

Carotenoids of lower plants—recent progress

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Abstract - Under the general topic "Structure and Stereochemistry" progress on carotenoids of lower plants during the last three years is discussed. Carotenoids of photosynthetic bacteria, non-photosynthetic bacteria, fungi including yeasts, lichens and algae are addressed.

INTRODUCTION

The lower plants encompass bacteria (photosynthetic and non-photosynthetic), fungi including yeasts, lichens and algae (microscopic phytoplankton and macroscopic algae). Within this area, my task is to cover the general topic "Structure and Stereochemistry." Progress during the last three years since the 6th International IUPAC Carotenoid Symposium (Ref.1) will be reviewed in a critical and selective manner. For the benefit of biochemists and biologists a chemosystematic approach will be used, treating the major biological subgroups separately, rather than a lay-out based on progress within each structural type of carotenoids (Ref.2). Published work will be evaluated and recent, unpublished findings from our own laboratory will be included. Further details on algal carotenoids studied by Eugster's group will be treated in his presentation (Ref.3). The progress in each area will be discussed on the background of previous knowledge and a general evaluation finally made.

Pertinent compilations and reviews serving as the bases for this treatment are available on carotenoids of lower plants (Ref.4), stereochemistry (Ref.5) and the progress reports from the last symposium (Ref.1).

GENERAL PROGRESS IN METHODOLOGY

Improved access to high precision mass spectrometers and exact mass measurements, CD instruments for chiroptical data and in particular to high resolution NMR instruments with companion spin decoupling, NOE and COSY techniques, has facilitated structural studies on the microgram scale.

Whereas the application of modern instrumentation has reduced the required sample size, the purity requirements have increased. The application of HPLC for general separations and separations of diastereomers (Ref.6) and geometrical isomers has become invaluable. Improved TLC systems have also been developed (Ref.7).

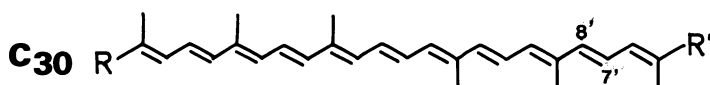
Analyses of mixtures of optical isomers by the HPLC-based camphanate (Ref.8) and more recently carbamate (Ref.9) methods already seem indispensable.

NON-PHOTOSYNTHETIC BACTERIA

A scattered distribution and unpredictable carotenoid pattern is encountered in non-photosynthetic bacteria (Refs.4,10), some of which have unique ability to synthesize either C₃₀-diapocarotenoids or higher (C₄₅- and C₅₀) carotenoids.

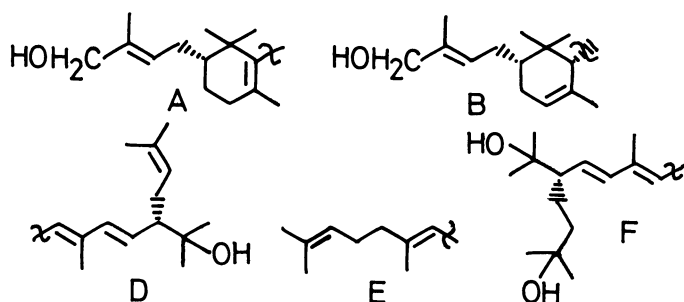
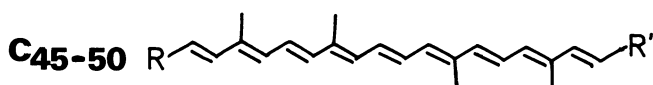
Staphyloxanthin has been assigned the C-30 diapocarotenoid structure **1** (α -O-glucopyranosyl-1-O-(4,4'-diaponeurosporen-4-oate)-6-O-(12-methyltetradecanoate), Scheme 1) (Ref.11). Acylated sugar residues are also encountered in carotenoid glycosides from myxobacteria (Ref.12). The exact position of the in-chain methyl groups and the α -linkage in **1** have not been proved.

The new C-30 diapocarotenoids 4,4'-diapocarotene-4,4'-dial (2), 4'-oxo-4,4'-diapocaroten-4-oic acid (3) and a β -D-glucosyl-4,4'-diapocaroten-4-oate (4), reported from mutants of *Pseudomonas rhodos* (Refs.13,14) appear related by the oxidative sequence aldehyde \rightarrow carboxylic acid \rightarrow glucosyl ester. A red strain of *Rhizobium* produces diglucosyl-4,4'-diapocaroten-4,4'-dioate (5) and glucosyl-4,4'-diapocaroten-4-oate-4-oic acid (6) (Ref.15), previously characterized from *P.rhodos* (Ref.13). A diapocarotenoid similar to 6 has also been characterized from another *Pseudomonas* sp. (Ref.16). Thus C-30 skeletal diapocarotenoids, not yet included in the official IUPAC nomenclature rules (Ref.17), are distributed outside *Streptomyces* and *Staphylococcus*.

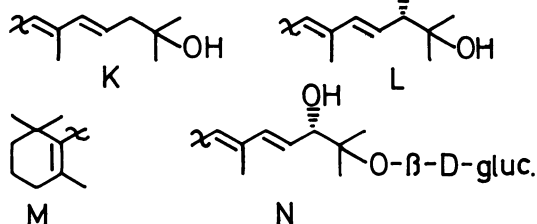
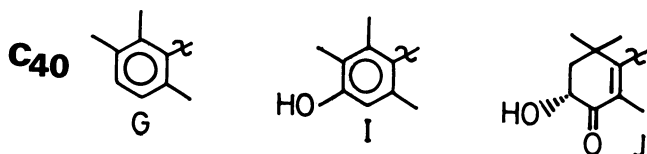


1 Staphyloxanthin, 7,8'-dihydro, R= COOgluc, R'=Me
2 R=R'=CHO
3 R=COOH, R'=CHO

4 R= COOgluc , R'=Me
5 R=R'= COO gluc..
6 R=COCH, R'=COOgluc.



7 C.p.450, R=R'=A
8 Decaprenoxanthin, R=R'=B
9 C.p.473, R=A, R'=D
10 C.p.482, R=D, R'=E
11 Bacterioruberin, R=R'=F



12 OH-Isorenieratene, R=I, R'=G
13 Di-OH-Isorenieratene, R=R'=I
14 Flexixanthin, R=J, R'=K
15 2'-OH-Flexixanthin, R=J, R'=L
16 Phleixanthophyll, R=M, R'=N

Scheme 1. Carotenoids from non-photosynthetic bacteria.

Within the C-50 series the structure of C.p. 450 has been revised to 7 (Ref.18) by H NMR including LIS. Total syntheses of optically inactive C.p. 450 (7), as well as of optically inactive 2,6-cis, 2',6'-cis decaprenoxanthin (8) have been accomplished (Ref.19). Comparative studies including H NMR, HPLC and TLC in favour of correct structural assignments for the natural carotenoids (7,8) have been effected (Ref.20).

By H NMR including LIS also C.p.473 was shown to have the two hydroxy groups at opposite ends of the molecule and assigned structure 9 (Ref.18). The chirality, elucidated by chiroptical studies (Refs. 21,22), was found to be the same as for other C-50 carotenoids, supporting a common biosynthetic isopentenylation. This was also true for the C-45 carotenoid C.p.482 (10), where the chirality was recently solved by a synthetic approach (Refs.22,23).

Syntheses of chiral acyclic C-15 skeletal alcohols suitable for the preparation of aliphatic C-45 and C-50 carotenoids of bacterioruberin (11) type, have recently been reported (Ref.24).

In the C-40 series the previously known phenolic carotenoids 3-hydroxyisorenieratene (12) and 3,3'-dihydroxyisorenieratene (13) from Streptomyces mediolani have now been reported from Brevibacterium linen (Ref.25).

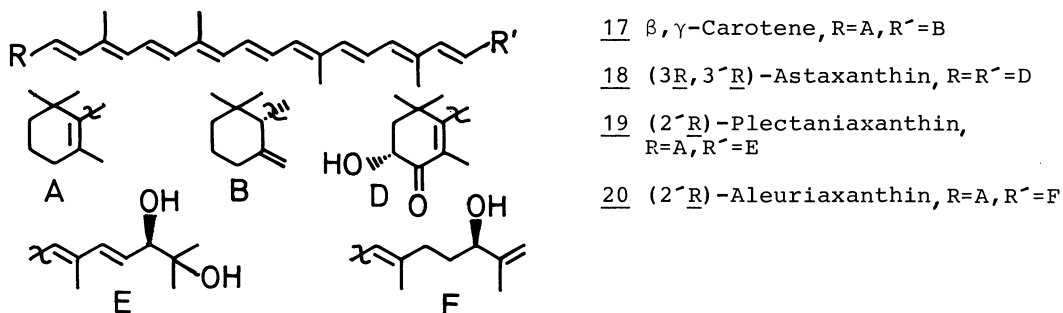
Chiralities have been assigned to flexixanthin (14) and 2'-hydroxyflexixanthin (15) (Refs.21,26) from chiroptical correlation based on the additivity hypothesis (Ref.27) for carotenoids of identical chromophores and the conformational rule (Ref.28). By a similar approach the chirality of (2S)-phleixanthophyll (16) has been solved (Ref.21).

PHOTOSYNTHETIC BACTERIA

The carotenoids of hardly any biological subgroup have been studied as extensively as those of photosynthetic bacteria (Refs.4,29,30,31). C-40 skeletal, achiral, aliphatic, mono- and diaryl carotenoids are common. These frequently carry tert. methoxy, hydroxy or occasionally glucosyloxy groups. 1,2-Dihydro features, keto groups in 2(2') or 4(4') positions or cross-conjugated aldehyde in 20-position are encountered. New structures have not been reported during the period. Unfortunately, the first natural carotenoid (C₄₀H₄₇O(OCH₃)₂S by high precision mass measurements) with sulfur bound directly to the carbon skeleton, represents a minor carotenoid, not invariably present in Chromatium purpuratum (Ref.32).

FUNGI

The carotenoid pattern of fungi, including yeasts, have recently been reviewed (Refs.4,33). C-40 aliphatic, mono- and dicyclic carotenes and carotenoids are common, and apocarotenoids such as neurosporaxanthin encountered. Sec./tert. hydroxy groups, keto groups in 2(2') or 4(4') positions, or carboxylic acid functions in 17' or 4'-positions are characteristic features. The chiralities of (6'S)-β,γ-carotene (17), Scheme 2) (Ref.34) from Caloscypha fulgens and of (3R,3'R)-astaxanthin (18) from Pfaffia rhodozyma (Ref.35) are noteworthy.



Scheme 2. Fungal carotenoids.

The absolute configuration of (2'R)-plectanixanthin (19), which could not be determined by the Horeau method, has been elucidated by chiroptical correlation of plectanixanthin acetone and (2'S)-16', 17'-dinorplectanixanthin acetone, synthesized from D-mannitol via 2,3-O-isopropylidene-D-glyceraldehyde as key synthon (Ref.36).

(2^rR)-Plectanixanthin (19) 2^r-esters and tetraacetates of 2^r- and 1^r-mono-β-D-glucosides have been prepared (Ref.37) and used as chiroptical standards in a CD correlation involving related β-monocyclic dodecaene carotenoids such as 14, 15 and 16, Scheme 1 (Ref.21).

Total syntheses of each of the two enantiomers of aleuriaxanthin (Ref.38) have confirmed the previous 2^rR-assignment for natural aleuriaxanthin (10) (Ref.39). The chiral synthons were prepared by Sharpless epoxidation (Ref.40), later also utilized for syntheses in the C-50 series (Ref.24).

It is interesting that the chiralities of the fungal carotenoids 17, 18 and 19 are opposite to those encountered in analogous bacterial and algal carotenoids.

LICHENS

Lichens are dual organisms of a fungus (mycobiont) and algae (phycobiont). Early work on carotenoids in lichens has been compiled (Ref.41). Systematic modern studies on lichen carotenoids for chemosystematic purpose have not been conducted.

β,β-Carotene and (3R,3^rR,6^rR)-lutein (27, Scheme 4) was recently characterized from *Dirina stenhammari* (Ref.42). Mutatoxanthin (zeaxanthin (28) 5,8-epoxide) has been claimed to be the dominant carotenoid in the genus *Xanthoria* (Ref.43). However, the identification must be considered most tentative, in contrast with the preceding conclusive stereochemical assignment of the diastereomeric mutatoxanthins (Ref.44).

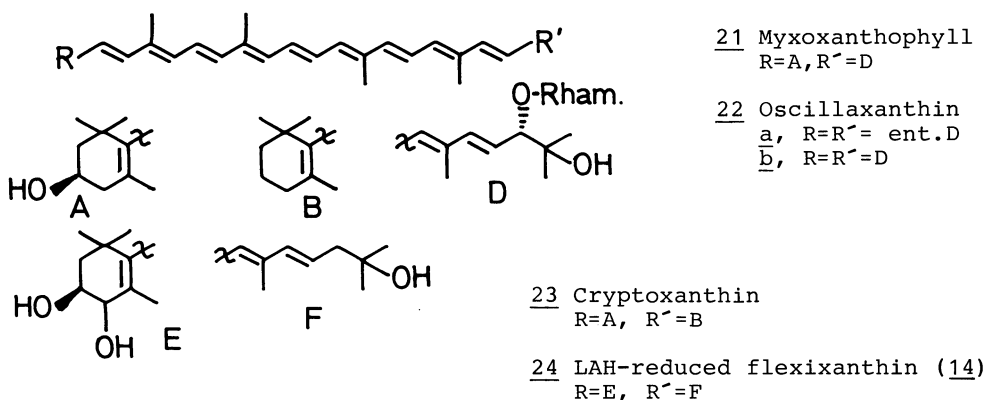
ALGAE

Structures, including stereochemistry, of the carotenoids encountered in the fifteen algal classes (Refs.45,46) have been reviewed until 1980 (Refs.4,47,48,49). Most of the algal classes have a characteristic carotenoid pattern. Carotenoids and chlorophylls represent major criteria for the identification of microscopic algae. Progress pertinent to particular algal classes will be discussed, following roughly the presumed evolutionary line.

Cyanophyceae

The procaryotic blue-green algae, now also classified as bacteria (Cyanobacter) (Ref.50), produce unique monocyclic and aliphatic carotenoid glycosides (rhamnoses and O-methyl-methylpentosides), notably myxoxanthophyll (21), Scheme 3, and oscillaxanthin (22).

In a chiroptical correlation 3R,2^rS-configuration (21) for myxoxanthophyll has recently been assigned (Ref.21). Its Cotton effect is dominated by the influence from the chiral β-ring with a smaller contribution from the aliphatic C-2^r center. The strong negative Δε at 280 nm suggested the same absolute configuration as for (3R)-cryptoxanthin (23). According to the conformational rule (Ref.28) and additivity hypothesis (Ref.27) the Cotton effect of the chiral β-ring may be eliminated by subtracting the Cotton effect of LAH-reduced flexixanthin (24). The difference curve is approximately conservative, closely similar in shape and opposite in sign to that of plectanixanthin (19, Scheme 2) 2^r-tetraacetyl-β-D-glucoside, leading to opposite chiralities at C-2^r for 21 and 19.

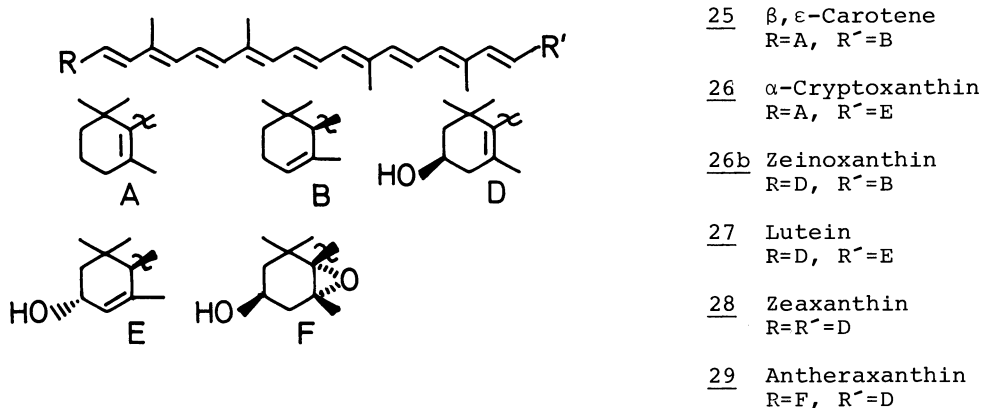


Scheme 3. Carotenoids from Cyanophyceae and relevant CD models.

The results casts doubt on the previous stereochemical assignment (22a) for oscillaxanthin (Ref.51). From biogenetic considerations, in comparison with myxoxanthophyll (21), oscillaxanthin is expected to be 2S, 2'S (22b). However, the required tridecaene chiroptical standards are not yet available. During this study we have learned that identical chiral C-2' end groups on β -monocyclic dodecaene and on acyclic tridecaene carotenoids may have very different effects on the CD spectra (Refs.21,52). Thus, hydrogenation or silylation of a chiral C-2' end may invert the observed CD spectrum in the acyclic series, but not in the β -series.

Rhodophyceae

Dicyclic carotenes with β - and ϵ - end groups and their 3,3'-dihydroxy derivatives are general and epoxides rare. In a recent study (Ref.53) the common configurations of (6'R) - β, ϵ -carotene (25, Scheme 4), (3'R, 6'R)- β, ϵ -caroten-3'-ol (α -cryptoxanthin (26), (3R, 3'R, 6'R)-lutein (27), (3R, 3'R)-zeaxanthin (26) and all-trans (3S, 5R, 6S, 3'R)-antheraxanthin (29) were established by H NMR and CD.

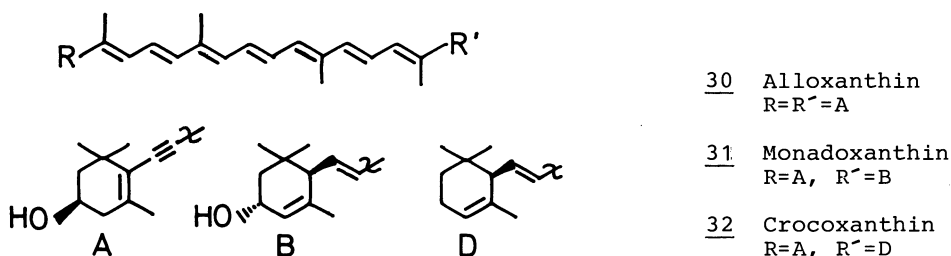


Scheme 4. Red algal carotenoids.

In this work the first documentation of α -cryptoxanthin (26) was presented by conclusive H NMR, CD and allylic methylation. It was suggested that the trivial name zeinoxanthin (Ref.54) should be maintained for the positional isomer (3R, 6'R)- β, ϵ -caroten-3'-ol (26b).

Cryptophyceae

ϵ -Type and acetylenic carotenoids are characteristic for this class with (3R, 3R)-alloxanthin (30), Scheme 5, as the typical cryptophyte indicator.



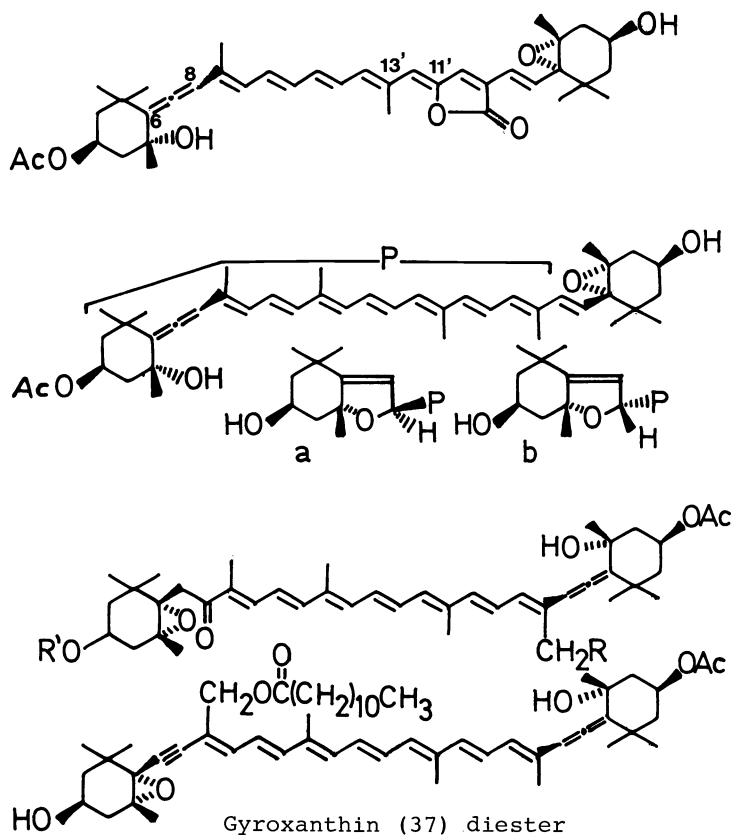
Scheme 5. Carotenoids from Cryptophyceae.

In a recent quantitative study selected cryptophytes were examined by techniques including HPLC, MS, H NMR and CD (Refs. 55,56). β, ϵ -Carotene (25) possessed the common 6R-configuration, and monadoxanthin (31) assigned 3'R, 6'R-chirality from H NMR and CD evidence; 3R-chirality being favoured on biogenetic grounds as for crocoxanthin (32) (Ref.57) in comparison with alloxanthin (30). No allenic precursors to the acetylenic carotenoids could be detected (cf. Ref.58).

Dinophyceae

Dinoflagellates produce structurally more complex carotenoids than other algal classes. Acetylenic and allenic carotenoids, epoxides and butenolides with C-37 skeletons are encountered. Peridinin (33) is the characteristic carotenoid, not produced by other algae.

Whereas the chirality of peridinin (33) has been previously elucidated (Ref.59), a study of peridinin stereoisomers by HPLC, H NMR (400 MHz) and CD has recently been conducted (Ref.60). The H NMR of the common all-*trans*-6*R* isomer (33) has now been fully assigned using spin decoupling, NOE and COSY, in good agreement with the simulated spectrum. From stored solutions or iodine catalyzed stereomutation mixtures of 33, the allenic 6*S* isomer (33b) has been isolated and characterized by the same criteria, VIS and CD spectroscopy. The Cotton effect differs only slightly from that of 33. Similar isomerism around the chiral allene function was first reported for fucoxanthin (Ref.61). We have now also characterized a 6*S*-isomer of neoxanthin (Ref.60). A neo U isomer of peridinin (33), isolated by TLC, consisted of neo UI and neo UII in equal proportion. Guided by previous H NMR generalizations (Ref.62) neo UI was assigned the 6*R*-11', 13'-*dicis* structure 33c (11'*E*, 13'*Z*) and neo UII the 6*R*-13'-*monocis* structure 33d (11'*Z*, 13'*Z*). The stereoisomeric set of peridinin thus offers two interesting features: the allene isomerism and the Δ 11'*E/Z* isomerism involving the butenolide ring.



- 33 Peridinin
all-*trans*-6*R*
33b all-*trans*-6*S*
33c neo UI
6*R*-11', 13'-*dicis*
33d neo UII
6*R*-13'-*monocis*

- 34 Dinoxanthin
35 Dinochromes
a (Epimer 1)
b (Epimer 2)

- 36 Fucoxanthin
acetate
R=H, R'=Ac
38 Fucoxanthin
R=R'=H
39 Hexanoyloxy-
fucoxanthin
R=OCC₅H₁₁, R'=H
40 Butanoyloxy-
fucoxanthin
R=OCC₃H₇, R'=H

Scheme 6. Carotenoids from Dinophyceae.

The dinochromes (35 a,b) are the C-8 epimeric furanoid rearrangement products of the epoxidic dinoxanthin (34) (Ref.63). In the recent extensive H NMR studies of carotenoid epoxides and furanoid oxides (Refs.44,64,65,66,67) unequivocal H NMR assignments of the two epimeric dinochromes have been made (Ref.66).

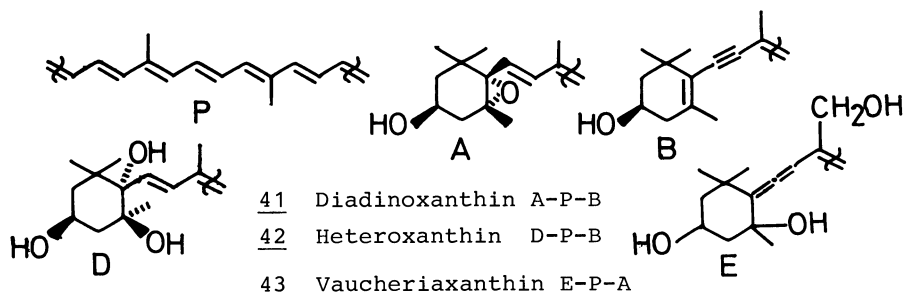
Fucoxanthin acetate (36) is a natural diacetate (Ref.68) and gyroxanthin (37) occurs as a natural diester (acetate and mainly dodecanoyl ester) in a *Gyrodinium* sp. (Refs.68,69). The acetylenic epoxide structure 37 is favoured. The same alga produces 19'-hexanoyloxy-fucoxanthin (39), first isolated from *Coccolithus huxleyi* (Prymnesiophyceae) in a mixture with fucoxanthin (38) (Ref.70).

During our recent study of *Gymnodinium breve*, responsible for the poisonous Florida red tide, two fucoxanthin-like carotenoids were identified as the hexanoyloxy derivative 39 and the new butanoyloxy derivative 40, fully characterized from a chrysophyte *Cocc.min.* Haltenbanken (Ref.7). HPLC separation of 38, 39 and 40 may now be achieved (Ref.7). The butanoyloxy derivative 40 had the predicted VIS, H NMR and MS properties, and methyl butanoate was identified by GC after alkaline hydrolysis of 40 and methylation.

The previously partly characterized polar carotenoid P457 (Ref.63) has been found to be typical of peridinin-producing dinoflagellates and considered as a disaccharide from MS evidence (Ref.71). Synthetic models, including peridinin (33) cellobioside, have been prepared by the Koenigs-Knorr reaction, which in addition to the expected β -D-glucosides and β -cellobioside afforded orthoesters, but no α -anomers. Further structural studies on this complex, minor, allenic, crossconjugated carotenal tetra(?) hexoside are reported at this symposium (Ref.37).

Raphidophyceae

The carotenoids of this class were recently re-examined by modern methods (Ref.72). Two definitive members of the class (*Gonyostomum semen* and *Vacuolaria virescens*) showed a similar carotenoid pattern including diadinoxanthin (41, major), dinoxanthin (34), heteroxanthin (42) and vaucherixanthin (43) 3,19-diacetate (*V. virescens*). The pigment composition with a dominance of acetylenic, allenic and epoxidic carotenoids resembles that of Xanthophyceae.



Scheme 7. Carotenoids from Raphidophyceae.

Two potential members *Chattonella japonica* and *Fibrocapsa japonica* contained no acetylenic carotenoids and fucoxanthin (38) as the major carotenoid.

Chrysophyceae

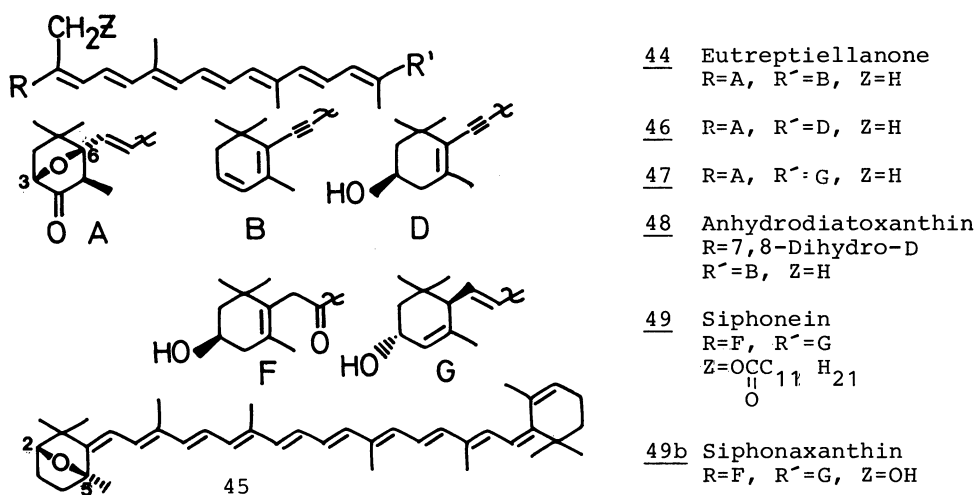
A recent survey of seven selected chrysophytes has been published (Ref.73). The carotenoid pattern includes fucoxanthin (38), diadinoxanthin (41) and other epoxidic, allenic and acetylenic carotenoids. The first isolation of 19'-butanoyloxyfucoxanthin (40) from *Cocc.min.* Haltenbanken (Ref.7) has already been mentioned. The CD spectrum of ϵ, ϵ -carotene from the same alga offered a surprise, suggesting $6S, 6'S$ -chirality (Ref.74).

Euglenophyceae

Proceeding now from the Chromophytes to the Chlorophytes the Euglenophyceae have recently been more closely examined because of the intriguing taxonomic position. The marine *Eutreptiella gymnastica*, examined in great detail, has offered new carotenoid structures (Refs.75,76).

Eutreptiellanone (44, Scheme 7) represents the first naturally occurring oxabicyclo [2.2.1] heptane carotenoid (Ref.75). Related 2,5-oxa-bicycloheptane carotenoids, such as 45, were previously prepared by partial synthesis in our laboratory (Ref.77). Detailed spectroscopic characterization and chemical derivatization lead to structure 44 for eutreptiellanone, including plausible chirality. Subsequently, the minor carotenoids 46 and 47 were shown to possess the same bicyclic end group (Ref.76).

Anhydrodiatloxanthin (48) with a new hydrocarbon terminus, also present in eutreptiellanone (44), has been fully characterized. Siphonein, with defined n -2-trans-2-dodecenoic esterifying acid, now assigned $3R(?), 3'R, 6'R$ -chirality (49) (Ref.75), has been isolated from two marine euglenophytes (Refs. 75,76). *Euglena gracilis*, the prototype of the class, is currently being re-examined for minor carotenoids (Ref.75). As in the Raphidophyceae (Ref.72) the acetylenic

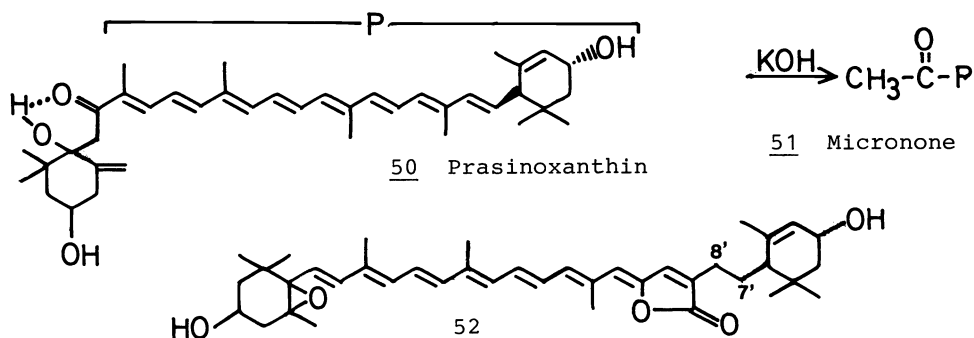


Scheme 8. Carotenoids from Euglenophyceae and a relevant model (45).

diadinoxanthin (41, Scheme 7) may be, but not invariably is, the major carotenoid of Euglenophyceae (cfr. Ref.4).

Prasinophyceae

Siphonein (49, Scheme 8) is also encountered in green flagellates (Ref.78). Xanthophyll K, considered peculiar to certain species of Prasinophyceae (Ref.79), was found to be identical with a carotenoid assigned structure 50 and named prasinoxanthin (Ref.80). Prasinoxanthin (50) with assigned 3^R, 6^R- and tentative 3^R, 6^R-chirality represents the first algal carotenoid with a γ -end group. It has a strongly hydrogen bonded *tert.* hydroxy group in the novel end group and undergoes facile retro-aldol cleavage to the methyl ketone 51 (micronone).



Scheme 9. Carotenoids from eucariotic ultraplankton clones.

In a recent scanning of eucariotic, non-flagellated ultraplankton clones (Prasinophyceae?) prasinoxanthin (50) was invariably the major carotenoid (Ref.81). One new minor carotenoid contained the same γ -end group and undergoes retro-aldol cleavage. A second new, minor carotenoid assigned structure 52 on the basis of H NMR (400 MHz) evidence, represents the first carotenoid butenolide encountered outside Dinophyceae.

The carotenoid chemistry of this algal class, including structurally complex carotenoids with presumed 7', 8'-dihydro features, is not yet fully explored.

Chlorophyceae

The carotenoid pattern of the green algae resembles that of higher plants, but offers some special carotenoids such as siphonaxanthin (49b, Scheme 8) and its ester siphonein (49). Lutein (27, Scheme 4) is a common carotenoid, and loroxanthin (53=19-hydroxylutein) may be encountered (Ref.4). The chirality of loroxanthin was recently settled as the biogenetically predicted (3^R, 3^R, 6^R)-

19-hydroxylutein (Ref. 82). In this connection, the synthesis of in-chain hydroxylated carotenoids using vinyl-anions generated by the Shapiro reaction have been effected (Ref.83). Astaxanthin, a secondary carotenoid of some green algae, is the optically pure, common (3*S*,3'*S*)-isomer (ent.10, Scheme 2) (Ref.84).

GENERAL EVALUATION

Some fifteen new carotenoids, including three new end groups, have been characterized from lower plants during the report period. Chiralities have been assigned to around another fifteen known carotenoids. Isomerism around chiral allene bonds in solution has been shown to be more general than suspected. Whereas chiralities have been assigned on the basis of comparative H NMR and CD or by comparison with synthetic models of known configuration, a breakthrough for X-ray analysis of chiral carotenoids finally seems to have been made with current studies on underivatized lutein (27) and zeaxanthin (28) (Ref.85).

Hitherto, de novo carotenoid producing organisms including lower plants, appear to synthesize optically pure carotenoids, a useful dogma in evaluating metabolism and in food-chain studies.

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