Synthesis of Violerythrin and Actinioerythrol

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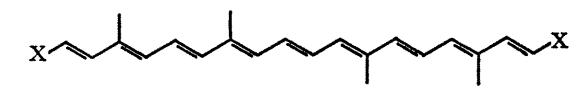
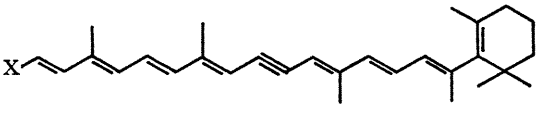
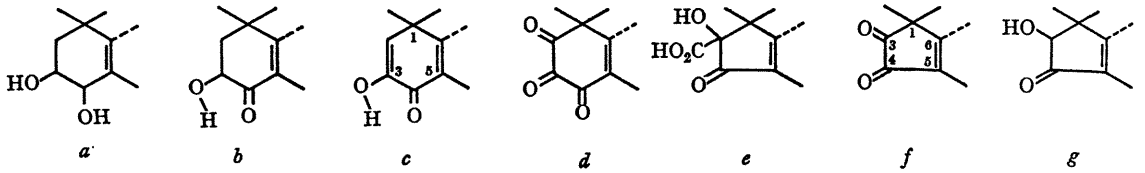
RECENTLY Hertzberg and Liaaen-Jensen[1] concluded that actinioerythrin, the red pigment of the sea anemone *Actinia equina*,[2] is a diester of the glycol (I), and that violerythrin, the blue pigment formed from it on treatment with alkali,[3] is the corresponding tetraketone (II). We report that carotenoids with these novel 2-nor end-groups may be prepared from the related diosphenols.[4]



(I) X=*g*; (II) X=*f*: (III) X=*c*
(IV) X=*b*



(V) X=*c*; (VI) X=*f*



a *b* *c* *d* *e* *f* *g*

Treatment of 15,15′-dehydro-β-carotene-3,4-dione (V)[4] in acetone with manganese dioxide at 20°, and chromatography of the product, gave (*ca.* 30%) the purple cyclopentenedione (VI), m.p. 179°; λ_{max} 524 (CS_2), 516 ($CHCl_3$), 500 (C_6H_6), 487 (Me_2CO), 476 (petrol) nm.; ν_{max} (KBr) 1758 and 1672 cm.$^{-1}$; τ 8·97 (6H), 8·59 (6H), 8·27 (3H), 8·01 (3H), 7·93 (6H), and 7·88 (6H); *m/e* 548·363 (*M*; $C_{39}H_{48}O_2$

requires 548·365). Its quinoxaline derivative had λ_{max} 481 ($CHCl_3$), 471 (Me_2CO) nm., *m/e* 620·413 (*M*; $C_{45}H_{52}N_2$ requires 620·413).

Under similar conditions, astacene (III)[4] yielded a mixture of products from which violerythrin was isolated (*ca.* 10%), m.p. 230°; λ_{max} 576 ($CHCl_3$), 546 (Me_2CO) nm.; ν_{max} (KBr) 1750, 1678, 1520 cm.$^{-1}$; τ ($CDCl_3$) 8·59, 7·98, and 7·93, relative intensities *ca.* 2 : 1 : 2; *m/e* 564·323 (*M*; $C_{38}H_{44}O_4$ requires 564·324). The fragmentation pattern closely resembled that of an authentic specimen from which it did not separate in mixed thin layer chromatograms on Kieselgel H (eluent: Me_2CO–petrol; EtOAc–C_6H_6, MeOH–C_6H_6, or $CHCl_3$–C_6H_6) or on alumina (eluent: Me_2CO–petrol). Its quinoxaline derivative had λ_{max} 501 and 530 (Me_2CO) nm., *m/e* 708·421 (*M*; $C_{50}H_{52}N_4$ requires 708·419).

Since the 3- and 3′-keto-groups in violerythrin may be selectively reduced with borohydride,[1] the results now reported also constitute a total synthesis of (optically inactive) actinioerythrol (I).

The oxidation of the diosphenols (*c*) to the cyclopentenediones (*f*) probably involves initial formation of the 2,3,4-triones (*d*), benzylic acid rearrangement to the hydroxy-acids (*e*), and further oxidation. A similar sequence has been suggested for the biosynthesis of actinioerythrin from astaxanthin (IV).[1] The cyclopentenediones were also observed as by-products in the oxidation of the cyclohexenediols (*a*) and the hydroxy-ketones (*b*) to the diosphenols (*c*) with either manganese dioxide or nickel dioxide.

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