Functionality Changes of Natural Antioxidants during Food Processing and Storage

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Abstract: Food raw materials and products contain inhibitors of oxidation reactions, both in the lipidic phase and the aqueous phase. The most important inhibitors are phenolic antioxidants. During food processing and storage, concentrations of antioxidants in the two phases reach an equilibrium. Phenolics react with lipidic free radicals, being converted into antioxidant free radicals, quinones, polymers and copolymers. Some degradation products possess an antioxidant activity, too. The relative antioxidant activity decreases with decreasing concentration of oxygen in the system and with increasing temperature. Antioxidants are more rapidly decomposed in surface layers. Health aspects of antioxidant degradation products are often neglected as the safety of antioxidant degradation products is mostly unknown.

Keywords: antioxidants; food technology; food storage; oxidation; phenolics

INTRODUCTION

The lipidic fraction of food raw materials and food products is rather sensitive against oxidation under conditions of food processing and storage. Therefore, it should be protected by phenolic antioxidants and other inhibitors of lipid oxidation. Fortunately, most foods contain a variety of oxidation inhibitors as their natural components, such as phenolic acids, lignans, flavonoids and anthocyanins [1]. Some nitrogen and sulphur derivatives also possess antioxidant activity, and some substituted and/or polyvalent organic acids act as synergists. They are subject to changes during food processing and storage, which affects their functionality [2]. As transient valency metals, present in foods, enhance oxidation reactions, chelating agents also act as oxidation inhibitors. In this contribution we shall discuss only the phenolic acids because they are the most important inhibitors of lipid oxidation.

Occurrence of antioxidants in foods

Most foods are dispersion systems, consisting of solid particles, lipidic liquid nonpolar phase, and aqueous polar phase. All these phases contain antioxidants. Antioxidants present in the solid phase can be extracted into the liquid phases during food processing and storage, especially, if enzymic reactions are involved. The most important group of antioxidants present in the nonpolar liquid phase are tocopherols [3], or the related tocotrienols, restricted to a few sources, such as cereals or palm fruits. Tocodienols and tocomonoenols are unimportant in food products. In some oilseed lipids and some other food lipids, additional phenolic antioxidants are present, too, such as hydroxytyrosol derivatives in olives, lignans in sesame or linseed oil, or sterol esters of ferulic acid in rice bran oil [4]. Phospholipids and some sterols (e.g. avenasterols) also increase the stability of fats and oils. The aqueous phase of most foods contains phenolic antioxidants, too, such as flavonoids or anthocyanins [5]. They are more polar than the above liposoluble substances, especially their glycosides and diglycosides. Several synergists and metal chelating agents are also dissolved in the aqueous phase. Some semipolar antioxidants are concentrated on the interface between the lipidic and the aqueous phases. The nonpolar moiety of the molecule is oriented towards the lipidic phase, while the polar moiety is oriented towards the aqueous phase. An equlibrium is attained during the storage between the concentration of antioxidants in the two liquid phases.

Changes of phenolic antioxidants during food processing and storage

Phenolic antioxidants react with free lipidoxy or peroxy radicals, which are reduced into inactive derivatives while phenolic substances are converted into phenolic free radicals. They possess only low reactivity so that they initiate the formation of other free radicals only in very small extent. The much more probable reactions are those with more reactive partners, such as follows [6]:

The reaction of a phenolic free radical with another lipid alkoxy or peroxy radical with formation of a quinone. Quinones possess only a limited antioxidant activity, but they more probably dimerize, react with an amine, a sulphide or a thiol group of amino acids with formation of substituted polyphenolic derivatives, which are often coloured. Quinones may be bound to proteins, too.

The reaction of a phenolic free radical with another phenolic free radicals forming a dimer, sometimes even a trimer. Spirotrimers formed from tocopherol free radicals were identified in oxidized vegetable oils. The dimers or oligomers possess a limited antioxidant activity, too.

The reaction of a phenolic free radical with a lipidic free radical, e.g. a linoleic peroxy radical, forming a copolymer. The copolymers possess a very moderate antioxidant activity.

Phenolic free radicals can react with water soluble free radicals, such as hydroxylic free radicals. Phenolic free radicals participate in numerous other free radicals occurring in food systems. Reaction products have mostly unknown chemical constitutions.

Application of Antioxidants to food products

Many food products, especially those containing high percentage of polyunsaturated lipids, have not enough natural antioxidants to keep the product stable against oxidation. It is possible to add synthetic antioxidants to such foods, but most consumers now prefer natural antioxidants. The most active natural antioxidants are those derived from herbs, such as tea leaves, or from spices, such as rosemary, sage, oregano, nutmeg or clove [1]. It is possible to add extracts, e.g. ethyl acetate or ethanolic extracts, whose application is not restricted by regulations as they are added not as antioxidants but as flavourings. The best way is, however, to add herbs or spices directly to food products, without any preliminary fractionation. Such ingredients are cheap, and subject to no restrictions as they are common food ingredients. The use of natural materials, which are not consumed as food, should be avoided, such as gingko leaves or creosot bush leaves (containing nordigydroguaiaretic acid), unless their safety has been tested by tests used for synthetic antioxidants.

Character of antioxidant changes occurring during food processing and storage

Changes occurring during food processing and storage belong to several reaction groups [2], all of them affecting the structure of antioxidants:

1. Processes requiring no thermal energy application:
   a) Reactions with specific chemicals, e.g. smoking or curing;
   b) Rections catalyzed by enzymes, e.g. during fermentation;
   c) Reactions occurring during storage, either at ambient temperature or during refrigerated or frozen storage.
2. Processes requiring energy input, differring in the energy transfer medium. The following media are the most common in the culinary technology:
   a) Water (boiling, pasteurization, sterilization, uperization, partly simmering, blanching, evaporation, extrusion, expansion cooking);
   b) Air (drying, baking, partly simmering, dry roasting);
   c) Oil (shallow or deep fat frying, oil roasting);
   d) Waves in air or water medium (microwave or induction oven heating, irradiation);

e) Application of ultrahigh pressure, usually in an aqueous medium.

The degree of antioxidant degradation during food processing or storage depends on the intensity of exposure of the respective food material to oxygen, either from air or dissolved in water or oil. For this reason, they are more evident on the surface of treated food than in inner layers. Changes are more pronounced during high temperature processing or during long term storage. The excess oxygen content on the surface of heated food favours rapid destruction of antioxidants, at least in the surface layers.

Changes of antioxidants during food processing

If no heat is applied during the food processing, changes of antioxidants are mostly negligible, excepting the drying operation. In natural food materials, lipid particles or membranes are protected against oxygen by layers of hydrated proteins or carbohydrates. During the drying, these layers are dehydrated and destroyed. The access of oxygen to lipids through the microchannels thus formed is rather easy in dried materials, and the oxygen molecules easily come in direct contact with the lipidic phase. A similar process takes place during frozen storage, where water is converted to ice crystals. The hydrated protein or carbohydrate layer around the lipid particles is destroyed by conversion of liquid water into ice. However, the oxidation rate is much lower in frozen foods than in dried foods, stored at ambient temperature, because of low temperature of frozen foods.

During extrusion or expansion cooking, the temperature is much lower than in case of conventional baking, especially in surface layers, and the heating time is very short, so that antioxidants are not appreciably destroyed in extruded material.

Boiling is a relatively mild operation, too, as the temperature is only about 100°C, and boiling water contains nearly no oxygen. The baking favours the oxidation, but only in surface layers. Inner layers are not heated to temperatures substantially higher than 100°C, and the oxygen access is limited. The oxidation is substantially faster during dry roasting as air has free access not only to surface layers, but also to dehydrated inner layers. On contrary, Maillard products, which may act as moderate oxidation inhibitors or metal chelators, are formed at substantially higher temperatures.

The deep fat frying in oil is an operation occurring at very high temperatures (mostly between 170 and 180°C or even higher) so that the destruction of antioxidants in frying oil is very rapid. Under these conditions, oxygen dissolved in oil is very rapidly consumed already in the process of preheating the frying medium. The further oxidation is thus limited only by the rate of oxygen diffusion in oil. The contact of frying oil with air is easier if frying oil starts foaming, which increases the air-oil interface several times. Fried foods are heated to the temperature of frying oil only on the surface [7], where the destruction of antioxidants is pronounced. However, the temperature does not usually exceed 100°C in inner layers, and the access of oxygen into inner layers is negligible, so that antioxidants are preserved there to high degree. Fried food, stored at ambient temperature after the process, is covered by a thin layer of frying oil, which is practically free of antioxidants. Therefore, deep fried foods are easily oxidized on further storage. For this reason, it is advisable to protect stored fried foods by application of antioxidants on the surface before the storage after frying.

Synthetic antioxidants can be added only in very low amounts (usually, only 0.02%, based on the lipid phase. according to the regulations) so that their concentration could be substantially reduced during thermal processes or long storage. In case of natural antioxidants, the maximum permitted concentration is not so strictly regulated as in case of synthetic antioxidants. As natural antioxidants are several times less reactive than synthetic antioxidants, their concentrations are usually several times higher, if the product is still acceptable from the standpoint of its sensory value. Therefore, substantial amounts of natural antioxidants still persist in food even after the thermal treatment.

Health aspects concerning antioxidant changes during food processing

Synthetic antioxidants may be considered as safe from the standpoint of the state of science as they were subject to complicated safety tests before their final approval by health authorities. In case of natural antioxidants, similar tests are usually lacking, but it is assumed they are relatively safe as they have been used as food for many generations. The situation is different in case of degradation products of both synthetic and natural antioxidants. Their structure is mostly known, and it is assumed, there exists no danger in their consumption, but no exact and complex results exist on their testing. They are considered as less reactive than the original antioxidants, but still, the degradation products may be carcinogenic or may damage liver or kidneys. More attention should be paid to medical aspects of natural antioxidants, which are often ortho-disubstituted phenolic components, more dangerous than para-substituted compounds, mostly used as synthetic antioxidants.

CONCLUSIONS

The activity of both synthetic and natural antioxidants has been tested in simple systems under storage conditions, but their application to complex foods requires additional tests in case of either synthetic or natural antioxidants. More attention should be paid to transformations of antioxidants during food preparation, and to the nutritional value and safety of their degradation products.

References

[1] Pokorný J., Yanishlieva N., Gordon M. (eds) (2001): Antioxidants in Foods. Woodhead Publishing, Cambridge, UK: .

[2] Pokorný J., Schmidt Š. (2003): In: Johnson I., Williamson G. (eds): Phytochemical Functional Foods. Woodhead Publ., Cambridge, UK.

[3] Kamal-Eldin A., Appelqvist L.-Å. (1996): Lipids, **31**: 671.

[4] Schmidt Š., Pokorný J., Vajdák M., Sekretár S., Gordon M.H. (2003): Bull. Potr. Výsk., **42**: 133.

[5] Pokorný J. (2003). In: Zeuthen P., Bogh-Sørensen L. (eds): Food Preservation Techniques. Woodhead Publ., Cambridge, UK.

[6] Pokorný J. (1987): In: Chan H.W.S. (ed.): Autoxidation of Unsaturated Lipids. Academic Press, London.

[7] Pokorný J. (2002): In: Henry C.J.K., Chapman C. (eds): Nutrition Handbook for Food Processors. Woodhead Publ., Cambridge, UK.