Fucoxanthin and Related Pigments

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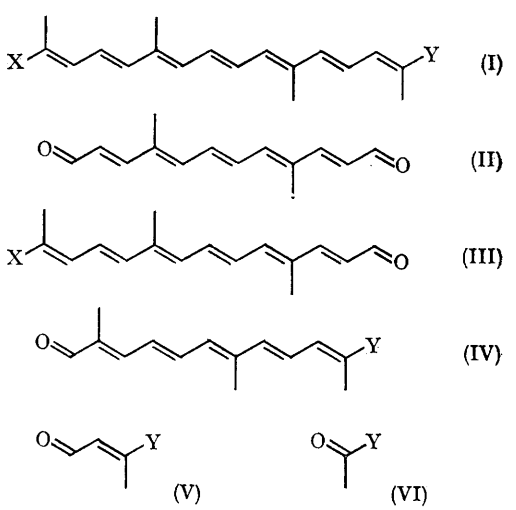
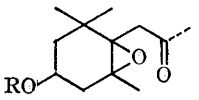
THE structure (I; X = *a*, Y = *k*) proposed[1] for fucoxanthin, the characteristic pigment of brown algae, has been confirmed. As reported previously,[1] the products of permanganate oxidation include the dimethylpentaenedial (II), the epoxyaldehyde (III; X = *a*) and a mixture of allenes. Chromatography of the latter yields the aldehyde (IV; Y = *k*), $C_{27}H_{36}O_4$,* the aldehyde (V; Y = *k*), $C_{17}H_{24}O_4$ and the methyl ketone (VI; Y = *k*), $C_{15}H_{22}O_4$, all of which exhibit the expected spectral (u.v., visible, i.r., n.m.r.) properties. Further support for the structure of (VI; Y = *k*) is afforded by a study of the fragmentation pattern, and by permanganate oxidation to αα-dimethylsuccinic acid (identified by g.l.c. of the methyl ester). The product reported by Jensen[2] from the ozonolysis of fucoxanthin benzoate, and for which structure (VI; Y = *k*) was proposed, is probably a mixture of (V; Y = *k*) and (VI; Y = *k*).

Reduction of fucoxanthin with lithium aluminium hydride gives the fucoxanthols[1,3] and semifucoxanthol.[3] Spectral studies show that the former have the structure (I; X = *c*, Y = *j*), $C_{40}H_{58}O_5$; semifucoxanthol is presumably the corresponding acetate (I; X = *c*, Y = *k*). Oxidation of the fucoxanthols with dichlorodicyanoquinone gives "fucoxanthinol" (I; X = *a*, Y = *j*), $C_{40}H_{56}O_5$, m.p. 146—148°, which on acetylation yields a diacetate, $C_{44}H_{60}O_7$, identical with fucoxanthin acetate (I; X = *b*, Y = *k*).[1]

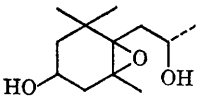
Treatment of the fucoxanthols with 0·01% hydrogen chloride in $CHCl_3$ gives a mixture of (epimeric) furanoid oxides (I; X = *d*, Y = *j*), $C_{40}H_{56}O_4$, from which one epimer, "fucochrome", $C_{40}H_{56}O_4$, m.p. 188—190°, crystallises. In its spectral (visible, i.r., n.m.r.) and chromatographic



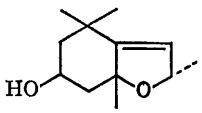
properties, and fragmentation pattern, the mixture of furanoid oxides closely resembles foliachrome (I; X = *d*, Y = *j*), m.p. 148°, and like the latter[4] yields zeaxanthin (I; X = Y = *n*), $C_{40}H_{56}O_2$,



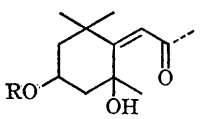
a, R = H
b, R = Ac



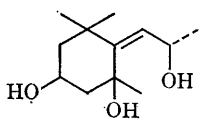
c



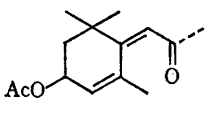
d



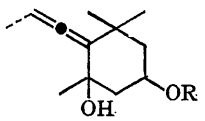
e, R = H
f, R = Ac
g, R = Bz



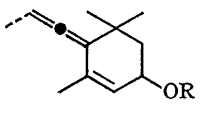
h



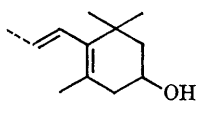
i



j, R = H
k, R = Ac



l, R = H
m, R = Ac



n

m.p. 203—205°, on reduction with lithium aluminium hydride by the method of Cholnoky *et al.*[4,5]

Dehydration ($POCl_3/C_5H_5N$) of fucoxanthin acetate (I; X = *b*, Y = *k*)[1] gives the "anhydroacetate" (I; X = *b*, Y = *m*), $C_{44}H_{58}O_6$, which is reduced by lithium aluminium hydride to the corresponding "anhydrofucoxanthols" (I; X = *c*, Y = *l*), $C_{40}H_{56}O_4$. Treatment of the latter, or the above mixture of furanoid oxides (I; X = *d*, Y = *j*), with 0·01% hydrogen chloride in $CHCl_3$ gives (I; X = *d*, Y = *l*), $C_{40}H_{54}O_3$.

During the isolation of fucoxanthin from *Fucus vesiculosus* by chromatography on alumina, three minor allenic pigments (ν_{max} *ca.* 1920 cm.$^{-1}$) were observed. Two of these, "isofucoxanthin", $C_{42}H_{58}O_6$, m.p. 144—146°, and "isofucoxanthinol", $C_{40}H_{56}O_5$, m.p. 207—209°, are formulated as (I; X = *e*, Y = *k*) and (I; X = *e*, Y = *j*) respectively. Both on reduction with lithium aluminium hydride give a (chromatographically) similar mixture of penta-ols (I; X = *h*, Y = *j*). Treatment of the latter with 0·01% hydrogen chloride in $CHCl_3$ gives a mixture of (epimeric) furanoid oxides (I; X = *d*, Y = *j*) with chromatographic and visible-light absorption properties identical with those of the mixture (I; X = *d*, Y = *j*) from the fucoxanthols.

Treatment of isofucoxanthin with benzoyl chloride in pyridine gives a monobenzoate (I; X = *g*, Y = *k*), $C_{49}H_{62}O_7$. On reaction with acetic anhydride in pyridine, both isofucoxanthin and isofucoxanthinol give "isofucoxanthin acetate" (I; X = *f*, Y = *k*), $C_{44}H_{60}O_7$. Dehydration ($POCl_3/C_5H_5N$) of the latter gives a pigment with visible-light absorption and chromatographic properties identical with those of the product (I; X = *i*, Y = *m*) described below.

Both isofucoxanthin and isofucoxanthinol are probably artefacts since they can be produced by treatment of fucoxanthin with alumina. Under similar conditions fucoxanthin acetate gives "isofucoxanthin acetate" (I; X = *f*, Y = *k*), $C_{44}H_{60}O_7$, and the anhydroacetate (I; X = *b*, Y = *m*) gives the "iso-anhydroacetate" (I; X = *f*, Y = *m*) $C_{44}H_{58}O_6$. Dehydration ($POCl_3/C_5H_5N$) of the latter gives (I; X = *i*, Y = *m*), $C_{44}H_{56}O_5$.

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* All molecular formulae quoted were determined by mass spectrometry on an MS.9 instrument.

[1] R. Bonnett, A. A. Spark, J. L. Tee, and B. C. L. Weedon, *Proc. Chem. Soc.*, 1964, 419.
[2] A. Jensen, *Acta Chem. Scand.*, 1964, **18**, 2005.
[3] A. Jensen, *Acta Chem. Scand.*, 1961, **15**, 1605.
[4] L. Cholnoky, K. Györgyfy, J. Szabolcs, E. S. Waight and B. C. L. Weedon, *Chem. Comm.*, 1966, 404.
[5] L. Cholnoky, J. Szabolcs, and Gy. Töth, unpublished results.