Carotenoids and Related Compounds. Part XXII.[1] Allenic Carotenoids in Sea Urchins

By **Gail Galasko, J. Hora, T. P. Toube,** and **B. C. L. Weedon,*** Department of Chemistry, Queen Mary College, Mile End Road, London E.1
D. André, M. Barbier, E. Lederer, and **V. R. Villanueva,** Institut de Chimie des Substances Naturelles, C.N.R.S., 91 Gif-sur-Yvette, France

Three pigments from sea urchins have been identified as fucoxanthin (II), fucoxanthinol (I), and a novel allenic ketone (V), 'paracentrone.'

PREVIOUS studies on the pigments of sea urchins demonstrated the presence of novel carotenoids in the gonads and coelomic epithelium.[2] This investigation has now been resumed with use of techniques not available when the original observations were made.

Four separate batches of 500 sea urchins, *Paracentrotus lividus*, were collected at Roscoff, France, during September and December 1967, and March and May 1968. They were extracted by the method previously outlined;[2] column chromatography on alumina was omitted, except for the first batch.† Thin-layer chromatography of the xanthophylls on silica gel, with chloroform–benzene–methanol (85 : 10 : 5) as eluant, gave two main pigments, R_F 0·24 and 0·35, and traces of a third, R_F 0·46

The most strongly adsorbed pigment (*ca.* 15 mg.) had m.p. 134—138° (from benzene–pentane at 0°); $\lambda_{\text{max.}}$ ‡ 487infl., *460*, and 436infl. nm.; $\nu_{\text{max.}}$ (Nujol) 3380 (OH), 1930 (C=C=C), 1650 (conjugated C=O), and 955 (*trans*-CH=CH) cm.$^{-1}$; τ 9·03 (3H), 8·98 (3H), 8·92 (3H), 8·78 (3H), 8·65 (6H), 8·18 (3H), 8·05 (3H), 8·02 (6H), 7·43 (1H, J 18 Hz), and 6·33 (1H, d, J 18 Hz); m/e 616 (2%, M^+, $C_{40}H_{56}O_5$ requires 616), 598 (6%, $M - 18$), 580 (8%, $M - 18 - 18$), 562 (4%, $M - 18 - 18 - 18$), 547 (2%), 524 (1·5%, $M - 92$), 119 (30%), 105 (37%), 91 (62%), and 43 (100%). These properties are in good agreement with those of *fucoxanthinol* (I), m.p. 146—148°. This known carotenoid has not previously been observed in nature, but has been prepared by reduction of fuxoxanthin (II) with lithium aluminium hydride and selective oxidation of the allylic hydroxy-groups in the resulting fucoxanthols (IV) with dichlorodicyanobenzoquinone.[3] Mixed t.l.c. on Kieselgel H with 40% acetone–petroleum, 70% ethyl acetate–petroleum, 70% ethyl acetate–benzene, or 25% ethanol–benzene as eluant confirmed the identity of the two pigments. Acetylation of the natural compound (acetic anhydride–pyridine; 20°) yielded the diacetate, $\lambda_{\text{max.}}$ 485infl., *457*, and 436infl. nm., m/e 700·438 (<1%; M^+, $C_{44}H_{60}O_7$ requires 700·434). This did not separate from fucoxanthin acetate (III) in mixed t.l.c. on Kieselgel H with 30% acetone–petroleum, 30% ethyl acetate–petroleum, or 20% ethyl acetate–benzene as eluant.

The second sea urchin pigment (*ca.* 16 mg.), after further t.l.c. on Kieselgel H, first with 40% acetone in petroleum as eluant and then with ethyl acetate, had $\lambda_{\text{max.}}$ 480, *456*, and 437infl. nm., $\nu_{\text{max.}}$ (CCl_4) 3610, 3420 (OH), 1924 (C=C=C), 1660, 1607 (conjugated C=O), 1046 (C–O), and 963 (*trans* -CH=CH) cm.$^{-1}$; τ 8·93 (3H), 8·66 (6H), 8·19 (3H), 8·06 (3H), 8·02 (6H), and 7·65 (3H) (the mass spectrum was similar to that of the crystalline material described later). Acetylation (acetic anhydride–pyridine) of a small portion yielded an acetate, $\nu_{\text{max.}}$ (CCl_4) 3602, 3420, 1923, 1738, 1654, 1600, 1023, and 954 cm.$^{-1}$; m/e 504·323 (5%, M$^+$, $C_{33}H_{44}O_4$ requires 504·324), 486 (5%, $M - 18$), 444 (1%, $M - 18 - 42$), 426 (2%, $M - 18 - 60$), 411 (1%, $M - 18 - 60 - 15$), 119 (18%), 105 (22%), 91 (40%), and 43 (100%). Reduction of a further portion with lithium aluminium hydride in ether furnished a product with $\lambda_{\text{max.}}$ 455, *427*, 404, and 385infl. nm., very similar to the values of the fucoxanthols (IV).[3] The natural pigment had m.p. 147—149° (from methanol–ethyl acetate–petroleum), $\lambda_{\text{max.}}$ 480, *456*, and 437infl. nm., (ϵ_{456} 84·7 × 10^3), m/e 462·313 (7%, M^+, $C_{31}H_{42}O_3$ requires 462·313), 444 (6%, $M - 18$), 426 (3%, $M - 18 - 18$), 411 (1%, $M - 18 - 18 - 15$), 119 (15%), 105 (18%), 91 (24%), and 43 (100%). The visible, i.r., and n.m.r. spectra contain many features in common with those of fucoxanthinol (I). The n.m.r. band at τ 7·65 indicates the presence of a methyl ketone. Structure (V) is therefore advanced for this new pigment, which we propose to name 'paracentrone'. The only C_{31} carotenoid previously reported is sintaxanthin (VI), from citrus hybrids.[4]

Both fucoxanthinol and paracentrone were detected by t.l.c. in the crude extracts from sea urchins. When fucoxanthin (II) was added to the initial extracts it was subsequently recovered unchanged after the usual work-up, and had the same R_F value as the minor, least strongly adsorbed, sea urchin pigment. It is therefore

---

† The gonads of *Strongylocentrotus* (= *Paracentrotus*) *lividus* contain mainly β-carotene and echinenone, whereas pentaxanthine and other xanthophylls are found in the coelomic epithelium.[2]

‡ Electronic absorption spectra were determined for solutions in benzene; the principal maximum is italicised. N.m.r. spectra were run for solutions in deuteriochloroform with a Varian A60 or HA100 instrument. Mass spectra were recorded with an A.E.I. MS9 or MS902 spectrometer; selected lines only are quoted (nominal mass units) and precision measurements where these were made.

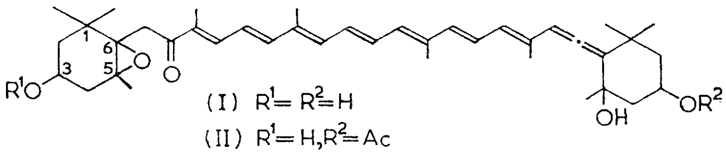
[1] Part XXI, preceding paper.

[2] E. Lederer, *Compt. rend.*, 1935, **201**, 300; *Bull. Soc. Chim. biol.*, 1938, **20**, 567.

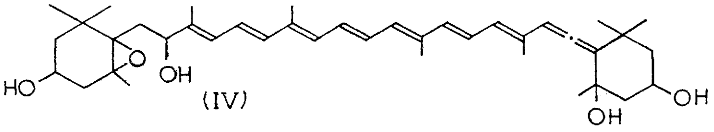
[3] R. Bonnett, A. K. Mallams, A. McCormick, J. L. Tee, and B. C. L. Weedon, *Chem. Comm.*, 1966, 515; R. Bonnett, A. K. Mallams, A. McCormick, A. A. Spark, J. L. Tee, and B. C. L. Weedon, *J. Chem. Soc.* (*C*), 1969, 429.

[4] H. Yokoyama, *J. Org. Chem.*, 1965, **30**, 3994.

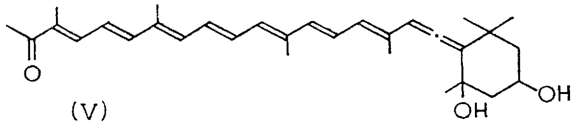
View Article Online



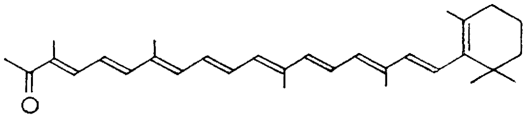
(I) $R^1 = R^2 = H$
(II) $R^1 = H, R^2 = Ac$
(III) $R^1 = R^2 = Ac$



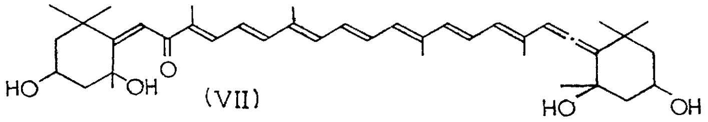
(IV)



(V)



(VI)



(VII)

conceivable that fucoxanthin, a common pigment of brown algae (Phaeophyceae) and diatoms, is absorbed by sea urchins from their diet and transformed *in vivo* into fucoxanthinol and paracentrone. Since fucoxanthinol has not been observed among the products produced on treatment of fucoxanthin with acids or bases *in vitro*,[3] any hydrolysis of fucoxanthin to fucoxanthinol in the sea urchin is presumably enzymatic. We suggest that paracentrone arises by a retro-aldol fission of a β-hydroxy-ketone, and that the latter is formed from fucoxanthinol (or one of its derivatives) by opening of the 5,6-epoxide ring to give a hydroxy-group at C-6.

The pigment pentaxanthine, m.p. 209—210°, which was isolated in the earlier studies, and for which a formula $C_{40}H_{56(\pm2)}O_5$ was proposed,[2] may have been isofucoxanthinol (VII), m.p. 207—209°, $C_{40}H_{56}O_5$.[3]

We thank the S.R.C. for a research assistantship (to J. H.) and Roche Products Ltd. for financial assistance (to B. C. L. W. and G. G.).

[8/1891 *Received, December 23rd,* 1968]