

## STRUCTURAL PECULIARITIES OF CAROTENOIDS USED AS FOOD COLORANTS

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### Abstract

*The carotenoids are a class of natural pigments that is very widespread and it was demonstrated that they occur in all the three domains of life, i.e. in the eubacteria, the archea and in the eucarya. Rich sources for carotenoids are the algae and more than 100 carotenoids have been isolated and characterized from these organisms. For humans the most important source for carotenoids are plants, where often the brilliant colors of the carotenoids are masked by chlorophyll, e.g. in green leaves. The carotenoids are responsible for the colors of many fruits (pine-apple, citrus fruits, tomatoes, paprika, rose hips) and flowers (Eschscholtzia, Narcissus), as well as the colors of many birds (flamingo, cock of rock, ibis, canary), insects (lady bird), and marine animals (crustaceans, salmon).*

**Keywords:** *carotenoids, -structure, food colorants*

### Introduction

The general structure of the carotenoids comprises a C<sub>40</sub> hydrocarbon chain made up of eight isoprenoid unit. Naturally occurring carotenoids exist mainly as the more stable trans isomers. β-carotene has 11 double bonds in conjugation, which is the reason for its yellow – orange color. Diversity in the carotenoids arises as a result of additional substituents at both terminals of the hydrocarbon chain (Bodea, 1966; Britton, 1982; Gârban, 2002).

The extent of the double bonds in the hydrocarbon chain as well as the stereochemistry of the molecule affect the molecule's absorption spectrum and determines the color displayed by the different

carotenoid compounds. A minimum of seven conjugated double bonds in the tetraterpenoid molecule is required before the carotenoid compound may have perceivable color. The presence of numerous double bonds in the carotenoid molecule also causes the compound to be very prone to oxidation, especially in the presence of light, enzymes, metals, and lipid hydroperoxides. Such reactions are believed stable over a wide pH range and are fat soluble.

Beta carotene is the most abundant carotenoid in nature, particularly in plant materials. It is the major coloring principle in carrot and as well as palm oil seed extracts. The extracts are oil soluble and impart a yellow color to food; they find application in dairy products, cakes, soup, and confectionery. It is also a known fact that beta carotene is a precursor of vitamin A while possessing antioxidation properties which may help in the prevention of cancer and other diseases. This has resulted in the incorporation of beta carotene in health products, such as functional or nutraceutical beverages, with increasing usage being predicted in the future (Miron, 2003).

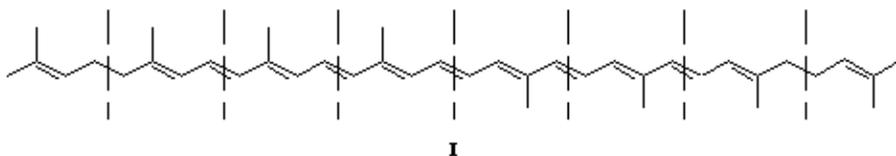
Although present in a lesser amount beta carotene, annatto, saffron and gardenia extracts are the more commonly used carotenoids for coloring foodstuffs. Paprika, tomato, carrot, and palm oil seed have also been utilized for the extraction of carotenoids. The carotenoids are used to provide orange and yellow colors in food, particularly in fat-based food products (Francis, 1982, 1987; Gârban, 2000; Branen, 2002).

### **Nomenclature and structure**

Carotenoids are a class of hydrocarbons (carotenes) and their oxygenated derivatives (xanthophylls). They consist of eight isoprenoid units joined in such a manner that the arrangement of isoprenoid units is reversed at the center of the molecule so that the two central methyl groups are in a 1,6-position relationship and the remaining nonterminal methyl groups are in a 1,5-position relationship.

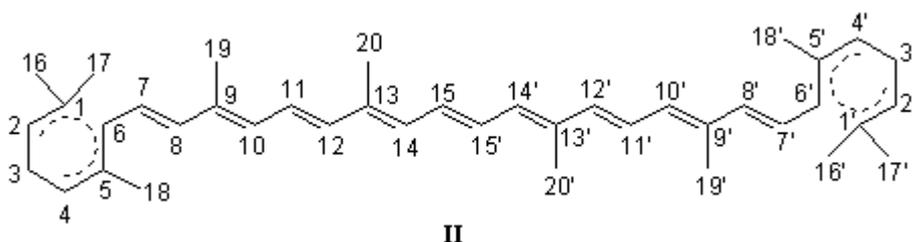
All carotenoids may be formally derived from the acyclic  $C_{40}H_{56}$  structure (I) (Fig. 1), having a long central chain of conjugated double bonds, by (1) hydrogenation, (2) dehydrogenation, (3) cyclization, or (4) oxidation, or any combination of these processes. The class also

includes compounds that arise from certain rearrangements or degradations of the carbon skeleton (I), provided that the two central methyl groups are retained.



**Fig. 1.** Carotenoids – general chemical structure

Rules for the nomenclature of carotenoids (semi systematic names) have been published by the International Union of Pure and Applied Chemistry (IUPAC) and IUPAC-International Union of Biochemists (IUB) Commissions on Nomenclature (1975). For the most common carotenoids trivial names are normally used. If these trivial names are used in a paper, the semi systematic name should always 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 fig. 2 (Bodea, 1964, 1966; Pop, 2005).



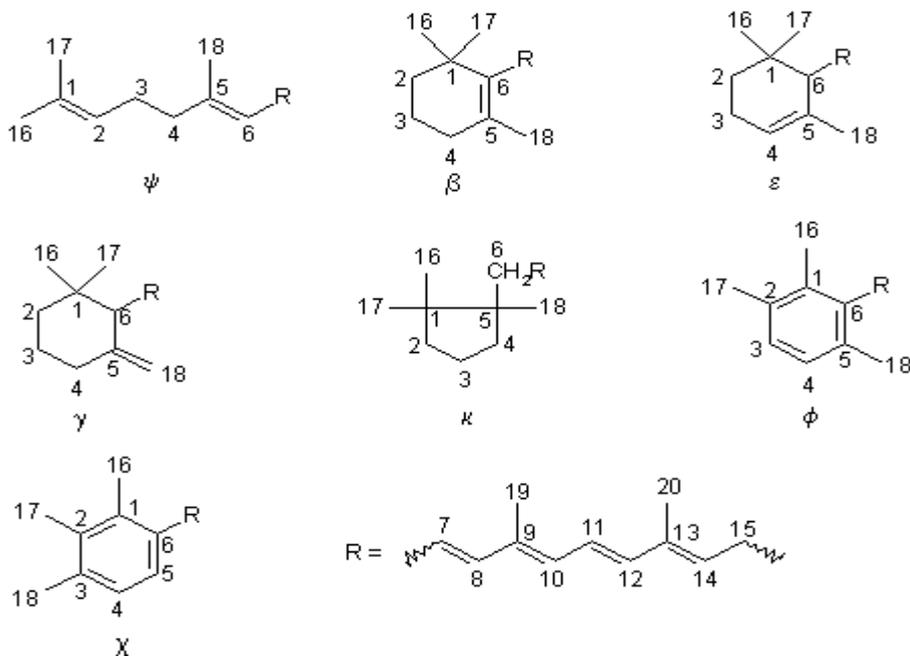
**Fig. 2.** Carotenoids – general formula and numbering

The name of a specific compound is constructed by adding two Greek letters as prefixes (Figure 3) to the stem name carotene; the Greek letter prefixes are cited in alphabetical order.

The oxygenated carotenoids (xanthophylls) are named according to the usual rules of organic chemical nomenclature. The functions most frequently observed are hydroxy, methoxy, carboxy, oxo, and epoxy.

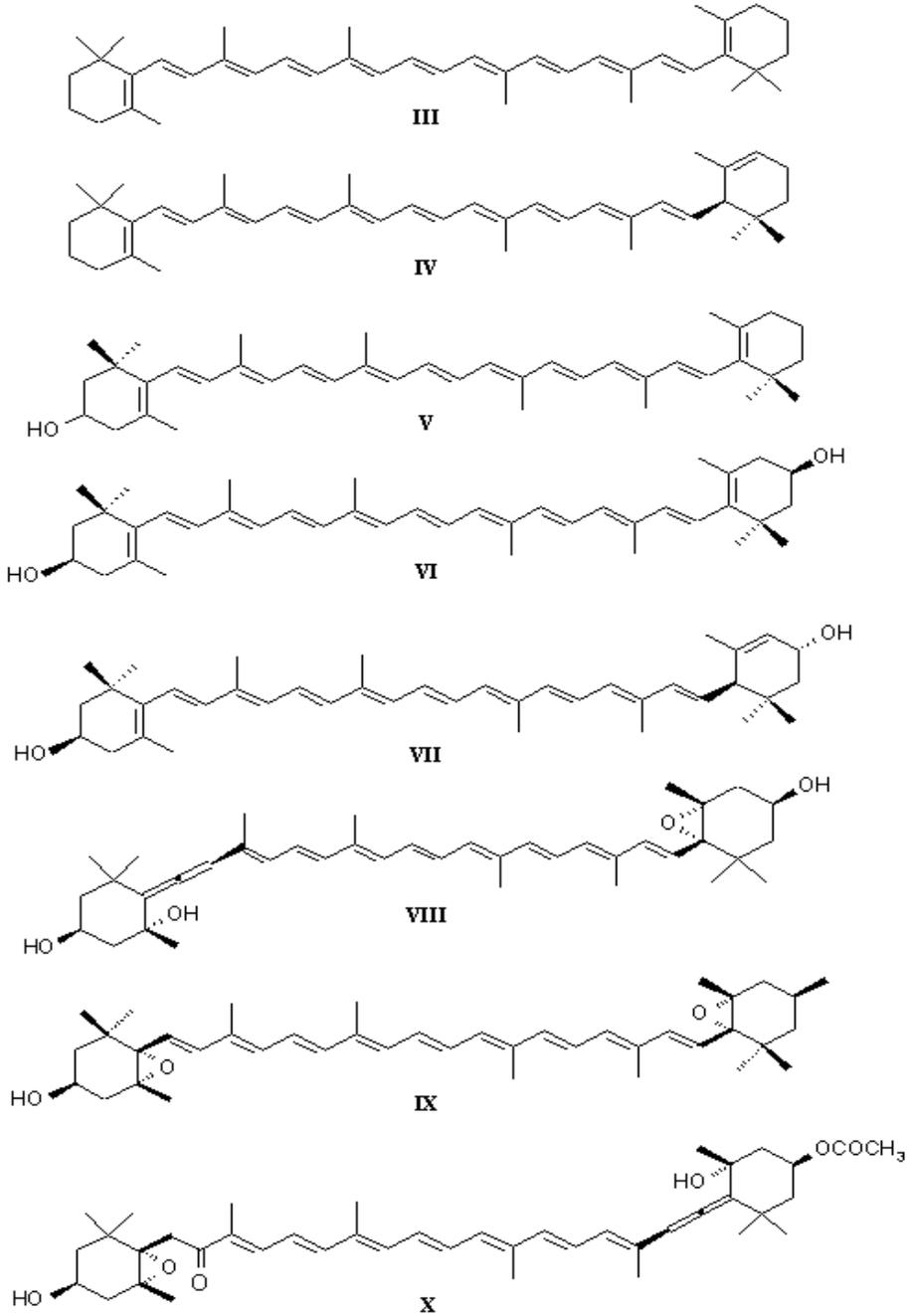
Important and characteristic carotenoids (Fig. 4 a and b) are lycopene (gamma,gamma-carotene) (I), beta-carotene (beta,beta-carotene) (III), alpha-carotene ((6'R)-beta,epsilon-carotene) (IV), beta-cryptoxanthin ((3R)-beta,beta-caroten-3-ol) (V), zeaxanthin ((3R,3'R)-

beta, beta carotene-3,3'-diol) (VI), lutein ("xanthophyll", (3R,3'R,6'R)-beta,epsilon-carotene-3,3'-iol)(VII), neoxanthin((3S,5R,6R,3'S,5'R,6'S)-5',6'-epoxy-6,7-didehydro-5,6,S',6'-tetrahydro-beta,beta-carotene-,5,3'-triol) (VIII), violaxanthin ((3S,5R,6R,3'S,5'R,6'S)-5,6,5',6'-diepoxy-5,6,5',6'-tetrahydro-beta,beta-carotene-3,3'-diol) (IX), fucoxanthin ((3S,5R,6S,3'S,5'R,6'R)-5,6-epoxy-3,3',5'-trihydroxy-6',7'-didehydro-5,6,7,8,5',6'-hexahydro-beta,beta-caroten-8-one3'-acetate) (X), canthaxanthin (beta,beta-carotene-4,4'-dione) (XI), and astaxanthin ((3S,3'S)-3,3'-dihydroxy-beta,beta-carotene-4,4'-dione) (XII).

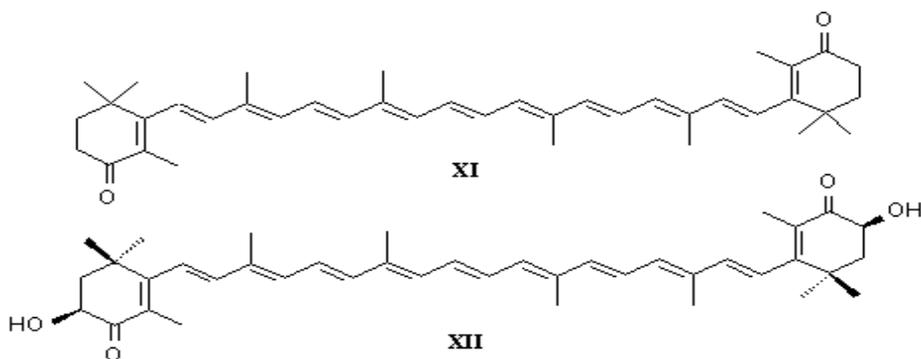


**Fig. 3.** Carotenoids- the Greek prefixes

This cis-trans or (E/Z)-isomerism of the carbon-carbon double bonds is another interesting features of the stereochemistry of the carotenoids, because it was demonstrated that the (E/Z)-isomers may have different biological properties. According to the number of double bonds a great number of (E/Z)-isomers exist for each carotenoid, e.g. 1056 for lycopene (I) and 272 for  $\beta$ -carotene (III).



**Fig. 4a.** Important and characteristic carotenoids – structural formula



**Fig. 4b.** Important and characteristic carotenoids – structural formula

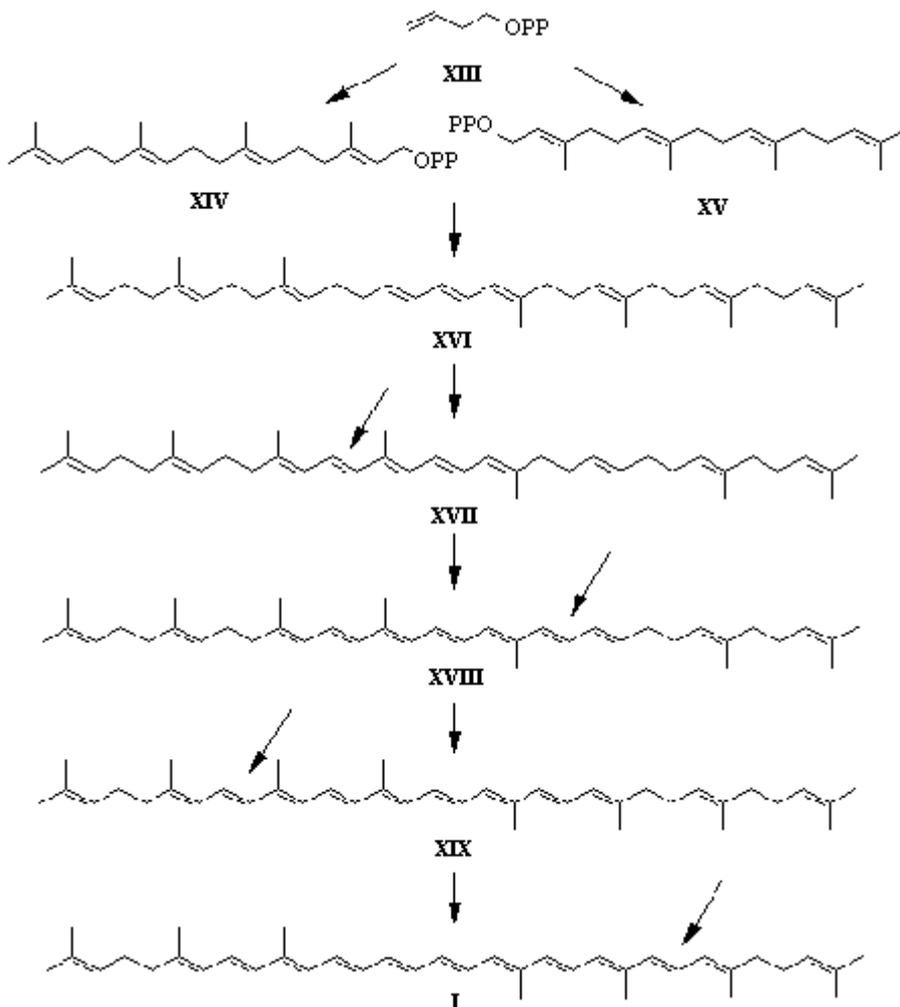
### **Biosynthesis of carotenoids**

Carotenoids are synthesized in nature by plants and many microorganisms. Animals can metabolize carotenoids in a characteristic manner, but they are not able to synthesize carotenoids. (Bodea, 1966; Britton, 1982; Istudor, 1988). Carotenoids, which are terpenoids, may be synthesized from the basic C<sub>5</sub>-terpenoid precursor, isopentenyl diphosphate which formula is shown in figure 5.

This compound is converted to geranylgeranyl diphosphate (C<sub>20</sub>) (XIV and XV). The dimerization of geranylgeranyl diphosphate leads to phytoene (7,8,11,12,7',8',11',12'-octahydro-gamma,gamma-carotene) (XVI) and the stepwise dehydrogenation via phytofluene (15Z,7,8,11,12,7',8'-hexahydro-gamma,gamma-carotene) (XVII), zeta-carotene (7,8,7',8'-tetrahydro-gamma,gamma-carotene) (XVIII), and neurosporene (7,8-dihydro-gamma,gamma-carotene) (XIX) gives lycopene (I). Subsequent cyclizations, dehydrogenations, oxidations, etc., lead to the individual naturally occurring carotenoids, but little is known about the biochemistry of the many interesting final structural modifications that give rise to the hundreds of diverse natural carotenoids (Britton, 1985; Rodriguez-Amaya, 1993).

There are now exciting prospects for rapid progress through the application of molecular genetics techniques in combination with other biochemical and chemical approaches. The benefits of this are not purely academic. The industrial production of natural carotenoids through microbial biotechnology is already established and expanding,

mainly through the exploitation of some microalgae (particularly *Dunaliella*) which can synthesize large amount of carotenoid.



**Fig. 5.** Important and characteristic carotenoids – structural formula

## Conclusions

Carotenoids have extensive applications as colors in foods and beverages, as pigments in poultry and fish and also as antioxidants in dietary supplements. Most carotenoids are produced by chemical

synthesis (e.g. vitamin A), although microbial fermentation processes have been developed for astaxanthin and  $\beta$ -carotene, whilst lycopene can also be obtained by extraction from natural sources. Food colorants play a very important role in enhancing the esthetic appeal of food. Regarding carotenoids, they have a double role, colorant and micronutrient.

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