



Computational study of the structure–free radical scavenging relationship of procyanidins



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ABSTRACT

Procyanidins (PCs) are effective free radical scavengers, however, their antioxidant ability is variable because they have different degrees of polymerisation, are composed by distinct types of subunits and are very susceptible to changes in conformation. In this work the structure–free radical scavenging relationship of monomers, dimers and trimers of PCs was studied through the hydrogen atom transfer (HAT), sequential proton-loss electron-transfer (SPLET) and single electron transfer followed by proton transfer (SET-PT) mechanisms in aqueous phase, employing the Density Functional Theory (DFT) computational method. The structure–free radical scavenging relationship of PCs showed a very similar behaviour in HAT and SET-PT mechanisms, but very different in the SPLET mechanism. The structural factor that showed more effects on the ability of PCs to scavenge free radicals in aqueous phase was the conformation.

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1. Introduction

The PCs are also known as proanthocyanidins or condensed tannins (Enomoto, Nagasako-Akazome, Kanda, Ikeda, & Dake, 2006) and represent one of the most abundant class of phenolic compounds produced by plant tissues (Andersen & Markham, 2006). The PCs have proven to be 30–50 times more effective free radical scavengers than vitamins C and E (Duda-Chodak, Tarko, Satora, Sroka, & Tuszyński, 2010; Saint-Cricq, Provost, & Vivas, 1999), so they have beneficial effects on the fruits and vegetable quality, in addition to the health of consumers (Jerez, Touriño, Sineiro, Torres, & Núñez, 2007; Khanal, Howard, & Prior, 2009). However, because PCs have very complex and diverse structures, their antioxidant ability is changeable and depends on the intermediates and oxidation products formed during the antioxidant reactions.

The PCs are flavonoids belonging to the flavan-3-ols class and are mainly composed of (–)-epicatechin and (+)-catechin subunits, which are linked to form oligomers or polymers (Enomoto et al., 2006). The subunit localised at the end of the chain is called terminal unit and the remaining subunits are called extension units (Fig. 1). Also the PCs are characterised by three chiral centres, C2, C3 and C4, which makes them very susceptible to changes in configuration and conformation. From C4 two conformations are

formed: compact and extended (Fig. 2). A way to distinguish these conformations is through the dihedral angles formed between the atoms involved in the interflavanoid linkage (C3–C4–C8–C9). Compact conformation is the one with positive dihedral angle values whereas the extended conformation has negative values. For dimers these values can range from +90° to –90° and for trimers from +100° to –70°, respectively (Khan, Haslam, & Williamson, 1997; Tarascou et al., 2007).

There is growing evidence indicating a strong relationship between the antioxidant ability of PCs and structural factors such as degree of polymerisation, type of subunit and conformation, but there are also many controversies about this issue (Leite, Laranjinha, Pereira, & de Freitas, 2003; Santos-Buelga & Scalbert, 2000). On the one hand, it is stated that the greater the degree of polymerisation of the PCs the greater their ability to scavenge free radicals (Arteel & Sies, 1999; Vennat, Bos, Pourrat, & Bastide, 1994). On the other hand, it is suggested that the PCs ability to scavenge free radicals is not necessarily greater at a higher degree of polymerisation, as in one study was reported that PCs trimers showed to be more efficient than dimers, but less efficient than monomers to scavenge the hydroxyl radical (Cheynier, Rigaud, & da Silva, 1992). There is a special interest to know the differences in the ability to scavenge free radicals amongst monomers, dimers and trimers, as these represent the most bioavailable forms compared to larger oligomers of PCs.

Regarding the type of subunit, most studies have reported higher activity for free radical scavenging in (–)-epicatechin against different free radicals (Cheynier et al., 1992; de Freitas,

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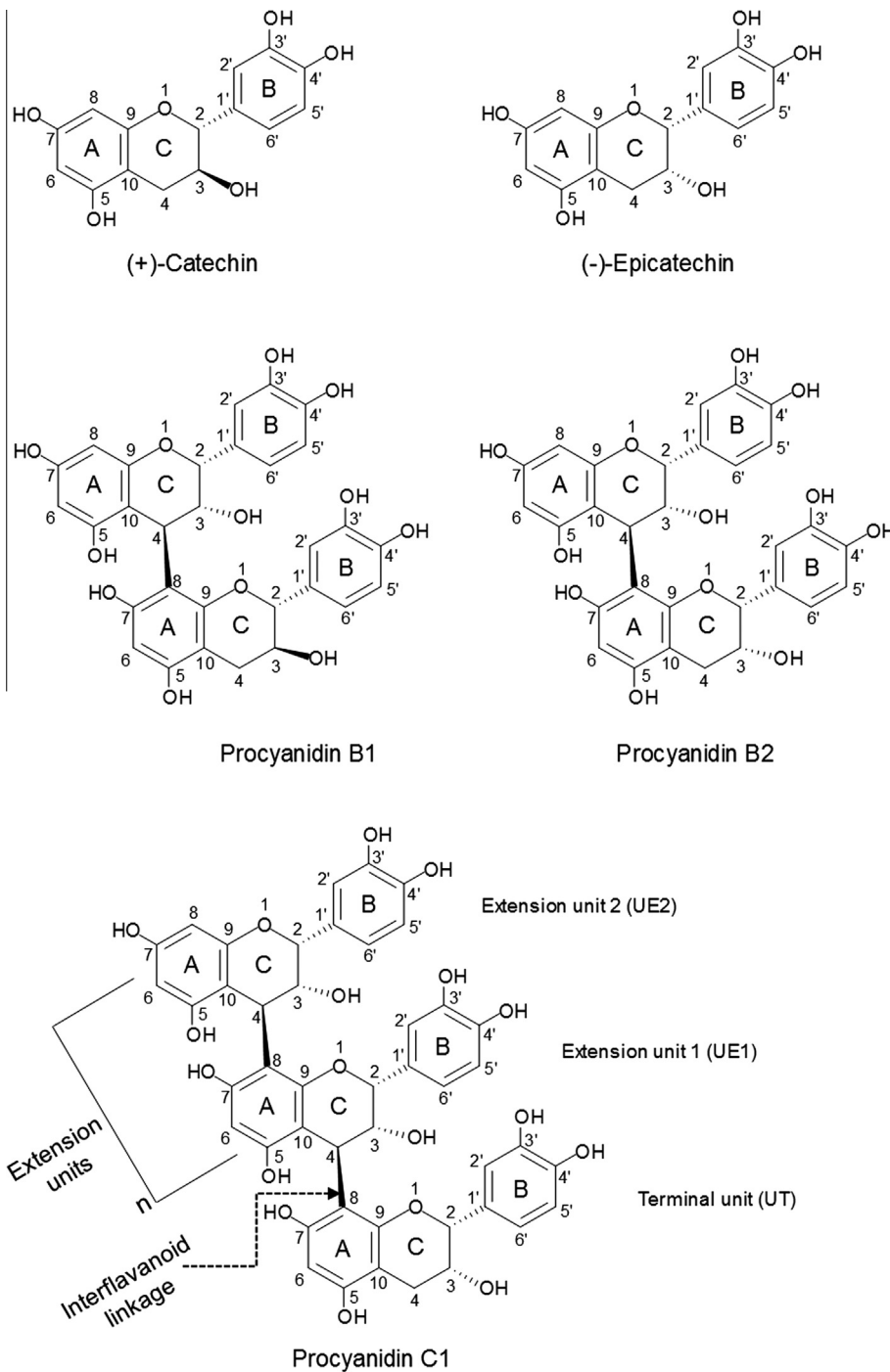


Fig. 1. Structure of (–)-epicatechin (E), (+)-catechin (C), procyanidin B1 (PB1), procyanidin B2 (PB2) and procyanidin C1 (PC1).

Glories, & Laguerre, 1998a); however, in an experimental-computational study conducted by Mendoza-Wilson et al. (2013), higher radical scavenging activity was found for (+)-catechin against the DPPH. In another computational study performed by Mendoza-Wilson and Glossman-Mitnik (2006) it was determined that (+)-catechin and (–)-epicatechin have comparable intrinsic reactivity properties, due to their similarity in structure (epimers). Nevertheless they have the ability to form distinct intermediates, which can make the difference in activity against free radicals between these isomers. Additionally, the predominant conformation (compact or extended) in a particular solvent (polar, non polar), is also

dependent on the type of subunit as extension unit (Hatano & Hemingway, 1997).

The intermediates and products that can be formed from the PCs during their reaction against free radicals are dependent primarily of the mechanism followed and their reactivity properties. There are three basic mechanisms for free radical scavenging: (1) HAT with a phenoxyl radical as intermediate; (2) SPLET with a phenoxide anion as intermediate, and (3) SET-PT with a radical cation as intermediate (Foti, Daquino, Mackie, DiLabio, & Ingold, 2008; Musialik, Kuzmicz, Pawlowski, & Litwinienko, 2009). The reactivity properties of PCs focus on the oxidation–reduction (redox)

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