Natural Antioxidants Review

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Introduction

Antioxidants are substances that delay or inhibit the oxidation of foods, and are therefore of great interest to food scientists. Antioxidants are naturally present in foods, but at very low levels. Therefore, additional quantities are added to control oxidation, increase shelf life, and improve overall quality. The mechanism by which this occurs is termed free radical termination, and is accomplished through the donation of an electron or hydrogen atom. Antioxidants can also protect food by the deactivation of metal ions and singlet oxygen.

The most extensively used synthetic antioxidants in foods are butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), Propyl Gallate (PG), and tert-butylhydroquinone (TBHQ). Due to the prooxidant effects of transition metal ions like magnesium, iron and copper, chelators are also used extensively in the food industry. Chelators such as citric acid (natural), ethylenediaminetetraacetic acid (EDTA) and polyphosphates or their derivatives, are used to chelate metal ions. For many years there has been strong debate and concern regarding the safety of certain synthetic antioxidants as potential carcinogens. BHA, BHT, PG and TBHQ still remain on the GRAS (Generally Recognized As Safe) list, although limitations to their use have been implemented in the U.S., while BHT, PG and TBHQ still lack approval in many countries. Therefore, there is growing interest by consumers and the food industry in replacing currently used synthetic compounds with natural alternatives that are perceived to be safer and have wider consumer acceptance.

There are two main categories of antioxidants: primary and secondary. Primary antioxidants interrupt the free-radical chain of oxidative reactions by contributing hydrogen from the phenolic hydroxyl groups, these forming stable free radicals that do not initiate or propagate further oxidation of lipids. Secondary antioxidants trap radicals, chelate metals, regenerate primary antioxidants, or act as emulsifying agents. Synergism among different primary antioxidants, and between primary and secondary antioxidants is often taken advantage of in food products and should be considered for all applications.

Market

Since the 1980s, consumer interest in and demand for, natural and organic products has increased, both in the U.S. and Europe. As a result, use of synthetic additives has declined while additives considered to be natural have grown, largely because the latter are perceived as safer. The natural trend, coupled with the growing market for premium food products, has driven the use of natural antioxidants like tocopherols (vitamin E), natural herbal flavorings, and ascorbic acid (vitamin C).

Many herbal extracts have antioxidant properties, and are therefore used as food antioxidants. The antioxidant function can generally be linked to the presence of phenolic compounds such as rosmanol, carnosic acid, carnosol, and rosmarinic acid. The herbal extract most commonly used as a food antioxidant is rosemary (Rosmarinus officinalis), which is native to most Mediterranean countries, and is now readily available throughout Europe (Frost and Sullivan et al., 2002). Although U.S. corporations lag behind the production capabilities of firms in the EU, some U.S. companies are growing rosemary in the southern states and increasing production capabilities.

Natural Antioxidants

Natural antioxidants are commonly derived from plant sources, and the efficacy is determined by plant species, variety, extraction and/or processing methods, and the growing environment. The mode of action for these substances will vary depending upon the source material, the presence of synergists and antagonists, and of course the food matrix applied to.

In order to use any antioxidant preparation in food, it must be safe; easy to incorporate; effective at low concentrations; possess no undesirable odor, flavor or color; be heat stable and have economic benefit. The possible effects of antagonists must be carefully considered since an antioxidant may become a prooxidant in the presence of certain other molecules or at high concentrations. For exam-
ple, chlorophylls may overwhelm the antioxidant effect of phenolics due to photosensitized oxidation and the presence of transition metal ions. Metal ions, such as magnesium, iron and copper, may render conditions favorable to oxidation.

Increased consumer demand for foodstuffs free from additives has led to a growing interest in products that are perceived as natural. Herbal and tocopherol/vitamin E-based products, in particular, are recognized by consumers as being natural. Furthermore, regulations permit the labeling of herbal extracts and/or tocopherols as natural, which is an appealing option to most food producers.

**Herbals**

Herbal extracts and flavorings in commercial production include rosemary, sage, and oregano, and are widely used in meat products. These substances contain varied but related antioxidative compounds, including carnosol, carnosic acid, rosmarinic acid, rosmanol and rosmarikinol. Extracts of rosemary, sage and oregano that have been deodorized and decolorized are now commercially available and their use in a variety of lipid-containing foods is increasing. Formulated herbal products are usually in liquid form, and are commonly added to meat products in the range of 500-5000 PPM (on a fat basis). The oleoresins, which have GRAS status, have been used in various products such as potato chips, sauces, dressings, processed meat/poultry, and seafood as well as cakes and crackers. The antioxidant activities of such extracts/oleoresins maybe comparable to, or exceed, those of BHA and BHT, and are comparable to the efficacy of tocopherols depending on the quality of the extract. These herbal products have also found value by making the ingredient label more “nature friendly.”

Rosemary has been used for centuries in foods for flavor and protection from rancidity. Rosemary, and other herbal products, have been accepted in the food industry because of their “clean labeling,” a direct reaction to the public’s demand for all-natural foods. These products have traditionally had limitations, including standardization of their antioxidant potency. Many factors, including climate, time of harvest, extraction process, and handling can affect the potency of herbal extracts. For example, a recent study examined the relationship between carnosic acid levels in rosemary and its growing conditions. The growing conditions were, average hours of sunshine and average daily temperature per month. As seen in Figure 1, a direct relationship was noted between the production of carnosic acid and the selected environmental conditions (Hildago et al., 1998). Many producers are now certifying their products on an activity basis vs. certifying specific levels of active chemicals.

![Figure 1. Relationship between carnosic acid level and rosemary growing environment.](image1)

It is generally recognized that carnosic acid has the highest antioxidant potency of all the compounds found in rosemary extracts. As carnosic acid oxidizes, it “cascades” from one antioxidant to another, acting as a primary antioxidant throughout this “cascade,” and protecting the food system (RFI et al.). The phenomenon has been termed, the Carnosic Acid Cascade. When carnosic acid donates a hydrogen to quench a free radical, it forms the antioxidant carnosol, which in turn forms another, rosmanol and so on. Carnosic acid thus has secondary and tertiary antioxidant formation mechanisms, although carnosol and rosmanol have only ~45% the potency of carnosic acid (RFI et al.). Many herbal extracts obtained from rosemary, sage, and oregano also contain hydrophilic antioxidants including compounds like rosmarinic acid that can act synergistically with the more lipophilic antioxidants. The blend of compounds is very important as it ensures a multi-phase food system will be broadly protected. Conversely, more lipophilic antioxidants like tocopherols may be blended with natural emulsifiers like lecithin, which increases dispersability within a multi-phase system, and increase the effectiveness of the formulations. As seen in Figure 2, herbal products can also take advantage of this emulsification effect (Haworth et al.)

![Figure 2. Emulsification effects on mixed tocopherols and a commercially available rosemary product.](image2)
Tocopherols and Tocotrienols

Natural antioxidants may also be obtained from crude, unrefined vegetable oils, including tocopherols and tocotrienols. These substances are present as constituents of unsaponifiable matter, and may occur together with phospholipids, carotenoids, chlorophylls and tripterpenyl alcohols. Deodorization of these oils via molecular distillation yields a significant amount of purified tocopherols and tocotrienols. Most of the global supply of tocopherols originates from soybean oil processing, while tocotrienols are obtained from palm and rice bran oils.

Tocopherols and tocotrienols are monophenolic and lipophilic compounds. Tocopherols are the most widely used of these two compounds, and occur in four main forms termed alpha-, beta-, gamma-, and delta-tocopherol depending on the number and position of the methyl groups. In terms of vitamin E activity, d-alpha-tocopherol is the reference compound with the highest biological potency; however, in food systems, the order of activity is delta>gamma>beta>>alpha. Tocopherols may be formulated as a 100% oil dispersible product, in dry form, or can be suspended/emulsified in water or brine solutions before inclusion into foods. Synergism between tocopherols and ascorbic acid or its derivatives has been well documented. Ternary mixtures of tocopherols, herbal extracts, lecithin or other phospholipids, chelators, and/or ascorbic acid or its derivatives exhibit excellent synergistic antioxidant activity in bulk oils, meat systems, and emulsified foods.

Antioxidant efficacy is determined by the suitability of antioxidants in each food system. In general, more hydrophilic antioxidants are better at stabilizing bulk oil than oil-in-water emulsions. The activity of lipophilic antioxidants follows the opposite trend (Frankel et al., 1998). There are many other parameters that must be taken into account when selecting antioxidants for food applications. Specific attention should be paid to the photosensitizing effect of chlorophylls in natural antioxidant products. In addition, the level of incorporation of antioxidants in foods should be optimized so that the antioxidant does not become a prooxidant at high levels. The use of chelating and emulsifying agents should also be considered.

Meats

The most important reference to the consumer when making a meat purchase decision is color. Consumers notice differences in color among meat products, and make purchase decisions based upon those differences. It has been estimated that up to 20% of all products are price reduced, discarded, or reprocessed due to discoloration and consumer perceptions of the product being rancid (Sherbeck et al., 1995). Many retailers increase the overall price of all meat products to compensate for lost margin associated with these problems.

Research has shown that natural antioxidants can improve the shelf life of meat products by delaying the onset of oxidation. Several studies have revealed that high dietary levels of vitamin E can improve the shelf life of the meat products (Stubbs et al. 2002). Work has also been done showing direct addition of primary and secondary natural antioxidants to meat products can prolong shelf life and help preserve the color associated with fresh product. Furthermore, many studies have shown that best results may be obtained if a combination of these tactics is employed.

In beef, the red color associated with a fresh cut is caused when the meat surface becomes oxygenated. This is caused by the myoglobin undergoing a process called “blooming” in which the meat becomes fully oxygenated to the oxymyoglobin state. Oxymyoglobin continues to react with oxygen, or be broken down by photo oxidation, and further oxidizes to the metmyoglobin state. Once ~70% of the myoglobin becomes oxidized and forms metmyoglobin, the meat surface becomes discolored or brown as seen in Figure 3 (Boles et al.). Meat blooms after it is exposed to oxygen for 20-30 minutes, and will maintain this color for about 2-3 days when displayed in a retail environment. Using antioxidants may extend the oxymyoglobin state for an additional 1-2 days in a retail environment.

![Figure 3. Interconversion of meat pigments.](image-url)
lar benefits. In a recent study published by the British Poultry Science Journal, poultry diets were supplemented with either vitamin E, rosemary extract, or sage extract. Results with all three treatments showed a marked improvement in the shelf life of the uncooked refrigerated white meat sections (Lopez-Bote et al., 1998).

**Summary**

In conclusion, the main goal of incorporating natural antioxidants into foods, specifically meats, is to increase product quality and overall appeal to consumers. Increasing the shelf life of meat products by incorporating natural antioxidants can be done in many ways including direct addition of primary and/or secondary antioxidants, bioavailability into the muscle via dietary administration, or combinations of the aforementioned. There is a growing consumer trend to seek natural ingredients, which bodes well for the use of natural antioxidants in foods for the years to come.

**References**

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