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Synthesis of Violerythrin and Actinioerythrol

RUTH HOLZEL, A. P. LEFTWICK, and B. C. L. WEEDON*

(Department of Chemistry, Queen Mary College, Mile End Road, London, E.1)

RECENTLY Hertzberg and Liaaen-Jensen¹ 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

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 (CS₂), 516 (CHCl₃),



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

500 (C₆H₆), 487 (Me₂CO), 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; C₃₉H₄₈O₂

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 (CHCl₃), 546 (Me₂CO) nm.; ν_{max} (KBr) 1750, 1678, 1520 cm.⁻¹; τ (CDCl₃) 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: Me₂CO-petrol; EtOAc-C₆H₆, 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 (Me₂CO) nm., m/e 708·421 (M; C₅₀H₅₂N₄ 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 2,3,4triones (d), benzylic acid rearrangement to the hydroxyacids (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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