Pectenoxanthin, Cynthiaxanthin, and a New Acetylenic Carotenoid, Pectenolone

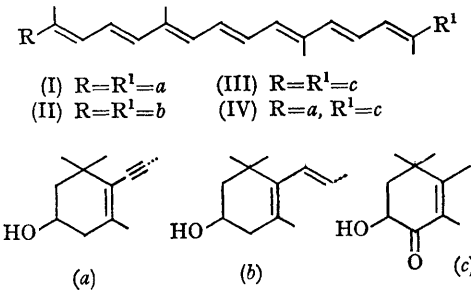
By SALLY A. CAMPBELL,[a] A. K. MALLAMS,[b] E. S. WAIGHT,[c] and B. C. L. WEEDON[b]*
([a]*Westfield College,* [b]*Queen Mary College, and* [c]*Imperial College of Science and Technology, University of London, England*)

and M. BARBIER, E. LEDERER, and A. SALAQUE
(*Institut de Chimie des Substances Naturelles, C.N.R.S., Gif-sur-Yvette, France*)

THE melting point and light absorption properties reported for pectenoxanthin, a pigment from the giant scallop *Pecten maximus*,[1,2] and cynthiaxanthin from the tunicate *Halocynthia papillosa*,[1-3] are similar to those recently observed with the diacetylenic carotenoid alloxanthin (I) from various Cryptomonas algae.[4,5] We have now shown that all these pigments, and another from the common mussel *Mytilus edulis*, are identical. We also report a new acetylenic carotenoid "pectenolone".

Partial separation of the carotenoids from 60 *H. papillosa* (collected at Naples in November 1966 through the courtesy of Professor R. A. Nicolaus) by thin-layer chromatography (t.l.c.) on Kieselgel gave cynthiaxanthin (5 mg.)†, m.p. 188—190°; λ_{max} 492 and 463 mμ; ν_{max} 3615 (OH), 2170 (C ≡ C), and 967 (*trans*-CH=CH) cm.$^{-1}$; τ‡ 8·85, 8·81, 8·11, 8·08, and 8·04; *m/e* 564·3945 corresponding to $C_{40}H_{52}O_2$ (Calc. 564·3967); it did not separate from alloxanthin on mixed t.l.c. The mixture of pigments also obtained was acetylated. The products were readily separated by t.l.c. on alumina giving: (i) cynthiaxanthin diacetate (3 mg.), m.p. 154—156°; λ_{max} 493 and 463 mμ; ν_{max} 2170 (C ≡ C), 1735 (OAc), and 964 (*trans*-CH=CH) cm.$^{-1}$; *m/e* 648·4204 corresponding to $C_{44}H_{56}O_4$ (Calc. 648·4178); hydrolysis gave cynthiaxanthin (mixed t.l.c. with the specimen described above); (ii) pectenolone diacetate (1 mg.); *m/e* 664·4154 corresponding to $C_{44}H_{56}O_5$ (Calc. 664·4128); it has the same u.v., i.r., and t.l.c. properties as the specimen described below; (iii) astaxanthin (III) diacetate (8 mg.), optically active, m.p. 198—199°; λ_{max} 482 mμ, $10^{-3}\epsilon$ 106; λ_{max} (EtOH) 474 mμ; ν_{max} 1733 (OAc), 1673 (C=O), and 980 (*trans*-CH=CH) cm.$^{-1}$; τ 8·79, 8·66, 8·11, 8·02, and 7·83; *m/e* 680 (*M*) and 620·3886 (*M* − 60) corresponding to $C_{44}H_{56}O_6$ (Calc. 620·3865 for *M* − 60); it did not separate from an authentic specimen on mixed t.l.c., and on reduction with potassium borohydride it gave a product λ_{max} (EtOH) 473 and 448 mμ.

The crude carotenoids from the gonads of 223 *Pecten maximus* (collected on the coast of Brittany in April 1967) were acetylated. Thin-layer chro-



(I) R=R¹=*a* (III) R=R¹=*c*
(II) R=R¹=*b* (IV) R=*a*, R¹=*c*

matography gave: (i) pectenoxanthin diacetate (5 mg.), m.p. 154—157°; λ_{max} 493 and 462 mμ; ν_{max} 2180, 1728, and 966 cm.$^{-1}$; *m/e* 648·4204; no separation was observed in mixed t.l.c. with cynthiaxanthin diacetate; (ii) pectenolone diacetate (4 mg.); λ_{max} 470 mμ; λ_{max} (EtOH) 463 mμ; ν_{max} 2175 (C ≡ C), 1730 (OAc), 1674 (C=O), and 967 (*trans*-CH=CH) cm.$^{-1}$; τ‡ 8·82, 8·80, 8·74, 8·67, 8·11, 8·03, 7·99, and 7·84; *m/e* 664 (*M*) and 604·3941 (*M* − 60) corresponding to $C_{44}H_{56}O_5$ (Calc. 604·3916 for *M* − 60); reduction with potassium borohydride gave a product, λ_{max} (EtOH) 478 and 451 mμ. Pectenolone is therefore formulated as (IV); no direct comparison with glycymerin[6] or hydroxyasteroidenone[7] has yet been possible; (iii) astaxanthin diacetate (0·5 mg.); λ_{max} 478 mμ; ν_{max} 1730, 1670 and 968 cm.$^{-1}$; *m/e* 680·4117 (Calc. 680·4077).

The intestines were excised from 200 mussels

† Yields and spectral data relate to chromatographically homogeneous products, and not necessarily to the crystalline material where m.p. (evacuated capillary, corrected) is given. Visible light absorption data were determined in benzene, unless otherwise indicated; where two bands are cited, the second was the more intense. I.r. and n.m.r. were determined in chloroform and deuterochloroform respectively; mass spectra were run on an A.E.I. MS9.

‡ A band at 8·76 indicated the presence of isomers with a *cis*-configuration about the acyclic double bond next to the triple bond; lipid impurities were also detected.

(collected at Brighton in May 1967). The carotenoids from the remaining organs were acetylated. Thin-layer chromatography indicated two main pigments, one of which (2 mg.) had m.p. 150—152°; λ_{max} 490 and 462 mμ; ν_{max} 2170, 1727 and 964 cm.$^{-1}$ *m/e* 648·4161. It did not separate from pectenoxanthin diacetate on mixed t.l.c. The same two pigments, but no zeaxanthin (II) diacetate, were detected by t.l.c. after acetylation of the carotenoids from the California sea mussel (*M. californianus*). Sheer[8] has previously reported that zeaxanthin is one of the principal carotenoids in these animals, but it is now known that zeaxanthin and pectenoxanthin cannot be reliably distinguished by the methods then used.

(*Received, July 21st*, 1967; *Com.* 755.)

[1] E. Lederer, *Compt. rend. Soc. Biol.*, 1934, **116**, 150; 1934, **117**, 411, 1086; *Bull. Soc. Chim. biol.*, 1938, **20**, 567.
[2] K. Nishibori, *Publ. Seto Mar. Biol. Lab.*, 1958, **7**, 181½ (*Chem. Abs.*, 1960, **54**, 18804); 1960, **8**, 317 (*Chem. Abs.*, 1961, **55**, 25073).
[3] Y. Tsuchiya and Y. Suzuki, *Tôhoku J. Agric. Research*, 1959, **10**, 397 (*Chem. Abs.* 1960, **54**, 18801).
[4] D. J. Chapman, *Phytochemistry*, 1966, **5**, 1331.
[5] A. K. Mallams, E. S. Waight, B. C. L. Weedon, D. J. Chapman, F. T. Haxo, T. W. Goodwin, and D. M. Thomas, *Chem. Comm.*, 1967, 301.
[6] E. Lederer, *Compt. rend. Soc. Biol.*, 1933, **113**, 1015.
[7] M. G. de Nicola, *Boll. sedute accad. Givenia sci. nat. Catania*, 1959, **5**, 201 (*Chem. Abs.*, 1961, **55**, 12684).
[8] B. T. Sheer, *J. Biol. Chem.*, 1940, **136**, 275.