Lipids: Their Role in the Formation of Endogenous Antioxidants during Food Processing

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Abstract: Lipids are important food nutrients and they also carry out other functions such as to be carriers of aromatic substances or to influence food texture, for example. However, polyunsaturated acids are also easily oxidised. In fact, oxidative rancidity of edible oils is a serious problem in the food industry. As an alternative to the use of synthetic antioxidants, the generation of endogenous antioxidants by carbonyl-amine reactions can be employed to increase food stability. These reactions are widely accepted to be produced as a consequence of Maillard reactions between carbohydrates and amino compounds. However, the contribution of lipid-derived carbonyl compounds to these reactions is much lesser known. This review discusses the role of lipid-derived antioxidants by analysing how they are formed and their antioxidative action.

Keywords: amino phospholipids; antioxidants; carbonyls-amine reactions; lipid-derived antioxidants; lipid oxidations; Maillard reactions

Formation of oxidised lipid/amine reaction products as a consequence of lipid oxidation in the presence of amino compounds

Lipid oxidation is the chemical reaction that most limits shelf life of foods, and it is increasingly being recognised as a major contributor to oxidative damage *in vivo*. Less recognised are, however, the co-oxidations that broadcast oxidative damage from lipids to all kinds of molecules via reactions of lipid free radicals in early stages of oxidation and later reactions of product epoxides and carbonyls as oxidation progresses (Schaich 2008).

Interactions between oxidised lipids and proteins are very complex, in part as a consequence of the contribution of both lipid hydroperoxides and their secondary products, and also because lipids and proteins possess several reactive functional groups (Pokorny *et al.* 2005). When proteins are exposed to peroxidised lipids, lipid-protein complexes are formed. The strength of these lipid-protein complexes can be defined by a series of extraction steps, and complexes may be broken with urea/sodium dodecyl sulphate (Kanazawa *et al.* 1975; Kanner & Karel 1976).

These complexes can also evolve into the formation of covalent bonds, which mainly takes place by reaction of the reactive groups of amino acid residues with the secondary lipid oxidation products. In fact, the formation of these adducts is an unavoidable consequence of lipid oxidation when it takes place in the presence of amino acids and proteins (Hidalgo & Zamora 2002).

Among the different oxidised lipid/amino acid reactions produced, some of them are nonreversible and different covalent compounds are formed. In fact, the formation of pyrroles (Hidalgo & Zamora 2000), dihydropyridines (Kikugawa *et al.* 1984), and pyridinium salts (Suyama & Adachi 1979), among other heterocyclic compounds, has been described. In addition, Michael adducts produced by reaction of the histidine imidazole ring with funcionalised α,β-unsaturated keto compounds are nowadays also well-known (Zamora *et al.* 1999).

In addition to amino acids and proteins, these reactions are also produced in amino phospholipids with the formation of analogous compounds (Zamora & Hidalgo 2003). However, those produced with the amino group of phospholipids are less hydrophilic than those produced with the amino group of amino acids (Zamora *et al.* 2005).

Antioxidative activity of oxidised lipid/amine reaction products

Many of the formed oxidised lipid/amine reaction products are antioxidants. Thus, when the 13-hydroperoxide of linoleic acid reacted with lysine, different fractions were isolated and most of them were able to protect soybean oil against oxidation (Ahmad *et al.* 1996). These activities were a consequence of the formation of different compounds in the amino group of the amino acid. Among them, the antioxidative activities of the formed pyrroles (Alaiz *et al.* 1995), dihydropyridines, pyridinium salts, and Michael adducts involving histidine residues have been shown (Alaiz *et al.* 1996).

This activity is also observed in damaged proteins. Thus, secondary lipid oxidation products were able to induce antioxidative activity in a bovine serum albumin at the same time that the protein was browned (Alaiz *et al.* 1997). This parallelism between browning and antioxidative activity is analogous to that produced as a consequence of the Maillard reaction. However, antioxidative activities and browning produced by oxidised lipids are higher at low temperatures, and lower at high temperatures, than those induced by carbohydrates (Alaiz *et al.* 1999).

Antioxidative activity of oxidised amino phospholipids

Analogously to the amino groups of amino acids, amino-carbonyl reactions can also be produced in the amino group of amino phospholipids and these reactions contribute to the antioxidative activity observed for these compounds (Husain *et al.* 1984). In fact, some studies have suggested that these reactions are contributing to increase the antioxidative activity of phosphatidylethanolamine, and not that of the phosphatidylcholine, as a consequence of oxidation (Hidalgo *et al.* 2005).

Amino-carbonyl reactions in phospholipids compete with those produced among oxidised phospholipid fatty acid chains and amino acids. However, different types of antioxidants are produced and this has a consequence in the antioxidative activities observed. Thus, when these reactions are produced *in situ* and the antioxidative activities of the formed compounds evaluated at the same time that they are produced, phosphatidylethanolamine/lysine mixtures always exhibited higher antioxidative activities than phosphatidylethanolamine in oils (Hidalgo *et al.* 2006). This is likely a consequence of the higher effectiveness of hydrophilic antioxidants in bulk oils, a trend that is opposite in oil-in-water emulsions (Frankel *et al.* 1994).

Synergism between oxidised lipid/amine reaction products and other antioxidants

Antioxidative activity of oxidised lipid/amine reaction products has been related to their ability for scavenging radical species (Zamora *et al.* unpublished), which is increased with the polymerisation suffered by some of the monomer oxidised lipid/amine reaction products initially formed (Hidalgo *et al.* 2003). However, the synergism observed between the antioxidative activities of these compounds and those of both natural (Hidalgo *et al.* 2007) and artificial antioxidants (Ahmad *et al.* 1998) is also noticeable.

Feed-back inhibition of lipid oxidation by oxidised lipid/amine reaction products

Because antioxidative activities of these compounds are able to protect lipids from oxidation, their formation has been proposed as a feed-back inhibition mechanism for the whole oxidative process when lipids are oxidised in the presence of amino compounds (Zamora *et al.* 1997; Hidalgo *et al.* 2001). In fact, a slight initial oxidation was observed to increase fatty acid stability in polyunsaturated fatty acid/protein mixtures (Alaiz *et al.* 1998).

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