Carotenoids

1. Chemistry

1.1 Structure and nomenclature

Carotenoids are a class of hydrocarbons (carotenes) and their oxygenated derivatives (xanthophylls). They consist of eight isoprenoid units joined in such a manner that their arrangement is reversed at the centre of the molecule, so that the two central methyl groups are in a 1,6-positional relationship and the remaining non-terminal methyl groups are in a 1,5-positional relationship. All carotenoids may be derived formally from the acyclic $C_{40}H_{56}$ structure, illustrated in Figure 1, with a long central chain of conjugated double bonds, by hydrogenation, dehydrogenation, cyclization or oxidation, or any combination of these processes. The class also includes compounds that arise from certain rearrangements or degradations of the carbon skeleton, provided that the two central methyl groups are retained. Retinoids, including retinol, all-*trans*-retinoic acid and 9-*cis*-retinoic acid (Fig. 2), are therefore not included in the class of carotenoids.

Rules for the nomenclature of carotenoids (semi-systematic names) have been published by the International Union of Pure and Applied Chemistry (IUPAC) and the IUPAC-International Union of Biochemistry Commissions on Biochemical Nomenclature (1975; Weedon & Moss, 1995). Trivial names are usually used for the most common carotenoids; however, when trivial names are used in a publication, it is recommended that the semi-systematic name be given, in parentheses or in a footnote, at the first mention. All specific names are based on the stem name 'carotene', which corresponds to the structure and numbering illustrated in Figure 3. The name of a specific compound is constructed by adding as prefixes two Greek letters that specify the two C_9 end groups (Fig. 4); these prefixes are cited in alphabetical order.

The oxygenated carotenoids (xanthophylls) are named according to the usual rules of organic chemistry. The functional groups most frequently observed are hydroxy, methoxy, carboxy, oxo and epoxy. Chirality and geometric configuration are designated conventionally as *R/S* or *E/Z*, respectively. In this handbook, the terms *trans* and *cis* are used for *E* and *Z*, respectively. Important, characteristic carotenoids (Fig. 5) are lycopene (φ,φ-carotene), β-carotene (β,β-carotene), α-carotene [(6′*R*)-β,ε-carotene], β-cryptoxanthin [(3*R*)-β,β-caroten-3-ol], zeaxanthin ((3*R*,3′*R*)-β,β-carotene-3,3′-diol), lutein (previously named 'xanthophyll' (3*R*,3′*R*,6′*R*)-β,ε-carotene-3,3′-diol), neoxanthin [(3*S*,5*R*,6*R*,3′*S*,5′*R*,6′*S*)-5′,6′-epoxy-6,7-didehydro-5,6,5′,6′-tetrahydro-β,β-carotene-3,5,3′-triol], violaxanthin [(3*S*,5*R*,6*S*,3′*S*,-5′*R*,6′*S*)-5,6:5′,6′-diepoxy-5,6,5′,6′-tetrahydro-β,β-carotene-3,3′-diol], fucoxanthin [(3*S*,5*R*,6*S*,-3′*S*,5′*R*,6′*R*)-5,6-epoxy-3,3′,5′-trihydroxy-6′,7′-didehydro-5,6,7,8,5′,6′-hexahydro-β,β-caroten-8-one 3′-acetate], canthaxanthin (β,β-carotene-4,4′-dione) and astaxanthin [(3*S*,3′*S*)-3,3′-dihydroxy-β,β-carotene-4,4′-dione].

Derivatives in which the carbon skeleton has been shortened by the formal removal of fragments from one end of a carotenoid are named 'apocarotenoids', the position of the point of cleavage being indicated, e.g. β-apo-8′-carotenal (8′-apo-β-caroten-8′-al). Derivatives in which fragments have been formally removed from both ends of the molecule are called 'diapocarotenoids', an example being bixin, the main component of the natural colorant annatto. Other structural variations are those of the norcarotenoids, in which one or more carbon atoms have been eliminated from within the typical C_{40} skeleton. A prominent example is the C_{37} skeleton of peridinin [(3*S*,5*R*,6*R*,3′*S*,5′*R*,-6′*R*)-5,6-epoxy-3,5,3′-trihydroxy-6,7-didehydro-5,6,5′,6′-tetrahydro-10,11,20-trinor-β,β-caroten-19′,11′-olide 3 acetate], which is characteristic of diatoms.

The structures and trivial and semisystematic names of all known naturally occurring carotenoids are listed in *Key to Carotenoids* (Pfander, 1987) and in the Appendix of *Carotenoids*,

Figure 1. The basic carotenoid skeleton, constructed from eight isoprenoid units

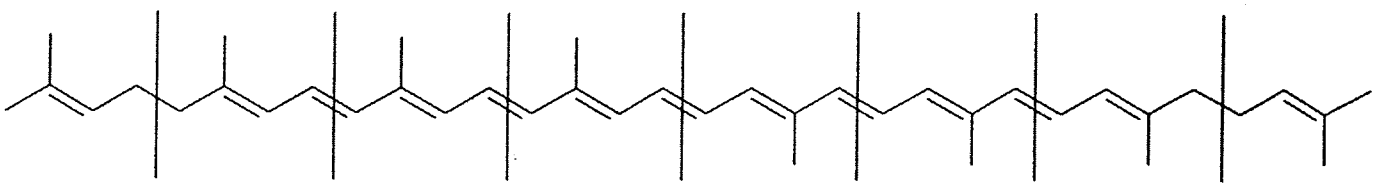


Figure 2. Structures of important retinoids

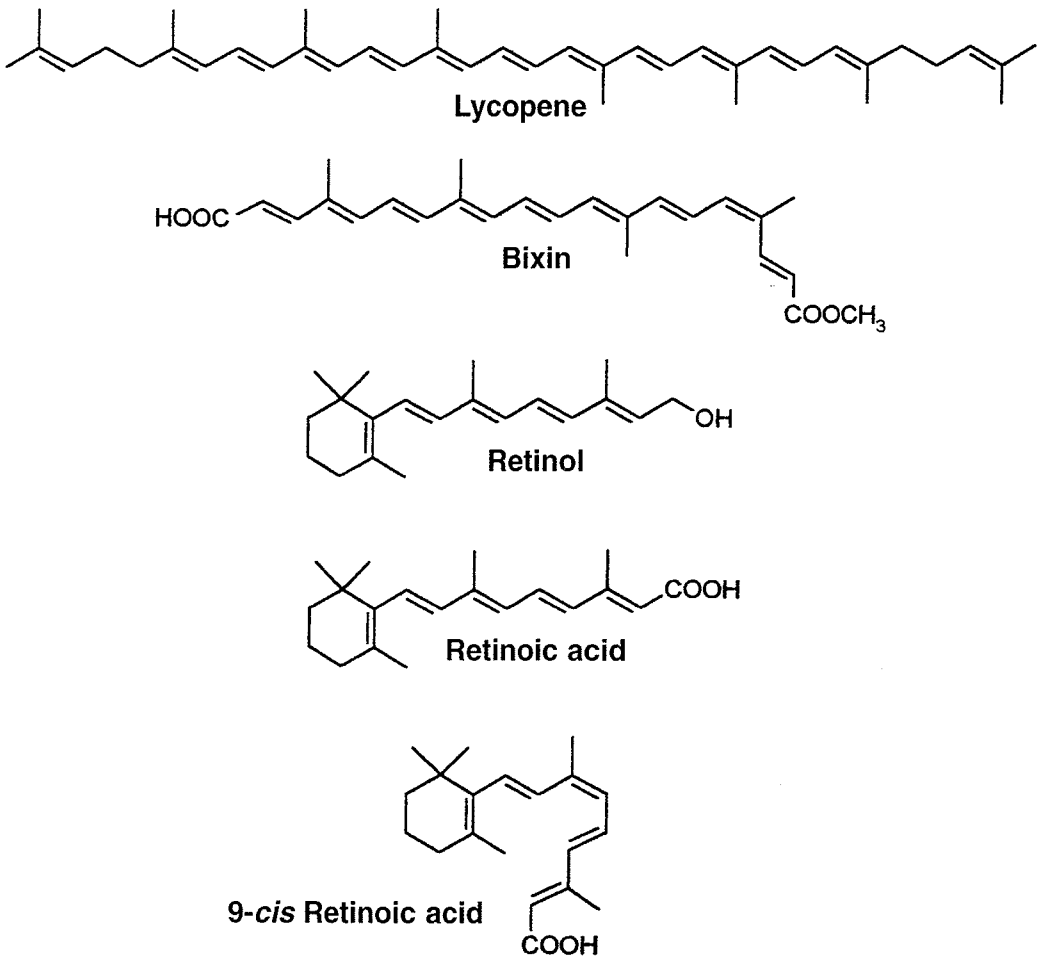


Figure 3. Numbering scheme for carotenoids

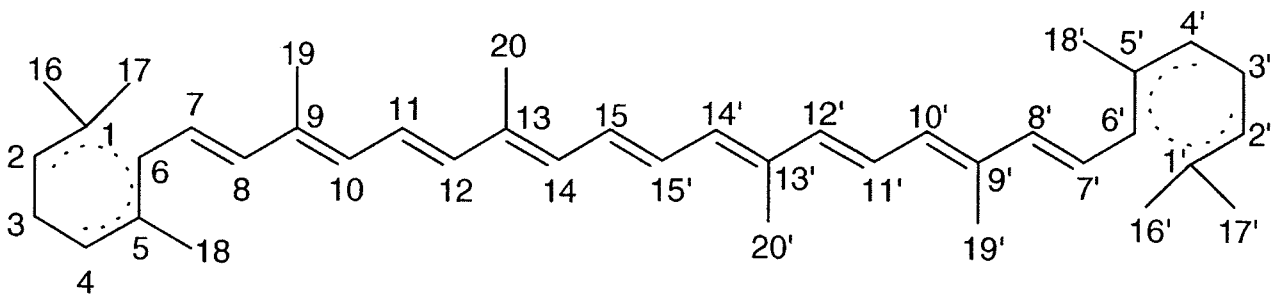
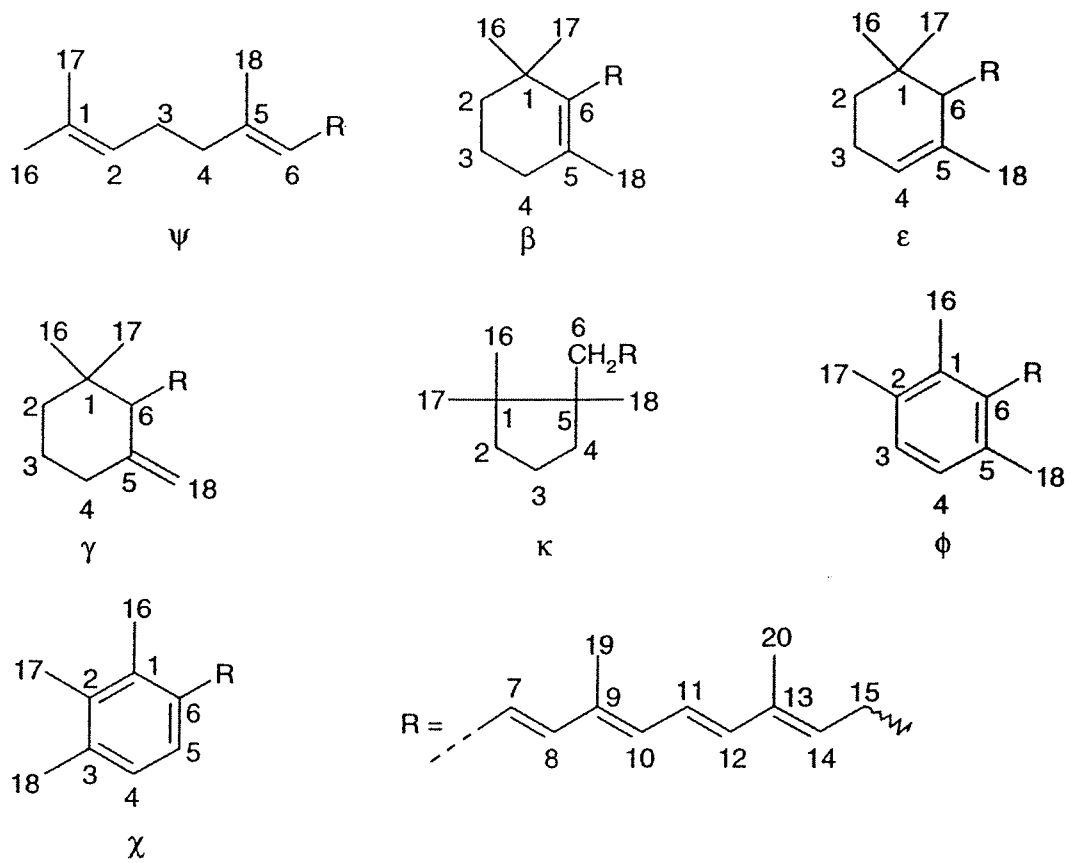


Figure 4. The seven end groups in carotenoids

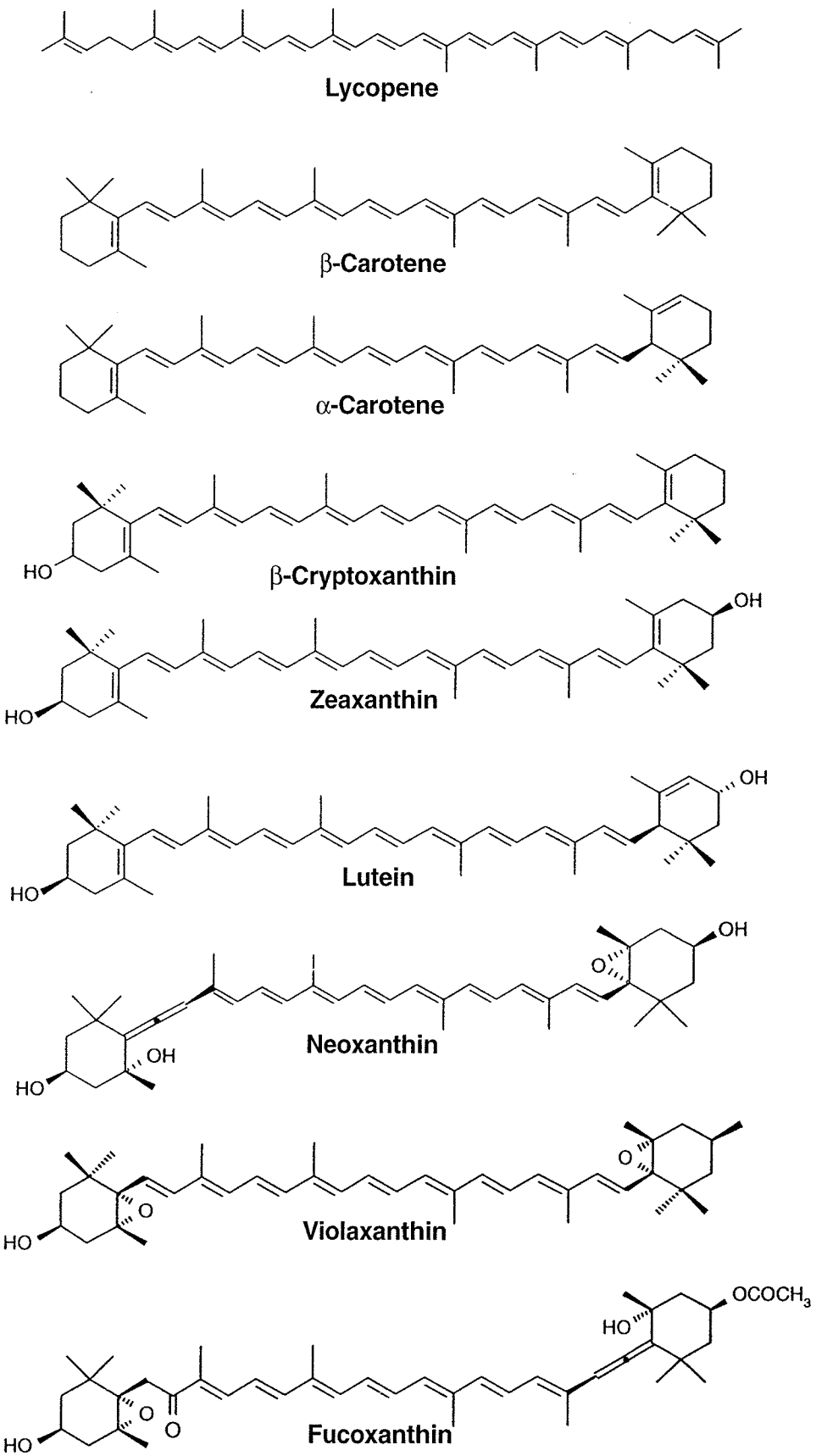


Volume 1A (Kull & Pfander, 1995), which also includes references for their spectroscopic and other properties. For many of the carotenoids listed, however, the structure (this term includes the stereochemistry) is still uncertain; in all these cases, reisolation followed by structural elucidation with modern spectroscopic methods (especially high-resolution nuclear magnetic resonance (NMR) spectroscopy) is absolutely necessary. About 370 of the naturally occurring carotenoids are chiral, bearing one to five asymmetric carbon atoms; most individual carotenoids occur in only one configuration in nature.

The *cis–trans* isomerism of the carbon–carbon double bonds is an important feature of the stereochemistry of carotenoids, because these geometric isomers may have different biological properties. The first comprehensive review of the *cis–trans* isomerism of carotenoids and vitamin A was published in 1962 (Zechmeister, 1962), and the literature in this field is extensive. Because of the number of double bonds, many geometric isomers (e.g. 1056 for lycopene and 272 for β-carotene) are theoretically possible. When in the *cis* configuration, the double bonds of the polyene chain can be considered as two groups: those with little steric hindrance (e.g. the central 15,15′ double bond and the double bonds that bear a methyl group, such as the 9,9′ and 13,13′ double bonds) and those with substantial steric hindrance (7,7′ and 11,11′ double bonds). Although isomers with sterically hindered *cis* double bonds are sometimes found, they are rare, and the number of *cis* isomers likely to be found is, in practice, reduced considerably, e.g. from a potential 1056 compounds to the actual number of 72 for lycopene.

Carotenoids usually occur in nature as all-*trans*-isomers, but exceptions are known, such as 9-*cis*-β-carotene in the alga *Dunaliella* and the 15-*cis*-phytoene isolated from carrots, tomatoes and other organisms. Some carotenoids readily undergo isomerization, and many *cis* isomers that are described in the literature as natural products may be artefacts. For experimental work, it must be kept in mind that geometric

Figure 5. Structures of important carotenoids



isomerization may occur when a carotenoid is kept in solution. The percentage of *cis* isomers is usually low but is enhanced as the temperature rises above the ambient. Furthermore, the formation of *cis* isomers is increased by exposure to light.

This section consists of two parts. In the first part, the general properties of carotenoids as a group are considered. The information is derived largely from a recent review of the structures and properties of carotenoids in relation to function (Britton, 1995a). In the second part, information is given on the individual compounds covered in this handbook. Although those listed are the main carotenoids identified in human blood and tissues, more than 100 are likely to be ingested in the general human diet, some of them, notably astaxanthin, bixin, capsanthin, capsorubin and others, in significant amounts. Some main dietary carotenoids, especially the epoxides violaxanthin and neoxanthin which are major carotenoids in all green plants are not found in blood or tissues.

1.2 General properties

1.2.1 Relationships between structure, properties and biological activity

The natural functions and biological actions of carotenoids are determined by the physical and chemical properties of the molecules, which themselves are defined by the molecular structure. Carotenoids are largely rigid molecules, but some flexibility is associated with the end groups. The overall molecular geometry, i.e. the size and shape of the molecule and the presence of functional groups, determines the solubility and is the main feature that determines the ability of the carotenoid to fit into cellular and subcellular structures. The conjugated double-bond system also determines the chemical and photochemical properties that form the basis of its biological actions and functions. A third factor, the importance of which is often overlooked, is interaction between carotenoids and other molecules in their immediate vicinity, which can greatly alter the properties of carotenoids and thus affect their functioning *in vivo*.

1.2.2 Molecular size and shape

All coloured carotenoids in the all-*trans* configuration have an extended system of conjugated carbon–carbon double bonds and are consequently linear. The *cis* isomers are not linear, and their shape differs substantially from that of the all-*trans* form, so their ability to fit into subcellular structures may differ greatly from that of the all-*trans* form. The size and shape of the end groups also affects their fit. Acyclic compounds such as lycopene are essentially long, linear molecules with flexible end groups. When cyclic end groups are present, the molecule is shorter; the effective bulk of cyclic end groups is greater and depends on the preferred conformation, as determined by steric factors and the presence of substituent groups. Structural changes that appear to be minor can result in significant alterations in shape.

1.2.3 Solubility

Virtually all carotenoids that are obtained from a normal human diet, and certainly those found in blood and body tissues, are extremely hydrophobic molecules which form aggregates or adhere nonspecifically to structural surfaces. The exceptions include the norcarotenoid carboxylic acid nor-bixin, which is present in preparations of annatto, and the glycosyl esters found in saffron. *In vivo*, free (i.e. not aggregated) carotenoids are therefore expected to be restricted to hydrophobic (lipophilic) environments.

1.2.4 Properties and molecular interactions of carotenoids in vivo

Almost all of the information about the properties of carotenoids is derived from studies of the molecules in simple organic solutions. *In vivo*, however, carotenoids are part of a much more complex system and are in close proximity to other components such as lipids and proteins, frequently in ordered structures. The overall size, shape and hydrophobicity of a carotenoid are thus major determinants of its ability to fit into subcellular structures. As noted above, the structural details that define individual carotenoids also determine the precise orientation and the nature of any molecular interactions with the surroundings.

Carotenoids are commonly located in membranes, where they may be an integral part of the ordered membrane structure. The positioning of the carotenoid in the membrane is strongly

dependent on structure, and differences are seen between carotenes and xanthophylls. The polar end groups of the xanthophylls interact with the polar, outer part of the membrane and allow the carotenoid to span the lipid bilayer (Gruszecki & Sielewiesiuk, 1990). Carotenes, with no polar end groups, are restricted to the hydrophobic inner core of the bilayer. Interactions between carotenoids and proteins are also of physiological importance, and the carotenoid is usually stabilized by such associations, which can significantly alter its physical and chemical properties.

Interactions between carotenoid molecules themselves can also affect their properties. The highly hydrophobic carotenoids show a strong tendency to aggregate and crystallize in aqueous media. This aggregation especially affects the light absorption and chemical reactivity of carotenoids and their effective size and solubility. This effect is particularly significant for the release of carotenoids from food matrices and their emulsification and absorption. In natural foods, carotenoids may be present in a microcrystalline form, e.g. lycopene in tomatoes, and their solubilization when in this form (or as crystalline supplements) can be very inefficient. This property clearly has important consequences for their bioavailability. *cis* Isomers generally have a lesser tendency to crystallize than all-*trans* isomers, so that the *cis* isomers may be more readily solubilized, absorbed and transported.

1.3 Properties of the conjugated polyene chain

1.3.1 Light absorption and photochemical properties

The characteristic strong absorption of light in the visible region is attributed to a transition from the electronic ground state to the second singlet excited state. As the main absorption bands lie in the 400–500-nm region, the carotenoids are strongly coloured yellow, orange or red. The ultraviolet (UV)–visible absorption spectrum provides the first criterion for identifying a carotenoid and is also the basis for quantitative analysis.

Direct formation of the carotenoid triplet state from the excited singlet state is not favoured. Nevertheless, its formation by triplet–triplet energy transfer from other triplet state molecules, e.g. photosensitizers, can be very efficient because the triplet-state energy of carotenoids that contain more than seven conjugated double bonds is low. Transfer of energy from triplet species to carotenoids is usually very efficient and prevents the alternative energy transfer to oxygen, which would generate the highly reactive and destructive singlet oxygen. Carotenoids can also accept excitation energy from singlet oxygen, if any should be formed. The triplet carotenoid has too little energy to generate other species by energy transfer, and the excitation energy is dissipated harmlessly to the surroundings.

1.3.2 Chemical properties

Chemical reactions involving carotenoid end groups are important in classical chemistry for characterization and derivatization. The conjugated polyene chain is a reactive, electron-rich system that is susceptible to attack by electrophilic reagents, is responsible for the instability of carotenoids towards oxidation and is the most important part of the molecule in relation to free-radical chemistry.

Carotenoids are rapidly destroyed by oxidation, especially by free radicals such as the hydroxy radical and various peroxy radicals. The important fundamental chemistry of carotenoid radicals and of the reactions of carotenoids with oxidizing free radicals is not well understood. Carotenoid radicals may be charged or neutral and are very short-lived species. In principle, removal of one electron from the carotenoid molecule by oxidation gives the radical cation $Car^{+\bullet}$, whereas the addition of one electron by reduction generates the radical anion $Car^{-\bullet}$ (Simic, 1992). These charged radicals can be detected by their distinctive spectroscopic properties, with intense absorption in the near infrared region. The abstraction of a hydrogen atom from a saturated carbon atom in a position allylic to the polyene chain, by homolytic cleavage, would generate a neutral radical $Car^{\bullet}$. In all these radicals, delocalization of the unpaired electron over the conjugated polyene chromophore has a

stabilizing effect and allows subsequent reactions to take place in many parts of the molecule. The same is true for carotenoid–adduct radicals which could be generated by the addition of a radical species such as a peroxy radical ROO• or the hydroxy radical HO• to the polyene chain.

The reactions between carotenoids (usually β-carotene) and peroxy radicals have been studied in organic solutions and in phospholipid liposomes. The reaction is usually attributed to direct addition of the peroxy radical to one of the suitable positions in the polyene chain of the carotenoid to give a resonance-stabilized, carbon-centred radical, e.g. ROO-Car•. At relatively low oxygen concentrations, a further peroxy radical could be added, to give a product that is not a free radical, e.g. ROO-Car-OOR. This process would consume peroxy radicals, and the carotenoid would act as an antioxidant. At higher oxygen concentrations, however, a carotenoid peroxy radical could be formed, e.g. Car-OO• or ROO-Car-OO•, and this could then act as a pro-oxidant, promoting hydrogen abstraction and peroxidation of unsaturated lipid and hence exacerbating damage (Burton & Ingold, 1984; Palozza & Krinsky, 1992a; Liebler, 1993). An alternative possibility is that the peroxy radical could abstract a hydrogen atom from a saturated CH_2 group allylic to the main polyene chromophore in a reaction analogous to the abstraction of hydrogen from an unsaturated lipid. Again, this could be followed by addition of a peroxy radical to generate a non-radical product, i.e. an antioxidant action, or of oxygen to generate a carotenoid–peroxy radical which would have prooxidant properties.

Series of apocarotenoids of different chain length have been reported to be products of chemical and free-radical oxidation of carotenoids and could be produced in tissues by nonspecific chemical or enzymic reactions or by specific excentric cleavage of carotenoids in the intestine.

All carotenoids react rapidly with oxidizing agents and free radicals, although the reactivity depends on the length of the polyene chromophore and on the nature of the end groups. Calculations show that the electron density is not uniform along the whole polyene chain but is greater towards the ends; there may therefore be preferred sites for reactions with electrophilic or free-radical species.

In discussing the mechanism by which β-carotene could act as an antioxidant or prooxidant, Truscott (1996) described interactions between radicals of β-carotene, vitamin E and vitamin C and concluded that β-carotene may quench or repair the vitamin E radical and vitamin C the β-carotene radical cation. This hypothesis highlights the need to consider possible interactions between carotenoids and other factors, in addition to the chemistry of the carotenoids themselves.

1.4 Isolation and analysis

Methods for the isolation and purification of carotenoids from natural sources are widely available and are described in detail, with worked examples, by Britton *et al.* (1995a), including many procedures for the high-performance liquid chromatography (HPLC) of carotenoids in blood, body tissues and foods. Details are also available of procedures for the analysis of the main carotenoids in blood plasma (Schüep *et al.*, 1995) and of geometrical isomers of β-carotene (Schierle *et al.*, 1995). More complex methods for the analysis of the many minor carotenoids present in blood have also been described (Khachik *et al.*, 1997). The use of spectroscopic methods for the analysis and characterization of carotenoids is discussed by Britton *et al.* (1995b). HPLC procedures are now available for the separation of mixtures of geometric isomers; however, very few isomers have been fully characterized and the position(s) of the *cis* double bond(s) established. A compound cannot be identified as a particular *cis* isomer without comparison with authentic (usually synthetic) standards. Therefore, in most published reports, use only of the general description '*cis* isomers' is justified.

1.4.1 General methods

As carotenoids are less stable than many other groups of substances, precautions and special procedures must be used to minimize the risk of degradation and formation of artefacts. In particular, exposure to oxygen, heat, light, acid and, in some cases, bases must be avoided

whenever possible (Schiedt & Liaaen-Jensen, 1995). All operations should be carried out in an inert atmosphere (nitrogen or argon), at low temperature (room temperature, about 20 °C), in the dark or diffuse light, under acid-free conditions and with freshly purified, peroxide-free solvents. After carotenoids have been extracted from tissues, even when they are pure and in the crystalline state, they are susceptible to oxidation and may be broken down rapidly if samples are stored in the presence of even traces of oxygen; solids must be stored under vacuum or an inert gas (nitrogen or argon). Carotenoids are also susceptible to oxidative damage *in vivo* if they are exposed to oxidizing species or to the free radicals that may be generated.

The usual indication of carotenoid breakdown is bleaching, i.e. loss of colour, due to breakage of the chromophore. A variety of breakdown products have been detected, most often apocarotenoids of various chain lengths produced by cleavage of any of the double bonds in the polyene chain (Palozza & Krinsky, 1992b; Liebler, 1993). Similar products are derived from the chemical reaction between carotenoids and singlet oxygen or other oxidizing agents. The products of oxidative breakdown or similar oxidation products formed by metabolism of carotenoids may have biological activity.

Geometrical (*cis–trans*) isomerization occurs readily when carotenoids are exposed to factors such as light or heat and even occurs slowly in isolated, purified samples. Plasma or tissue samples should be stored at –70 °C or less to minimize degradative reactions or isomerization. Even carotenoid samples that are nominally all-*trans* usually contain small amounts of various *cis* isomers.

1.4.2 Identification

The following criteria must be fulfilled for identification of a carotenoid as a known compound (Schiedt & Liaaen-Jensen, 1995): (i) The UV–visible absorption spectrum (λ_{max} and fine structure) in at least two solvents must be consistent with the chromophore and identical to that of an authentic sample. (ii) The chromatographic properties must be identical to those of an authentic sample in two systems, preferably thin-layer chromatography and HPLC, and co-chromatography with an authentic sample should be demonstrated. If possible a mass spectrum should be obtained which allows at least confirmation of the molecular mass.

Full elucidation of the structure requires a fully assigned NMR spectrum and, for chiral compounds, comparison of a circular dichroism spectrum with that of an authentic reference sample. A first criterion for identification is the UV–visible spectrum, which is characteristic of the chromophore of the molecule but generally gives no information about functional groups, except carbonyl groups conjugated with the polyene system. Not only the position of the λ_{max} but also the overall shape or fine structure of the spectrum convey information. A discussion of the relationship between chromophore and spectrum, with tabulated lists of λ_{max} values for natural carotenoids in several solvents, is given by Britton (1995b).

1.4.3 Quantitative analysis

The UV–visible spectrum also provides the basis for quantitative analysis of carotenoids. Tables of values for $A^{1\%}$ (usually in the order of 2500) and ε_{mol} (usually about 100 000) are also given by Britton (1995b).

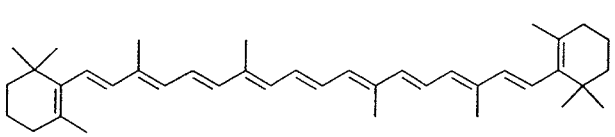
1.5 Data on individual compounds

1.5.1 β-Carotene

IUPAC name
β,β-Carotene

Chemical Abstracts Services Registry Number
7235-40-7 (9*Z*, 13312-52-2; 13*Z*, 6811-73-0; 15*Z*, 19361-58-1)

Structure



Molecular formula
$C_{40}H_{56}$

Relative molecular mass
536

Melting-point
183 °C (from benzene–petroleum)

UV–visible spectrum
λ_{max} 425, 450, 477 nm (hexane, petroleum); 429, 452, 478 nm (acetone); 435, 462, 487 nm (benzene). $A^{1\%}$, 2592; ε_{mol}, 138 900 (450 nm, petroleum); $A^{1\%}$, 2337; ε_{mol}, 125 300 (462 nm benzene) (Britton, 1995b)

Mass spectrometry
M^+ 536; major fragment ion at *m/z* 444 (M-92)

^{1}H-NMR (Englert, 1995)

^{13}C-NMR (Englert, 1995)

Infrared
(Bernhard & Grosjean, 1995)
Isolation
From green and other plant tissues (Britton, 1995c)

Natural sources
All green fruit and vegetables, carrots, many orange and yellow fruit

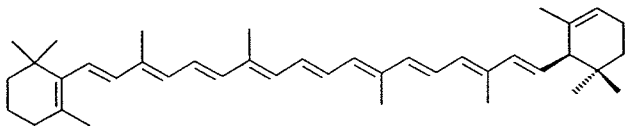
Geometrical isomers
(9-*cis*), (13-*cis*), (15-*cis*). Resolved by HPLC on Vydac 218TP54 C_{18} RP column (Schierle *et al.*, 1995), Vydac 201TP54 C_{18}RP column (Emenhiser *et al.*, 1995) or C_{30}RP column (Emenhiser *et al.*, 1995).

1.5.2 α-Carotene

IUPAC name
(6′*R*)-β,ε-Carotene

Chemical Abstracts Services Registry Number
7488-99-5

Structure



Molecular formula
$C_{40}H_{56}$

Relative molecular mass
536

Melting-point
187 °C (from petroleum or benzene–methanol)

UV–visible spectrum
λ_{max} 422, 445, 473 nm (hexane, petroleum); 424, 448, 476 nm (acetone); 432, 456, 485 nm (benzene). $A^{1\%}$, 2710; ε_{mol}, 145 300 (445 nm, hexane) (Britton, 1995b)

Mass spectrometry
M^+ 536; major fragment ions at *m/z* 480 (M-56), 444 (M-92), 413 (M-123)

^{1}H-NMR
(Englert, 1995)
^{13}C-NMR
(Englert, 1995)

Infrared
(Bernhard & Grosjean, 1995)

Isolation
From green and other plant tissues (Britton, 1995c)

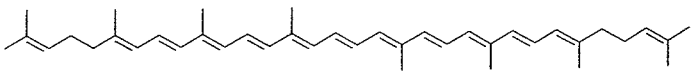
Sources
Carrots; some green fruit and vegetables; some yellow–orange fruit. Usually found with larger amounts of β-carotene

1.5.3 Lycopene

IUPAC name
ψ,ψ-Carotene

Chemical Abstracts Service Registry Number
502-68-5 (9*Z*, 64727-64-6; 13*Z*, 13018-46-7; 15*Z*, 59092-07-8)

Structure



Molecular formula
$C_{40}H_{56}$

Relative molecular mass
536

Melting-point
174 °C (from hexane or petroleum)

UV–visible spectrum
λ_{max} 444, 470, 502 nm (petroleum); 448, 474, 505 nm (acetone), 455, 487, 522 nm (benzene). $A^{1\%}$, 3450; ε_{mol}, 184 900 (470 nm, petroleum); $A^{1\%}$, 3370; ε_{mol}, 180 600 (487 nm, benzene) (Britton, 1995b)

Mass spectrometry
M^+ 536; main fragment ions at *m/z* 467 (M-69), 444 (M-92), 430 (M-106)

^{1}H-NMR
(Englert, 1995)

^{13}C-NMR
(Englert, 1995)

Infrared
(Bernhard & Grosjean, 1995)

Isolation
From tomato (Britton, 1995c)

Sources
Tomato and tomato products; small amounts in some fruits, e.g. watermelon

Geometrical isomers
Natural lycopene is mainly all-*trans*, accompanied by 5*Z*, 9*Z*, 13*Z* and other isomers, which are separated by HPLC on C_{30} RP columns (Hengartner *et al.*, 1992; Emenhiser *et al.*, 1995). Prolycopene (7,9,7′,9′-tetra*cis*) occurs naturally in tangerine, tomato and some other fruit, e.g. passion fruit.

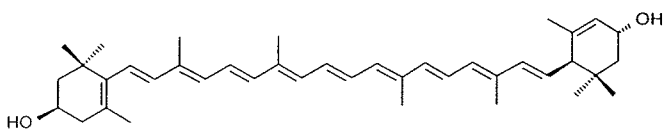
Comments
Poorly soluble in most solvents and natural oils; crystallizes readily; very unstable in the presence of oxygen

1.5.4 Lutein

IUPAC name
(3*R*,3′*R*,6′*R*)-β,ε-Carotene-3,3′-diol

Chemical Abstracts Services Registry Number
127-40-2

Structure



Molecular formula
$C_{40}H_{56}O_2$

Relative molecular mass
568

Melting-point
193 °C (from methanol)

UV–visible spectrum
λ_{max} 422, 445, 474 nm (ethanol); 432, 458, 487 nm (benzene). $A^{1\%}$, 2250; ε_{mol}, 144 800 (445 nm, ethanol); $A^{1\%}$, 2236; ε_{mol}, 127 000 (458 nm, benzene) (Britton, 1995b)

Mass spectrometry
M^+ 568; major fragment ions at *m/z* 550 (M-18), 476 (M-92), 458 (M-18-92), 430 (M-138)

^{1}H-NMR
(Berset & Pfander, 1985)

^{13}C-NMR
End-group assignment (Englert, 1995)

Isolation
From green leaves (Britton, 1995c)

Sources
Main carotenoid in all green fruit and vegetables; also present in other yellow–orange fruit, e.g. pumpkin; major carotenoid in egg yolk

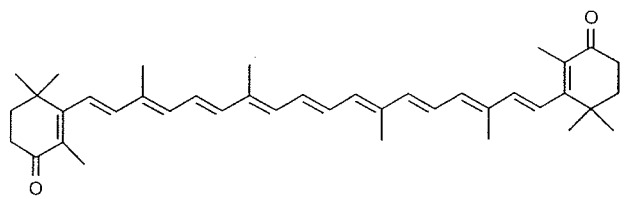
Geometrical isomers
For separation and characterization of *cis* isomers, see Berset and Pfander (1985).

1.5.5 Canthaxanthin

IUPAC name
β-Carotene-4,4′-dione

Chemical Abstracts Services Registry Number
514-78-3

Structure



Molecular formula
$C_{40}H_{52}O_2$

Relative molecular mass
564

Melting-point
213 °C (from dichloromethane–methanol)

UV–visible spectrum
λ_{max} 474 nm (ethanol); 484 nm (benzene); 466 nm (petroleum); no fine structure. $A^{1\%}$, 2200; ε_{mol}, 124 100 (466 nm, petroleum); $A^{1\%}$, 2092; ε_{mol}, 118 000 (484 nm, benzene) (Britton, 1995b)

Mass spectrometry
M^+ 564; fragment ion at *m/z* 472 (M-92). No diagnostic fragment ions

^{1}H-NMR
(Englert, 1995)

^{13}C-NMR
End-group assignment (Englert, 1995)

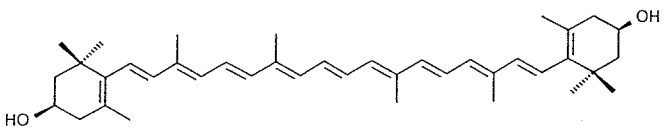
Infrared
(Bernhard & Grosjean, 1995)

Sources
Characteristic carotenoid in marine animals, especially crustaceans (with astaxanthin); main pigment in trout; not a major human dietary component.

1.5.6 Zeaxanthin

IUPAC name
(3*R*,3′*R*)-β,β-Carotene-3,3′-diol
Chemical Abstracts Services Registry Number
144-68-3, 29472-68-2

Structure



Molecular formula
$C_{40}H_{56}O_2$

Relative molecular mass
568

Melting-point
215 °C (from methanol)

UV–visible spectrum
λ_{max} 428, 450, 478 nm (ethanol); 430, 452, 479 nm (acetone); 440, 463, 491 nm (benzene). $A^{1\%}$, 2480; ε_{mol}, 140 900 (450 nm, ethanol); $A^{1\%}$, 2340; ε_{mol}, 132 900 (452 nm, acetone) (Britton, 1995b)

Mass spectrometry
M^+ 568; fragment ions at *m/z* 550 (M-18, low intensity), 476 (M-92)

^{1}H-NMR
(Englert, 1995)

^{13}C-NMR
(Englert, 1995)

Infrared
(Bernhard & Grosjean, 1995)

Sources
Main food source: maize; also present in small amounts in many green and other fruits and vegetables; commonly present in egg yolk; also produced in high concentrations in some bacteria

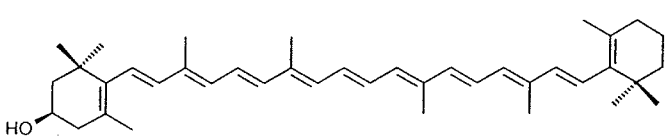
Geometric isomers
Separation and characterization of 9-*cis*, 13-*cis* and others given by Englert *et al.* (1992) and Emenhiser *et al.* (1995).

1.5.7 β-Cryptoxanthin

IUPAC name
(3*R*)-β,β-Caroten-3-ol

Chemical Abstracts Services Registry Number
472-70-8

Structure



Molecular formula
$C_{40}H_{56}O$

Relative molecular mass
552

Melting-point
169 °C (from benzene–methanol)

UV–visible spectrum
λ_{max} 428, 450, 478 nm (ethanol); 425, 449, 476 nm (petroleum); 435, 463, 489 nm (benzene). $A^{1\%}$, 2386; ε_{mol}, 131 900 (449 nm, petroleum) (Britton, 1995b)

Mass spectrometry
M^+ 552; fragment ions at *m/z* 534 (M-18, low intensity), 460 (M-92)

^{1}H-NMR
End-group assignment (Englert, 1995)

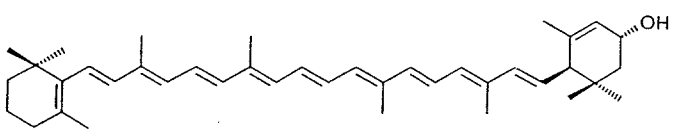
^{13}C-NMR
End-group assignment (Englert, 1995)

Sources
Present, usually in small amounts, in yellow–orange fruits and in maize; best sources: orange, peach, papaya; not a major dietary component

1.5.8 α-Cryptoxanthin

IUPAC name
(3′*R*, 6′*R*)-β,ε-Caroten-3-ol
Chemical Abstracts Services Registry Number
24480-38-4

Structure



Molecular formula
$C_{40}H_{56}O$

Relative molecular mass
552

UV–visible spectrum
λ_{max} 423, 446, 473 nm (ethanol); 421, 445, 475

nm (hexane); 433, 459, 488 nm (benzene). $A^{1\%}$, 2636; ε_{mol}, 145 500 (hexane); $A^{1\%}$, 2355; ε_{mol}, 130 000 (459 nm, benzene) (Britton, 1995b)

Mass spectrometry
M^+ 552; fragment ions at *m/z* 534 (M-18, low intensity), 496 (M-56), 460 (M-92), 414 (M-138)

^{1}H-NMR
End-group assignment (Englert, 1995)

^{13}C-NMR
End-group assignment (Englert, 1995)

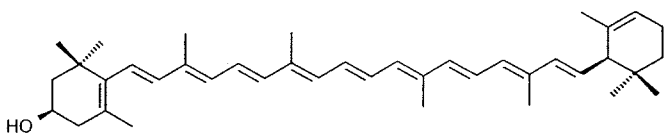
Sources
No major source; likely to be a minor component in many fruit and vegetables; often measured as part of cryptoxanthin.

1.5.9 Zeinoxanthin

IUPAC name
(3*R*,6′*R*)-β,ε-Caroten-3′-ol

Chemical Abstracts Services Registry Number
472-69-5

Structure



Molecular formula
$C_{40}H_{56}O$

Relative molecular mass
552

UV–visible spectrum
As for α-cryptoxanthin

Mass spectrometry
M^+ 552; fragment ions at *m/z* 534 (M-18 high density), 496 (M-56), 460 (M-92), 442 (M-18-92), 429 (M-123)

^{1}H-NMR
End-group assignment (Englert, 1995)

^{13}C-NMR
End-group assignment (Englert, 1995)

Sources
No major source; likely to be a minor component of many fruit and vegetables; often measured as part of cryptoxanthin