

# Comparative Efficacy of Natural and Synthetic Antioxidants in Preventing Rancidity

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**Abstract**—Rancidity is the main cause of wastage of food stuff which contains oils and fats in their composition. To prevent rancidity various antioxidants are being used which are mainly synthesized chemically. Among the synthetic types, the most frequently used to preserve food are butylatedhydroxyanisole (BHA), butylatedhydroxytoluene (BHT), propyl gallate (PG) and tert-butyl hydroquinone (TBHQ). Reports revealing that BHA and BHT could be toxic, and the higher manufacturing costs and lower efficiency of natural antioxidants such as tocopherols, together with the increasing consciousness of consumers with regard to food additive safety, created a need for identifying alternative natural and probably safer sources of food antioxidants. The replacement of synthetic antioxidants by natural ones may have benefits due to health implications and functionality. The protection that fruits and vegetables provide against several diseases has been attributed to the various antioxidants, vitamin C, vitamin E,  $\alpha$ -tocopherol, beta carotene and polyphenolic compounds. In living systems, dietary antioxidants ( $\alpha$ -tocopherol,  $\beta$ -carotene, ascorbic acid) and endogenous enzymes (superoxide dismutase, glutathione peroxidase, and catalase) protect against oxidative damage. Several studies have shown that phenolic compounds reduce in vitro oxidation of low density lipoprotein; particularly those phenolic with multiple hydroxyl groups which are generally the most efficient for preventing lipid and low density lipoproteins (LDL) oxidation and therefore, by inference, atherogenesis (Meyer, Heinonen & Frankel, 1998; Meyer, Jepsen & Sørensen, 1988; Moon & Terao, 1998; Nakagawa et al., 1999).

**Keywords:** BHT, TBHQ, Synthetic Antioxidants, carotenes.

## Introduction

The increasing interest in the substitution of synthetic food antioxidants by natural ones has fostered research on vegetable sources and the screening of raw materials for identifying new antioxidants. Oxidation reactions are not an exclusive concern for the food industry, and antioxidants are needed to prevent deterioration of other oxidisable goods, such as cosmetics, pharmaceuticals and plastics. In addition, other biological properties such as anti carcinogenicity, anti mutagenicity, anti allergenicity and anti aging activity have been reported for natural and synthetic antioxidants. Special attention is given on their extraction from inexpensive or

residual sources from agricultural industries. The replacement of synthetic antioxidants by natural ones may have benefits due to health implications and functionality. The protection that fruits and vegetables provide against several diseases has been attributed to the various antioxidants, vitamin C, vitamin E,  $\alpha$ -tocopherol, beta-carotene and polyphenolic compounds (Abushita, Hebshi, Daood & Biacs, 1997; Aruoma, 1998). In living systems, dietary antioxidants ( $\alpha$ -tocopherol, beta-carotene, ascorbic acid) and endogenous enzymes (superoxide dismutase, glutathione peroxidase, catalase) protect against oxidative damage. Several studies have shown that phenolic compounds reduce in vitro oxidation of low density lipoprotein; particularly those phenolics with multiple hydroxyl groups which are generally the most efficient for preventing lipid and low density lipoproteins (LDL) oxidation and therefore, by inference, atherogenesis (Meyer, Heinonen & Frankel, 1998; Meyer, Jepsen & Sørensen, 1988; Moon & Terao, 1998; Nakagawa et al., 1999). Recent scientific studies have proved that antioxidants are capable of protecting cells from free radical damage (Saint-Cricq de Gaulejac, Provost & Vivas, 1999). Furthermore, other physiological activities of natural anti-oxidants have been described, such as antibacterial, antiviral, antimutagenic (Ikken, Morales, MartõÁnez, MarõÁn, Haza & Cambero, 1999), anticarcinogenic effects (Carrol, Kurowska & Guthrie, 1999; Kawaii, Tomono, Katase, Ogawa & Yano, 1999), antimetastasis activity (Maeda-Yama-moto, Kawahara, Tahara, Tsuji, Hara & Isemura, 1999), platelet aggregation inhibition, blood-pressure increase inhibition (Ito et al., 1998), antiulcer activity (Saito, Hosoyama, Ariga, Kataoka & Yamaji, 1998; Vilegas, Sanomimiya, Rastrelli & Pizza, 1999) and anticariogenicity (Tanabe, Kanda & Yanagida, 1995). Wang, Cao and Prior (1996) and Kalt, Forney, Martin and Prior (1999) published works about strong antioxidant compounds found in fruits. For example, antioxidants with important activity have been found in berries (Abuja, Murkovic & Pfannhauser, 1998; Heino-nen, Lehtonen & Hopia, 1998; Heinonen, Meyer & Frankel, 1998; Prior et al., 1998), cherries (Wang, Nair, Strasburg, Booren & Gray, 1999;

Wang, Nair, Strasburg, Chang, Booren & Gray, 1999; Wang, Nair, Strasburg, Chang, Booren, Gray & DeWitt, 1999), citrus (Saleh, Hashem & Glombitza, 1998) and in kiwi fruit (Dawes & Keene, 1999) prunes (Donovan, Meyer & Waterhouse, 1998) and olives (Romani, Mulinacci, Pinelli, Vincieri & Cimato, 1999). High activity antioxidants were found in olive oil (Blekas & Boskou, 1998; Papadopoulus & Boskou, 1991) and also in fruit juices (Chambers, Lambert, Plumb & Williamson, 1996; Spanos & Wrolstad, 1990, 1992; Van Buren, de Vos & Pilnik, 1976; Wen, Wrolstad & Hsu, 1999). Recently a comprehensive review summarised the role of phenolic compounds in the oxidative process of fruits.

Antioxidants are frequently applied to food as a protection against lipid oxidation. The efficiencies of the two types of antioxidants are very difficult to compare, but generally both of them act by similar mechanisms so that their antioxidant activities depend only on their chemical structure and polarity. No factors specific for natural compounds are involved. Synthetic antioxidants have been developed for the stabilization of bulk fats and oils or foods rich in lipids. In these substrates, they are substantially more efficient than  $\alpha$ -tocopherol and other natural antioxidants, which are usually less liposoluble. The highest concentration allowed by law (0.02% on the lipid basis) is sufficient in most cases of synthetic antioxidants for the stabilization of real foods, such as lard, perhaps except for extraordinarily long storage or long deep-fat frying.

Natural antioxidants are mostly much more polar than synthetic antioxidants, except for carotenes, tocopherols and their esters, and sesame seed lignans. Therefore, natural phenolic antioxidants are usually not sufficiently soluble in the lipid phase, which limits their efficiency in bulk lipids. They are not pure substances so that the active fraction is usually much lower than the actual addition, while synthetic antioxidants are nearly 100% pure. Generally, it is necessary to add natural antioxidants in higher concentrations, such as 0.1–0.5%, or even more.

Many attempts have been made to prevent the oxidative deterioration of lipids by using natural antioxidants. Some components in natural products such as carotenoids, flavonoids, anthocyanins, and phenolic compounds are known to function as radical scavengers. In particular, the potential antioxidant activity of polyphenolic compounds has been reported for a number of natural plant extracts including grapes and their residues, almond hulls (*Prunus amygdalus*) and pine sawdust (*Pinus pinaster*), green teas, berries, and murta fruits and leaves. Botanical extracts with antioxidant activity generally quench free radical oxygen with phenolic compounds as well (Halliwell *et al.*, 1987). The most widely encountered way of antioxidant formation is the synthesis of antioxidants by various microorganisms, fungi, even animals, and most often by plants. They are called natural antioxidants. They are preferred by most consumers, as the consumers believe that benign Mother Nature produces antioxidants in all

organisms for the benefit of mankind. This is, of course, only a superstition, as plants synthesize antioxidants for their own benefit as a protection against pests, mostly microorganisms, and against herbivores, including human consumers.

Fruits and vegetables contain significant levels of biologically active components that impart health benefits beyond basic nutrition (Oomah and Mazza, 2000). Polyphenols are secondary plant metabolites which were earlier considered as anti-nutrients because some (tannins) were shown to have adverse effects in human metabolism, but recently the recognition of antioxidative properties of these phenolics has evoked a rethinking towards the health benefits of these secondary metabolites. Polyphenols account for the majority of antioxidant activity when compared with ascorbic acid in fruits (Wang *et al.*, 1996; Deighton *et al.*, 2000). The antioxidant properties of phenolics is mainly because of their redox properties, which allow them to act as reducing agents, hydrogen donors and singlet oxygen quenchers (Rice-Evans *et al.*, 1997).

## Reference

- [1] Abuja, P. M., Murkovic, M., & Pfannhauser, W. (1998). Antioxidant and prooxidant activities of Elderberry (*Sambucus nigra*) extract in Low-Density-Lipoprotein oxidation. *Journal of Agricultural and Food Chemistry*, 46, 1040-1046.
- [2] Abushita, A. A., Hebshi, E. A., Daood, H. G., & Biacs, P. A. (1997). Determination of antioxidant vitamins in tomatoes. *Food Chemistry*, 60, 207-212.
- [3] Aruoma, O. I. (1998). Free radicals, oxidative stress and antioxidants in human health and disease. *Journal of the American Oil Chemists' Society*, 75, 199-212.
- [4] Blekas, G., & Boskou, D. (1998). Antioxidative activity of 3, 4-dihydroxyphenyl acetic acid and  $\alpha$ -tocopherol on the triglyceride matrix of olive oil. Effect of acidity. *Grasas y Aceites*, 49, 34-37.
- [5] Carrol, K. K., Kurowska, E. M. & Guthrie, N. (1999). Use of citrus limonoids and avonoids as well as tocotrienols for the treatment of cancer. *Int. Patent WO9915167*.
- [6] Chambers, S. J., Lambert, N., Plumb, G. W., & Williamson, G. (1996). Evaluation of the antioxidant properties of a methanolic extract from 'Juice Plus fruit' and 'Juice Plus vegetable' (dietary supplements). *Food Chemistry*, 57, 271-274.
- [7] Dawes, H. W., & Keene, J. B. (1999). Phenolic composition of kiwi-fruit juice. *Journal of Agricultural and Food Chemistry*, 47, 2398-2403.
- [8] Deighton, N., Brennan, R., Finn, C. & Davies, H.V. (2000). Antioxidant properties of domesticated and wild *Rubus* species. *Journal of the Science of Food and Agriculture*, 80, 1307-1313.
- [9] Donovan, J. L., Meyer, A. S., & Waterhouse, A. L. (1998). Phenolic composition and antioxidant activity of prunes and prune juice (*Prunus domestica*). *Journal of Agricultural and Food Chemistry*, 46, 4, 1247-1252.
- [10] Halliwell B, Gutteridge JMC, Aruoma OI. The deoxyribose method: a simple "test tube" assay for determination of rate constants for reactions of hydroxyl radicals. *Anal. Biochem* 1987; 165: 215-219.
- [11] Heinonen, M., Lehtonen, P. J., & Hopia, A. L. (1998). Antioxidant activity of berry and fruit wines and liquors. *Journal of Agricultural and Food Chemistry*, 46, 25-31.

- [12] Heinonen, M., Meyer, A. S., & Frankel, E. N. (1998). Antioxidant activity of berry phenolics on human low-density-lipoprotein and liposome oxidation. *Journal of Agricultural and Food Chemistry*, 46, 107-4112.
- [13] Ikken, Y., Morales, P., MartoAnez, A., MaroAn, M. L., Haza, A. I., & Cambero, M. I. (1999). Antimutagenic effect of fruit and vegetable ethanolic extracts against N-nitrosamines evaluated by the Ames test. *Journal of Agricultural and Food Chemistry*, 47, 3257-3264.
- [14] Ito, A., Shamon, L. A., Yu, B., Mata-Greenwood, E., Lee, S. K., van Breemen, R. B., Mehta, R. G., Farnsworth, N. R., Fong, H. H. S., Pezzuto, J. M., & Kinghorn, A. D. (1998). Antimutagenic constituents of *Casimiroa edulis* with potential cancer chemopreventive activity. *Journal of Agricultural and Food Chemistry*, 46, 3509-3516.
- [15] Kalt, W., Forney, C. F., Martin, A., & Prior, R. L. (1999). Antioxidant capacity, vitamin C, phenolics, and anthocyanins after fresh storage of small fruits. *Journal of Agricultural and Food Chemistry*, 47, 4638-4644.
- [16] Kawaii, S., Tomono, Y., Katase, E., Ogawa, K., & Yano, M. (1999). HL-60 Differentiating activity and flavonoid content of the readily extractable fraction prepared from Citrus juices. *Journal of Agriculture*.
- [17] Maeda-Yamamoto, M., Kawahara, H., Tahara, N., Tsuji, K., Hara, Y., & Isemura, M. (1999). Effects of tea polyphenols on the invasion and matrix metalloproteinases activities of human breast carcinoma HT1080 cells. *Journal of Agricultural and Food Chemistry*, 47, 2350-2354.
- [18] Meyer, A. S., Heinonen, M., & Frankel, E. N. (1998). Antioxidant interactions of catechin, cyanidin, caffeic acid, quercetin, and ellagic acid on human LDL oxidation. *Food Chemistry*, 61, 71-75.
- [19] Meyer, A. S., Jepsen, S. M., & Surensen, N. S. (1998). Enzymatic release of antioxidants for human low-density lipoprotein from grape pomace. *Journal of Agricultural and Food Chemistry*, 46, 2439-2446.
- [20] Moon, J. H., & Terao, J. (1998). Antioxidant activity of caffeic acid and dihydrocaffeic acid in lard and human low-density lipoprotein. *Journal of Agricultural and Food Chemistry*, 46, 5062-5065.
- [21] Nakagawa, K., Ninomiya, M., Okubo, T., Aoi, N., Juneja, L. R., Kim, M., Yamanaka, K., & Miyazawa, T. (1999). Tea catechin supplementation increases antioxidant capacity and prevents phospholipid hydroperoxidation in plasma of humans. *Journal of Agricultural and Food Chemistry*, 47, 3967-3973.
- [22] Oomah, B.D., Mazza, G., 2000. Functional foods. In: Francis, F.J. (Ed.), *The Wiley Encyclopedia of Science and Technology*, vol. 2, 2nd ed. Wiley, New York, NY, pp. 1176-1182.
- [23] Papadopoulos, G., & Boskou, D. (1991). Antioxidant effect of natural phenols on olive oil. *Journal of the American Oil Chemists' Society*, 68, 669-671.
- [24] Prior, R. L., Cao, G., Martin, A., So, E., McEwen, J., O'Brien, C., Lischner, N., Ehlenfeldt, M., Kalt, W., Krewer, G., & Mainland, C. M. (1998). Antioxidant capacity as influenced by total phenolic and anthocyanin content, maturity, and variety of *Vaccinium* species. *Journal of Agricultural and Food Chemistry*, 45, 2686-2693.
- [25] Rice-Evans, C.A., Miller, N.J., & Paganga, G. (1997). Antioxidant properties of phenolic compounds. *Trends in Plant Science*, 4, 304-309.
- [26] Rice-Evans, A. C. Measurement of total antioxidant action as a marker of antioxidant status in vivo. *Proceedings and limitations. Free Radical Research* 33 (2000) 59-68.
- [27] Romani, A., Mulinacci, N., Pinelli, P., Vincieri, F. F., & Cimato, A. (1999). Polyphenolic content in vegetable Tuscan cultivars of *Olea europaea* L. *Journal of Agricultural and Food Chemistry*, 47, 964-967.
- [28] Saint-Cricq de Gaulejac, N., Provost, C., & Vivas, N. (1999). Comparative study of polyphenol scavenging activities assessed by different methods. *Journal of Agricultural and Food Chemistry*, 47, 425-431.
- [29] Saito, M., Hosoyama, H., Ariga, T., Kataoka, S., & Yamaji, N. (1998). Antitumor activity of grape seed extract and procyanidins. *Journal of Agricultural and Food Chemistry*, 46, 1460-1464.
- [30] Saleh, M. M., Hashem, F. A. E.-M., & Glombitza, K. W. (1998). Study of Citrus taitensis and radical scavenger activity of the flavonoids isolated. *Food Chemistry*, 63, 397-400.
- [31] Spanos, G. A., & Wrolstad, R. E. (1990). Influence of processing and storage on the phenolic composition of Thompson seedless grape juice. *Journal of Agricultural and Food Chemistry*, 38, 1565-1571.
- [32] Spanos, G. A., & Wrolstad, R. E. (1992). Phenolics of apple, pear, and white grape juices and their changes with processing and storage, a review. *Journal of Agricultural and Food Chemistry*, 40, 1478-1487.
- [33] Tanabe, M., Kanda, T., & Yanagida, A. (1995). Fruit polyphenol; process for production thereof; and antioxidant, hypotensive agent, antimutagenic agent, antiallergenic agent and anticarcinogenic agent, each comprising said polyphenol. EP0657169.
- [34] Van Buren, J., de Vos, L., & Pilnik, W. (1976). Polyphenols in golden delicious apple juice in relation to method of preparation. *Journal of Agricultural and Food Chemistry*, 24, 448-451.
- [35] Vilegas, W., Sanomimiya, M., Rastrelli, L., & Pizza, C. (1999). Isolation and structure elucidation of two new flavonoid glycosides from the infusion of *Maytenus aquifolium* leaves. Evaluation of the anti ulcer activity of the infusion. *Journal of Agricultural and Food Chemistry*, 47, 403-406.
- [36] Wang, H., Cao, G., & Prior, R. L. (1996). Total antioxidant capacity of fruits. *Journal of Agricultural and Food Chemistry*, 44, 701-705.
- [37] Wang, H., Cao, G.H. & Prior, R.L. (1996). Total antioxidant capacity of fruits. *Journal of Agricultural Food Chemistry*, 44, 701-705.
- [38] Wang, H., Nair, M. G., Strasburg, G. M., Booren, A. M., & Gray, J. I. (1999). Novel antioxidant compounds from tart cherries (*Prunus cerasus*). *Journal of Natural Products*, 62, 86-88.
- [39] Wang, H., Nair, M. G., Strasburg, G. M., Chang, Y.-C., Booren, A. M., & Gray, J. I. (1999). Antioxidant polyphenols from tart cherries (*Prunus cerasus*). *Journal of Agricultural and Food Chemistry*, 47, 840-844.
- [40] Wang, H., Nair, M. G., Strasburg, G. M., Chang, Y.-C., Booren, A. M., Gray, J. I., & DeWitt, D. L. (1999). Antioxidant and anti-inflammatory activities of anthocyanins and their aglycon, cyanidin, from tart cherries. *Journal of Natural Products*, 62, 294-296.
- [41] Wen, L., Wrolstad, R. E., & Hsu, V. L. (1999). Characterization of sinapyl derivatives in pineapple (*Ananas comosus*) and sage (*Salvia officinalis*) by enzyme-assisted ensiling (ENLAC). *Journal of Agricultural and Food Chemistry*, 47, 2959-2962.