Trends in Food Science & Technology 54 (2016) 165–174

Contents lists available at ScienceDirect

Trends in Food Science & Technology

journal homepage: http://www.journals.elsevier.com/trends-in-food-science-and-technology

The triple defensive barrier of phenolic compounds against the lipid oxidation-induced damage in food products

Rosario Zamora, Francisco J. Hidalgo*

Instituto de la Grasa, Consejo Superior de Investigaciones Científicas, Carretera de Utrera km 1, Campus Universitario, Edificio 46, 41013 Seville, Spain

ARTICLE INFO

Article history:
Received 25 January 2016
Received in revised form
30 May 2016
Accepted 8 June 2016
Available online 15 June 2016

Keywords:
Carbonyl-scavenging ability
Lipid-derived reactive carbonyls
Lipid oxidation
Phenolic compounds
Structure-activity relationship

ABSTRACT

Background: Although prooxidant activities have also been described, phenolic compounds can act as chelating and free radical scavengers. These protective functions would be their first and second defense barriers against the lipid-induced damage in foods. In addition, recent studies have shown that they can act as lipid-derived carbonyl scavengers, therefore avoiding that these toxic and very reactive compounds can modify essential food components such as aminophospholipids, amino acids, and proteins. These results point out to phenolic compounds also as responsible for a third defense barrier against the lipid oxidation-induced damage in foods.

Scope and approach: This review collects the scattered information existing on the role of phenolic compounds as lipid-derived carbonyl scavengers and introduces a general lipid oxidation scheme in which the triple function of phenolic compounds can be clearly understood by pointing out where they are acting as a function of their structure.

Key findings and conclusions: The structural requirements for the three barriers are different and phenolic compounds are suggested to be classified into seven groups as a function of the number and kind(s) of function(s) exhibited. This better classification and understanding of how different phenolic compounds protect foods will help to the food industry to employ the most appropriate phenolic compounds in each formulation and will also contribute to better understand the biological functions of these compounds.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Lipid oxidation is a major food problem because it causes consumer rejection and potential safety problems. Thus, it is responsible for the deterioration of polyunsaturated lipids and produces changes in flavor, texture, appearance, and nutritional quality in food products (Waraho, McClements, & Decker, 2011). This traditional problem in the food industry has got worse in recent years because of the removal of hydrogenated fats, the addition of more unsaturated fatty acids to improve nutritional content, and the consumer desire to remove synthetic food additives including antioxidants. Because of that, the search of satisfactory strategies for inhibiting lipid oxidation has been (and still is) a constant for the food industry.

The assayed strategies have included the use of both primary antioxidants (those that disrupt the oxidative free radical chain reaction) and secondary antioxidants (those that prevent lipid oxidation by deactivating singlet oxygen, chelating metal ions, absorbing ultraviolet radiation, scavenging oxygen, or helping to regenerate primary antioxidants) (Senanayake, 2013). Among the different compounds assayed, natural phenolic compounds have been shown to effectively scavenge free radicals and to chelate transition metals, thus stopping progressive autoxidative damage and production of off-odours and off-tastes (Brewer, 2011). In addition, phenolic compounds are also able to scavenge the carbonyl compounds produced in the lipid oxidation pathway, providing in this way an additional protection to foods against the consequences of lipid oxidation. On the other hand, prooxidant activities of phenolic compounds have also been described (Chedea, Choueiri, Jisaka, & Kefalas, 2012; Halliwell, 2008; Masuda, Inai, Miura, Masuda, & Yamauchi, 2013), although they will not be discussed in depth in the present review.

The main purpose of this review is to collect the scattered information existing on the role of phenolic compounds as lipid-

* Corresponding author.
E-mail addresses: rzamora@ig.csic.es (R. Zamora), fhidalgo@ig.csic.es (F.J. Hidalgo).

http://dx.doi.org/10.1016/j.tifs.2016.06.006
0924-2244/© 2016 Elsevier Ltd. All rights reserved.

derived carbonyl scavengers, and to elaborate a general scheme of lipid oxidation in which the different functions of phenolic compounds in the protection of lipid oxidation consequences (as chelating agents, as free radical scavengers and as carbonyl trapping agents) can be easily understood.

2. The lipid oxidation pathway as a source of both free radicals and carbonyl compounds

Lipid oxidation is a free radical chain reaction that proceeds through the common stages of initiation, propagation and termination (Schaich, 2013). However, many of the secondary and tertiary products formed by free radical reactions are very reactive and react covalently with the surrounding food components, therefore extending lipid oxidation consequences (Zamora & Hidalgo, 2005).

The generation of primary free radicals is a thermodynamically unfavorable reaction and needs to be facilitated by the presence of oxidation initiators such as light, heat, ionizing radiation, transition metals, metalloproteins, oxidants, various hemolysis-prone substances and enzymes (Senanayake, 2013). In any case, the result will be the abstraction of a hydrogen atom from an unsaturated fatty acid and the formation of the corresponding alkyl radical (equation (1)).

$$LH + \text{initiator} \rightarrow L^{\bullet} \quad (1)$$

In mixtures of acyl chains with different unsaturation degree, the abstracted proton is usually a proton bonded to a doubly allylic carbon and the produced radical suffers then a rearrangement to produce a conjugated diene system. The formed alkyl radical reacts faster with oxygen than with lipids. Therefore the next step in the propagation reaction is the formation of the corresponding peroxyl radical (LOO•). This is a reversible reaction because the peroxyl radical can suffer a β-elimination reaction to produce again the alkyl radical, although the produced rearrangements would not be reversed (equation (2)).

$$L^{\bullet} + O_2 \leftrightarrow LOO^{\bullet} \quad (2)$$

This new radical is relatively slow to abstract an hydrogen from a new lipid molecule. Therefore, there is plenty of time for alternative reaction pathways that may compete and change the direction of the oxidation.

The reaction that continues the free radical chain is the hydrogen abstraction from a new lipid molecule (equation (3)).

$$LOO^{\bullet} + LH \rightarrow LOOH + L^{\bullet} \quad (3)$$

However, when these new lipid molecules are not immediately available during oxidation, peroxyl radicals react by alternative pathways. The most facile pathway is addition to a neighboring double bond. If this double bond belongs to the same molecule (a *cis* double bond two carbons away from the peroxyl radical) a cyclic product (epidioxide radical) is formed. This new radical reacts rapidly with oxygen to produce the corresponding epidioxide peroxyl radical (equation (4)).

$$LOO^{\bullet} \rightarrow \text{epidioxide radical} \rightarrow \text{epidioxide peroxyl radical} \quad (4)$$

If the carbon-carbon double bond belongs to a different molecule, a dimer is produced, which either can continue polymerizing afterwards or can produce monomeric products (epoxides).

Peroxyl radicals can also suffer a disproportionation reaction to produce alkoxyl radicals (LO•), although these last radicals are also produced by decomposition of lipid hydroperoxides (equation (5)).

$$LOOH \rightarrow LO^{\bullet} + OH^{\bullet} \quad (5)$$

LO• radicals are much more reactive than LOO• by several orders of magnitude. This is the reason for the very rapid oxidation that takes place in the second stages of oxidation after a very slow oxidation in the induction period. This radical suffers a cascade of reactions including: hydrogen abstraction to continue the free radical chain at the same time that they are converted into alcohols; internal rearrangements to produce epoxides; addition to double bonds to produce polymerization; and scissions to produce a mixture of carbonyl compounds (aldehydes, ketones, keto-acids), fatty acids, alcohols, alkanes, and alkenes.

The favored pathways in this cascade of reactions are determined by the reaction conditions, the solvent, and the lipid concentration and conformation. In any case, it produces a complex mixture of products, some of which are stable but others are able to react with the surrounding food components, therefore broadcasting the oxidative damage from lipids to all kind of molecules. Among the different produced reactions, carbonyl-amine reactions are particularly important because they have been shown to produce important changes in foods with both positive and negative consequences (Hidalgo & Zamora, 2004; Zamora & Hidalgo, 2008, 2015). A detailed description of these reactions is out of the scope of this review and they have been described somewhere else (Hidalgo & Zamora, 2016; Zamora & Hidalgo, 2005).

3. The chelating ability of phenolic compounds

The first function of phenolic compounds as inhibitors of lipid oxidation is to chelate or to form complexes with the transition metal catalysts responsible for the initiation of lipid degradations. Many phenolics have a strong capacity for binding ferric ions due to the presence of iron-binding motifs (Khokhar & Owusu Apenten, 2003). Fig. 1 shows the chemical structure of two major flavonoids: catechin and quercetin. The molecular structure of flavonoids consist of a benzopyran (rings A and C) and a phenyl ring (ring B), which have a hydroxylation pattern that is characteristic for each flavonoid. Their chelating ability depends on this hydroxylation pattern because flavonoids have a tendency to serve as hydrogen donors, which contributes to the formation of metal coordination complexes with good stability (Mira et al., 2002). In addition, the structure of the complex formed depends on a number of factors, including the coordination number and oxidation state of the metal ion, the number and proximity of electron donors in the flavonoid, and the chelating conditions such as temperature and pH (Selvaraj, Krishnaswamy, Devashya, Sethuraman, & Krishnam, 2013). Although other complexes can also be produced, when the carbonyl group is available, commonly the metal ion complexes are preferentially formed between the keto group in the C-4 and the hydroxyl group in C-5, resulting in either 1:1 or 1:2 metal-flavonoid complexes. In the case of catechin, where the carbonyl group is absent, its ability to chelate cupric ions has been attributed to the presence of the catechol group in the B-ring (Mira et al., 2002). These last hydroxyl groups have also been implied in the formation of 2:1 complexes between cupric ions and quercetin (Bukhari, Memon, Mahroof-Tahir, & Bhanger, 2009).

The complexation of the metal ions produces a special spatial orientation in the flavonoid, which has been related to the pharmacological activity described for these complexes. The biological activities described for flavonoid-metal ion complexes include anti-inflammatory, anti-bacterial, anti-diabetic, anti-tumor, and antioxidant activities both *in vitro* and *in vivo* (Selvaraj et al., 2013).

On the other hand, combinations of antioxidants and metal ions generate reactive oxygen species under *in vitro* conditions as shown by using electron spin resonance (ESR) (Iwasaki et al., 2014).

Download English Version:

https://daneshyari.com/en/article/2098506

Download Persian Version:

https://daneshyari.com/article/2098506

Daneshyari.com