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ABSOLUTE CONFIGURATION OF FUCOXANTHIN

K Bernhard, G.P. Moss, Gy. Tóth, and B.C.L. Weedon
Department of Chemistry, Queen Mary College,
Mile End Road, London, E1 4NS.

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Summary The common natural isomer of the allenic carotenoid fucoxanthin has the 3S,5R,6S,3'S,5'R,6'R configuration.

The stereochemistry of fucoxanthin (1) has been determined except for that of the 5,6-epoxide group.[1] The provisional 5R,6S assignment[2] for this feature of the major natural carotenoid has now been confirmed.

Reduction of fucoxanthin with lithium aluminium hydride gives a mixture of fucoxanthols (2 and 3) which, on treatment with chloroformic hydrogen chloride, is converted into a mixture of fucochromes (4 and 5) [3] We find that, by chromatography on calcium carbonate, each of these products can be separated into the two isomers (a less polar than b) Comparison of the n.m.r. properties of the two fucochromes with those of the four 5,8-epoxides (6 - 9) in the (3R-) lutein series[2] (Table) shows that they are epimeric at C-8 with the trans-arrangement of the oxygen functions at C-5 and C-3. They must therefore have the 5R configurations given in (4) and (5)

On treatment of the fucoxanthols (2) and (3) individually with traces of acid, both reacted (but at significantly different rates) to give both fucochromes (4) and (5) in the same ratio (1 1). This excludes the possibility[2] that one fucochrome is formed from (2), and the other from (3), with retention of configuration at C-8 but inversion at C-5 No intermediate could be detected in these transformations, even in the products of incomplete reaction, or when the reactions were monitored spectroscopically. Furthermore related erythro and threo 5,6-glycols do not react under the acidic conditions used.[2] It is therefore concluded that conversion of the fucoxanthols into the fucochromes involves loss of configuration at C-8 but retention at C-5. Whether this involves a normal polyene allylic dehydration to give initially all-trans neoxanthin (10), which would rearrange rapidly in the presence of acids to give both fucochromes,[2,4] or a rearrangement of the intermediate C-8 carbonium ion to a 5,8-epoxide, followed by loss of a proton, does not affect the conclusion. It follows that fucoxanthin has the 3S,5R,6S,3'S,5'R,6'R configuration shown in (1), and that its allenic isomer detected in some batches of seaweed, and formed on stereomutation,[5] is the 3S,5R,6S,3'S,5'R, 6'S isomer.

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References

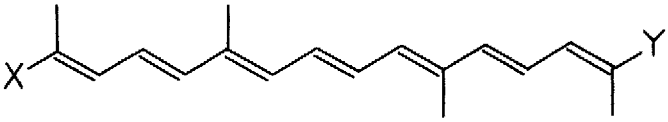
[1] B.C L. Weedon in "Carotenoids", p 267, ed. O Isler, Birkhauser Verlag, Basel, 1971.

[2] D. Goodfellow, G P. Moss, J. Szabolcs, Gy Tóth, and B.C.L. Weedon, Tetrahedron Letters, 1973, 3925.

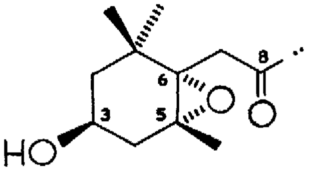
[3] R. Bonnett, A.K Mallams, A.A. Spark, J.L Tee, B.C.L. Weedon and A. McCormick, J. Chem Soc. (C), 1969, 429.

[4] L. Cholnoky, K Gyorgyfy, A. Rónai, J. Szabolcs, Gy Tóth, G. Galasko, A.K. Mallams, E.S. Waight, and B.C.L. Weedon, J. Chem. Soc. (C), 1969, 1256.

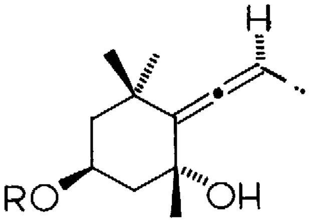
[5] K. Bernhard, G.P. Moss, Gy. Tóth, and B.C.L. Weedon, Tetrahedron Letters, 1974, 3899.



(1) X = a, Y = b (6) X = f, Y = j
(2) X = d, Y = c (7) X = g, Y = j
(3) X = e, Y = c (8) X = h, Y = j
(4) X = f, Y = c (9) X = i, Y = j
(5) X = g, Y = c (10) X = k, Y = c

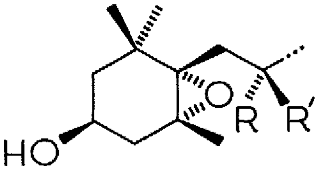


a



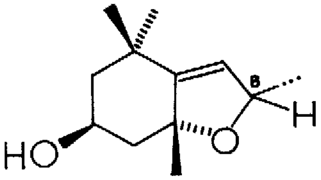
b, R = Ac

c, R = H



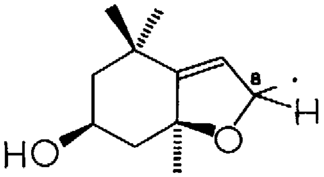
d, R = H, R' = OH

e, R = OH, R' = H



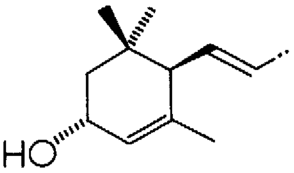
f and g

(epimers at C-8)

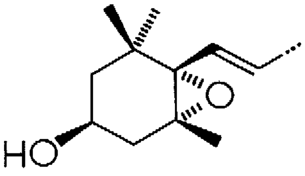


h and i

(epimers at C-8)



j



k

Table Characteristic n.m.r. bands of 5,6- and 5,8-epoxides

(δ, $CDCl_3$, 100 MHz, bands associated with relevant half of molecule only).

	1-Me's		5-Me	9-Me	13-Me	7-H and 8-H	
Fucoxanthin (1)	0.96	1.03	1.21	1.94	1.98	2.59	3.65
Fucoxanthol a (2 or 3)	1.20	1.20	1.42	1.83	1.95		
Fucoxanthol b (3 or 2)	1.09	1.13	1.37	1.83	1.95		
Fucochrome a (4 or 5)	1.17	1.33*	1.61	1.71	1.94	5.16	5.25
Fucochrome b (5 or 4)	1.19	1.33*	1.68	1.80	1.95	5.06	5.30 (J = 2Hz)
Chrysanthemaxanthin (6 or 7)†	1.16	1.31	1.60*	1.70	1.94	5.15	5.23
Flavoxanthin (7 or 6)†	1.19	1.33	1.67	1.80	1.95	5.04	5.27 (J = 2Hz)
Lutein-5,8-epoxide b (8 or 9)§	1.14	1.20	1.45	1.74	1.95	5.16	5.24
Lutein-5,8-epoxide a (9 or 8)§	1.14	1.22	1.47	1.79	1.94	5.09	5.33 (J = 2Hz)

* Signal not resolved from band associated with the other half of molecule

† Derived from natural lutein-5,6-epoxide

§ Derived from semi-synthetic lutein-5,6-epoxide