

Studies on algal carotenoids

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Abstract - Selected examples are given of recent structural studies on algal carotenoids. Interdisciplinary aspects such as algal chemosystematics and food chain studies are exemplified.

INTRODUCTION

Of the ca. 580 structurally defined naturally occurring carotenoids (ref. 1) around 100 are encountered in algae. Interdisciplinary aspects such as chemosystematics, functional aspects and food chain relations have been a special challenge for structural studies on algal carotenoids.

CHEMOSYSTEMATICS

Algal carotenoids are usually C₄₀-skeletal. Dinoflagellates also synthesize C₃₇-norcarotenoids. Characteristic end groups of algal carotenoid are given in Scheme 1. Carotenoids are recognized as useful chemosystematics markers for algae (Table 1).

Scheme 1

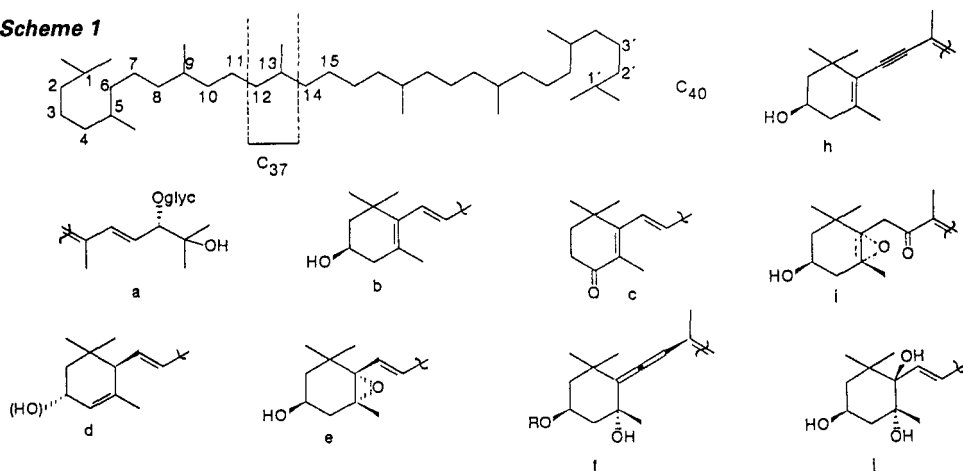


TABLE 1. Characteristic structural features of the major carotenoids of the various algal classes.

ALGAL CLASS	STRUCTURAL FEATURES OF MAJOR CAROTENOIDS												
	a	b	c	d	e	f	g	h	i	j	k	l	m
Cyanophyceae	+	+	+										
Rhodophyceae		+		+									
Cryptophyceae		+		+				+					
Eustigmatophyceae		+			+	+	?					+	
Xanthophyceae		+			+	+	+	+			+		
Raphidophyceae I		+			+	+	+	+			+	+	
II		+			+	+	+		+				
Dinophyceae II		+			+	+	+	+					+
I		+			+	+	+	+					
Prymnesiophyceae		+			+	+	+	+	+			+	
Bacillariophyceae		+			+	+	+	+	+				
Chrysophyceae		+			+	+	+						
Phaeophyceae		+			+	+	+						
Euglenophyceae		+	+		+	+		+				+	
Prasinophyceae		+			+	+				+		+	
Chlorophyceae		+	+	+	+	+						+	+

a) monocyclic glycosides, b) bicyclic xanthophylls, c) 4-keto, d) ϵ -rings, e) 5,6-epoxides, f) allenenes, g) acetates, h) acetylenic, i) 8-keto, j) 5,6-diol, k) 19-acyloxy, l) C₃₇-skeletal, m) 2-OH.

STRUCTURAL STUDIES

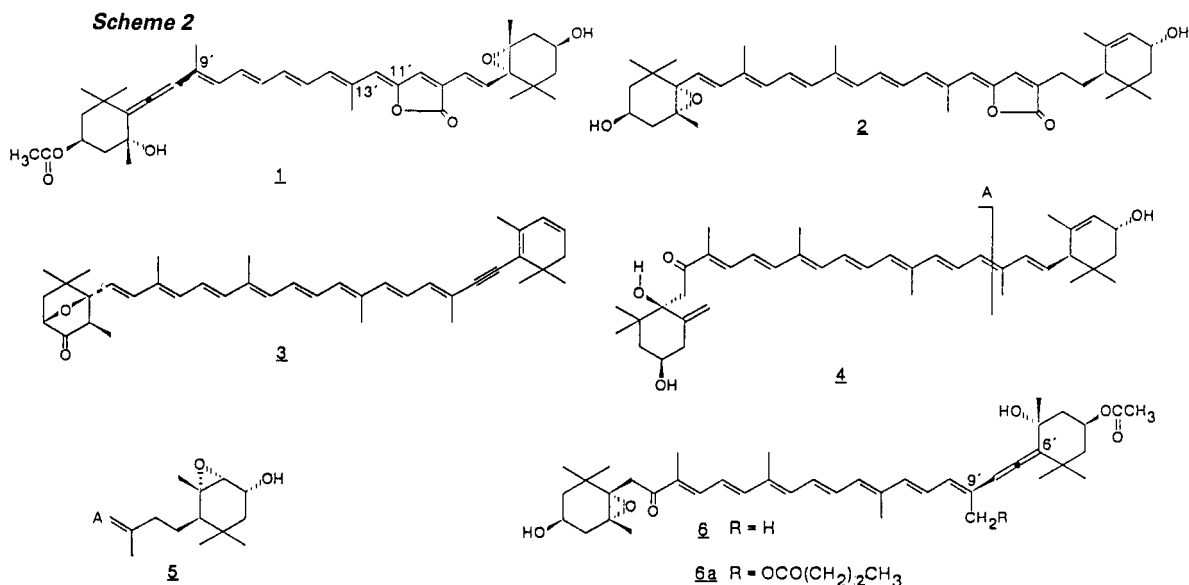
Examples are given on recent structural studies on algal carotenoids carried out in our laboratory.

Peridinin (**1**, Scheme 2) is the prototype of C₃₇-skeletal carotenoids. Recent complete ¹H NMR assignments confirm the structure. Three *Z*-isomers obtained upon iodine catalyzed stereomutation have been assigned 9-*cis*, 13'-*cis* and 11',13'-*dicis* configuration by ¹H NMR. The butenolide structural element was recently also encountered in a new C₄₀-carotenoid uriolide (**2**) from a prasinophyte (ref. 2).

The structure of the first naturally occurring oxabicycloheptane carotenoid eutreptiellane (**3**) is discussed, as well as related 3,6-oxabicycloheptane derivatives (refs. 3,4). *In vitro* formation of 2,5-oxabicycloheptane carotenoids from caroten-2-ols with BF₃ is referred to (ref. 5).

Spectroscopic and chemical evidence for the novel C₄₀-ketocarotenoids prasinoxanthin(**4**) and dihydroprasinoxanthin epoxide(**5**) are treated in some detail (refs. 6,2).

New allenic C₄₀-ketocarotenoids are the naturally occurring fucoxanthin(**6**) derivatives 19'-hexanoyloxyfucoxanthin (ref. 7) and 19'-butanoyloxyfucoxanthin (**6a**). HPLC and 2D ¹H NMR data are given.



Optical isomerism is possible for allenic carotenoids such as **6**. By analogy with the stereospecific, photosensitized oxidation of a chiral cyclohexenol reported by Isoe *et al.* (ref. 8), it has been suggested that (6'*S*)-fucoxanthin was the biosynthetic precursor of the more stable (6'*R*)-isomer (**6**) (ref. 8). The formation of (6'*S*)-fucoxanthin upon iodine catalyzed stereomutation (ref. 9) is being disproved. Detailed ¹H NMR ROESY (rotating frame NOE) experiments for all-*trans* **6a** and 9'-*cis* **6a** in collaboration with Englert suggest that (6'*R*)-9'-*cis*-fucoxanthin has been misidentified as all-*trans*-(6'*S*). CD data are supportive.

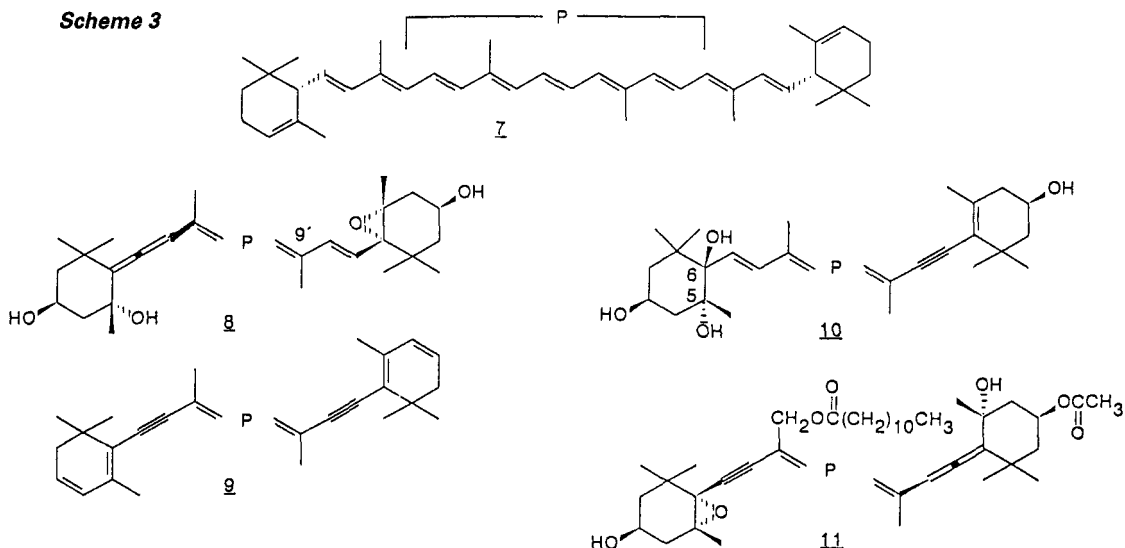
(6'*S*,6'*S*)- ϵ,ϵ -Carotene (**7**, Scheme 3), isolated from a chrysophyte, possesses negative Cotton effect and is the first example of an algal carotenoid with (6'*S*)-configured ϵ -end group.

All-*trans* carotenoids are usually the naturally occurring geometrical isomer with few classical exceptions. Recently we have demonstrated that 9'-*cis*-neoxanthin is the naturally occurring isomer in green leaves, spinach and the algae studied. In solution 9'-*cis* is gradually converted to all-*trans* (**8**).

New algal acetylenic carotenoids from Euglenophyceae include the highly unsaturated carotene **9**. The chirality we had previously assigned to heteroxanthin has been reversed by Eugsters group at C-5,6 to **10** (ref. 10).

Gyroxanthin from dinoflagellates is the first known allenic, acetylenic carotenoid. Also the acetylenic, epoxidic end group represents a new structural feature. Gyroxanthin occurs as a natural diester (**11**). Spectroscopic data including COSY ¹H NMR are given.

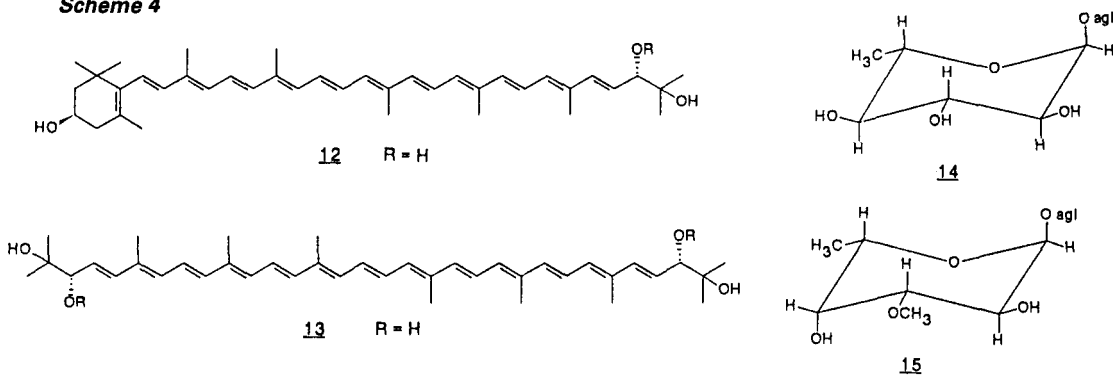
Scheme 3



Blue-green alga (cyanobacteria) produce sec., allylic glycosidic carotenoids derived from the hypothetical aglycones myxol (12, Scheme 4) of known (ref. 11), and oscillol (13) of tentative chirality. In a recent reinvestigation the sugar moiety bound to 12 in *Oscillatoria agardhii* was shown to be α -linked chivonose (14) and the *O*-methyl methyl-pentose bound to 12 in *O. bornetti* to be α -linked 3-*O*-methyl-fucose (15) (ref. 12).

Currently a carotenoid tetra (?) saccharide P457 from dinoflagellates is being studied.

Scheme 4



FOOD CHAIN STUDIES

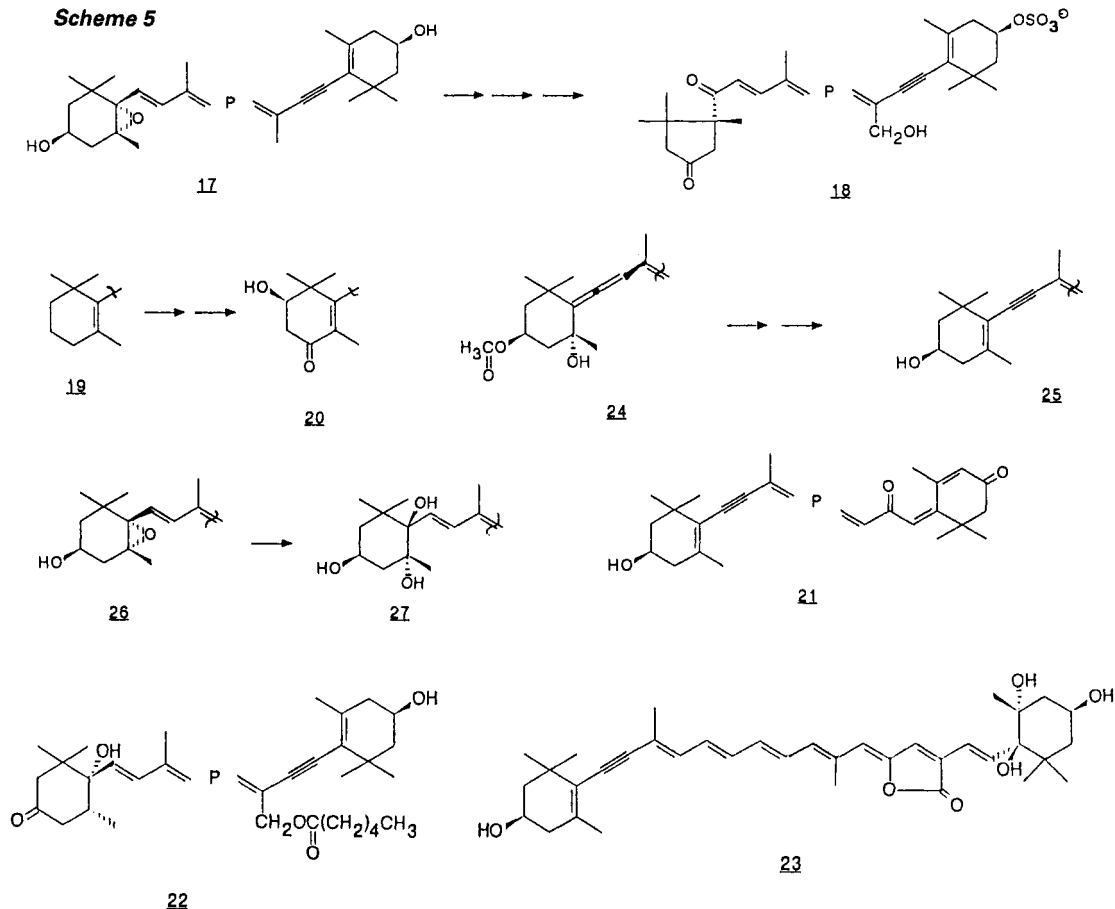
Carotenoids are synthesized de novo by algae, which represent the bottom of the marine food chain. Carotenoids are selectively resorbed and metabolized along the food chain.

Sulfated carotenoids, the bastaxanthins, including bastaxanthin g (16, Scheme 5), possess cyclopentanone rings. Isolated from a marine sponge they are likely metabolic products of microalgal, dietary diadinoxanthin (17) (ref. 13).

Experimentally documented is the selective resorption of β,β -carotene (19) from a green alga by the zooplankton *Daphnia magna*, and the metabolic transformation to new (2R)-2-hydroxy-4-keto-carotenoids (20) (ref. 14).

Selective resorption of fucoxanthin (6), 19'-hexanoyloxyfucoxanthin, diadinoxanthin (17) and peridinin (1, C₃₇-skeletal) from algal unicultures by *Mytilus edulis* (edible mussel), and metabolic transformations of the carotenoids resorbed, have recently been studied. Twenty different carotenoids, including three new metabolites, anhydro-amarouciaxanthin B (21), 19'-hexanoyloxyisomytiloxanthin (22) and hydrato-pyrrhoxanthinol (23), have been structurally identified. General metabolic reactions included hydrolysis of carotenoid acetates, conversion of allenic (24) to acetylenic (25) end groups and transformation of 5,6-epoxides (25) to 5,6-glycols (27).

Scheme 5



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