. These, in ether, were treated with lithium aluminium hydride (100 mg). After 10 min, the excess of hydride was decomposed by addition of wet ether, and the product was isolated in the usual way. Chromatography on alumina (grade IV), and crystallisation from ethyl acetate–methanol, gave 15,15′-didehydro-β,β-carotene-3,3′-diol (40 mg), m.p. and mixed m.p. 213°; $\lambda_{max.}$ (petroleum) 457 and 430 nm ($10^{-3}\varepsilon$ 87 and 101); $\nu_{max.}$ 3 600, 2 160, and 980 $cm^{-1}$; δ see Table [Isler *et al.*[38] give m.p. 207—208° (uncorr.); $\lambda_{max.}$ (petroleum) 458 and 430 nm]. The product did not separate from an authentic sample on mixed t.l.c.

Partial hydrogenation in ethyl acetate, and stereomutation of the product, gave zeaxanthin, m.p. and mixed m.p. 206—208°; $\lambda_{max.}$ (petroleum) 480 and 452 nm ($10^{-3}\varepsilon$ 100 and 113); δ see Table. It did not separate from an authentic sample on mixed t.l.c.

β,β-*Carotene*-3,4,3′,4′-*tetraol* (7).—Potassium borohydride (80 mg) was added to a solution of astacene (55 mg) in benzene (12 ml) and ethanol (110 ml). The mixture was boiled under reflux for 3 h, then cooled and poured onto 2N-hydrochloric acid. The mixture was extracted with chloroform–ethanol (1 : 1) and the extract was washed with aqueous sodium hydrogen carbonate, and then with aqueous ethanol (1 : 1). The solution was concentrated, and the solid which separated was collected, giving the tetraol (20 mg), $\lambda_{max.}$ ($CHCl_3$) 476 and 461 nm; *m/e* 600 ($M^{+\cdot}$, $C_{40}H_{56}O_4$).

*Astaxanthin* (3,3′-*Dihydroxy*-β,β-*carotene*-4,4′-*dione*) (1).—2,3-Dichloro-5,6-dicyano-*p*-benzoquinone (150 mg) was added to a solution of the preceding tetraol (100 mg) in dioxan (250 ml), and the mixture was kept at 20 °C for 15 min. Chloroform (500 ml) was added and the mixture was washed rapidly with 2N-sodium hydroxide and then water. Evaporation, and preparative t.l.c. of the residue on kieselgel (20% acetone–light petroleum) gave *astaxanthin* (2.5 mg), which crystallised from acetone–light petroleum as needles, m.p. 182—183°; $\lambda_{max.}$ ($CS_2$) 503 nm; $\lambda_{max.}$ (MeOH) 472; $\lambda_{max.}$ (hexane) 466—467 nm; $\lambda_{max.}$ ($CHCl_3$) 485 nm; $\nu_{max.}$ 3 620, 3 510, 1 660, 1 610, and 975 $cm^{-1}$; δ see Table (Found: $M^{+\cdot}$, 596.386. $C_{40}H_{52}O_4$ requires $M$, 596.386). It did not separate on mixed t.l.c. on kieselgel or Micro-Gel from samples of natural astaxanthin from the common lobster, *Homarus gammarus* (from Professor D. F. Cheesman and Dr. P. F. Zagalsky) and from the sea water crayfish, *Jasus lalandei* (from Dr. D. H. S. Horn), both of which had $\lambda_{max.}$ ($CS_2$) 503 nm; $\lambda_{max.}$ ($CHCl_3$) 484 nm; $\lambda_{max.}$ (MeOH) 470 nm. A sample of the synthetic astaxanthin was shown by Dr. P. F. Zagalsky to combine with the appropriate apoprotein to form α-crustacyanin, $\lambda_{max.}$ 630 nm.

Treatment of synthetic astaxanthin with acetic anhydride in pyridine yielded the diacetate, $\lambda_{max.}$ ($CHCl_3$)

482 nm. It did not separate from the diacetate of natural astaxanthin in mixed t.l.c. on kieselgel, Micro-Cel, or alumina.

During t.l.c. on alumina, both synthetic and natural astaxanthin were rapidly oxidised to astacene. Exposure of synthetic astaxanthin, and its diacetate, in methanolic 15% potassium hydroxide to air also led to astacene.

15,15′-*Didehydroastaxanthin* (1′).—2,3-Dichloro-5,6-dicyano-*p*-benzoquinone (50 mg) was added to a solution of the acetylenic tetraol (20 mg) in dioxan (10 ml) and the mixture was kept at 15 °C for 48 h. Chloroform was added, and the solution was washed with 2N-sodium hydroxide and then with water. Evaporation and t.l.c. (25% acetone–light petroleum) gave 15,15′-didehydroastaxanthin (4 mg), $\lambda_{max.}$ ($CHCl_3$) 452 nm. Treatment with acetic anhydride in pyridine yielded the diacetate (2 mg), which, in ethyl acetate (5 ml) containing a trace of quinoline, was shaken in hydrogen in the presence of Lindlar catalyst (4 mg) for 12 h. Removal of catalyst and solvent, iodine-catalysed stereomutation in benzene, and t.l.c. (20% acetone–light petroleum), gave astaxanthin acetate (0.5 mg), $\lambda_{max.}$ ($CHCl_3$) 478 nm. It did not separate from an authentic sample in mixed t.l.c. on kieselgel, Micro-Cel, or alumina.

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