Carotenoids and Related Compounds. Part XXXIV.[1] Synthesis of Violerythrin and other Cyclopentenediones †

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On treatment with manganese dioxide, carotenoid diosphenols are converted into 2-nor-analogues with a cyclopentenedione end group. Thus astacene (3,3'-dihydroxy-2,3,2',3'-tetradehydro-β,β-carotene-4,4'-dione) yields the blue pigment violerythrin (2,2'-dinor-β,β-carotene-3,4,3',4'-tetraone).

Most carotenoids are yellow or red. By alkaline hydrolysis of actinioerythrin, the red pigment of the sea anemone *Actinia equina*, Heilbron *et al.* prepared the first blue carotenoid, violerythrin.[2] This was later formulated by Liaaen-Jensen and her collaborators as the C_{38} tetraketone (1), and actinioerythrin as a mixture of fatty acid esters of the related bis-acyloin, actinioerythrol (2).[3,4] The oxidation involved in the formation of violerythrin is formally analogous to that which occurs

† The principal trivial names used for convenience in this paper are defined in the Experimental section.

[1] Part XXXIII, R. E. Coman and B. C. L. Weedon, *J.C.S. Perkin I*, 1975, 2529.

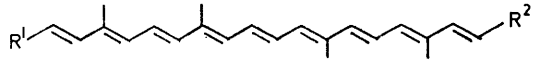
[2] I. M. Heilbron, H. Jackson, and R. N. Jones, *Biochem. J.*, 1936, **29**, 1384.

[3] S. Hertzberg and S. Liaaen-Jensen, *Acta Chem. Scand.*, 1968, **22**, 1714.

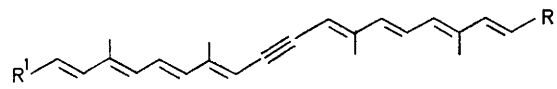
[4] S. Hertzberg, S. Liaaen-Jensen, C. R. Enzell, and G. W. Francis, *Acta Chem. Scand.*, 1969, **23**, 3290.

readily with astaxanthin (3) under alkaline conditions to give astacene (4).[5] The latter exists almost entirely as the enolic bis-diosphenol and is red.

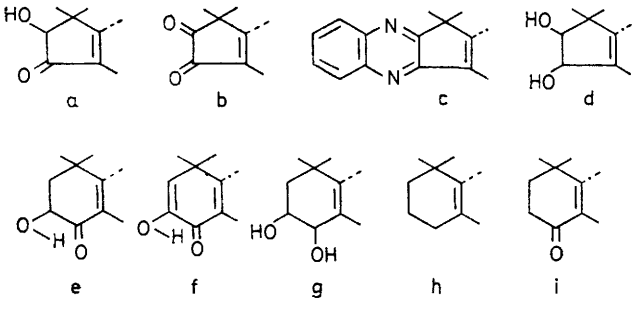
During studies on the synthesis of astaxanthin and related carotenoids by selective oxidation of 3,4-dihydroxy-carotenoids with manganese dioxide or nickel dioxide we frequently observed the formation of mauve-blue impurities, and found that these resulted



(1) $R^1 = R^2 = b$ (7) $R^1 = f, R^2 = i$
(2) $R^1 = R^2 = a$ (8) $R^1 = b, R^2 = i$
(3) $R^1 = R^2 = e$ (9) $R^1 = R^2 = j$
(4) $R^1 = R^2 = f$ (10) $R^1 = R^2 = c$
(5) $R^1 = f, R^2 = h$ (11) $R^1 = R^2 = d$
(6) $R^1 = b, R^2 = h$ (12) $R^1 = b, R^2 = f$



(13) $R^1 = f, R^2 = h$ (17) $R^1 = b, R^2 = i$
(14) $R^1 = c, R^2 = h$ (18) $R^1 = R^2 = f$
(15) $R^1 = b, R^2 = h$ (19) $R^1 = R^2 = b$
(16) $R^1 = f, R^2 = i$



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from slow oxidation of the diosphenols, common by-products in the desired process.[5] Prolonged treatment of the C_{40} diosphenol (13) in acetone with manganese dioxide gave a purple, almost black, crystalline pigment in *ca.* 30% yield. Precision mass spectrometry established that it was a nor-carotenoid, $C_{39}H_{48}O_2$, and the n.m.r. spectrum revealed that the diosphenol end group had been replaced by one with a novel shielding pattern; a six-proton singlet at δ 1.41 was attributed to the geminal methyls in the new end group, and another six-proton peak at δ 2.07 to the C-5 and C-9 methyls. The i.r. spectrum included two prominent carbonyl bands at 1 758 and 1 672 cm^{-1} consistent with an α-diketone in a cyclopentene ring. Reaction of the C_{39} pigment with *o*-phenylenediamine yielded the expected quinoxaline derivative (14). The blue pigment was therefore formulated as the 2-nor-carotenoid (15). An analogous ring contraction, with loss of one carbon atom, on treatment of a diosphenol with manganese dioxide has been reported in the steroid field.[6,7]

Reaction of the diosphenol (5) with manganese dioxide similarly gave the nor-carotenoid (6), whilst (16) and (7) gave the expected triketones (17) and (8), respectively. Under appropriate conditions 15,15′-didehydroastacene (18) gave the dinor-tetraketone (19). Astacene (3), obtained by total synthesis *via* canthaxanthin (9),[5] was converted into the required tetraketone (1) in *ca.* 10% yield. It yielded the expected bis-quinoxaline derivative (10), and its electronic absorption, i.r., and mass spectra were in good agreement with those of a sample of violerythrin prepared from actinioerythrin. The synthetic and semi-synthetic samples had identical chromatographic properties. Further direct comparisons were made with the violerythrols (11) formed on hydride reduction.[3,4] These results[8] confirmed the structure assigned to violerythrin, and hence that of actinioerythrin.[3] Subsequently Liaaen-Jensen *et al.* isolated the unsymmetrical intermediate (12) in our conversion of astacene into violerythrin and identified it with roserythrin, the product formed by treatment of a minor pigment (Ester X) in *Actinia equina* with alkali.[9] The conversion of 'natural' violerythrin into a mixture of optically inactive actinioerythrols (2) has been described,[3,4] and a preliminary account has recently been given of a new synthesis of violerythrin.[10]

All the cyclopentenediones reported in this paper exhibit very broad absorption bands at long wavelengths. The positions of these bands are markedly solvent dependent, and replacement of the central double bond by a triple bond results in a bathochromic shift (*ca.* 43 nm) considerably larger than that observed in other series (Table 1).[11] The n.m.r. properties of these nor-carotenoids are summarised in Table 2.

EXPERIMENTAL

N.m.r. spectra were determined for dilute solutions in deuteriochloroform. Polyenes were handled in an atmosphere of nitrogen, and without exposure to bright light. Solutions were evaporated under reduced pressure. Light petroleum refers to the fraction b.p. 60—80°, unless the contrary is indicated.

2-Nor-15,15′-didehydro-β,β-carotene-3,4-dione (15).—Manganese dioxide (Harringtons) (100 mg) was added to a solution of 3-hydroxy-2,3,15,15′-tetradehydro-β,β-caroten-4-one (50 mg) in acetone (25 ml). The mixture was shaken at 15 °C in the dark for 15 h, then filtered, and the filtrate was evaporated. The residue in benzene was spread on an alumina t.l.c. plate. Elution with 20% acetone in light petroleum, isolation of the main mauve product (15 mg, 30%), and crystallisation from ethanol gave the nor-carotenoid (8 mg) as plates, m.p. 179°; for $\lambda_{max.}$ see Table 1;

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[7] K. Yoshida and T. Kubota, *Chem. and Pharm. Bull. (Japan)*, 1964, **14**, 370.
[8] Preliminary report, R. Holzel, A. P. Leftwick, and B. C. L. Weedon, *Chem. Comm.*, 1969, 128.
[9] G. W. Francis, S. Hertzberg, R. R. Upadhyay, and S. Liaaen-Jensen, *Acta Chem. Scand.*, 1972, **26**, 1097.
[10] F. Kienzle, *Pure Appl. Chem.*, 1976, in the press.
[11] B. C. L. Weedon, *Progr. Chem. Org. Natural Products*, 1969, **27**, 81.

$\nu_{max.}$ (KBr) 2 182, 1 758, 1 672, and 996 cm^{-1}; for δ see Table 2; *m/e* 548 ($M^{+\cdot}$ 75%), 533 (M − 15, 2.5), 520 (M − 28, 0.3), 518 (M − 30, 0.3), 458 (M − 90, 1), 442 (M − 106, 1), 406 (M − 142, 15), 394 (M − 154, 20), and 196 (100) (Found: $M^{+\cdot}$ 548.363. $C_{39}H_{48}O_2$ requires M, 548.365). The same product was obtained from a similar oxidation of 15,15′-didehydro-β,β-carotene-3,4-diol.

A solution of the nor-carotenoid (4.0 mg) and *o*-phenylenediamine (10 mg) in glacial acetic acid (5 ml) was heated at 100 °C for 4 h, then cooled and diluted with water (10 ml). Isolation of the product with chloroform and t.l.c. (silica gel; 15% acetone in light petroleum) gave the *quinoxoline derivative* (14); $\lambda_{max.}$ (Me_2CO) 500infl, 472, and 398infl nm; $\lambda_{max.}$ ($CHCl_3$) 510infl, 481, and 409infl nm; *m/e* 620 ($M^{+\cdot}$, 6%), 514 (M − 106, 5), and 57 (100) (Found: $M^{+\cdot}$, 620.413. $C_{45}H_{52}O_2$ requires M, 620.413).

2-*Nor*-β,β-*carotene*-3,4-*dione* (6).—Manganese dioxide (300 mg) was added to 3-hydroxy-2,3-didehydro-β,β-caroten-4-one (150 mg) in acetone (100 ml). The mixture was stirred in the dark at 20 °C until t.l.c. showed the optimum formation of purple product with a minimum of starting material and decomposition products (48 h). The mixture was then filtered through Hiflo-Supercel, and the solid was washed thoroughly with chloroform. The combined washings and filtrate were evaporated to dryness and the residue was purified by column chromatography (grade IV alumina; gradient elution with 25—35% benzene in light petroleum). Isolation of the product (25 mg, 17%) from the major purple band, and crystallisation from chloroform–hexane gave the *nor-carotenoid* as black needles, m.p. 205—206°; for $\lambda_{max.}$ see Table 1; $\nu_{max.}$ (KBr) 1 750, 1 675, and 970 cm^{-1}; for δ see Table 2; *m/e* 550.380 ($M^{+\cdot}$, 29%), 534 (M − 16, 1.7), 522 (M − 28, 2), 520 (M − 30, 2), 472 (M − 78, 1.1), 460 (M − 92, 6), 444 (M − 106, 5), 392 (M − 158, 18), and 91 (100) (Found: $M^{+\cdot}$, 550.380. $C_{39}H_{50}O_2$ requires M, 550.381).

2-*Nor*-15,15′-*didehydro*-β,β-*carotene*-3,4,4′-*trione* (17).—Manganese dioxide (60 mg) was added to a solution of 3-hydroxy-2,3,15,15′-tetradehydro-β,β-carotene-4,4′-dione (25 mg) in acetone (25 ml). The mixture was stirred at 20 °C in the dark until t.l.c. (silica gel; 25% acetone in light petroleum) showed the optimum formation of a purple product with a minimum of starting material and decomposition products (18 h). The crude product was filtered through Hiflo-Supercel, and the solid was washed with chloroform. The combined filtrate and washings were evaporated and the residue was purified by column chromatography (grade IV alumina; gradient elution with 50—100% benzene in light petroleum, and finally 4% chloroform in benzene); isolation of the product in the major purple-red band, and crystallisation from chloroform–hexane gave the *trione* (8 mg, 32%) as purple crystals, m.p. 181—182°; for $\lambda_{max.}$ see Table 1 [$\lambda_{max.}$ (EtOH) 502 nm]; $\nu_{max.}$ (KBr) 2 140, 1 755, 1 690, 1 660, and 960 cm^{-1}; for δ see Table 2; *m/e* 562 ($M^{+\cdot}$, 17%), 547 (M − 15, 0.6), 534 (M − 28, 0.1), 506 (M − 56, 0.3), 472 (M − 90, 0.2), 456 (M − 106, 0.6), and 420 (M − 142, 2) (Found: $M^{+\cdot}$, 562.345. $C_{39}H_{46}O_3$ requires M, 562.345).

2-*Nor*-β,β-*carotene*-3,4,4′-*trione* (8).—3-Hydroxy-2,3-didehydro-β,β-carotene-4,4′-dione (75 mg) in acetone (50 ml) was treated with manganese dioxide (150 mg) and the crude product was isolated as in the previous experiment. Chromatography (grade IV alumina; 30% acetone in light petroleum), followed by t.l.c. (silica gel; 35% acetone in light petroleum), and crystallisation from chloroform–hexane gave the *trione* (15 mg, 20%), m.p. 183—185°; for $\lambda_{max.}$ see Table 1; $\nu_{max.}$ (KBr) 1 750, 1 680, and 965 cm^{-1}; for δ see Table 2; *m/e* 564 ($M^{+\cdot}$, 25%), 536 (M − 28, 0.1), 486 (M − 78, 1), 462 (M − 92, 3.6), 458 (M − 106, 2%), and 91 (100) (Found: $M^{+\cdot}$, 564.360. $C_{39}H_{48}O_3$ requires M, 564.360).

2,2′-*Dinor*-15,15′-*didehydro*-β,β-*carotene*-3,4,3′,4′-*tetraone* (19).—3,3′-Dihydroxy-2,3,15,2′,3′,15′-hexadehydro-β,β-carotene-4,4′-dione (120 mg) in acetone (100 ml) was stirred with manganese dioxide (500 mg) in the dark, and the reaction was monitored by t.l.c. After 24 h the crude product was isolated in the usual way. Chromatography (grade IV alumina; gradient elution with 50—100% benzene in light petroleum, then 2% chloroform in benzene), and crystallisation of the main component from chloroform–

TABLE 1

Visible light absorption maxima (nm) of nor-carotenoids in various solvents

	Light petroleum	Benzene	Acetone	Chloroform	Carbon disulphide
Violerythrol (11) (synthetic)			500, 469, 447	509, 478, 453	
Violerythrol (semi-synthetic)			503, 470, 447	511, 479, 453	
Actinioerythrin (natural)	525, 492, 467 *	544, 512, 484 *	532,* 505, 480 *	550,* 518	568, 532, 498 *
Violerythrin (1) (synthetic)		592,* 556, 520 *	547	580	614,* 574, 538 *
Violerythrin (semi-synthetic)		590,* 556, 522 *	549	581	616,* 574, 538 *
Acetylenic analogue (19)		538,* 511, 455 *	512	536	577,* 531
Triketone (8)		536	524	550	558, 538 *
Acetylenic analogue (17)		492, 404	485	507, 416 *	516, 433 *
Diketone (6)	552,* 524	544	530	565	570
Acetylenic analogue (15)	476, 390 *	500	487	516, 412 *	524

* Inflection.

TABLE 2

Principal ^1H n.m.r. bands (δ values) of cyclopentenediones in deuteriochloroform

	1-Me_2	5-Me	9-Me	13-Me	13′-Me	9′-Me	5′-Me	1′-Me_2
Violerythrin (1)	1.41	2.07	2.07	2.03	2.03	2.07	2.07	1.41
Acetylenic analogue (19)	1.41	2.08	2.08	2.15	2.15	2.08	2.08	1.41
Triketone (8)	1.41	2.06	2.06	2.00	2.00	2.00	1.86	1.18
Acetylenic analogue (17)	1.40	2.06	2.06	2.12	2.12	2.00	1.85	1.18
Diketone (6)	1.41	2.07	2.07	2.00	1.99	1.98	1.72	1.03
Acetylenic analogue (15)	1.41	2.07	2.07	2.12	2.12	1.99	1.71	1.03

hexane gave the *tetraone* (30 mg, 25%), m.p. 218—219°; for $\lambda_{max.}$ see Table 1; $\nu_{max.}$ (KBr), 2 140, 1 750, 1 682, and 960 cm^{-1}; for δ see Table 2; *m/e* 562 ($M^{+\cdot}$, 46%), 547 (M − 15, 2), 534 (M − 28, 0.6), 532 (M − 30, 1), 506 (M − 56, 0.7), 504 (M − 58, 1.4), 489 (M − 15 − 58, 1.3), and 196 (100) (Found: $M^{+\cdot}$, 562.30. $C_{38}H_{42}O_4$ requires M, 562.308).

Violerythrin (2,2′-*Dinor*-β,β-*carotene*-3,4,3′,4′-*tetraone*) (1).—Manganese dioxide (2 g) was added to a solution of astacene (3,3′-dihydroxy-2,3,2′,3′-tetradehydro-β,β-carotene-4,4′-dione) (700 mg) in acetone (300 ml). The mixture was shaken in the dark at 20 °C for 15 h, then filtered, and the solid was washed with acetone. The combined filtrate and washings were evaporated and the residue was purified by column chromatography (grade IV alumina; 30% acetone in light petroleum), followed by t.l.c. (silica gel H; 30% acetone in light petroleum). The main mauve-blue band was collected, the carotenoid was extracted with chloroform, and the solution was evaporated. Crystallisation from ethanol, and then from chloroform–hexane gave violerythrin (70 mg, 10%), m.p. 243°; for $\lambda_{max.}$ see Table 1; $\nu_{max.}$ (KBr) 1 750, 1 675, 970, and 950 cm^{-1}; for δ see Table 2; *m/e* 566 (M + 2, 16%), 564 ($M^{+\cdot}$, 23), 562 (M − 2, 9), 550 (M − 14, 0.6), 506 (M − 58, 0.3), 504 (M − 60, 0.5), 474 (M − 90, 5), 472 (M − 92, 1), 460 (M − 104, 4), and 458 (M − 106, 1). The relative intensities of the M + 2, M, and M − 2 peaks changed appreciably during the determination of the spectrum (Found: $M^{+\cdot}$, 564.326. $C_{38}H_{44}O_4$ requires 564.324) (Found: M + 2, 566.338, $C_{38}H_{46}O_4$ requires 566.340) (Found: M − 2, 562.311. $C_{38}H_{42}O_4$ requires 562.308).

The synthetic violerythrin did not separate on mixed t.l.c. from an authentic sample, obtained from actinioerythrin (silica gel H; 30% acetone in light petroleum, 20% ethanol in benzene, or 1% methanol in benzene : alumina; 30% acetone in light petroleum, or 20% ethanol in benzene).

A solution of (synthetic) violerythrin (2 mg) and freshly repurified *o*-phenylenediamine (2 mg) in glacial acetic acid (3 ml) was heated at 100 °C for 4 h (monitoring by t.l.c. showed the formation of first a mono- and then a bis-quinoxaline derivative). The mixture was allowed to cool and diluted with water (5 ml), and the product was isolated with chloroform. T.l.c. (silica gel; 40% acetone in light petroleum) yielded the bisquinoxaline derivative (9), $\lambda_{max.}$ (Me_2CO) 565infl, 531, and 506infl nm; *m/e* 708 ($M^{+\cdot}$, 18%), 616 (M − 92, 2.2), and 602 (M − 106, 5.7) (Found: $M^{+\cdot}$, 708.421. $C_{50}H_{52}N_4$ requires M, 708.419). Hertzberg *et al.*[4] give $\lambda_{max.}$ (Me_2CO) 565infl, 530, and 510infl nm; *m/e* 708 (24%), 616 (M − 92, *ca.* 6), and 602 (M − 106, *ca.* 7.5).

Violerythrol (2,2′-*Dinor*-β,β-*carotene*-3,4,3′,4′-*tetraol*) (11).—Lithium aluminium hydride (20 mg) was added to a solution of (synthetic) violerythrin (*ca.* 2 mg) in ether (2 ml) and tetrahydrofuran (10 ml), and the mixture was stirred in ice–salt. An instantaneous colour change to yellow was observed (t.l.c. gave three yellow spots). The mixture was left for 3 h though no further change was observed. Ethyl acetate was added to destroy the excess of hydride, followed by a saturated solution of sodium potassium tartrate. More ethyl acetate was added and the organic phase was separated from the colourless aqueous phase and evaporated. Crystallisation of the residue from ether gave violerythrol as a mixture of diastereoisomers, m.p. 138°; for $\lambda_{max.}$ see Table 1 [$\lambda_{max.}$ (EtOH) 499, 468, and 446 nm]; $\nu_{max.}$ (KBr) 3 400 and 960 cm^{-1}; *m/e* 572 ($M^{+\cdot}$, 4%), 554 (M − 18, 11), 536 (M − 18 − 18, 20), 520 (M − 18 − 18 − 16, 4.7), 504 (M − 18 − 18 − 16 − 16, 0.7), 480 (M − 92, 1), 466 (M − 106, 1.7), and 91 (100) (Found: $M^{+\cdot}$, 572.386. $C_{38}H_{52}O_4$ requires M, 572.387).

Both synthetic violerythrol and a semisynthetic sample prepared from actinioerythrin were mixtures of three isomers with identical visible light absorption spectra. There was no separation of the respective components in the two series on mixed t.l.c. [silica gel H; 35% acetone in light petroleum (b.p. 40—60°), 60% ether in benzene, 20% acetone in benzene, or 20% ethanol in benzene : alumina, 20% ethanol in benzene, or 35% acetone in light petroleum (b.p. 40—60°)].

Actinioerythrin.—Dark red *Actinia equina*, collected near Brighton, were washed well with water, minced at −10 °C, and extracted repeatedly at 5 °C with acetone. The acetone extracts were diluted with water, and the pigment was isolated with benzene.

The crude product in dichloromethane was spread on t.l.c. plates (silica gel H) and the chromatograms were developed with 20% acetone in light petroleum. Isolation of the main pigment and crystallisation from methanol gave actinioerythrin, m.p. 90—91°; for $\lambda_{max.}$ see Table 1; $\nu_{max.}$ (KBr) 1 740, 1 695, 985, and 960 cm^{-1}; $\nu_{max.}$ (CCl_4) 1 750, 1 710, and 970 cm^{-1}; δ ($CDCl_3$) 0.90 (6 H, t, *J* 6 Hz), 1.18 (6 H, s), 1.29 (*ca.* 30 H, s), 1.44 (*ca.* 6 H, s), 1.93 (6 H, s), 2.02 (12 H, s), 2.48 (*ca.* 4 H, t, *J* 7 Hz), 5.17 (2 H, s), 5.35 (4 H, m), 7.1—6.1 (*ca.* 15 H, m); *m/e* 984, 872, 844, 842, 816, 790, 738, 724, 710, 698, 684, 660, 646, 632, 592, 552, 550, 536, 534, 458, 444, 430, and 428 (base peak at *m/e* 55). Hertzberg *et al.*[4] give m.p. 90—91°; $\lambda_{max.}$ (petrol) 529, 496, and 470infl nm; $\lambda_{max.}$ (Me_2CO) 538, 508, and 480infl nm; $\lambda_{max.}$ ($CHCl_3$) 550infl and 518 nm; $\nu_{max.}$ (KBr), 1 738, 1 695, 990, and 960 cm^{-1}; δ ($CDCl_3$) 0.90 (6 H, m), 1.28 (*ca.* 28 H, s), 1.21 (*ca.* 6 H, s), 1.42 (*ca.* 6 H, s), 1.92 (*ca.* 5 H, s), 2.02 (*ca.* 11 H, s), 2.40 (*ca.* 4 H, m), 5.18 (*ca.* 2 H, s), 5.35 (*ca.* 3 H, t, *J* 7 Hz), and 7—6.3 (*ca.* 11 H, m); *m/e* 862, 834, 806, 780, 756, 742, 728, 714, 700, 688, 686, 674, 672, 664, 650, 636, 622, 620, 618, 582, 568, 552, 550, 536, 534, 519, 460 (552 − 92), 458 (550 − 92), 446 (552 − 106), and 440 (550 − 106) (base peak at *m/e* 28). The differences in the two mass spectra may be due at least partially to differences in the composition of the fatty acid residues in the two samples examined.

Semi-synthetic Violerythrin (1).—A solution of actinioerythrin (*ca.* 40 mg) in light petroleum (20 ml) was carefully shaken with a 2.5% solution of potassium hydroxide in methanol (20 ml), and the reaction was monitored by t.l.c. After 30 min the bright red mixture was diluted with water and 5% acetic acid was added until the solution was slightly acid. The product was isolated with ether. Chromatography (silica gel plates; 35% acetone in light petroleum), and extraction of the major purple fraction with acetone, yielded violerythrin (*ca.* 2 mg); for $\lambda_{max.}$ see Table 1; $\nu_{max.}$ (KBr) 1 750, 1 675, 970, and 950 cm^{-1}; *m/e* 566 (M + 2, 43%), 564 ($M^{+\cdot}$, 52), 562 (M − 2, 11), 550 (M − 14, 0.6), 536 (M − 28, 0.4), 534 (M − 30, 0.3), 506 (M − 58, 5), 504 (M − 60, 5), 486 (M − 78, 1.3), 474 (M − 90, 11), 472 (M − 92, 4.5), 460 (M − 104, 12), and 458 (M − 106, 4.7) (Found: $M^{+\cdot}$, 564.323. $C_{38}H_{44}O_4$ requires M, 564.324). Hertzberg *et al.*[4] give m.p. 236°; $\lambda_{max.}$ (Me_2CO) 556 nm; $\lambda_{max.}$ ($CHCl_3$) 580 nm; $\nu_{max.}$ (KBr) 1 750, 1 675, 970, and 950 cm^{-1}; no satisfactory n.m.r. spectrum was obtained, but signals at δ ($CDCl_3$) 2.05 and 1.41 were tentatively assigned to the methyl groups attached to the polyene chain and to the *gem*-dimethyls respectively; *m/e* 564 ($M^{+\cdot}$,

100%), 536 (M − 28, *ca.* 3), 506 (M − 58, *ca.* 3%), 472 (M − 92, *ca.* 10%), and 458 (M − 106, *ca.* 11%).

Semi-synthetic Violerythrol (11).—Lithium aluminium hydride (20 mg) was added to actinioerythrin (*ca.* 40 mg) in ether (10 ml), and the mixture was stirred at −20 °C for 1 h. Ethyl acetate was added to destroy the excess of hydride, followed by a saturated solution of sodium potassium tartrate. Isolation of the product with chloroform, and crystallisation from chloroform–hexane gave violerythrol, m.p. 140°; for $\lambda_{max.}$ see Table 1 [$\lambda_{max.}$ (EtOH) 500, 469, and 446 nm]; $\nu_{max.}$ (KBr) 3 420 and 960 cm^{-1}; *m/e* 572 ($M^{+\cdot}$, 18%), 554 (M − 18, 17), 536 (M − 18 − 18, 16), 520 (M − 18 − 18 − 16, 9), 504 (M − 18 − 18 − 16 − 16, 2), 480 (M − 92, 2), 466 (M − 106, 4), and 91 (100) (Found: $M^{+\cdot}$, 572.387. $C_{38}H_{54}O_4$ requires M, 572.387). Hertzberg *et al.*[4] give $\lambda_{max.}$ (Me_2CO) 500, 470, and 446infl nm; $\lambda_{max.}$ ($CDCl_3$) 506, 478, and 455infl nm; *m/e* 572 ($M^{+\cdot}$, 27%), 554 (M − 18, 30), 536 (M − 18 − 18, 17), 520 (M − 18 − 18 − 16, 7), 480 (M − 92, 11), and 466 (M − 106, 17); and (for a mixture of two of the three isomers) m.p. 192—194°.

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