



Review

Applications of computational chemistry to the study of the antiradical activity of carotenoids: A review



Debora Luana Monego*, Marcelo Barcellos da Rosa, Paulo Cícero do Nascimento

Department of Chemistry, Federal University of Santa Maria, Avenida Roraima, 1000, Santa Maria 97105900, RS, Brazil

ARTICLE INFO

Article history:

Received 14 June 2016

Received in revised form 22 August 2016

Accepted 22 August 2016

Available online 24 August 2016

Keywords:

Carotenoids

Free radicals

Antiradical activity

Quantum chemistry calculations

ABSTRACT

A summary of the various quantum chemical analyses that have been employed to evaluate the free radical scavenger capacity of carotenoid molecules are tabulated in this review and the most important observations are discussed. These molecules are able to interact with reactive oxygen species through singlet oxygen scavenging, electron transfer, hydrogen atom abstraction and radical adduct formation. Most studies employ density functional theory to compare the antiradical capacity of different carotenoids with the ones that are most explored theoretically, such as lycopene and β -carotene. A significant number of these applications have been directed towards understanding the electron transfer mechanism, and a useful tool called the FEDAM (full-electron donor-acceptor map) was developed to better evaluate this mechanism. Important aspects that may affect the radical scavenging capacity of carotenoids, such as synergistic effects and solubility, are sometimes overlooked, and a greater number of such compounds should be explored.

© 2016 Elsevier Ltd. All rights reserved.

Contents

1. Introduction	37
2. Computational studies evaluating free radical and reactive oxygen scavenging activity of carotenoids	39
2.1. Quenching singlet oxygen mechanism	39
2.2. Electron transfer mechanism	40
2.3. Hydrogen atom transfer and radical adduct formation mechanisms	42
3. Conclusions	43
Funding	43
Acknowledgements	43
References	43

Abbreviations: B3LYP, Becke, three-parameter, Lee-Yang-Parr exchange-correlation functional; BPW91, combination of GGA exchange functional of Becke and GGA correlation functional of Perdew and Wang; CAR, carotenoid; CASMP2, complete active space Møller-Plesset 2nd order perturbation theory; DFT, density functional theory; EA, electron affinity; FEDAM, full-electron donor-acceptor map; GGA, generalized gradient approximation; HOMO, highest occupied molecular orbital; IE, ionization energy; LUMO, lowest unoccupied molecular orbital; LYC, lycopene; PCM, polarizable continuum model; PM3, parametric method 3; R, radical; UB3LYP, unrestricted Becke, three-parameter, Lee-Yang-Parr exchange-correlation functional.

* Corresponding author.

E-mail address: debora.monego@gmail.com (D.L. Monego).

1. Introduction

Carotenoids are a class of natural pigments derived from a basic structure of 40 carbon atoms in a polyene chain. In human nutrition, these molecules are the major sources of retinol, besides showing pro-vitamin A activity and important role as antioxidant agents (Krinsky, 1989; Lachance, 1988). Due to this antioxidant potential, a diet rich in carotenoids is associated with a reduced risk of development of several disorders caused by oxidative stress, such as various types of cancer, cardiovascular and ophthalmologic diseases (Krinsky, 1988; Mayne, 1996; Peto, Doll, Buckley, & Sporn, 1981).

Computational chemistry is a multidisciplinary field of research with applications to many important problems in chemistry, biology and materials science. The study of the fundamental properties of atoms and molecules using quantum mechanics and thermodynamics is nowadays a consolidated approach and long considered as a “must-have” tool by the scientific community (Krieger, 1997).

Uses of computational chemistry in the area of carotenoids have gained attention especially in the last two decades. Carotenoids are usually studied by chromatographic and spectrometric methods, which impose limitations concerning important factors that may influence their biological functions, such as solubility and synergistic effects (Böhm, Edge, McGarvey, & Truscott, 1998; Young & Lowe, 2001). Also, the large molecular size of carotenoids has restricted many of these studies to the semiempirical level. This makes computations on them very useful in order to develop a better understanding of the mechanisms underlying these functions, improving the accuracy of predictions of their *in vivo* actions.

Based on the study of the reaction of carotenoid molecules with different radical species, mechanisms through which carotenoids react with active oxygen species have been suggested (Burton & Ingold, 1984; Everett et al., 1996; Hill et al., 1995; Liebler & McClure, 1996). Since then, a great number of splendid reviews have been written aiming to elucidate the mechanisms and the effects of this interaction on human health. Edge, McGarvey, and Truscott (1997) for instance, analyzed relevant data regarding the antioxidant activity of carotenoids and discussed their possible mechanisms of action. According to the authors, carotenoids have

the ability to act as a catalyst and quench singlet oxygen ($^1O_2^*$). They also observed that the extent of this capacity is directly related to the number of conjugated double bonds and to the carotenoid triplet energy level. Among the biological occurring carotenoids, lycopene presents the greatest ability to quench $^1O_2^*$ (Di Mascio, Kaiser, & Sies, 1989) by the direct energy transfer, as follows:



The carotenoid then returns to the ground state by dissipating its energy as heat through rotational and vibrational interactions with the surrounding solvent.

Additionally, carotenoids are able to chemically interact with free radicals *in vivo* by many different mechanisms (Krinsky, 2001; Krinsky & Yeum, 2003; Mortensen, Skibsted, & Truscott, 2001; Rice-Evansa, Sampson, Bramley, & Holloway, 1997). The most important are the electron transfer (II), hydrogen atom abstraction by the radical (III), and radical addition to the carotenoid to form adduct (IV):



where Hx stands for the abstracted hydrogen and $[CAR \dots R]^\cdot$ is the adduct formed.

Table 1
Structure of common carotenoid molecules.

Compound	Structure
Lycopene/ Ψ - Ψ -carotene/ $C_{40}H_{56}$	
β -carotene/ β - β -carotene/ $C_{40}H_{56}$	
Zeaxanthin/(3R,3'R)- β - β -carotene-3,3'-diol/ $C_{40}H_{56}O_2$	
Lutein/(3R,3'R,6'R)- β - ϵ -carotene-3,3'-diol/ $C_{40}H_{56}O_2$	
β -cryptoxanthin/(3R)- β - β -carotene-3-ol/ $C_{40}H_{56}O$	
Astaxanthin/3,3'-dihydroxy- β , β -carotene-4,4'-dione/ $C_{40}H_{52}O_4$	

Download English Version:

<https://daneshyari.com/en/article/1184727>

Download Persian Version:

<https://daneshyari.com/article/1184727>

[Daneshyari.com](https://daneshyari.com)