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STEREOISOMERS OF FUCOXANTHIN

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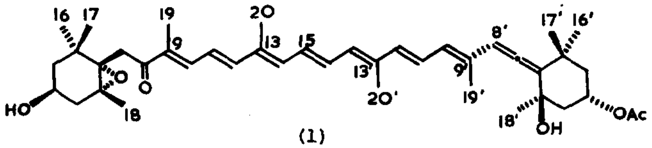
Summary: Three new isomers of fucoxanthin have been characterised; one has the S axial chirality postulated in biosynthetic schemes, the others are the 13-*cis* and 13'-*cis* isomers.

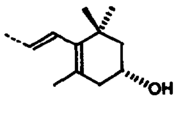
Fucoxanthin (1) in brown algae, and the related neoxanthin present in all green leaves, are the two major natural allenes and both have R axial chirality.[1] It has been suggested[2] that their biosynthesis involves a photochemical oxidation of a carotenoid with the diene unit (2) to give an allene with the S configuration, and its subsequent isomerisation to R. We now report a re-investigation of the stereomutation of fucoxanthin. This provides the first identification of a carotenoid S-allene and illustrates its easy conversion to the R-isomer.

Strain *et al.*[3,4] reported the occurrence of three interconvertible forms of fucoxanthin. The isomer with longest wavelength light absorption predominates after stereomutation, and is the principal natural isomer.[3-5] It is assigned the all-*trans* configuration (1).[5-7]

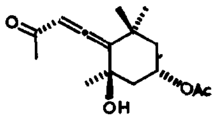
We find that stereomutation of fucoxanthin in benzene containing a trace of iodine occurs rapidly in the presence of diffuse light. Chromatography on calcium carbonate (with 5-7% acetone in benzene) gives isomers I, II, III, IV, and the all-*trans* form (in order of decreasing adsorption) in the proportions *ca.* 1:1:2:0.1:8. An identical set was produced in the presence of dimethylaniline,[3,4] but in boiling benzene in the dark isomers I, II, III, V and the all-*trans* form were obtained (*ca.* 1:1:0.2:0.2:8). When kept, the isomers revert to a mixture consisting mainly of all-*trans* fucoxanthin.



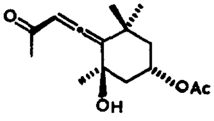
(1)



(2)



(3)



(4)

Chromatography on columns of powdered sugar indicated that the neofucoxanthin A of Strain et al.[4] was probably a mixture of isomers I and II, and that their neofucoxanthin B was identical with isomer III.

The physical properties of the four main isomers are summarised in the Table. The c.d. properties of the isomers I, II, and III are markedly different from those of the all-trans. Both I and II are mono-unhindered-cis forms[6] (2-4 nm shift in $\lambda_{max.}$ in benzene with strong cis-peaks[6]); neither is 15-cis (no i.r. band near 780 cm^{-1}), 9-cis (strong cis-peak in borohydride reduction product), or 9'-cis ($\delta_{8'H}$ similar to that in all-trans). The δ values for the 16-, 17- and 18-methyls suggest that the cis-bond is nearer the epoxide end group in I than in II; this deduction is supported by the relative intensities of the cis-peaks before and after borohydride reduction. The isomers I and II are formulated as 13-cis and 13'-cis respectively.

The isomer III has no cis-peak; a di- or poly-cis configuration is excluded by the small shift in $\lambda_{max.}$ (2 nm in benzene). It is therefore regarded as the allenic isomer in which the chiral axis is S, and not R as in (1).[7] There are significant shifts in the δ values for the 16'- and 17'-methyls, and a major shift in that for the 8'-proton. The corresponding signals differ in the racemates (3) and (4) which have the same (relative) structural relationship.[1] Irradiation of (4) is reported[2] to give an equilibrium mixture (1:1) of (3) and (4). Iodine catalysed stereomutation of isomer III gave the same mixture of isomers as the all-trans form.

TABLE

	isomer I	isomer II	isomer III	all-*trans*
m.p.	112-115°	98-99°	106-108°	168-169°
u.v. & visible[9]				
$\lambda_{max.}$ (C_6H_6)	458	456	458	460
cis-peak	339	340	-	-
$\lambda_{max.}$ (EtOH)	445	446	446	451
cis-peak	334(0.49)	335(0.41)	-	-
$\lambda_{max.}$ (EtOH/$NaBH_4$)	419	419	420	424
cis-peak	314(0.35)	314(0.33)	-	-
c.d.[10]				
$\Delta\varepsilon$ (227)	-0.75	-0.65	-1.70	+0.44
$\Delta\varepsilon$ (265)	+1.50	+0.15	+1.60	-0.55
$\Delta\varepsilon$ (331)	-1.00	-0.5±0.1	-0.45	+0.29
n.m.r.[11]				
16-Me	0.2	-0.1	0.2	(0.96_1)
17-Me	0.7	0.1	0.2	(1.03_1)
18-Me	0.6	-0.1	-0.4	(1.21_6)
19-Me	0.2	-0.9	-1.1	(1.94_9)
20-Me 20'-Me	-1.2	-0.7	-0.8	(1.99_0)
19'-Me	-0.6	-0.2	-0.8	(1.81_6)
18'-Me	-0.1	-0.2	0.2	(1.38_2)
17'-Me	0.0	0.3	1.8	(1.35_0)
16'-Me	-0.1	0.3	1.6	(1.07_0)
Ac	-0.4	-0.2	-0.7	(2.03_2)
8'-H	0.	0.	50.	(6.04_7)

Fucoxanthin from *Fucus serratus* collected near Trondheim (in May 1973)[8a] contained *ca*. 6% of isomer III, that from *F. serratus* collected near Edinburgh (June 1973)[8b] contained isomer II (*ca*. 1%) but no isomer III could be detected.

These results support the view that allenes such as isomer III are precursors in the biosynthesis of fucoxanthin and neoxanthin.[1,2]

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References and footnotes

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[8] Kindly supplied by (a) Dr. A. Jensen, and (b) Dr. J.W. Wells.

[9] Wavelengths in nm. Figures in parentheses after *cis*-peaks indicate intensity relative to that of the principal absorption band.

[10] In EtOH, wavelengths in nm. Great reliance cannot be placed on the quantitative values in view of the instability of the isomers, particularly II.

[11] In $CDCl_3$. For the all-*trans* isomer δ values are given in parentheses. For other isomers $10^2\Delta\delta$ are cited, i.e. $(\delta_{cis} - \delta_{trans})\times 10^2$. No significance is attached to the $10^2\Delta\delta$ values between -0.5 and 0.5.