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Protective effect of phenolic compounds on carbonyl-amine reactions produced by lipid-derived reactive carbonyls

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2,4-Heptadienal (PubChem ID: 5283321)
4,5-Epoxy-2-heptenal (PubChem ID: 6444055)
4,5-Epoxy-2-decenal (PubChem ID: 15825667)
4-Oxo-2-hexenal (PubChem ID: 6365145)
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ABSTRACT

The degradation of phenylalanine initiated by 2-pentenal, 2,4-heptadienal, 4-oxo-2-pentenal, 4,5-epoxy-2-heptenal, or 4,5-epoxy-2-decenal in the presence of phenolic compounds was studied to determine the structure-activity relationship of phenolic compounds on the protection of amino compounds against modifications produced by lipid-derived carbonyls. The obtained results showed that flavan-3-ols were the most efficient phenolic compounds followed by single *m*-diphenols. The effectiveness of these compounds was found to be related to their ability to trap rapidly the carbonyl compound, avoiding in this way the reaction of the carbonyl compound with the amino acid. The ability of flavan-3-ols for this reaction is suggested to be related to the high electronic density existing in some of the aromatic carbons of their ring A. This is the first report showing that carbonyl-phenol reactions involving lipid-derived reactive carbonyls can be produced more rapidly than carbonyl-amine reactions, therefore providing a satisfactory protection of amino compounds.

1. Introduction

Lipid oxidation is responsible for the deterioration of polyunsaturated fatty acyl chains in food lipids and the later changes produced in flavor, texture, appearance, and nutritional quality of food products (Liu, Gao, McClements, & Decker, 2016; Lv et al., 2016; Przybylski, Firdaous, Chataigne, Dhulster, & Nedjar, 2016). These changes are a consequence of both the formation of lipid oxidation products with undesirable properties, and the ability of some of these products to modify important macromolecules, including nucleic acids (Kozekov et al., 2010), aminophospholipids (Zamora & Hidalgo, 2003), amino acids (Hidalgo & Zamora, 2016), and proteins (Zamora & Hidalgo, 2005). Among them, amino acid modifications produced by oxidized lipids during food processing are a recognized source of both desirable beneficial compounds and compounds with deleterious properties, which can also be precursors of processing-related food toxicants such acrylamide (Hidalgo, Leon, & Zamora, 2016; Zamora & Hidalgo, 2008).

Lipid oxidation and its consequences have been traditionally controlled by the use of antioxidants, among which the use of phenolic compounds has received a considerable attention. Thus, these last compounds have been shown both to effectively scavenge free radicals and to chelate transition metals, and, consequently, to stop progressive autoxidative damage and the corresponding production of off-odors and off-flavors (Akhtar, Ismail, Fraternale, & Sestili, 2015; Balboa, Conde, Moure, Falque, & Dominguez, 2013). More recently, some authors have also pointed out to the ability of phenolic compounds to scavenge the carbonyl compounds produced during lipid oxidation, including alkanals, dialdehydes,

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alkenals, and 4-hydroxyl-2-alkenals, analogously to their better known ability to trap small reactive carbonyls such as glyoxal or methylglyoxal (Delgado, Hidalgo, & Zamora, 2016a; Hidalgo & Zamora, 2014; Lo, Hsiao, & Chen, 2011; Zhu et al., 2009a, 2009b). In fact, carbonyl–phenol adducts have been found to be produced in food products as a consequence of frying (Zamora, Aguilar, Granvogl, & Hidalgo, 2016). These last results have allowed to describe the protection offered by phenolic compounds against lipid oxidation as a triple defensive barrier by, successively, being able of chelating transition metals to inhibit the formation of the first radicals, scavenging lipid radicals to prevent the broadcasting of the initial damage, and, finally, trapping the produced lipid-derived reactive carbonyls to avoid the consequences of carbonyl–amine reactions (Zamora & Hidalgo, 2016).

Because the effectivity of this last defensive barrier is still poorly understood, this manuscript studies the stability of phenylalanine, as model amino acid, in the presence of both lipid-derived carbonyls and phenolic compounds in an attempt to compare the effectiveness of different kinds of phenolic compounds to protect amino acids against carbonyl-amine reactions produced by lipid-derived carbonyl compounds.

2. Materials and methods

2.1. Materials

As model lipid-derived carbonyl compounds, an alkenal (2-pentenal), an alkadienal (2,4-heptadienal), an oxoalkenal (4-oxo-2-hexenal), and two epoxyalkenals (4,5-epoxy-2-heptenal and 4,5-epoxy-2-decenal) were employed. 2-Pentanal and 2,4-decadienal were purchased from Sigma-Aldrich (St. Louis, MO), 4-oxo-2-hexenal was prepared from 2-ethylfuran by ring opening (Zamora, Alcon, & Hidalgo, 2013), and 4,5-epoxy-2-heptenal and 4,5-epoxy-2-decenal were synthetized from their corresponding alkadienals (2,4-heptadienal and 2,4-decadienal) by epoxidation with 3-chloroperoxybenzoic acid (Zamora, Gallardo, & Hidalgo, 2006).

As phenolic compounds a wide array of model compounds as well as flavonoids were employed. They are collected in Fig. 1. They included simple *m*-diphenols: resorcinol (**1**), 2-methylresorcinol (**2**), 2,5-dimethylresorcinol (**3**), and 2,6-dihydroxybenzoic acid (**4**); other simple phenols: 4-methylcatechol (**5**), hydroquinone (**6**), and sesamol (**7**); flavonols: quercetin (**8**), myricetin (**9**), and

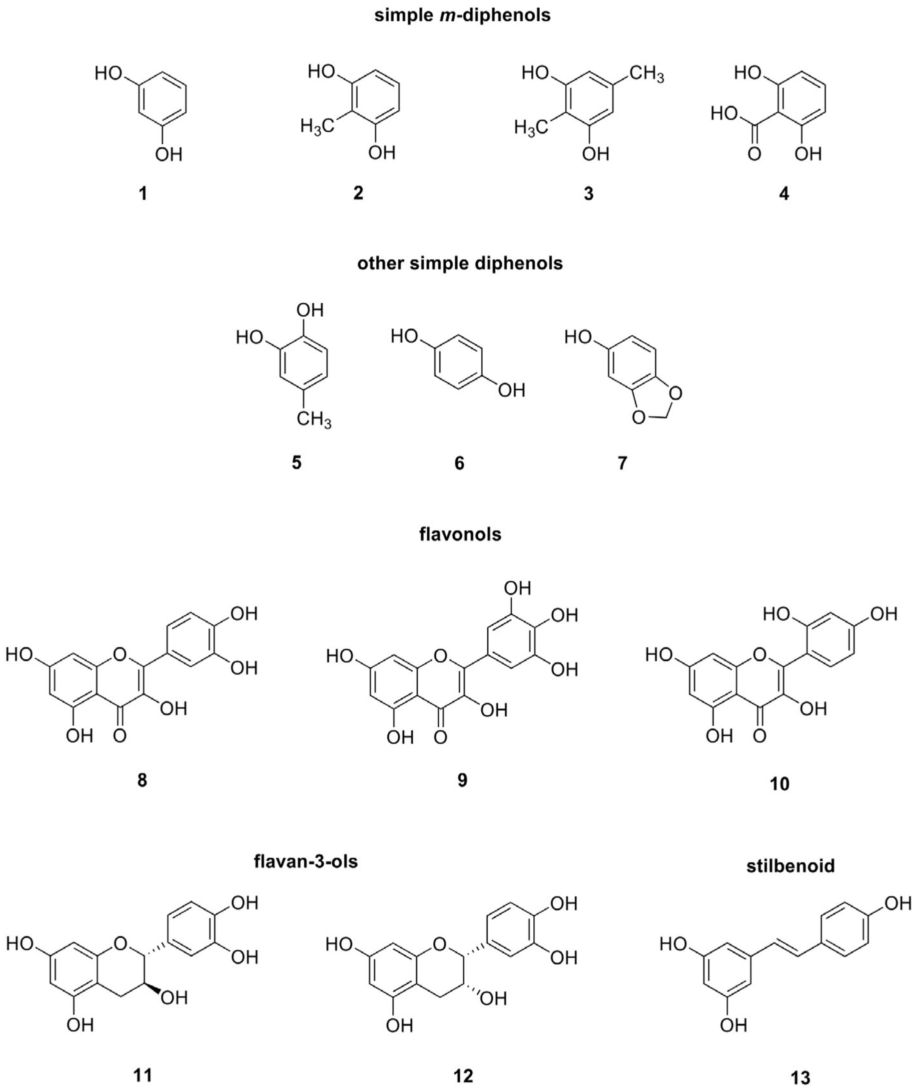

Fig. 1. Chemical structures of the phenolic compounds employed in the study.