

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.

Algal Carotenoids

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

three new, crystalline derivatives of fucoxanthin, for which the names fucoxanthol a (80 mg), fucoxanthol b (140 mg), and semifucoxanthol (5 mg) are proposed. Fucoxanthol a (m.p. 187–189°C, $E_{1\text{cm}}^{1\%} = 2510$ at 421 $m\mu$) and fucoxanthol b (m.p. 181–182°C, $E_{1\text{cm}}^{1\%} = 2150$ at 421 $m\mu$) showed identical absorption properties in the

visible and infra-red regions, λ_{max} 398, 421, 448 $m\mu$ (petroleum ether) and main absorption bands at 3340, 2930, 1930, 1450, 1360, 1135, 1030 and 960 cm^{-1} (KBr-disc). Elementary analyses gave C 76.47; H 9.36 and C 75.48; H 9.50 for fucoxanthol a and b, respectively. Calc. for $\text{C}_{40}\text{H}_{60}\text{O}_6$: C 75.43; H 9.50. Iodine catalysed isomerisation gave two different stereois-

Table 1. J_2 -catalysed isomerisation of fucoxanthol a and b.

Fucoxanthol a	λ_{max} , $m\mu^a$	Rel. amount	R_F 20 % ^b
Trans-fucoxanthol a	398, 421, 448	—	54
Equilibrium mixture	396, 419, 447	—	—
Trans	398, 421, 448	63 %	54
Neo U	395, 417, 444	37 %	52
<i>Fucoxanthol b</i>			
Trans-fucoxanthol b	398, 421, 448	—	—
Equilibrium mixture	396, 419, 447	—	—
Neo A	396, 418, 447	21 %	49
Trans	397, 421, 448	48 %	42
Neo U	394, 417, 442	32 %	36

^a in petroleum ether. ^b $R_F \times 100$, 20 % acetone in petroleum ether.

Table 2. Acetylation of fucoxanthol b.

Zone No.	R_F^a	Carotenoid in % of total after reaction time in minutes				Tentative identification
		2	15	60	200	
8	11	90	18.2	4.2	0	fucoxanthol b
7	26	6	20.5	9.6	0	monoacetates
6	33	4	12.9	5.8	2.6	
5	37	0	8.8	9.8	0	
4	42	0	6.0	5.6	0	diacetates
3	53	0	23.4	32.0	11.5	
2	58	0				
1	75	0	10.2	33.2	85.9	triacetate

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

Table 3. Partition ratios⁷ of the fucoxanthols.

Compound	Partitions ratios in pet. ether/aq. methanol		
	85 %	60 %	50 %
Fucoxanthol a	0:100	5:95	15:85
Fucoxanthol b	0:100	5:95	15:85
Fucoxanthol b acetate	33:67	—	—
Semifucoxanthol	2:98	45:55	63:37
Zeaxanthin ⁷	40:60	—	—

meric sets as shown by paper chromatography (see Table 1).

Semifucoxanthol had absorption maxima at 398, 421 and 448 $m\mu$ (petroleum ether) and showed main absorption bands at 3 340, 2 930, 1 930, 1 725, 1 450, 1 365, 1 245, 1 150, 1 030 and 960 cm^{-1} (KBr-disc.).

Acetylation of fucoxanthol b in pyridine-acetic anhydride was followed by paper chromatography. The results are shown in Table 2.

The acetate of fucoxanthol b ($R_F = 75$) was purified by chromatography, and melted at 168°C after two crystallisations from ether-petroleum ether, $E_{1\text{cm}}^{1\%} = 1\ 800$ at 421 $m\mu$, λ_{max} 398, 421, 449 $m\mu$ (petroleum ether). Elementary analyses gave C 73.39; H 8.59; CH_3CO 14.77. Calc. for the triacetate $C_{46}H_{66}O_8$: C 72.41; H 8.72; CH_3CO 16.92. (The diacetate $C_{44}H_{64}O_6$ requires CH_3CO 11.94).

Partition ratios⁷ for the compounds above are given in Table 3. While solutions of fucoxanthin and its acetate in ether both gave a strong and stable blue colour reaction with 25 % hydrochloric acid, the reduction products gave a rather faint and unstable, but unmistakable, blue colour with this reagent.

The data presented above prove that the fucoxanthin molecule contains two, non-identical carbonyl groups, one of which is conjugated with the rest of the chromophore. By reduction of the conjugated keto function, the semifucoxanthol was formed. This compound still contained one carbonyl group, as evident from the infra-red absorption at 1 725 cm^{-1} . Further reduction gave the fucoxanthols which showed no absorption in the carbonyl region of the spectrum. These three compounds exhibited pronounced fine structure absorption spectra in visible light, confirming that the conjugation with the carbonyl group had been broken. The position of the absorption maxima coincided completely with those of flavoxanthin⁸, which has eight conjugated carbon-carbon double bonds in an aliphatic chromophore.

The fucoxanthols a and b were formed without loss of oxygen, a fact that rules

out the suggested presence of an ester group in the fucoxanthin molecule.

The behaviour of fucoxanthol b during acetylation (Table 2) was similar to that expected for an unsymmetrical triol containing three about equally accessible hydroxyl groups, during the acetylation of which three monoacetates, three diacetates and one triacetate should occur. The formation of one single end product makes it very unlikely that any of the compounds of Table 2 were *cis-trans* isomers. Therefore the course of the acetylation of fucoxanthol b, together with the elementary analysis and the acetoxy content of the product strongly indicate that it was a triacetate. The R_F -value and the partition ratio suggest the presence of at least two free hydroxyl groups in this acetate. If the blue colour reaction of the fucoxanthols a and b with concentrated aqueous hydrochloric acid was caused by an epoxy or a furanoid function, the number of free hydroxyl groups in the acetate could not exceed two.

A detailed report of this work will be published elsewhere. Further studies on the structure of fucoxanthin is in progress.

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Received September 13, 1961.