

## Fucoxanthin and Related Pigments

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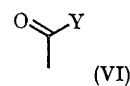
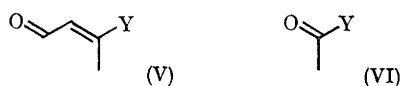
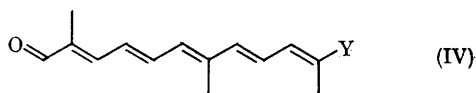
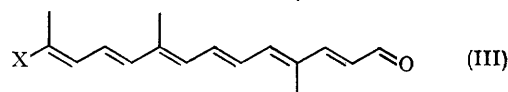
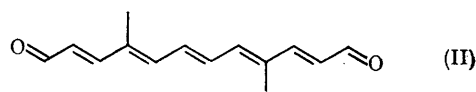
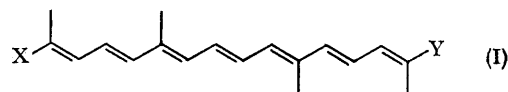
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THE structure (I;  $X = a$ ,  $Y = k$ ) proposed<sup>1</sup> for fucoxanthin, the characteristic pigment of brown algae, has been confirmed. As reported previously,<sup>1</sup> the products of permanganate oxidation include the dimethylpentaenedial (II), the epoxy-aldehyde (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  $\alpha\alpha$ -dimethylsuccinic acid (identified by g.l.c. of the methyl ester). The product reported by Jensen<sup>2</sup> 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;  $Y = k$ ).

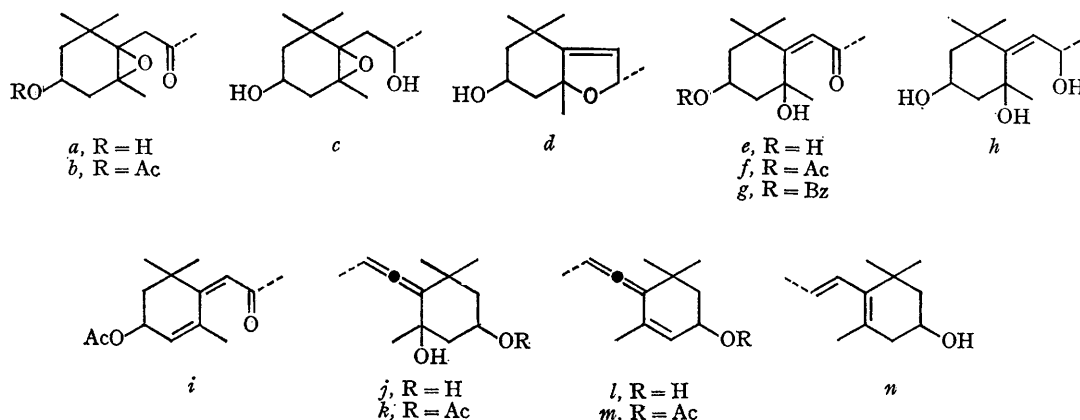
Reduction of fucoxanthin with lithium aluminium hydride gives the fucoxanthols<sup>1,3</sup> and semi-fucoxanthol.<sup>3</sup> Spectral studies show that the former have the structure (I;  $X = c$ ,  $Y = j$ ),  $C_{40}H_{56}O_5$ ; semi-fucoxanthol is presumably the corresponding acetate (I;  $X = c$ ,  $Y = k$ ). Oxidation of the fucoxanthols with dichlorodicyanquinone 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;  $X = b$ ,  $Y = k$ ).<sup>1</sup>

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<sup>4</sup> yields zeaxanthin (I;  $X = Y = n$ ),  $C_{40}H_{56}O_2$ ,



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

Dehydration ( $POCl_3/C_5H_5N$ ) of fucosanthin acetate (I; X = b, Y = k)<sup>1</sup> gives the "anhydroacetate" (I; X = b, Y = m),  $C_{44}H_{58}O_6$ , which is reduced by lithium aluminium hydride to the corresponding "anhydrofucosanthols" (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 fucosanthin from *Fucus vesiculosus* by chromatography on alumina, three minor allenic pigments ( $\nu_{max}$  ca. 1920  $cm^{-1}$ ) were observed. Two of these, "isofucosanthin",  $C_{42}H_{58}O_6$ , m.p. 144—146°, and "isofucosanthinol",  $C_{40}H_{56}O_5$ , 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 fucosanthols.

Treatment of isofucosanthin 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 isofucosanthin and isofucosanthinol give "isofucosanthin 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 isofucosanthin and isofucosanthinol are probably artefacts since they can be produced by treatment of fucosanthin with alumina. Under similar conditions fucosanthin acetate gives "isofucosanthin 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.

<sup>1</sup> R. Bonnett, A. A. Spark, J. L. Tee, and B. C. L. Weedon, *Proc. Chem. Soc.*, 1964, 419.

<sup>2</sup> A. Jensen, *Acta Chem. Scand.*, 1964, 18, 2005.

<sup>3</sup> A. Jensen, *Acta Chem. Scand.*, 1961, 15, 1605.

<sup>4</sup> L. Cholnoky, K. Györgyfy, J. Szabolcs, E. S. Waight and B. C. L. Weedon, *Chem. Comm.*, 1966, 404.

<sup>5</sup> L. Cholnoky, J. Szabolcs, and Gy. Tóth, unpublished results.