Pure Appl. Chem., Vol. 71, No. 12, pp. 2263–2272, 1999.
Printed in Great Britain.

New carotenoids: Recent progress*

Adriana Z. Mercadante

Department of Food Science, Faculty of Food Engineering, State University of Campinas, PO Box 6121, 13083-970, Campinas, Brazil

Abstract: Progress on the identification of new carotenoids over the six years 1993–1999 is reviewed. Carotenoid structures with the normal C_{40} skeleton, carotenoid derivatives such as sulfates and glycoside esters, and apocarotenoids from higher plants, marine organisms, bacteria and algae, and metabolites in fishes and human serum are covered. Whenever possible, comments are made about biosynthetic and biological implications.

INTRODUCTION

This review covers the new carotenoids reported in the literature during the period 1993–1999. The carotenoids presented here were identified by the combined information given by their UV–visible, mass and nuclear magnetic resonance (NMR) spectra, and from circular dichroism (CD) spectral data for chiral carotenoids. In a few cases, synthesis was carried out to confirm the structure assigned. The new carotenoids will be treated according to their structural similarities.

The structures of carotenoids isolated from natural sources are shown in the book, *Key to Carotenoids* [1], and in the Appendix: List of New Carotenoids [2], which together, cover the literature up to the end of 1992. In addition, progress on the chemistry of marine carotenoids was previously reviewed by Liaaen-Jensen, covering up to 1990 [3].

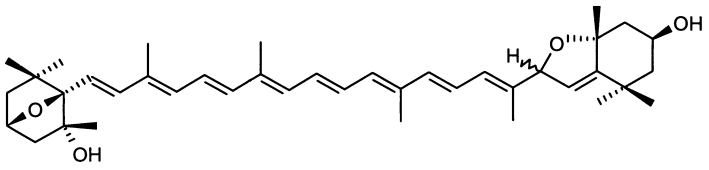
NEW C_{40} CAROTENOIDS

In the past few years, many new carotenoids with the 3,6-epoxide group have been isolated from different varieties of red paprika. These include the diastereoisomeric pair (8′*R* and 8′*S*) of cucurbitachrome ((3*S*,5*R*,6*R*,3′*S*,5′*R*)-5,8:3′,6′-diepoxy-5,6,5′,6′-tetrahydro-β,β-carotene-3,5′-diol (**1**) [4] and examples with the κ-end group, such as 5,6-diepicapsokarpoxanthin ((3*S*,5*S*,6*S*,3′*S*,5′*R*)-5,6-dihydro-3,5,6,3′-tetrahydroxy-β,κ-caroten-6′-one (**2**) [5]. The occurrence of (3*S*,5*R*,6*S*)-**1** and (3*S*,5*S*,6*S*)-**2** in paprika can be explained by the enzyme-catalysed hydrolysis of (3*S*,5*R*,6*S*)-5,6-epoxy carotenoids, such as violaxanthin, via the formation of a carbenium ion at C-5. In this way, the configuration at C-5 may change, but the configuration at C-6 remains unchanged (Scheme 1).

Two lycopene metabolites with a novel five-membered ring end group were isolated from human serum and breast milk and identified as the diastereoisomeric pair I (**3**) (Scheme 2) and II of 2,6-cyclolycopene-1,5-diol [6]. Although the relative configurations at the three asymmetric centres at C-2, C-5 and C-6 were determined by NMR studies, the absolute configurations have not yet been established. These carotenoids may result from the metabolic oxidation of lycopene to 5,6-epoxy-lycopene, which, due to its instability, undergoes rearrangement to form an epimeric mixture of 2,6-cyclolycopene 1,5-epoxides. The enzymatic or acidic hydrolysis of these epoxides may then yield an epimeric mixture of **3** and 2,6-cyclolycopene-1,5-diol II.

Two new trihydroxy-keto-carotenoids, (2*R*,3*S*,3′*S*)-2-hydroxyastaxanthin and (2*R*,3*S*,3′*R*)-2-hydroxy-adonixanthin, were isolated from an astaxanthin-producing marine bacterial strain SD-212, from Japan

* Lecture presented at the 12th International Symposium on Carotenoids, Cairns, Australia, 18–23 July 1999, pp. 2205–2302.
Correspondence: E-mail: mercadan@obelix.unicamp.br



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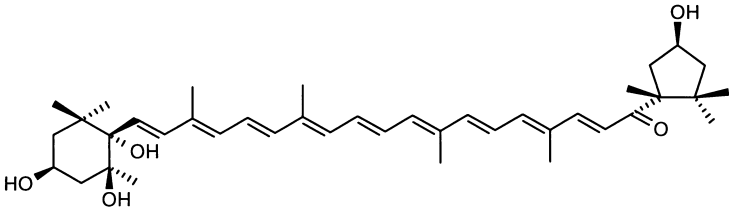

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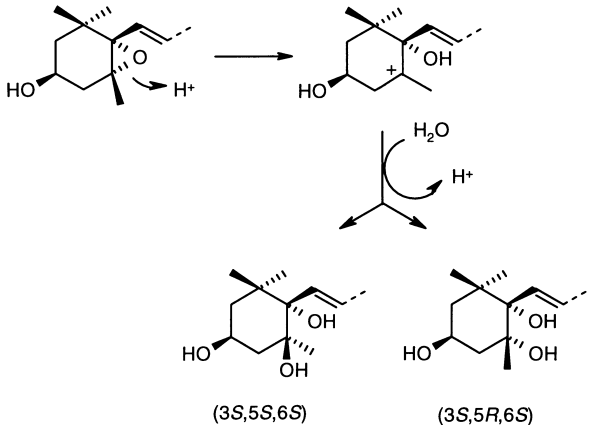
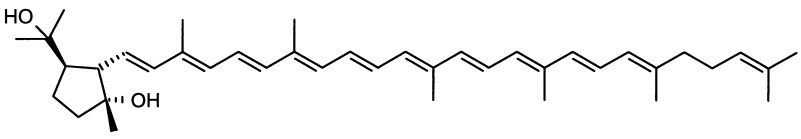


Scheme 1



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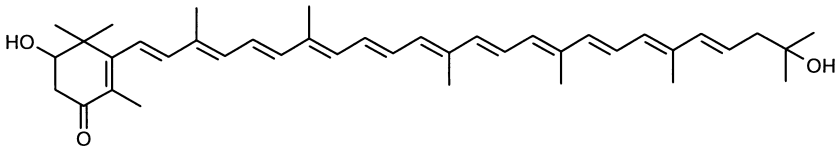
Scheme 2

[7], and had the same chirality at C-3 and C-3′ as the corresponding homologues astaxanthin and adonixanthin, respectively. Erythroxanthin, (3*S*,2′*R*,3′*R*)-3,2,3′-trihydroxy-β,β-caroten-4-one, was also isolated in the free form [7]. It had only previously been reported as a sulfate derivative [8].

Also with a hydroxyl group at C-2, deinoxanthin (**4**), 2,1′-dihydroxy-3′,4′-didehydro-1′,2′-dihydro-β,ψ-caroten-4-one, was isolated from *Deinococcus radiodurans* (Scheme 3). As the amount of pigment available was not sufficient to perform ^{13}C NMR experiments, the allylic position of the keto group with respect to the double bond in the β-ring was indicated by positive reduction with $NaBH_4$. Elimination of

water by treatment with base was also in accordance with the properties of the 2-hydroxy-4-keto-β-end group. Although CD was measured, the stereochemistry remains unknown because no reference compound with known stereochemistry was available [9].



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Scheme 3

A purple carotenoid, with λ_{max} at 514 nm in ether, was isolated from *Rhodobacter capsulatus* and identified as (13*Z*)-1,1′-dimethoxy-3,4,3′,4′-tetradehydro-1,2,1′,2′-tetrahydro-ψ,ψ-caroten-20-al [10].

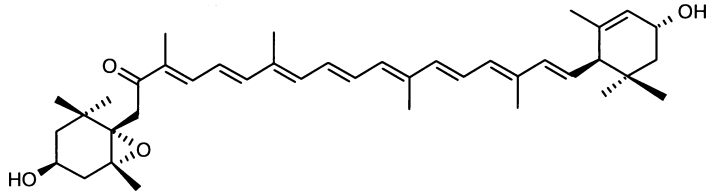
A new diacetylenic carotenoid, (3*S*,3′*S*)-3,3′-dimethoxy-7,8,7′,8′-tetradehydro-β,β-carotene, given the common name suberixanthin, was isolated from the sponge *Suberites massa* from the lagoon in Venice [11]. The *S* chirality was suggested by its CD spectrum, which showed opposite features to that of the structurally related alloxanthin, which possesses (3*R*,3′*R*) chirality.

Continuing their enormous work on carotenoids, Liaaen-Jensen's group evaluated the carotenoid profile of members of the algal class Prasinophyceae, analysing *Bathycoccus prasinos*, *Micromonas pusilla*, *Mantoniella squamata* [12], *Pyramimonas amylifera*, *Codium fragile*, *Prasinococcus capsulatus*, *Nephroselmis olivacea* [13]. This class of alga displayed a wide range of carotenoid structures, including 30 identified carotenoids of which about 14 possess special structural features peculiar to this class. Based on the carotenoid composition of 13 species, a chemosystematic evaluation at the ordinal level was proposed according to the following prototypes: type 1 with common green algal carotenoids such as lutein and violaxanthin; type 2 presenting common algal carotenoids together with carotenoids of the siphonaxanthin series; and type 3 with common green algal carotenoids along with carotenoids of the prasinoxanthin and micromonal/uriolide series. Preprasinoxanthin (**5**) (Scheme 4), with a rare 5,6-epoxy-8-keto end group, is a new carotenoid from the prasinoxanthin series. The micromonal series represents novel carotenoids with an aldehyde group or the corresponding primary alcohol in the 19′-position, such as (3*R*,3′*R*,6′*R*)-3,3′-dihydroxy-7′,8′-dihydro-β,ϵ-caroten-19′-al, named micromonal (**6**) (Scheme 4), micromonol ((3*R*,3′*R*,6′*R*)-7′,8′-dihydro-β,ϵ-carotene-3,3′,19′-triol) and the corresponding anhydromicromonal ((3*R*,6′*S*)-3-hydroxy-3′,4′-didehydro-7′,8′-dihydro-β,ϵ-caroten-19′-al) and anhydromicromonol. Deepoxyuriolide, 3′-dehydrouriolide and anhydrouriolide (**7**) (Scheme 4) are three new derivatives of uriolide. Dihydrolutein, a lutein derivative with the same hydrogenated double bond at C-7′,8′, found in some of the above new carotenoids, was isolated from *M. squamata* and *P. capsulatus*.

Three novel (9*Z*,9′*Z*)-carotenoids, cucumariaxanthin A ((9*Z*, 9′*Z*)(5*S*,6*S*,5′*S*,6′*S*)-5,6,5′,6′-tetrahydro-β,β-carotene-4,4′-dione), B ((9*Z*,9′*Z*)(5*S*,6*S*,4′*S*,5′*S*,6′*S*)-4′-hydroxy-5,6,5′,6′-tetrahydro-β,β-caroten-4-one) and C ((9*Z*,9′*Z*)(4*S*,5*S*,6*S*,4′*S*,5′*S*,6′*S*)-5,6,5′,6′-tetrahydro-β,β-carotene-4,4′-diol), were found in sea cucumbers of the order Dendrochirotida, but they were not found in those of the order Aspidochirotida [14,15]. Cucumariaxanthin A (**8**) (Scheme 5) was found as a major carotenoid in some parts of *Cucumaria japonica*, *C. echinata* and *Pentacta australis*, along with canthaxanthin. These new carotenoids may come from a reductive and isomeric metabolic pathway from canthaxanthin.

During reinvestigation of the β-echinenone fraction in parts of the sea urchin *Pseudocentrotus depressus*, Tsushima and Matsuno [16] found a greater abundance of (9′*Z*)-β-echinenone (76–78% of the total echinenone fraction) in the ovary and testis. The authors suggested that the (*Z*)-carotenoid may have a specific function in the urchin, probably related to reproduction.

The enzymatic reductive conversion *in vitro* of violaxanthin into a novel retro carotenoid, (3*S*,5*R*,3′*S*,5′*R*)-5,5′-dihydro-3,5,3′,5′-tetrahydroxy-β,β-carotene (**9**) (Scheme 6), occurred in chromoplasts of flowers after supplementation with reduced nicotinamide adenine dinucleotide (phosphate) (NAD(P)H) in the presence of protoporphyrin IX, under anaerobic conditions [17].



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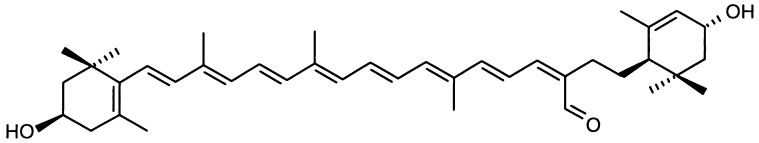

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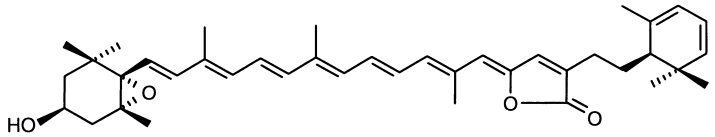

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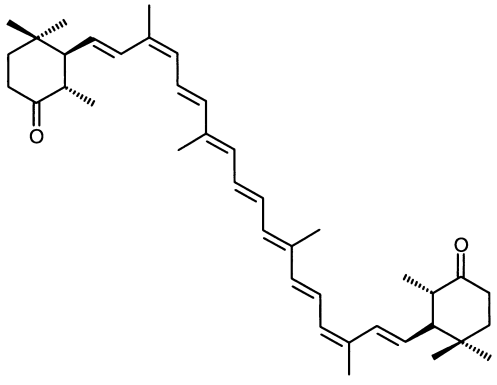
Scheme 4



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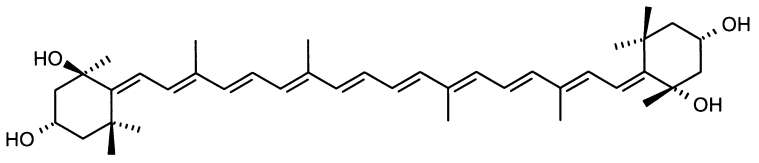
Scheme 5



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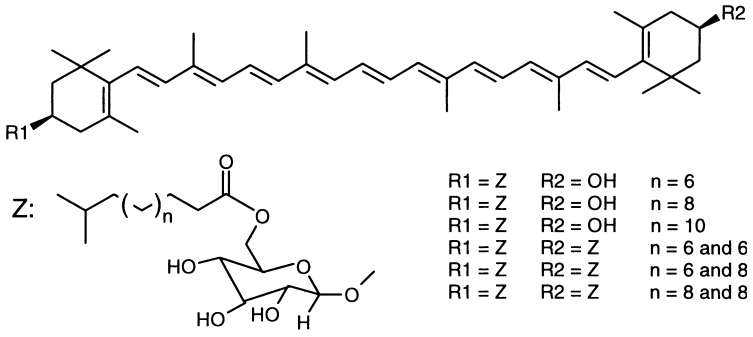
Scheme 6

CONJUGATED DERIVATIVES

Two new carotenoid glycosides, (3*S*,3′*S*)-astaxanthin-3-β-D-glucoside and (3*S*,3′*R*)-adonixanthin-3-β-D-glucoside, were isolated from the astaxanthin-producing marine bacterium *Agrobacterium aurantiacum* [18].

Many groups have reported new carotenoid glycoside esters from thermophilic bacteria. The so-called thermozeaxanthins and thermocryptoxanthins were isolated from *Thermus thermophilus* [19,20]. The thermozeaxanthin group comprises mono- and di-β-D-glucoside fatty acid esters (6–10 carbons) or zeaxanthin (**10**) (Scheme 7). It has been reported that membrane reinforcement is one of the biological functions of bacterial carotenoids, based on the fact that the carotenoid molecule length is similar to that of the lipid bilayer. This is the case with the thermozeaxanthins, which have a hydrophobic–hydrophilic–hydrophobic structure consisting of zeaxanthin, glucose and fatty acids [19]. The thermocryptoxanthins comprise β-D-glucose fatty acid esters (4, 6 and 8 carbons) linked at C-3 of cryptoxanthin. The results of treatment with inhibitors suggested that the thermocryptoxanthins were intermediates in the biosynthesis of thermozeaxanthins [20]. The proposed biosynthetic pathway resembles that in *Erwinia* [21] in which zeaxanthin diglucoside is the end product. However, *Thermus* showed an additional esterification of the glucose moiety with fatty acids of various chain lengths.



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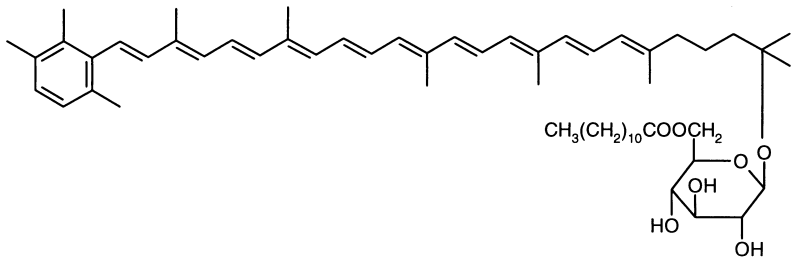
Scheme 7

The major pigment in *Meiothermus ruber*, previously *Thermus ruber*, was identified as 1′-β-glucopyranosyloxy-3,4,3′,4′-tetradehydro-1′,2′-dihydro-β,ψ-caroten-2-one, esterified at the 6-position of the sugar with C-10 to C-18 fatty acids, $C_{10:1}$ being the major fatty acid [22].

Three new carotenoiods were identified from the thermophilic green sulfur bacterium *Chlorobium tepidum*, namely 1′,2′-dihydro-γ-carotene, 1′,2′-dihydrochlorobactene and hydroxy-chlorobactene glucoside laurate (**11**) (Scheme 8) [23].



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Scheme 8

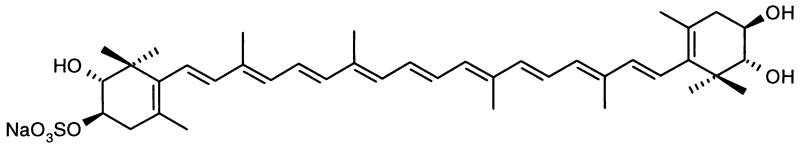
The major carotenoid in the green filamentous bacterium *Chloroflexus aurantiacus* was identified as 1′-[(6-*O*-acyl-β-D-glucopyranosyl)oxy]-1′,2′-dihydro-β,ψ-carotene, esterified mainly with $C_{16:1}$ and $C_{16:0}$ fatty acids [24].

From the myxobacterium *Polyangium fumosum*, 3,4,3′,4′-tetradehydro-1,2,1′,2′-tetrahydro-ψ,ψ-carotene-1,1′-diol and its mono β-glucoside and glucoside fatty acid (11-methyl laurinoate) were isolated [25].

For the purpose of the production of astaxanthin glucosides, which are expected to be a useful group of carotenoids due to their water solubility, two transformed strains of *Escherichia coli* were produced by introduction of seven kinds of carotenoid biosynthetic genes. These strains produced astaxanthin β-glucoside (naturally known) [18] and astaxanthin di-β-glucoside (new, not natural) [26].

The structure of P457, a minor carotenoid disaccharide found in several dinoflagellates, was completely elucidated as (3*S*,5*R*,6*R*,3′*S*,5′*R*,6′*S*)-(13′*Z*)-7′,8′-dihydroneoxanthin-20′-al-3′-β-lactoside [27].

New polar carotenoid sulfates [28] were isolated from marine bacterium, strain PC-6, provisionally identified as a *Flavobacterium* sp., and were assigned as (2*R*,3*S*,2′*R*,3′*R*)-4-ketonostoxanthin-3′-sulfate and (2*R*,3*R*,2′*R*,3′*R*)-nostoxanthin-3-sulfate (**12**) (Scheme 9). Only three groups of carotenoid sulfates had previously been reported: bastaxanthins from sponge [29], ophioxanthin and its dehydro derivative from an ophiuroid [30] and erythroxanthin sulfate and caloxanthin sulfate from a photosynthetic bacterium [31]. Ketonostoxanthin and nostoxanthin sulfates are the fourth group of naturally occurring carotenoid sulfates with a 2-hydroxy-3-sulfate-β-ring moiety.



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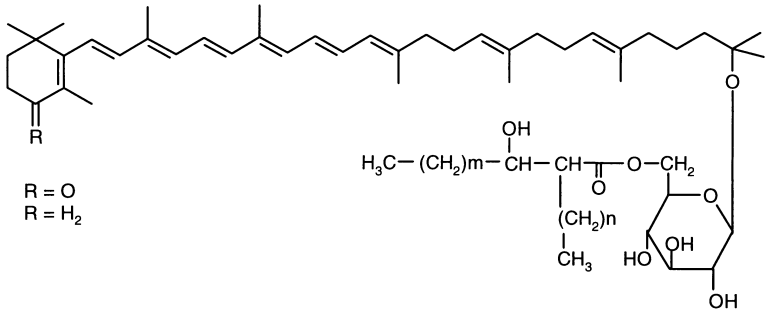
Scheme 9

From five strains of *Rhodococcus rhodochrous*, two carotenoid glucoside mycolic acid monoesters (**13**) (Scheme 10) were isolated and identified [32]. This is a new type of carotenoid derivative that has not yet been reported in any other organism.



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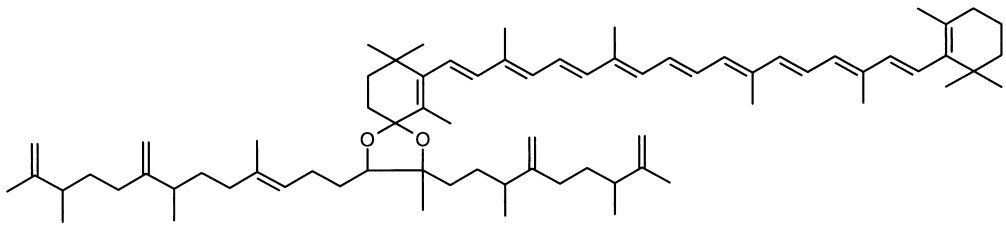
Scheme 10

Okada and co-workers [33–35] examined the relationship between colony colour and hydrocarbon production in three races (A, B and C) of the green microalga *Botryococcus braunii*. Five new carotenoids conjugated via ether linkages to alkylphenol and tetramethylsqualene structures were reported. Botryoxanthin A (**14**) (Scheme 11), α-botryoxanthin and botryoxanthin B were detected in two strains (Berkeley and Kawaguchi-1) in the race B. Braunixanthins 1 ($n = 8$) (**15**) (Scheme 12) and 2 ($n = 9$) were isolated from the Kawaguchi-1 strain.



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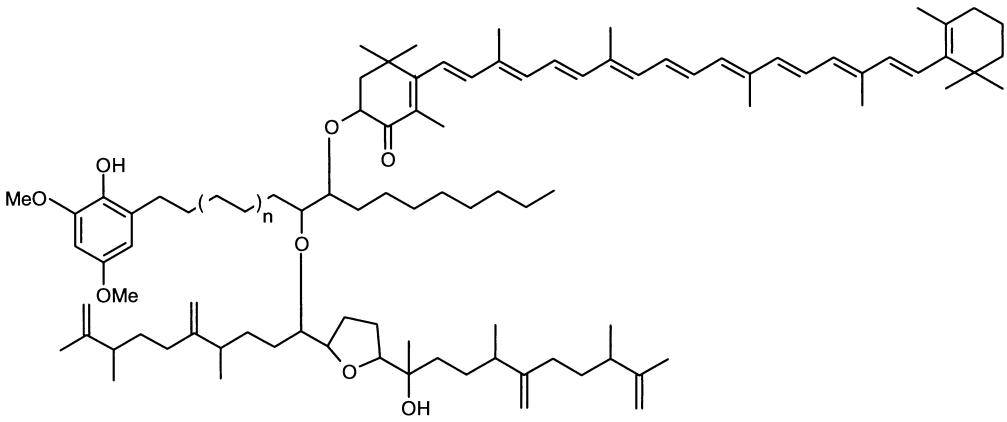
Scheme 11



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Scheme 12

More complex carotenoid derivatives with 69 carbons, in which the carotenoids violaxanthin, antheraxanthin or neoxanthin cross-linked to tocopherol, were isolated from the seeds of *Pittosporum tobira* by Maoka and Matsuno [36,37]. The carotenoids with two 5,6-epoxy groups were called pittosporumxanthins A1 (**16**) (Scheme 13) and A2, and those with one 5,6-epoxy group were called pittosporumxanthins B1 and B2. The allenic carotenoids with a 5,6-epoxy group were named pittosporumxanthin C1 (**17**) (Scheme 13) and C2. They occurred as *R* and *S* isomeric pairs at C-12.

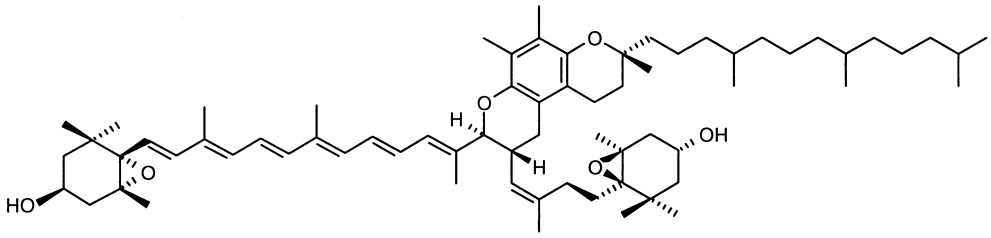
APOCAROTENOIDS

Maoka [38] reported the presence of apoalloxanthinal (3*R*)-3-hydroxy-7,8-didehydro-8′-apo-β-caroten-8′-al) in Japanese sea mussel (*Mytilus coruscus*) and oyster *Crassostrea gigas*. This C_{30} apocarotenoid is probably a metabolite derived from the oxidative cleavage of alloxanthin.

From 10 kg of the integuments of the black bass *Micropterus salmoides*, the following four novel apocarotenols were isolated [39]: α-micropteroxanthin A ((3*S*,6*S*)-11′,12′-dihydro-10′-apo-ϵ-carotene-3,10′-diol), α-micropteroxanthin B ((3*R*,6*S*)-11′,12′-dihydro-10′-apo-ϵ-carotene-3,10′-diol), β-micropteroxanthin (**18**) ((3*R*)-11′,12′-dihydro-10′-apo-β-carotene-3,10′-diol) (Scheme 14) and 7,8-didehydro-β-micropteroxanthin ((3*R*)-7,8-didehydro-11′,12′-dihydro-10′-apo-β-carotene-3,10′-diol).

Plant roots are often colonized by mycorrhizal fungi, which form typical structures such as arbuscules and internal hyphae. These structures improve the uptake of nutrients and water from the soil. Mycorradicin (10,10′-diapocarotene-10,10′-dioic acid) (**19**) (Scheme 15) was found to be the main pigment responsible for the yellow colour of maize roots upon mycorrhizal colonization [40].

More than 80% of the carotenoids in annatto (*Bixa orellana*) seeds consist of bixin, which has been encountered to date only in these seeds. Recently, eleven new minor carotenoids were isolated and



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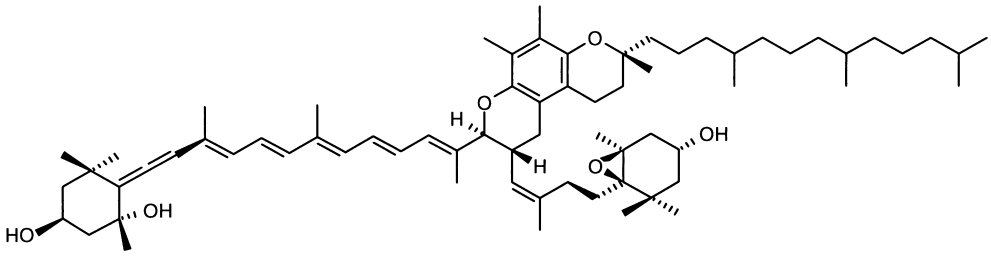

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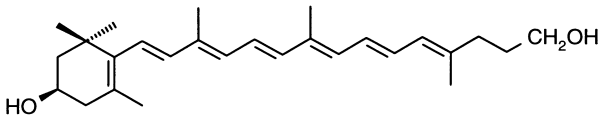
Scheme 13



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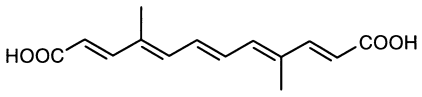
Scheme 14



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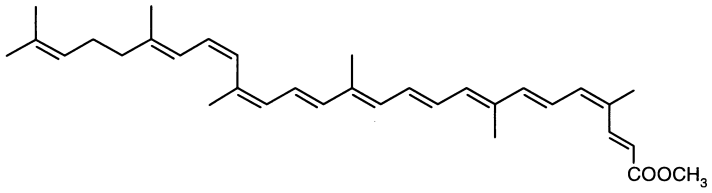
Scheme 15

identified by means of spectroscopic data [41–44]. They can be arranged into three groups. First, methyl esters of apocarotenoids (C_{30} and C_{32}) which comprise two new geometrical isomers, (9′*Z*)- and (7*Z*,9*Z*,9′*Z*)-, of methyl-apo-6′-lycopenoate (**20**) (Scheme 16), (all-*E*)- and (9*Z*)-methyl-apo-8′-lycopenoate, and methyl-8′-apo-β-caroten-8′-oate. The latter has already been synthesized, but this is the first time that this apocarotenoid has been found in nature. Secondly, diapocarotenoids with methyl ester, ketone or aldehyde end groups (C_{19}, C_{22}, C_{24} and C_{25}), such as dimethyl-(9*Z*,9′*Z*)-6,6′-diapocarotene-6,6′-dioate, methyl-(9*Z*)-10′-oxo-6,10′-diapocaroten-6-oate (**21**) (Scheme 16) and methyl-(9*Z*)-6′-oxo-6,6′-diapocaroten-6-oate, were also isolated. The first reported naturally occurring carotenoid acids esterified with the geranylgeranyl group are found in the third group, which comprises methyl-6-geranylgeranyl-8′-methyl-6,8′-diapocarotene-6,8′-dioate, 6-geranylgeranyl-6′-methyl-(9′*Z*)-6,6′-diapocarotene-6,6′-dioate (**22**) (Scheme 16) and 6-geranylgeranyl-6′-methyl-6,6′-diapocarotene-6,6′-dioate. Although no alkali was used during the extraction and isolation procedures, the presence of the new keto-C_{26} apocarotenoiod, methyl-(9*Z*)-6′-oxo-6,5′-diapocaroten-6-oate, is most likely an artefact arising



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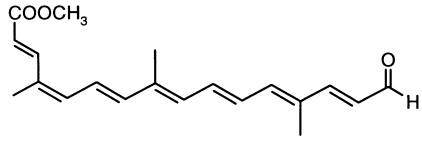

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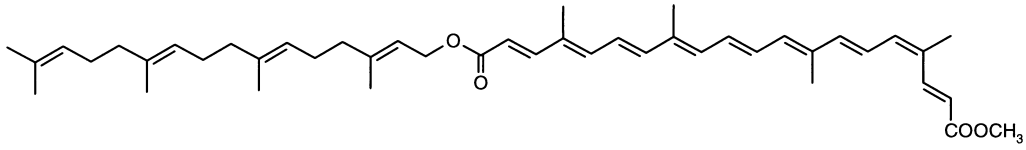

22

Scheme 16

from an aldol condensation of methyl-(9Z)-8′-oxo-6,8′-diapocaroten-6-oate with the acetone from the mobile phase used in the TLC on MgO [43]. The other minor carotenoids may be considered as natural metabolites derived from C_{40}-carotenes by enzymatic oxidative cleavage.

ACKNOWLEDGEMENTS

The author thanks FAPESP and MCT-CNPq-PRONEX for their financial support, and Prof. Hanspeter Pfander from Switzerland.

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