

Short Communications

Algal Carotenoids

I. Fucoxanthin Monoacetate

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Fucoxanthin, the characteristic carotenoid of brown algae (and of diatoms), was isolated in the crystalline state for the first time in 1914 by Willstätter and Page¹ who ascribed to it the molecular formula $C_{40}H_{54}O_6$. More recent authors have favoured the formulas $C_{40}H_{56}O_6$,^{2,3} and $C_{40}H_{50}O_6$.^{4,5} Active hydrogen determinations have indicated between four and six hydroxyl groups in the molecule^{3,6}. Attempts to determine the number of hydroxyl functions by acetylation have failed, as only about two hydroxyls could be esterified³. Although several investigations have been made to elucidate the structure of fucoxanthin¹⁻⁷, no satisfactory constitution has hitherto been suggested. The proposed formulations^{4,8} are not in accordance with the known properties of the compound, as has been pointed out by a number of authors⁹⁻¹¹.

During a study of the content of carotenoids of Norwegian brown algae, a limited amount of chromatographically pure fucoxanthin became available. The crystalline compound, mainly isolated from *Fucus serratus*, m.p. 158–159°C (uncorr.), λ_{max} (425), 449, 478 $m\mu$ (petroleum ether), $E_{1\%}^{1\text{cm}} = 1650$ (449 $m\mu$), showed main absorption bands at 3450, 2940, 1930, 1730, 1663, 1647, 1610, 1530, 1450, 1355, 1240, 1030 and 955 cm^{-1} (KBr-disc). The acetylation in pyridine-acetic anhydride at room temperature was followed by paper chromatography¹² (Table 1). The reaction came to a standstill after 3–4 h. Treatment over-night did not lead to

Table 1. Acetylation of fucoxanthin.

Reaction time minutes	Starting material		Product	
	R_F^a	Percentage ^b	R_F^a	Percentage ^b
2	45	83	72	17
60	44	20	74	80
180	44	trace	73	100

^a Relative mobility $\times 100$ in petroleum ether containing 10 % of acetone.

^b Relative amounts in the reaction mixture.

further acetylation. After chromatography on calcium carbonate and two crystallisations from petroleum ether, the acetate melted at 118–119°C (uncorr.). The light absorption properties were very similar to those of fucoxanthin both in the visible and in the infra-red regions ($E_{1\text{cm}}^{1\%} = 1560$ at 449 $m\mu$ in petroleum ether). Elementary analyses gave C 74.77; H 8.84; calc. for $C_{42}H_{58}O_7$: C 74.74; H 8.66.

Partition ratios for fucoxanthin and the acetate were determined according to

Table 2. Partition ratios¹³ of fucoxanthin and fucoxanthin monoacetate.

Compound	Partition ratios in petroleum ether/aq.methanol			R_F^a
	85 % methanol	60 % methanol	50 % methanol	
Fucoxanthin	2:98	72:28	92:8	49
Fucoxanthin monoacetate	29:71	—	—	73
Zeaxanthin ¹³	40:60	—	—	73
Lutein ¹³	43:57	—	—	78

^a Relative mobility $\times 100$ in petroleum ether containing 10 % of acetone.

Petracek and Zechmeister¹³, and the results are given in Table 2.

The formation of a monoacetate of fucoxanthin under the conditions employed strongly indicates the presence of only one secondary (or primary) hydroxyl group in the native pigment. The infra-red spectrum of the acetate showed the presence of more hydroxyl functions, and on partition between petroleum ether and aqueous methanol the compound was more hypophasic than the dihydroxy carotenoids zeaxanthin and lutein. The R_F -value of the acetate was close to those of zeaxanthin and lutein although the former had a shorter chromophore. We therefore suggest that fucoxanthin contains at least two hindered, presumably tertiary, hydroxyl groups in the molecule. Weak absorption bands occurring at 1 140 and 900 cm^{-1} in the infra-red spectra of both fucoxanthin and the monoacetate may belong to these groups^{14,15}.

The spectral absorption curve of fucoxanthin (λ_{max} at (425), 449, 478 μ in petroleum ether) is very similar in shape and position to that of β -citraurin (λ_{max} at 425, 448, 477 μ in hexane¹⁶). The latter compound has eight carbon-carbon and one carbon-oxygen double bonds in conjugation. Fucoxanthin may therefore have a similar arrangement, or, if the chromophore is terminated by an allene group (the presence of which is indicated by the absorption at 1 930 cm^{-1} in the infra-red) it may consist of one terminal allene group, seven carbon-carbon and one carbon-oxygen double bonds which are all conjugated.

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Received September 13, 1961.

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II. The Fucoxanthols — Reduction Products of Fucoxanthin

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The presence of carbonyl functions in the fucoxanthin molecule was first suggested in 1935 by Heilbron and Phipers¹ who based this assumption mainly on chemical grounds. Later², the poorly defined spectral absorption curve of fucoxanthin dissolved in polar solvent relative to that for the pigment dissolved in nonpolar solvent, was taken as an indication of the presence of one or more ketonic groups in the molecule. More recently absorption bands at 1 730 and 1 660 cm^{-1} in the infra-red spectrum of fucoxanthin have been demonstrated, and the presence of one conjugated and one isolated keto group³, or of one conjugated carbonyl and one saturated carbonyl or unsaturated ester group⁴ have been proposed. It should be pointed out, however, that the methyl esters of bixin and of crocetin, which each contain two identical, conjugated carbonyl groups, give rise to two separate carbonyl bands in the infra-red absorption spectrum⁵ namely at approximately 1 630 and 1 730 cm^{-1} . The above assignments therefore needed some further support.

Crystalline fucoxanthin⁶ (480 mg) was treated with lithium aluminium hydride, and from the reaction mixture were isolated