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Mini-review

Health protective effects of carotenoids and their interactions with other biological antioxidants

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ABSTRACT

Carotenoids are natural pigments attracting attention of physicists, chemists and biologists due to their multiple functions in the nature. While carotenoids have unusually high extinction coefficients, they do not exhibit adequate emission. This fact has resulted in detailed studies of photophysical and photochemical properties of carotenoids and their role as light-harvesting pigments in photosynthesis. Carotenoids are abundantly present in fruits and vegetables and are considered as important species with beneficial effect on human health by decreasing the risk of various diseases, particularly decreasing the incidence of cancers and eye disease. More trials are needed to ascertain the role of carotenoids in prevention of cardiovascular disease and metabolic disease. Carotenoids effectively scavenge peroxyl radicals and act predominantly as antioxidants. However, under conditions of increased concentration of oxygen and carotenoid concentration, beta-carotene was found to exhibit prooxidant behaviour. Photophysical properties of carotenoids are the main aims of this review. In addition, the localization of carotenoids in biological membranes, their interactions and reactions with ascorbic acid (vitamin C) and alpha-tocopherol (vitamin E) as well as their redox potentials are discussed in view of their antioxidant properties as beneficial species in preventing various diseases.

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1. Introduction

Carotenoids are natural pigments characterised by a wide variety of functions in nature [1]. Carotenoids have many important functions mainly in view of their interactions with light. In fact, carotenoid photophysics has always been a key research area of carotenoids because processes linked with photon absorption play important roles in understanding the mechanisms of photoprotection of carotenoids as well as the roles of carotenoids as lightharvesting systems [2].

Carotenoids play important roles in deactivating a wide variety of reactive radical species in biological systems [3]. Such properties are termed antioxidant properties. However, under certain conditions, which are not fully understood, carotenoids are known to behave as prooxidants [3]. Carotenoids acting as prooxidants in biological systems are currently of increased interest due to their potentially serious health consequences.

0223-5234/\$ - see front matter © 2013 Elsevier Masson SAS. All rights reserved. http://dx.doi.org/10.1016/j.ejmech.2013.09.054 The aim of this review is to discuss the chemical, biological and physical properties of carotenoids. Special attention is devoted to their antioxidant properties. A possible role of carotenoids as prooxidants, including conditions under which a switch between antioxidant and prooxidant state may occur will also be discussed.

2. Characterization of carotenoids

2.1. General properties

Carotenoids are pigments that are found in plants and microorganisms [4]. There are over 600 carotenoids occurring in nature which are classified as carotenes, xanthophylls and lycopene.

Carotenoids have been shown to play a range of roles in the prevention against various health disorders, including cancer, metabolic disease and possibly cardiovascular disease [5]. The positive health effects of carotenoids is related to their antioxidant activity which arises as a result of the ability of the conjugated double bond structure to delocalise unpaired electrons [6]. This feature is primarily responsible for the excellent ability of carotenoids to physically quench singlet oxygen and terminate reactive free radicals formed in tissues.





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Fig. 1. Structures of selected carotenoids.

Carotenoids are hydrophobic molecules with very low solubility in water functioning in hydrophobic areas of the cell [7]. Polar functional groups attached to the polyene chain may modify the polarity of carotenoids which in turn may influence their localization within biological membranes and their interactions with various molecules.

The natural functions of carotenoids are predominantly determined by their molecular properties such as size, geometry, presence of functional groups and other characteristics [8]. Of importance is also double bond conjugation which is linked with photochemical properties and chemical reactivity towards molecules including free radicals. The chemical structures of selected carotenoids are shown in Fig. 1.

2.2. Structural characteristics of carotenoids

The most typical feature of the carotenoid molecules is the long system of conjugated double bonds in which π -electrons are effectively delocalized over the length of the polyene chain. Carotenoids may exist in different configurations due to isomerism around the C=C bonds [8]. The configurations around a double bond are termed E or Z, which generally corresponds to *trans* and *cis*, however there are some exceptions [9]. *Cis* isomers are usually less thermodynamically stable than trans isomers, mainly due to the sterical hindrance between adjacent hydrogens and methyl groups. Therefore the *trans* form of carotenoids is more prevalent in the nature. In addition, rotation around a single C-C bond is also possible, thus the carotenoid molecules can exhibit many shapes and conformations.

The conjugated polyene chain is stable mainly due to the existence of coplanar double bonds. Free rotation around the C-6,7 single bond in carotenoids containing cyclic-end groups can generate many possible geometries. It is rational to assume, that coplanarity between the ring and chain may result in steric crowding [9]. Thus it has been concluded, that the preferred conformation is 6-s-cis, but departure of approximately 40° from planarity is necessary to relieve steric hindrance between the



Fig. 2. Energy levels of a carotenoid molecule. The green line denotes $S_0 - S_2$ transition and the red lines denote transient signals observed after excitation. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

methyl group on ring carbon-5 and the carbon-8 hydrogen from the polyene chain.

Carotenoids in all-*trans* configurations are linear and rigid molecules and have an extended conjugated double bond system. On the contrary, *cis*-isomers have different molecular geometries, they are not linear molecules and therefore their ability to act within subcellular structures may be greatly affected [10]. *Cis*-isomers have higher solubility than all *trans*-isomers and thus they can be more readily absorbed and transported within cellular compartments.

3. Carotenoids in photochemistry, photophysics and photosynthesis

3.1. Photochemistry of carotenoids

Two original papers published four decades ago, dealing with the interpretation of the electronic absorption spectra of polyenes (related to carotenoids) have shown that there are anomalous spectroscopic and photochemical properties of π -electron conjugated molecules [11,12]. These were 1) in computed and experimental lifetimes from absorption spectra, 2) solvent dependent shifts in the absorption and fluorescence spectra and 3) large differences between absorption and emission bands. These anomalies were explained on the basis of spectroscopy measurements using short polyenes and carotenoid analogs. The results have shown that anomalies were caused by the presence of a dark excited state located below the absorbing state. The structure of the conjugated polyenes including most of the carotenoids belongs to the C_{2h} point symmetry group. It has been shown that the lowest excited state of polyenes is not the B_{u}^{+} state, but the A_{g}^{-} state which has lower energy than the B^+_u state into which transition is allowed. The lowest excited state of polyenes (A_g⁻ state) is of the same symmetry with the S₀ ground state and therefore the transition into this state is forbidden (Fig. 2). The lowest excited electronic state A_g^- is denoted as the S_1 state and B_u^+ state is commonly denoted S_2 . Precise calculations of the excited states of long polyenes including carotenoids have shown that such molecules may have alternative Download English Version:

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