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### Performance of Antioxidative Compounds under Frying Conditions. A Review

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## Performance of Antioxidative Compounds under Frying Conditions. A Review

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**ABSTRACT**

Although much study has been done assessing activity of antioxidants at ambient and accelerated storage temperatures, the results cannot correctly depict their performance under frying conditions. Due to the stringent conditions imposed, most conventional antioxidative compounds failed under frying conditions, suggesting the need for a continuous modification to improve their effectiveness. Although syntheses and performance evaluation of over a hundred (semi)synthetic antioxidants have been reported in literature, only a small fraction have been specifically designed and/or evaluated under frying conditions. Here, the performance under frying conditions of major natural and synthetic antioxidants is reviewed. The recent trend in the designing of antioxidants for frying applications is also reviewed with the view of stimulating further study in this direction.

Keywords: Natural antioxidants, synthetic antioxidants, frying stability, endogenous minor components

## INTRODUCTION

As the name implies, antioxidants are compounds possessing the ability to inhibit oxidation when present in food or biological systems. Depending on their structural features, antioxidants can scavenge free radicals, inactivate prooxidant metals, quench singlet oxygen, or inactivate sensitizers. The different type of antioxidants and their respective points of antioxidant activity are depicted in Figure 1. Besides their structural features, the effectiveness of antioxidants also depends on the concentration used, the applied temperature, exposure to light, and type of substrates (Yanishlieva and Marinova, 2001).

A number of antioxidants occur naturally in food where they offer protection against oxidative damage. These endogenous antioxidants are part of the unsaponifiable components of fats and oils, representing less than 5% of the total lipid composition. However, due to inherent shortcomings in their applicability and performance, a number of synthetic antioxidants such as butylated hydroxytoluene (BHT), butylated hydroxyanisole (BHA), and tert-butyl hydroxyquinone (TBHQ) were prepared. Unfortunately, the use of these common synthetic antioxidants has also been limited due to their failure to meet performance expectations, especially under frying conditions, and their perceived detrimental effect on human health (Frankel, 2007). Consequently, there is a growing interest in development of new antioxidants with improved antioxidant activity and thermal stability, but prepared from natural precursors. The new trend in this direction is leading to modification of existing natural antioxidants. A number of these synthetic (or semi-synthetic) antioxidants have been approved by appropriate authorities in several nations (Torres et al., 2008). For instance, fatty acid esters of vitamin C

(ascorbyl palmitate, stearate, oleate and linoleate; E304) have been synthesized to enhance the lipophilicity of vitamin C for stabilization of lipids (LoNostro et al., 2000; Song, 2004).

The activity of antioxidative compounds is usually evaluated by chemical assays such as DPPH, ORAC, FRAP, ABTS, TBA, and  $\beta$ -carotene bleaching, excellently reviewed by Huang et al. (2005), Apak et al. (2007), Yoo et al. (2007), Singh and Singh (2008), Magalhaes et al. (2008), Moon and Shibamoto (2009), and Gülcin (2012). Unfortunately, however, these indirect methods often correlate poorly with the ability of compounds to inhibit oxidation in real food systems due to their inability to account for a number of important variables such as the physical location of the antioxidant and its interaction with other food components (Decker et al., 2005). In real food applications, most of the antioxidant studies has been conducted under ambient or accelerated storage conditions. However, the activity of antioxidative compounds under ambient and accelerated storage tests may not correctly depict their performance during frying, considering the wide differences in operational conditions including: (i) temperatures; (ii) oxygen pressure; (iii) water content; (iv) thermooxidative degradation of components and their interactions with antioxidative compounds; (v) volatilization, degradation, and thermal inactivation of antioxidants; and (vi) continuous changes in relative locations of antioxidant, oxidant, and substrates due to constant agitation during boiling.

In this review, the performance of common natural and synthetic antioxidants under frying conditions is summarized. The recent trend in the designing of antioxidant for frying applications is also reviewed with the view of stimulating further study in this direction.

## ***NATURAL ANTIOXIDANTS***

### *Tocochromanols*

A number of naturally occurring minor components in edible oils possess antioxidant activity, and are of great importance to both storage and frying stability of oils. The most important and often studied antioxidants are the tocopherols and tocotrienols, collectively referred to as tocochromanols. The structural difference between tocopherols and tocotrienols is in the unsaturation of the phytyl side chain (Figure 2). Depending on the position and the number of a methyl substitution on the chromanol ring, four homologues,  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$ , are recognized for each tocopherol and tocotrienol. Of these, the  $\alpha$ - and  $\gamma$ -tocopherols are the most abundant in frying oils (Seppanen et al., 2010).

More often than not, edible oils rely on tocochromanols for protection against oxidative degradation, mainly because of their excellent radical scavenging activity. It has been reported that lipid peroxy radicals react with tocopherols much faster ( $10^4$  to  $10^9$   $M^{-1}s^{-1}$ ) than with lipids ( $10$  to  $60$   $M^{-1}s^{-1}$ ) (Choe and Min, 2006). According to Kamal-Eldin and Appelqvist (1996), one tocopherol molecule can protect about  $10^3$  to  $10^8$  polyunsaturated fatty acid molecules at low peroxide value. A very strong positive correlation was reported between the radical scavenging capacity of different refined oils and the total content of tocochromanols (Rossi et al., 2007).

A number of studies has evaluated the ability of tocochromanols to protect oils under frying conditions (Table 1). According to Nogala-Kalucka et al. (2005), the addition of 100, 500, or 1000  $\mu g/g$  of  $\delta$ -tocopherol to Planta, a commercial blend of hydrogenated canola oil and palm oil resulted in a significant decrease in the peroxide value, *p*-anisidine value, and hexanal formation during heating at 160°C for 2 h in a Rancimat. Supplementing technical triolein with 100 or 400  $\mu g/g$  of  $\gamma$ -tocopherol significantly inhibited polymer formation during frying of potato

chips at 190°C for 6 h (Neff et al., 2003). The effect of  $\alpha$ -tocopherol and  $\alpha$ -tocotrienol on the performance of antioxidant stripped canola oil at a high temperature was reported by Romero et al. (2007). The pure canola oil triacylglycerols were supplemented with  $\alpha$ -tocopherol and  $\alpha$ -tocotrienol at various concentrations: 155 and 432  $\mu\text{g/g}$  tocopherol; 138  $\mu\text{g/g}$  tocotrienol; and a mixture of 66  $\mu\text{g/g}$  tocopherol and 72  $\mu\text{g/g}$  of tocotrienol. The samples were heated at 180°C for 18 h in a Rancimat apparatus, and performance assessed by measurement of the amount of total polar components. The authors reported a significant level of protection by both  $\alpha$ -tocopherol and  $\alpha$ -tocotrienol, although the later was significantly less effective. They also observed that increasing the level of  $\alpha$ -tocopherol from 155 to 432  $\mu\text{g/g}$  did not improve its antioxidative activity. In a similar study, Lampi and Kamal-Eldin (1998) evaluated the antioxidant activity of  $\alpha$ - and  $\gamma$ -tocopherol in purified high oleic sunflower triacylglycerols. The oil with or without  $\alpha$ - and  $\gamma$ -tocopherol was heated for 24 h at 185°C in an oven. Thermooxidative changes in oil were measured by analysis of polymerized materials, and both tocopherols significantly inhibited polymerization of the oil; however, the  $\gamma$ -isomer was more effective. The authors did not observe any synergistic relationship between the two isomers when they were added as a mixture. On the contrary, Warner and Moser (2009) observed that samples of purified mid-oleic sunflower oil triacylglycerols containing a mixture of  $\alpha$ ,  $\gamma$ , and  $\delta$  tocopherols accumulated significantly lower amounts of the total polar components compared to effectiveness of individual isomers during frying of tortilla chips. Similarly, Barrera-Arellano et al. (2002) reported a synergistic interaction between  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$  tocopherols during thermal treatment of purified palm olein and soybean oil triacylglycerols at 180°C for 10 h in a Rancimat as assessed by the amounts of polymers formed. The tocochromanol mixtures isolated from canola, rice bran and palm oils significantly

inhibited thermooxidation of canola oil triacylglycerol during a model frying of formulated food at 185°C as measured by the amount of total polar compounds and the rate of volatile carbonyl compounds and hydroxynonenal formation (Aladedunye and Przybylski, 2012a). Interestingly, no significant difference was observed in the performance of the tocopherol mixture despite the differences in isomeric composition, suggesting an absence of synergies among tocopherol and tocotrienol isomers. Romero et al. (2007) also found no increase in the antioxidant activity when a mixture of  $\alpha$ -tocopherol and  $\alpha$ -tocotrienol was added to antioxidants stripped canola oil as compared to when only tocotrienol was added.

Normand et al. (2001) compared the frying stability of regular and three modified canola oils during a 72-hour actual frying operation, and performance was assessed by the analysis of free fatty acids and total polar components. The rate of tocopherol degradation was reported as the major factor determining the frying stability of the oils. This was in agreement with the conclusion by Petukhov et al. (1999) during frying of potato chips in regular, high oleic low linolenic, and hydrogenated canola oils.

The  $\alpha$ - and  $\gamma$ - isomers of tocopherol are the most common tocopherol components of frying oils, and whereas there is a general agreement on their relative stability under oxidative and storage conditions, the controversy on their relative stability during frying still remains. In Table 1, the major studies regarding the stability of tocopherol isomers under frying conditions are presented. For studies conducted using actual frying experiments, it is generally agreed that the loss of  $\gamma$ -tocopherol was more rapid than  $\alpha$ -tocopherol (Miyagawa et al., 1991; Aggelousis and Lalas, 1997; Simonne and Eitenmiller, 1998; Matthäus, 2006; Aladedunye and Przybylski, 2009a, 2009b; Bansal et al., 2010; Juárez et al., 2011; Al-Khusaibi et al., 2012). Conversely,



majority of the studies involving heating the oil in an oven or a Rancimat apparatus concluded that  $\alpha$ -tocopherol was less stable than the  $\gamma$ - isomer (Lampi and Kamal-Eldin, 1998; Barrerra-Arellano et al., 1999; Barrerra-Arellano et al., 2002; Marmesat et al., 2008). However, the chemical reactions taking place during actual frying of food are different from those during continuous heating (Chang et al., 1978; Fritsch, 1981; Kalogianni et al., 2010). Thus, the activity of tocopherols can be better assessed during an actual frying or in a frying test that truly mimics actual deep fat frying conditions (Aladedunye and Przybylski, 2011). Based on available data (Table 1), it can be deduced that the relative stability of  $\alpha$ - and  $\gamma$ -tocopherol under frying conditions depends on: (1) The relative amounts of the isomers in the initial oil, with the isomer present in the higher amount degrading much faster than the one present in lesser amount (Warner and Moser, 2009); (2) frying temperature and period; and (3) experimental set up, that is, frying of food vs heating; heating with vs heating without air, water, or agitation etc.

Tocopherols are thermally unstable, and are known to be easily removed during frying by evaporation/distillation (Marmesat et al., 2010). The loss of tocopherols has been attributed to both oxidative and thermal degradation, with the rate being significantly slower in unsaturated oils than in saturated oils (Yuki and Ishikawa, 1976; Yoshida et al., 1991; Jorge et al., 1996; Normand et al., 2001). A number of tocopherol degradation products notably,  $\alpha$ -tocopherolquinone, 4a,5-epoxy- $\alpha$ -tocopheroxyquinone, 5,6-epoxy- $\alpha$ -tocopheroxyquinone, and 7,8-epoxy- $\alpha$ -tocopheroxyquinone have been identified both in model systems and during actual deep fat frying (Murkovic et al., 1997; Verleyen et al., 2001; Rennick and Warner, 2006). However, despite the prevalence of oligomerization during frying, oligomers of tocopherols are rarely encountered (Marmesat et al., 2010), presumably because coupling of tocopheroxyl

radicals with lipid peroxy and alkyl radicals predominates over the formation of tocopherol oligomers through self-coupling (Kamal-Eldin and Appelqvist, 1996). The prooxidant effect observed for tocopherols under thermooxidative conditions has been attributed to their oxidation products. Rietjens et al. (2002) suggested that increased levels of oxidized  $\alpha$ -tocopherol could result in increased levels of intermediate radicals, which can initiate lipid oxidation. Jung and Min (1992) reported that the oxidative stability of soybean oil at 55°C was significantly reduced in the presence of oxidized  $\alpha$ ,  $\gamma$ , and  $\delta$  tocopherols, the observed prooxidant effect being more pronounced with oxidized  $\alpha$ -tocopherol. According to Pokorny et al. (1973), tocopherol oxidation products can react with other food components such as protein to generate several other products.

Apart from their antioxidant/prooxidant activity, little is known about other biological activities of tocopherol degradation products.

### *Phytosterols*

Phytosterols are the major constituents of unsaponifiables present in edible oils (Rudzińska et al., 2009). They are triterpenic compounds, structurally different from cholesterol only in the side chain configuration. The most common phytosterols in edible oils are  $\beta$ -sitosterol, campesterol, stigmasterol,  $\Delta^5$ -avenasterol, and brassicasterol (Figure 3). In vegetable oils, phytosterols are the dominant class of minor components and occur primarily as free sterols or steryl fatty acid esters (Piironen et al., 2000).

There is a general agreement in publications that phytosterols offer no protection to oils under storage conditions or low temperature applications (<120°C) (Kochhar, 2001; Cercaci et

al., 2007). However, under frying conditions, phytosterols have been reported to inhibit thermo-oxidative alterations of frying oils. Sims et al. (1972) investigated the ability of some phytosterols to inhibit thermooxidation of safflower oil by heating it to 180°C, and the extent of thermooxidation was assessed by iodine value. Fucosterol,  $\Delta^7$ -avenasterol, and vernosterol offered significant protection to the oil, while ergosterol,  $\beta$ -sitosterol, and stigmasterol were either ineffective or slightly prooxidant. In a similar study, Gordon and Magos (1983) reported that the addition of fucosterol and  $\Delta^5$ -avenasterol to technical triolein and heating it to 180°C inhibited thermooxidation as measured by iodine value. According to Kochhar and Gertz (2004), a mixture of phytosterols isolated from canola or sunflower oils significantly increased value of the Oxidative Stability at Elevated Temperature (OSET) index of canola oil heated at 170°C, indicating antioxidant activity. In a recent study, Winkler and Warner (2008a) observed an oil dependent activity of phytosterols. A mixture of phytosterols was added to purified soybean and high oleic sunflower oil triacylglycerols. The oils were heated at 180°C for up to 12 h, and formation of polymers was quantified by high performance size exclusion chromatography (HPSEC). The authors reported that the added phytosterols significantly decreased thermal polymerization of soybean oil triacylglycerols; however in high oleic sunflower oil triacylglycerols polymerization was significantly increased. Thus, the phytosterol mixture was effective in unsaturated oil but ineffective in the more saturated oil. A mixture of endogenous phytosterol isolated from canola (SCAN) and rice bran oil (SRBO) offered a concentration dependent protection for canola oil triacylglycerol during a model frying (Aladedunye and Przybylski, 2012a). When 500  $\mu\text{g/g}$  of SCAN was added, no protective activity was observed. On the contrary, at this low concentration the protection by SRBO was comparable to the

observed for endogenous tocopherols isolated from canola or rice bran oils. This is presumably due to the presence of higher amount of sterols with known antioxidant activity such as avenasterol in RBO (Aladedunye and Przybylski, 2012a). When 3,000  $\mu\text{g/g}$  was added, however, the protection offered by SCAN was 20% better than tocopherols and comparable to SRBO as measured by the amount of TPC at the end of the frying period.

White and Armstrong (1986) compared the antioxidant activity of pure  $\beta$ -sitosterol and a purified oat sterol containing mixture of  $\Delta^5$ -avenasterol and  $\beta$ -sitosterol using soybean oil heated to 180°C. Thermooxidative degradations were followed by changes in fatty acids, conjugated diene formation and polymerization. At all tested concentrations, samples containing  $\Delta^5$ -avenasterol were more stable than the control - soybean oil without additives. In contrast, samples containing  $\beta$ -sitosterol were altered at the same rate as the control. Because observed antioxidant activity appeared to be restricted to sterols with ethylidene side chain configuration, such as avenasterol, fucosterol, vernosterol and citrostadienol, the mechanism of phytosterol antioxidant activity has been ascribed to the formation of an allylic free radical at C-29 followed by isomerisation to a relatively stable tertiary free radical at C-24 (Figure 4) (Sims et al., 1972; Gordon and Magos, 1983; White and Armstrong, 1986). However, there is a lack of supporting experimental data, showing presence of phytosterol side chain oxidation products to support this mechanism. Furthermore, since the phytosterol mixtures evaluated by Kochhar and Gertz (2004), Winkler and Warner (2008a), and Aladedunye and Przybylski (2012a) were mainly composed of  $\beta$ -sitosterol, stigmasterol, and campesterol, phytosterols without ethylidene side chain configurations, a more plausible explanation is required for their observed inhibitory activity.

A further study of the effect of structure on phytosterol antioxidant activity was undertaken by Winkler and Warner (2008b). Endogenous minor components were removed from soybean oil by molecular distillation. Various concentrations of pure phytosterols mixture containing  $\beta$ -sitosterol, sitostanol, stigmasterol, fucosterol, brassicasterol, and ergosterol were added back to the stripped oil, and the samples heated at 180°C for 8 h. As measured by the amounts of polymers formed at the end of the heating period, all phytosterols with two or more double bonds, regardless of the presence of an ethylidene group in the side chain, provided protection against polymerization of the oil. The best protection was offered by ergosterol with three double bonds. The authors concluded that the degree of phytosterol unsaturation was more important for its antioxidant activity than the presence of an ethylidene group. According to Monu (2007), whereas free phytosterols inhibited the degradation of canola oil heated at 190°C for up to 12 h, the corresponding phytosterol esters offered no protection, attributing the protection of free phytosterol to activity of the terminal hydroxyl functional group. However, Lengyel et al. (2012) recently showed that the hemolytic cleavage of phytosterol hydroxyl O-H bond required significantly larger energy in comparison with a number of alternative C-H bonds. In a more recent study, Singh (2013) reported an antioxidative effect of sitosterol in triolein, canola, flaxseed and high oleic sunflower oils as measured by the amount of polymers formed at the end of heating at 180°C for 72 h. Conversion of sterol to steradiene by a 1, 2 elimination of water was suggested as the antioxidative mechanism of sitosterol at frying temperatures.

In our recent study (Aladedunye and Przybylski, 2012a), it was observed that whenever tocopherols were added to the sterol fraction isolated from canola and rice bran oil, the level of thermooxidative degradation in the oil was similar to the amounts accumulated when the

substrate contained only tocopherols. This indicates the lack of synergistic interaction between these components and suggested that the antioxidant effect of phytosterols might not be realized in the presence of tocopherols, presumably due to the lower activation energy of the latter.

Like tocopherols, phytosterols can undergo thermooxidative degradation under the conditions employed during deep frying, leading to a variety of polar and nonpolar compounds. The formation of phytosterol oxidation products have been studied both in model heating systems and under actual deep frying conditions (Ghavami and Morton, 1984; Dutta and Appelqvist, 1996; Dutta, 1997; Oehri et al., 2001; Soupas et al., 2004; Soupas et al., 2005; Tabee et al., 2008). Dutta et al. (1997) assessed the contents of phytosterol oxides in a hydrogenated canola/palm blend, sunflower oil, high oleic sunflower oils, and French fries fried in the various oils.  $7\alpha$ -, and  $7\beta$ -hydroxysterols, 7-ketosterols,  $5\alpha,6\alpha$ -epoxysterols, and dihydroxysterols were the major phytosterol oxides identified. Soupas et al. (2004) evaluated the effects of the degree of unsaturation of both the phytosterols and the lipid medium on the formation of phytosterol oxides under different temperatures (60 – 180°C). Stigmasterol (unsaturated phytosterol) and sitostanol (saturated phytosterols) were added as model compounds to tripalmitin and canola triacylglycerols. The authors reported a significant influence of lipid matrices and temperature on the level and reaction pathway of phytosterol oxidation. For instance, after 3 h of heating at 180°C, the stigmasterol oxide contents were 24.2 and 7.4% in tripalmitin and purified canola oil, respectively. However, heating at 100°C yielded 0.3 and 26.5% stigmasterol oxide in tripalmitin and canola oil, respectively. It was also observed that the level of oxidation products from the unsaturated phytosterol was significantly higher than the level from the saturated phytosterol. In a similar study, Oehri et al. (2001) monitored the formation of phytosterol oxidation products in

canola, coconut, peanut, and soybean oils during heating at 100, 150, and 180°C for 20 h. The authors reported that the amounts and varieties of phytosterol oxidation products were significantly higher at 100 and 150°C than at 180°C, presumably due to their participation in oligomerization reactions at frying temperatures.

Oxidized phytosterols have been identified as the precursors for oligomers at frying temperatures (Lampi et al., 2009; Rudzińska et al., 2009; 2010). Rudzińska et al. (2009) heated phytosterol standards at 60, 120, and 180°C for up to 24 h in the presence of pure oxygen, and the level of oligomers was monitored by HPSEC. It was observed that at frying temperatures, oligomers were the main products, accounting for 60-74% phytosterol transformation. Several volatile degradation products of phytosterols were identified and quantified in the study. In a recent study, Struijs et al. (2010) reported a broad range of dimers with different polarity during thermooxidation of stigmasterol at 180°C for 3 h and the most abundant dimers were found to be linked by carbon-carbon bonds.

Whereas the biological activity of phytosterol oxidation products has been well studied and reviewed (Adcox et al., 2001; Maguire et al., 2003; Ryan et al., 2005; Ryan et al., 2009; O'Callaghan et al., 2010; Alemany et al., 2012), their influence, antioxidative or prooxidative, on thermooxidative stability of frying oil is yet to be studied.

### ***Gamma-Oryzanol***

Gamma-oryzanol, a mixture of ferulic acid steryl esters is a major antioxidant found in rice bran oil. At least 16 steryl ferulates have been identified (Nakayama et al., 1987; Xu and

Godber, 1999; Akihisa et al., 2000; Collins et al., 2002; Fang et al., 2003; Parrado et al., 2003; Miller and Engel, 2006). Major components are presented in Figure 5.

Studies on the activity of  $\gamma$ -oryzanol during frying are scarce, and are conducted by heating the oils rather than assessing during actual deep frying. It was reported that the addition of  $\gamma$ -oryzanol to refined canola and sunflower oils resulted in lower accumulation of dimers and polymers during an OSET test at 170°C (Gertz et al., 2000; Kochhar and Gertz, 2004). Sitostanyl ferulate prevented polymerization in antioxidant stripped high oleic sunflower oil during heating at 180°C for 6 h (Nyström et al., 2007). The thiobarbituric acid-reactive substances (TBARs) in lard heated in the oven at 180°C for up to 10 days were significantly reduced in the presence of  $\gamma$ -oryzanol. In a recent study, Winkler-Moser et al. (2012) compared the ability of corn steryl ferulate and  $\gamma$ -oryzanol on the thermooxidative stability of refined, bleached, deodorized soybean oil in a 2-day frying experiment using a miniature frying protocol with potato cubes. The components were added at 0.5% concentration and the performance was assessed by the rate of polymerized triacylglycerol (PTAG) formation. Both corn steryl ferulate and  $\gamma$ -oryzanol significantly delayed the formation of PTAG with corn steryl ferulate offering a markedly superior performance lasting for the entire frying period. The protection by  $\gamma$ -oryzanol, on the other hand, was only significant on the first day of frying. The authors attributed the differences in the performance of corn steryl ferulate and rice steryl ferulate ( $\gamma$ -oryzanol) to structural differences and differential interactions with endogenous tocopherols; while corn steryl ferulate had a protective effect on the tocopherols naturally present in soybean oil,  $\gamma$ -oryzanol increased their degradation.



The capacity of rice bran oil to improve the thermooxidative stability of its blends with other frying oils is usually attributed to the  $\gamma$ -oryzanol component (Chotimarkorn and Silalai, 2008; Farhoosh and Kenari, 2009). However, rice bran oil also contains a number of other minor components like tocopherols and tocotrienols, and their influence cannot be neglected. Furthermore, the resulting changes in fatty acid and triacylglycerol composition arising from such blending will also affect thermooxidative stability of the oils. According to Mezouari and Eichner (2007), raising the amount of rice bran oil from 10 to 50% in a sunflower/rice bran oil blend will increase OLO, OLP, PPL, OOO, OPO, oleic and palmitic acids, and decrease LLL, LLO and linoleic acid contents to a level that can significantly influence thermooxidative stability. Changes in the triacylglycerol composition have been reported to exert a strong influence on stability of frying oils (Kim et al., 1988; Neff et al., 1992; Neff et al., 1994; Neff and El-Agaimy, 1996). Indeed, according to Kim et al. (1988), the influence of changes in triacylglycerol composition on foaming of oils during frying exceeded that of the fatty acid composition.

There is no agreement in the available literature on the relative antioxidant effectiveness of  $\gamma$ -oryzanol and tocopherols in oils. According to Gertz et al. (2000), polymerization of canola and sunflower oils was better inhibited by  $\gamma$ -oryzanol than  $\alpha$ -tocopherol during heating at 170°C for 2 h. Nyström et al. (2007), on the other hand, reported a superior activity of  $\alpha$ -tocopherol over sitostanyl ferulate during heating of high oleic sunflower triacylglycerols at 180°C for 6 h. Differences in experimental conditions could be responsible for the divergence in conclusions. However, unlike studies regarding antioxidant activity, all available data agreed that  $\gamma$ -oryzanol possessed a higher thermal stability than tocopherols (Mezouari and Eichner, 2007; Nyström et

al., 2007; Chotimarkorn and Silalai, 2008; Jennings and Akoh, 2009; Winkler-Moser et al., 2012). Although, the antioxidant activity of steryl ferulates is attributed to the radical scavenging activity of the ferulic acid moiety, their high thermal stability makes them a better antioxidant under frying conditions than ferulic acid (Marinova and Yanishlieva, 1994; Nyström et al., 2007).

### *Lignans*

Lignans are compounds with a dibenzylbutane skeleton formed by coupling of two coniferyl alcohol residues that are present in the plant cell wall (Touré and Xueming, 2010). Sesamin, sesamol, sesamolin, sesaminol and sesamolol (Figure 6) are lignan compounds naturally present in sesame oil, and have been implicated in the oil's high stability (Yoshida, 1994; Namiki 1995). The ability of sesamol, sesamin and sesamolin to inhibit lipid oxidation in model systems has been reported. Sunflower oil containing sesamol, sesamin, and sesamolin extracted from roasted sesame seed oil was heated at 180°C for 10 h, and thermooxidative degradation assessed by conjugated diene contents, *p*-anisidine value, and fatty acid composition. Samples containing sesame lignans showed significantly higher stability compared to sunflower oil without them (Lee et al., 2007). The effect of sesame lignans on thermooxidation of methyl linoleate during heating at 180°C for 1 h in a Rancimat was assessed by Lee et al. (2008). The contents of conjugated dienes and the *p*-anisidine value were significantly lower when lignans were added to oil than samples without lignans. The frying stability of soybean oil also increased after addition of sesamin and sesamolin (Hemalatha and Ghafoorunissa, 2007). Thermooxidative deterioration of lard heated at 180°C for up to 2 h was significantly inhibited in the presence of

sesamol as measured by DPPH, conjugated dienoic acid, and anisidine value (Yeo et al., 2010; 2011). During heating of soybean oil at 180°C for 8 h, sesamol and sesamin delayed oligomer formation and loss of bisallylic and olefinic protons monitored by <sup>1</sup>H-NMR, with sesamol being significantly more effective than sesamin especially at higher concentrations (Hwang et al., 2012). Lee et al. (2008) also reported the superior performance of sesamol over sesamin during thermooxidation of methyl linoleate as measured by anisidine value. On the contrary, sesamin was found to be more effective when assessment was done by level of conjugated dienoic acid, a measure of lipid primary oxidation products, suggesting possible differences in antioxidative mechanisms between the two lignans (Lee et al., 2008).

Secoisolariciresinol diglycoside (SDG) and matairesinol (Figure 6) are the main flaxseed oil lignans (Touré and Xueming, 2010). Literature reports on the antioxidant activity of flaxseed lignans in oils are rather scarce, and the only available report was the recent study by Hwang et al. (2012) on the antioxidant activity of some minor flaxseed lignans, namely, secoisolariciresinol and pinoresinol. Interestingly, pinoresinol (also a minor component of sesame lignan) and secoisolariciresinol reportedly offered better protection against thermooxidation of heated soybean oil than sesamin, the predominant sesame lignan. Further, at low and intermediate concentrations (200 and 400 µg/g), the activity of this minor lignans was also comparable to that of sesamol, the most active sesame lignan, as measured by oligomer formation and loss of bisallylic and olefinic protons (Hwang et al., 2012.). The superior performance of pinoresinol over sesamin may be due to structural differences in which the opening of the two dioxolane groups in sesamin structure resulted in two phenolic OHs in

pinoresinol (Figure 6). SDG, and its aglycone, secoisolariciresinol, significantly improved the Oxidative Stability Index of canola oil at 110°C (Hosseini et al., 2006).

### *Carotenoids*

Carotenoids are a group of naturally occurring tetraterpenoids, consisting of isoprenoid units (Choe and Min, 2006). They are lipid-soluble pigments that contribute to the yellow or deep orange colour of oils. Depending on source and variety, crude palm oil may contain up to 0.5% carotenoids (Kochhar, 2001).  $\beta$ -Carotene is the most widespread carotenoid present in vegetable oils (Achir et al., 2010). Although the antioxidant activity of carotenoids against photo-oxidation has been recognized, their antioxidant activity during storage without light exposure or at elevated temperature remains controversial (Fakourelis et al., 1987; Lee and Min, 1988; Miller et al., 1996). Yanishlieva et al. (2001) observed a prooxidant effect when  $\beta$ -carotene was added to antioxidant free sunflower oil triacylglycerols during accelerated storage at 100°C. However, in the same study, an antioxidant activity was reported for regular sunflower oil. The observed activity was attributed to a synergistic action between  $\beta$ -carotene and the endogenous  $\alpha$ -tocopherol in the sunflower oil. According to Schroeder et al. (2006), the addition of 100 – 1000  $\mu\text{g/g}$   $\beta$ -carotene to antioxidant depleted palm olein did not extend the induction period in a Rancimat stability test at 120°C. In a recent study, Zeb and Murkovic (2010) evaluated the effects of  $\beta$ -carotene on the oxidation of triacylglycerols. They observed that addition of  $\beta$ -carotene significantly increased the peroxide value of model triacylglycerols during oxidation at 110°C in a Rancimat apparatus. Procida et al. (2009) reported that  $\beta$ -carotene inhibited the formation of some deleterious carbonyl compounds such as pentanal during frying in olive oil. It

was also reported that  $\beta$ -carotene protected  $\alpha$ -tocopherol and tocotrienols during deep frying using palm olein, thus improving the frying performance of the oil (Schroeder et al., 2006). Edge et al. (1998) observed that a 7, 7'-dihydro- $\beta$ -carotene derivative of  $\beta$ -carotene, was able to regenerate  $\alpha$ -tocopherol from the tocopheroxyl radical. A small but significant protection was offered by lutein against thermooxidative degradation of sunflower oil during heat treatment at 180°C for 120h as monitored by the formation of polar compounds and *trans* fat (Filip et al., 2011).

With regard to antioxidant activity of carotenoids during high temperature processing of lipids, there are two major possible mechanisms proposed for their reaction with lipid radical species: (1) According to Burton and Ingold (1984), a lipid peroxy radical (ROO $\cdot$ ) can add at any place across the carotenoid (CAR) polyene chain, resulting in the formation of a resonance stabilized carbon centered radical, ROO-CAR $\cdot$ . Because this reaction interferes with the propagation step of lipid oxidation, it is being used to explain some of the reported antioxidant effects of carotenoids (Paloza and Krinsky, 1992). However, it has been suggested that the carotenoid-peroxy addition radical, ROO-CAR $\cdot$  could react reversibly with molecular oxygen to form a new peroxy radical, ROO-CAR-OO $\cdot$  which is believed to be responsible for some of the reported prooxidant activity of carotenoids at high oxygen concentrations (Krinsky and Yeum, 2003); (2) Depending on the chemical structure of the carotenoids and the reduction potential of the free radicals, carotenoids can donate hydrogen to free radicals, exhibiting antioxidant activity (Woodall et al., 1997; Choe and Min, 2006). Lee et al. (2003) reported that  $\beta$ -carotene with a high reduction potential of 1060 mV had great difficulty donating hydrogen to alkyl and peroxy radicals with reduction potentials of 600 and 1000 mV, respectively. However,  $\beta$ -carotene can

donate hydrogen to hydroxyl and alkoxyl radicals formed from the decomposition of hydroperoxides, because of their relatively higher reduction potentials.

### *Squalene*

Squalene is a triterpene hydrocarbon widely distributed in vegetable oils, with olive (10 – 1200 mg/kg) and rice bran oils (100 – 330 mg/kg) containing the highest amounts. The capacity of squalene to protect oils against oxidative degradation has been evaluated by Rao and Achaya (1968), Boskou and Katsikas (1979), Psomiadou and Tsimidou (1999), Shahidi and Wanasundara (1999), Dessi et al. (2002), Psomiadou and Tsimidou (2002a), and Mateos et al. (2003). Literature reports, however, on squalene antioxidant activity remain controversial, highly dependent on the model used (Amarowicz, 2009).

Although all available data on the antioxidant activity of squalene under frying conditions are obtained by heating the oils and not during actual deep fat frying, it is generally agreed that squalene inhibits thermooxidative degradation of frying oils. Addition of squalene at 0.5% significantly reduced the thermooxidative degradation of safflower oil during intermittent heating at 180°C for 7 h per day for 4 days (Sims et al., 1972). Malecka (1991, 1994) reported a significant increase in thermooxidative stability of canola oil heated at 170°C for 35 h in the presence of different concentrations of squalene (0.1 – 1.0%). Addition of squalene isolated from shark and olive oils at a concentration of 0.25% also increased the frying stability of sunflower and canola oils as evaluated by an OSET index (Gertz et al., 2000). A synergistic interaction between tocopherols and squalene has been suggested by Kochhar (2001) and Psomiadou and

Tsimidou (2002a, 2002b). Nevertheless, investigations on the protective effect of squalene during actual deep fat frying are still required.

### *Phospholipids*

Phospholipids such as phosphatidylcholine (PC), phosphatidylethanolamine (PE), phosphatidylserine (PS), phosphatidylinositol (PI), and phosphatidic acid (PA) are endogenous minor components of oils.

Unlike studies describing the antioxidant activity of phospholipids under accelerated storage conditions, rather fragmented information is available on their application under frying conditions, probably because of their adverse effects on colour and foaming of oils (Dobarganes et al., 2000). The addition of 0.1% soy lecithin remarkably inhibited thermooxidative alteration of oils during frying (Chu, 1991; Kourimska et al., 1994; Gordon and Kourimska, 1995b). The thermooxidative stability of salmon oil heated at 180°C was significantly improved in the presence of a phospholipid fraction isolated from bluefish (King et al., 1992). The antioxidant effect of egg yolk during frying of flour dough containing different amounts of egg yolk powder was attributed to phospholipids present in this ingredient (Kim and Choe, 2008). According to Kourimska et al. (1994), addition of soy lecithin in an amount not higher than 0.2% had no negative effect on foaming of the oil and the quality of the prepared French fries. In a recent study, the performance of PC and PE was evaluated during a model frying of a mixture of starch, glucose and silica (4:1:1) in canola oil triacylglycerol at 185°C (Aladedunye and Przybylski (2012a). At a concentration of 500µg/g, neither PC nor PE offered any protection to canola oil triacylglycerol. However, at higher concentrations (1,000 and 2,000µg/g), both phospholipids

significantly inhibited thermooxidative degradation of the oil as measured by the amount of total polar compounds and the rate of volatile carbonyl compounds and hydroxynonenal formation.

The observed antioxidant activity of phospholipids has been attributed to: (1) their synergistic activity with phenolic antioxidants such as tocopherols (Dziedzic and Hudson, 1984; Weng and Gordon, 1993; Lambelet et al., 1994; Koga and Terao, 1995; Bandarra et al., 1999; Khan and Shahidi, 2000; Judde et al., 2003; Ramadan, 2008); (2) the ability of the phosphate group to chelate prooxidant metals (Pokorny et al., 1992; Drusch et al., 2008); (3) the formation of nonenzymatic browning reaction products between amino phospholipids and sugar or lipid oxidation products (Husain et al., 1984; Hidago et al., 2005; 2006; 2007; Zamora et al., 2011); and (4) the ability of phospholipids to form an oxygen barrier between the oil and air interface (Porter, 1980; Calvo et al., 1994).

### *Polyphenolics*

A recent trend in the search for natural antioxidants is the application of extracts and isolates from different plants. The most prominent compounds present in those extracts are polyphenols (Shahidi and Naczki, 1995). The structures of common simple phenolic and polyphenolic compounds are presented in Figure 7. The isolation of polyphenolic compounds, their antioxidant activities and applications in biological and food systems has been extensively reviewed by Moure et al. (2001), Schieber et al. (2001), Yao et al. (2004), Shi et al. (2005), Balasundram et al. (2006), Pandey and Rizvi (2009), Perron and Brumaghim (2009), Raederstorff (2009), Serrano et al. (2009), Valls et al. (2009), Nichols and Kaliyar (2010), and Xia et al. (2010). Whereas there are several reports on the antioxidant activities of plant extracts



and their polyphenolic components in vegetable oil under oxidative conditions ( $\square$  120°C), corresponding investigations under frying conditions, however, have not received such attention. Major studies in this regards are presented in Table 2.

Generally, extracts from different parts of spices, herbs and fruits studied so far indicated their efficacy in inhibiting thermooxidative degradation and extend the fry life of vegetable oils (Table 2). Besides, the extracts and their isolated polyphenolic components effectively inhibited the formation of toxic thermooxidative degradation products including heterocyclic amines during pan frying of beef patties, and acrylamide during deep-frying of potato and bread sticks (Britt et al., 1998; Shin et al., 2003; Tsen et al., 2006; Cheng et al., 2007; Zhang and Zhang, 2007; Cheng et al., 2010; Dong et al., 2011). Available data indicated that the addition of plants extracts to frying oil did not negatively affect the sensory attributes of the fried products (Jawir et al., 2000; Che Man and Jawir, 2000; Zhang and Zhang, 2007; Nor et al., 2009a; 2009b), lending credence to their utilization as antioxidants for frying applications.

Whereas the efficacy of many conventional antioxidants including tocopherols and BHT dramatically decrease at frying temperatures, on the contrary, the effectiveness of polyphenolic compounds improved with temperature as indicated by a number of studies. For instance, whereas mixed tocopherol was more effective than rooibos tea polyphenolic extract at protecting antioxidant-free soybean oil at 120 and 140°C, the polyphenolic extract was significantly more effective at 160 and 180°C (Fukasawa et al., 2009). Elhamirad and Zamanipoor (2012) evaluated the temperature-dependent antioxidant activity of  $\alpha$ -tocopherol, simple phenolic acids (gallic and caffeic acids) and representative polyphenolic compounds (catechin and quercetin) during thermal oxidation of sheep tallow olein in a Rancimat. At 120°C gallic and caffeic acids were

markedly more effective than the polyphenolic compounds, but at 180°C, quercetin was the most effective, catechin was comparable to gallic acid and more effective than caffeic acid. At all temperatures the polyphenolic compounds were more effective than  $\alpha$ -tocopherol with the difference more pronounced at 180°C (~1.3 times at 120°C and up to 5.1 times at 180°C). The temperature effect may in part explain why no significant positive effect was observed for black tea and garlic bulb polyphenolic extracts during heating of corn oil at 140°C for 48h (Navas et al, 2006).

Although plant extracts and polyphenols show good potential as natural antioxidants for frying applications, nevertheless, a major set-back is their poor solubility in oils. For improved effectiveness, it is required of applied antioxidant to be soluble or optimally dispersed in the substrate. The observed improved efficiency of polyphenolic compounds with temperature may as well be related to increased solubility or dispersal at higher temperature. The solubility and dispersal of polyphenolic compounds in oil is also a very important factor that can affect the level of performance observed in a model frying involving heating of oil to a frying temperature without food, compared to actual frying experiment. During heating of oil without food, water or aeration, ‘caramelization’ of extracts (forming black sediments), with consequent inactivation of polyphenolic active ingredients is not unlikely. It is expected, however, that during frying of food, water from the food, agitation of the oil arising from escaping water vapor and aeration will improve polyphenolic solubility and dispersal. Investigations into methods to enhance the lipophilicity of polyphenolic compounds through appropriate modifications are therefore warranted.

***SYNTHETIC ANTIOXIDANTS***

A broader application of natural antioxidants in the protection of oils against thermo-oxidative degradation is hampered by some inherent shortcomings. For instance, the poor thermal stability of tocopherols and carotenoids limits their applications for extended institutional frying operations. The poor solubility of phenolic and polyphenolic compounds and variability in composition, and hence variable activity of the extracts limit their applications in fats and oils (Pokorny, 2007). Consequently, synthetic antioxidants have been developed, and a number of these have been approved for food applications (Torres et al., 2008)

Synthetic antioxidants are often added to processed oils to retard oxidative degradation during storage and frying (Warner, 2004). The most widely used synthetic antioxidants include: BHA; BHT; TBHQ; and propyl gallate (PG) (Figure 8). Transition metal chelators such as citric acids are also used to counteract the deleterious effects of metals such as iron and copper. Although BHT and BHA are effective antioxidants at ambient and accelerated storage temperatures (Gordon and Kourimska, 1995a; Khan and Shahidi, 2001; Nenadis et al., 2003; Yeo et al., 2010), they offer little or no protection during frying of food. They are known to evaporate and thus do not remain in the frying oil long enough to provide protection against thermooxidative degradation (Peled et al., 1975; Augustin and Berry, 1983; Tsaknis et al., 2002; Warner, 2004). For instance, 75% of the added BHT and 86% of the original BHA were lost after 6 h of intermittent frying of potato chips in palm olein (Augustin and Berry, 1983). TBHQ, on the other hand, has been reported to possess better thermal stability and effectiveness during frying (Gordon and Kourimska, 1995a). Che Man et al. (1999) found that TBHQ was more efficient than  $\alpha$ -tocopherol in inhibiting thermooxidative degradation during frying in palm olein.

Nevertheless, Asap and Augustin (1986) reported a 95% loss of the initial amount of TBHQ after 5 h of frying in palm olein. The loss of TBHQ was attributed to steam distillation, thermal decomposition, and absorption of TBHQ by the fried food. The nature, toxicity and antioxidant activity of common synthetic antioxidants have been a subject of several review articles (Johnson and Chichester, 1971, Kim and Pratt, 1992; Shahidi and Wanasundara, 1992; Valenzuela and Nieto, 1996; Frankel, 2007; Marmesat et al., 2010) and will not be reiterated here. Suffice to say, however, that the isolation of BHT, one of the major synthetic antioxidants, from a natural source (*Litchi Chinensis* Sonn.) has just been reported (Jiang et al., 2013). And the effect of the modification of TBHQ to form lauryl tert-butylated hydroquinone on its toxicity is yet to be reported (Zhang et al., 2004).

Aside from poor protection, especially under frying conditions, use of common synthetic antioxidants has also been limited due to their perceived detrimental effect on human health (Frankel, 2007). Consequently, there is a growing interest in development of new antioxidants with improved antioxidant activity and thermal stability, but prepared from natural precursors. The new trend in this direction is leading to modification of existing natural antioxidants.

For instance, in addition to commercially available tocopherol derivatives such as  $\alpha$ -tocopheryl acetate,  $\alpha$ -tocopheryl succinate and racemic trolox (Figure 9), a number of tocopherol derivatives have been synthesized. These are excellently reviewed by Cerecetto and López (2007). Ascobyl palmitate and stearate (E304), propyl (E310), octyl (E311), and dodecyl (E312) gallates are relevant modifications of some existing natural antioxidative compounds for improved lipophilicity and probable antioxidant activity. The reported synergy between tocopherols and carotenoids (Edge et al., 1998; Yanishlieva et al., 2001) prompted the

development of synthetic antioxidants incorporating these antioxidant substructures (Larsen et al., 1998; Naalsund et al., 2001; Palozza et al., 2002). FeAOX-6 (Figure 9) is an example of such a group of antioxidants reportedly possessing potent radical scavenging activity (Palozza et al., 2002). The study by Naalsund et al. (2001) esterified trolox, the water soluble tocopherol analogue, carotenoid, and a selenium fatty acid to a glycerol backbone. The ‘triantioxidant’ (Figure 9), however, only showed additive effect of trolox and carotenoid in a DPPH radical scavenging assay. Likewise, the reported synergistic activity between ascorbic acid and  $\alpha$ -tocopherol prompted the development of a series of novel antioxidants derived from molecular combination of ascorbic acid and tocopherol analogues (Figure 9) (Morisaki and Ozaki, 1996; Manfredini et al., 2000). Although no improvement in inhibitory activities against tyrosinase-catalyzed melanin formation, active oxygen species, and free radicals were observed from these molecular combinations, the ascorbic acid- $\alpha$ -tocopherol hybrid exhibited significantly higher thermal stability than the parent components (Morisaki and Ozaki, 1996). Similarly, Voisin-Chiret et al. (2007) reported the synthesis of a series of thermally stable ascorbic-ferulic acid hybrids. Again, exploiting the variously reported synergistic interactions between tocopherol and phosphatidylcholine, Koga et al. (1994) reported the synthesis of phosphatidylchromanol (Figure 9) in which tocopherol’s phytyl chain was substituted for a phosphatidyl moiety. The induction period for the new phosphatidylchromanol was longer than that with the mixture of tocopherol and phosphatidylcholine during autoxidation of lard at 60°C (Koga and Terao, 1994).

Available literature on the chemical and enzymatic syntheses and modification of (poly)phenolic compounds have been recently reviewed by Chebil et al. (2006), Fernandez-Bolanos (2008), Viskupicova et al. (2009), and Wang et al. (2010). Recently, Hamdi et al. (2008)

reported the synthesis of a series of dicoumarol and epoxydicoumarin derivatives exhibiting good radical scavenging activity against the ABTS radical. Rajan et al. (2001) described the synthesis of new caffeic acid amides exhibiting good antioxidant activity. Jung et al. (2002) also reported the synthesis of 4-hydroxyphenylacetic acid amide possessing potent analgesic and antioxidant activities. The synthesis of caffeic acid amides possessing antimicrobial activities was recently reported by Fu et al. (2010). The syntheses of several gallic and ferulic acid derivatives with enhanced lipophilicity and radical scavenging activity have also been reported by Belin et al. (2003) and Zheng et al. (2010). In a recent study, Lorentz et al. (2010) reported a lipase catalyzed synthesis of two new 4-O- and 3-O-palmitoyl chlorogenic acids; however, the new chlorogenic acid derivatives exhibited weaker radical scavenging activities against DPPH radical, compared to the original chlorogenic acid. Zhong et al. reported the synthesis and the antioxidant activities of a series of lipophilized epigallocatechin gallate (EGCG) derivatives with fatty acids (Zhong and Shahidi, 2011; 2012; Zhong et al., 2012). The lipophilized EGCG derivatives exhibited greater ORAC, DPPH and  $\beta$ -carotene bleaching radical scavenging activity than unmodified EGCG. At lower concentration ( $\square$  0.35  $\mu\text{mol/g}$  of oil) EGCG stearic acid derivative showed a significantly higher antioxidant activity than EGCG in purified corn oil using Rancimat at 100°C, but EGCG was a better antioxidant at higher concentration (0.87  $\mu\text{mol/g}$  of oil). It was hypothesized that at lower concentration, the effect of solubility on antioxidant performance dominates over interfacial phenomenon (Zhong and Shahidi, 2012).

Studies on enzymatic lipophilization of simple phenolic acids up to 2005 were reviewed by Figueroa-Espinoza and Villeneuve (2005). More recent studies are presented in Table 3. Although syntheses and performance evaluation of over a hundred (semi)synthetic antioxidants

have been reported in literature (Figuerola-Espinoza and Villeneuve, 2005; Chebil et al., 2006; Cerecetto and López, 2007; Fernandez-Bolanos, 2008; Viskupicova et al., 2009; Wang et al., 2010; Zhong and Shahidi, 2011; 2012; Reddy et al., 2012), only a negligible fraction have been specifically designed and/or evaluated under frying conditions. Irrespective of their performance under chemical and lipid model antioxidant assays, evaluations of these antioxidants for frying application is still warranted. For instance, the decrease in radical scavenging activities of the two new 4-O- and 3-O-palmitoyl chlorogenic acids against DPPH radical (which is not unexpected considering the blockage of an active OH site by the palmitoyl group) may have no relevance to their performance under frying conditions as the expected improved lipophilicity (leading to a better dispersal in oil), and thermal stability may be more important than radical scavenging activity (Zhong and Shahidi, 2012). Recently, we reported the synthesis of a series of caffeic acid amides and evaluated their performance during frying of formulated food in canola oil triacylglycerols (Aladedunye et al., 2012). It was observed that although the DPPH radical scavenging activity of a number of these novel compounds were not significantly different from the caffeic acid precursor, nevertheless, they were markedly better antioxidants under frying condition. By coupling simple phenolic acids, caffeic, ferulic, gallic, synapic, and syringic acids to the chromanol ring of tocopherol (mainly responsible for its antioxidant activity), their antioxidative performance including thermal stability during frying in canola oil was markedly improved (Catel et al., 2010; 2012). However, whereas the gallic acid derivative, possessing highest number of OH groups, showed the highest radical scavenging activity, it was significantly less effective compared with other derivatives with weaker radical scavenging activity regarding performance under frying condition, suggesting that evaluation of new

antioxidants for frying application should never be hampered by their supposedly poor radical scavenging activity.

The classical view of antioxidant synergy is a situation in which the combined effect of the two antioxidants is better than the contribution from each of the antioxidative components, and arises when each of the antioxidants is operating by separate but complementary mechanisms (for instance, a radical scavenger and a metal chelator) (Frankel, 2007). However, it may also be possible to harness the inherent presence of various potential catalysts in oils and food (water, acid, alkali, metal ions, etc), and the high operational temperature during the frying process, for a targeted *in situ* generation of secondary antioxidative compounds through reactions between the primary antioxidants, as a technique for improving and extending the antioxidant performance. For instance, it was recently observed that the reactions between endogenous phytosterols and added phenolic acids during frying can create a synergistic relationship through *in situ* formation of steryl ferulates, the secondary antioxidant (Aladedunye and Przybylski, 2012b). Investigations into the influence of components' molar ratios and other conditions, however, are subjects for further studies. For instance, according to Nasibullin et al. (2002), depending on the molar ratio, a stable, hydrogen bond-mediated complex can be formed between quercetin and phospholipids by mixing at room temperature. This knowledge was recently applied by Ramadan (2012) in the formulation of a quercetin-enriched lecithin (phenolipid) that exhibited synergistic action during accelerated storage of triolein and sunflower oil at 60°C for 15d.

Formation of Maillard reaction products is another example of heat-induced *in situ* generation of antioxidants during frying. Their formation, nutritional, biological and antioxidant



activities have been extensively reviewed (Kato, 1973; Yamaguchi, 1969; Namiki, 1988; Wanasundara et al., 1997; Hidalgo and Zamora, 2000; Manzocco et al., 2001; Anese and Fogliano, 2001; Lee and Shibamoto, 2002; Echavarria et al., 2012). Maillard reaction products are formed by the reaction between amine from amino acid or protein and carbonyl moiety of sugar. However, in addition to amino acids and proteins, it has been recognized that amino phospholipids such as phosphatidylethanolamine can react via their amine group with aldehydic moiety of lipid oxidation products during frying to generate analogous compounds with potent antioxidant activity (Husain et al., 1984; Hidago et al., 2005; 2006; 2007; Zamora et al., 2011). In a recent study, Kitrytá et al. (2012) observed that the products isolated from a model heating of amino acids (glycine, lysine, arginine) and lipid oxidation-derived aldehydes (hexanal, (E)-2-hexenal) at 125°C for 2 h showed significantly stronger radical scavenging activity than the corresponding unheated initial reaction mixtures, suggesting a heat-induced *in situ* formation of melanoidin-like antioxidant compounds. According to Vhangani and Wyk (2013), the antioxidant activity of Maillard reaction products isolated from fructose-lysine model system heated at 60, 80, and 120°C for up to 2 h increased with increased reaction temperature, thus, it is likely that many of the Maillard reaction products will offer improved antioxidant performance at frying temperatures. Apart from their radical scavenging activity, it is expected that their formation through reactions involving lipid oxidation-derived aldehydic compounds will extend the fry life of oils through removal of these prominent secondary lipid oxidation products.

## CONCLUSION

Deep frying is a very complex phenomenon, and the harsh conditions employed places a huge demand on the applied antioxidants, resulting in common failure of traditional antioxidants.

However, the formation of a host of potentially toxic degradation products during frying, coupled with an ever increasing demand for fried food necessitates the development of safe, yet potent antioxidants for frying applications. Presently, only a very negligible fraction of the available (semi)synthetic antioxidants in the literature has been evaluated under frying conditions presumably due to: (1) the presupposition that their radical scavenging activity in a chemical test or antioxidant activity under oxidative condition correlates with their performance during frying, which is not necessarily true because usually different conditions are applied; (2) lack of an official fast and reliable frying test that truly mimics actual frying conditions to evaluate small amounts of developed antioxidants considering the large amounts required for a typical restaurant-type frying; (3) the time and resources required to assess toxicity of potential antioxidant for frying applications, considering the innumerable number of an antioxidant's decomposition products that are possible under frying conditions; and (4) the impact of antioxidants and their decomposition products on sensory attributes of fried food. Nevertheless, the need to develop a safe, potent, and stable antioxidant for frying application still remains an appealing task.

Based on current knowledge of the antioxidant mechanisms of activity, compounds with antioxidative properties generated from non-toxic natural precursors and possessing the following functional groups and properties could behave as effective antioxidants for frying: (i) at least two phenolic hydroxy functional groups, for enhanced radical scavenging activity; (ii) a catechol moiety, for possible metal chelating activity; (iii) an amino and/or amide functional group, for possible removal of carbonyl compounds through condensation reaction; (iv) relatively high molecular weight for reduced volatility under frying conditions; (v) composed of

independent small antioxidant units which may still exhibit some antioxidant activity consequent to thermooxidative or hydrolytic degradation; (vi) made of components offering different mechanism of antioxidative activity; and (vii) at least moderate lipophilicity for better dispersal in oil. Thus, the evaluation of performance during frying of lipophilized phenolic acid derivatives and a number of semi-synthetic antioxidant hybrids such as ascorbic acid- $\alpha$ -tocopherol, tocopherol-carotenoid, ascorbic-phenolic acid, amino phospholipid-chromanol, and tocopherol-sterol is warranted.

**REFERENCES**

- Abdalla, A. E. M., Darwish, S. M., Ayad, E. H. E., and El-Hamahmy, R. M. (2007). Egyptian mango by-product 2: Antioxidant and antimicrobial activities of extract and oil from mango seed kernel. *Food Chem.* **103**: 1141–1152.
- Abd-ElGhany, M. E., Ammar, M. S., and Hegazy, A. E. (2010). Use of olive waste cake extract as a natural antioxidant for improving the stability of heated sunflower oil. *World Appl. Sci. J.* **11**: 106–113.
- Achir, N., Randrianatoandro, V. A., Bohuon, P., Laffargue, A., and Avallone, S. (2010). Kinetic study of  $\beta$ -carotene and lutein degradation in oils during heat treatment. *Eur. J. Lipid Sci. Technol.* **112**: 349–361.
- Adcox, C., Boyd, L., Oehrl, L., Allen, J., and Fenner, G. (2001). Comparative effects of phytosterol oxides and cholesterol oxides in cultured macrophage-derived cell lines. *J. Agric. Food Chem.* **49**: 2090–2095.
- Aggelousis, S., and Lalas, S. (1997). Quality changes of selected vegetable oils during frying of doughnuts. *Riv. Ita. Sostanze Gr.* **74**: 559–562.
- Akihisa, T., Yasukawa, K., Yamaura, M., Ukiya, M., Kimura, Y., Shimizu, N., and Arai, K. (2000). Triterpene alcohol and sterol ferulates from rice bran and their anti-inflammatory effects. *J. Agric. Food Chem.* **48**: 2313–2319.

Aladedunye, F. A., and Przybylski, R. (2009a). Degradation and nutritional quality changes of oil

during frying. *J. Am. Oil Chem Soc.* **86**: 149–156.

Aladedunye, F. A., and Przybylski, R. (2009b). Protecting oil during frying: A comparative study. *Eur. J. Lipid Sci.Technol.* **111**: 893–901.

Aladedunye, F. A., and Przybylski, R. (2011). Rapid assessment of frying performance using small size samples of oils/fats. *J. Am. Oil Chem Soc.* **88**: 1867–1873.

Aladedunye, F. A., Catel, Y., and Przybylski, R. (2012). Novel dihydrocaffeic acid amides: synthesis, radical scavenging activity, and evaluation as antioxidants under storage and frying conditions. *Food Chem.* **130**: 945–952.

Aladedunye, F. A., and Przybylski, R. (2012a). Frying performance of canola oil triacylglycerides as affected by vegetable oils minor components. *J. Am. Oil Chem Soc.* **89**: 41–53.

Aladedunye, F. A., and Przybylski, R. (2012b). Antioxidative properties of phenolic acids and interaction with endogenous minor components during frying. *Eur. J. Lipid Sci.Technol.* **113**: 1465–1473.

Al-Bandak, G., and Oreopoulou, V. (2011). Inhibition of lipid oxidation in fried chips and cookies by *Majorana syriaca*. *Int. J. Food Sci. Technol.* **46**: 290–296.

Alemany, L., Laparra, J. M., Barbera, R., and Alegria, A. (2012). Evaluation of the cytotoxic effect of 7-keto-stigmasterol and 7-keto-cholesterol in human intestinal (caco-2) cells. *Food Chem. Toxicol.* **50**: 3106–3113

Ali, R. F. M. (2010). Improvement the stability of fried sunflower oil by using different levels of

- pomposia (*Syzygium cumini*). *EJEAFChe* **9**: 396–403.
- Al-Khusaibi, M., Gordon, M. H., Lovegrove, J. A., and Niranjana, K. (2012). Frying of potato chips in a blend of canola oil and palm olein: changes in levels of individual fatty acids and tocopherols. *Int. J. Food Sci. Technol.* **47**: 1701–1709
- Amarowicz, R. (2009). Squalene: A natural antioxidant? *Eur. J. Lipid Sci. Technol.* **11**: 411–412.
- Anese, M., and Fogliano, V. (2001). The Maillard reaction in foods: chemical, technological and nutritional aspects. *Ind. Aliment-Italy* **40**: 385 – 399.
- Apak, R., Guclu, K., Demirata, B., Ozyurek, M., Celik, S. E., Bektasoglu, B., Berker, K. I., and Ozyurt, D. (2007). Comparative evaluation of various total antioxidant capacity assays applied to phenolic compounds with the CUPRAC assay. *Molecule* **12**: 1496–1547.
- Aranha, C. P. M., and Jorge, N. (2012). Antioxidant potential of oregano extract (*Origanum vulgare* L.). *Br. Food J.* **114**: 954–965.
- Asap, R., and Augustin, M. A. (1986). Effect of frying oil quality and TBHQ on the shelf-life of potato crisps. *J. Sci. Food Agric.* **37**: 1045–1051.
- Augustin, M. A., and Berry, S.K. (1983). Efficacy of the antioxidants BHA and BHT in palm olein during heating and frying. *J. Am. Oil Chem. Soc.* **60**: 1520–1523
- Aydeniz B., and Yilmaz, E. (2012). Enrichment of frying oils with phenolic extracts to extend the usage. *Eur. J. Lipid Sci. Technol.* **114**: 933–941.
- Balasundram, N., Sundram, K., and Samma, S. (2006). Phenolic compounds in plants and agric-

- industrial by-products: Antioxidant activity, occurrence, and potential uses. *Food Chem.* **99**: 191–203.
- Bandarra, N. M., Campos, R. M., Batista, I., Nunes, M. L., and Empis, J. M. (1999). Antioxidant synergy of  $\alpha$ -tocopherol and phospholipids. *J. Am. Oil Chem. Soc.* **76**: 905–913.
- Bansal, G., Zhou, W., Barlow, P. J., Lo, H-L, and Neo, F-L. (2010). Performance of palm olein in repeated deep frying and controlled heating processes. *Food Chem.* **121**: 338–347.
- Barrera-Arellano, D., Ruiz-Mendez, V., Velasco, J., Marquez-Ruiz, G., and Dobarganes, C. (2002). Loss of tocopherols and formation of degradation compounds at frying temperatures in oils differing in degrees of unsaturation and natural antioxidant content. *J. Sci. Food Agric.* **82**: 1696 – 1702.
- Barrera-Arellano, D., Ruiz-Mendez, V., Velasco, J., Marquez-Ruiz, G., and Dobarganes, C. (1999). Loss of tocopherols and formation of degradation compounds in triacylglycerol model systems heated at high temperature. *J. Sci. Food Agric.* **79**: 1923 – 1928.
- Belin, F., Barthelemy, P., Ruiz, K., Lacombe, J.M., and Pucci, B. (2003). Synthetic gallic acid derivatives as models for a comprehensive study of antioxidant activity. *Helv. Chim. Acta.* **86**: 247–265.
- Betalleluz-Pallardel, I., Chirinos, R., Rogez, H., Pedreschi, R and Campos, D. (2012). Phenolic compounds from andean mashua (*Tropaeolum tuberosum*) tubers display protection against soybean oil oxidation. *Food Sci. Technol. Int.* **18**: 271–280.
- Boskou, D., and Katsikas, H. (1979). Effect of olive oil hydrocarbons and triterpene alcohols on the stability of heated cotton seed oil. *Acta. Aliment.* **8**: 317–320.

- Botega, D. Z., Bastida, S., Marmesat, S., Pérez-Olleros, L., Ruiz-Roso, B., and Sánchez-Muniz, F. J. (2009). Carob fruit polyphenols reduce tocopherol loss, triacylglycerol polymerization and oxidation in heated sunflower oil. *J. Am. Oil Chem. Soc.* **86**: 419–425.
- Britt, B., Gomaa, E. A., J. Ian Gray, J. I., and Booren, A. M. (1998). Influence of cherry tissue on lipid oxidation and heterocyclic aromatic amine formation in ground beef patties. *J. Agric. Food Chem.* **46**: 4891-4897
- Burton, G. W., and Ingold, K. U. (1984).  $\beta$ -Carotene: An unusual type of lipid antioxidant. *Science* **224**: 569–573.
- O'Callaghan, Y. C., Foley, D. A., O'Connell, N. M., McCarthy, F. O., Maguire, A. R., and O'Brien, N. M. (2010). Cytotoxic and apoptotic effects of the oxidized derivatives of stigmasterol in the U937 human monocytic cell line. *J. Agric. Food Chem.* **58**: 10793 – 10798.
- Calvo, L., Cocero, M. J., and Diez, J. M. (1994). Oxidative stability of sunflower oil extracted with supercritical carbon dioxide. *J. Am. Oil Chem. Soc.* **71**: 1251–1254.
- Catel, Y., Aladedunye, F.A., and Przybylski, R. (2010). Synthesis, radical scavenging activity, protection during storage, and frying by novel antioxidants. *J. Agric. Food Chem.* **58**: 11081–11089.
- Catel, Y., Aladedunye, F.A., and Przybylski, R. (2012). Radical scavenging activity and performance of novel phenolic antioxidants in oils during storage and frying. *J. Am. Oil Chem. Soc.* **89**: 55–66.
- Cercaci, L., Passalacqua, G., Poerio, A., Rodriguez-Estrada, M. T., and Lercker, G. (2007).



- Composition of total sterols (4-desmethyl-sterols) in extravirgin olive oils obtained with different extraction technologies and their influence on the oil oxidative stability. *Food Chem.* **102**: 66–76.
- Cerecetto, H., and Lopez, G. V. (2007) Antioxidants derived from vitamin E: An overview. *Mini Rev. Med. Chem.* **7**: 315–338.
- Chang, S. S., Peterson, R. J., and Ho, C. T. (1978). Chemical reactions involved in deep-fat frying of foods. *J. Am. Oil Chem. Soc.* **55**: 718–727.
- Che Man, Y. B., and Jaswir, I. (2000). Effect of rosemary and sage extracts on frying performance of refined, bleached and deodorized (RBD) palm olein during deep-fat frying. *Food Chem.* **69**: 301–307.
- Che Man, Y. B., Jialong, L., and Liu, J. L. (1999). The effects of TBHQ and  $\alpha$ -tocopherol on quality characteristics of refined-bleached and deodorized palm olein (RBDPO) during deep-fat frying. *J. Food Lipids*, **6**: 117–129.
- Chebil, L., Humeau, C., Falcimaigne, A., Engasser, J. M., and Ghoul, M. (2006). Enzymatic acylation of flavonoids. *Process Biochem.* **41**: 2237–2251.
- Cheng, K-W., Qingli, W. U., Zheng, Z. P., Peng, X., Simon, J. E., Chen, F., and Wang, M. (2007). Inhibitory effect of fruit extracts on the formation of heterocyclic amines. *J. Agric. Food Chem.* **55**: 10359–10365
- Cheng, K-W., Shi, J-J., Ou, S-Y., Wang, M., and Jiang, Y. (2010). Effect of fruit extracts on the formation of acrylamide in model reactions and fried potato crisps. *J. Agric. Food Chem.* **58**: 309–312
- Chiou, A., Kalogeropoulos, N., Salta, F. N., Efstathiou, P., and Andrikopoulos, N. K. (2009).

- Pan-frying of French fries in three different edible oils enriched with olive leaf extract: Oxidative stability and fate of microconstituents. *LWT – Food Sci. Technol.* **42**: 1090–1097.
- Chirinos, R., Haumán, M., Betalleluz-Pallardel, I., Pedreschi, R., and Campos, D. (2011). Characterisation of phenolic compounds of Inca muña (*Clinopodium bolivianum*) leaves and the feasibility of their application to improve the oxidative stability of soybean oil during frying. *Food Chem.* **128**: 711–716.
- Choe, E., and Min, D. B. (2006). Mechanisms and factors for edible oil oxidation. *Compr. Rev. Food Sci. Food Safety* **5**: 169–186.
- Choo, W-S., and Birch, E.J. (2009). Radical scavenging activity of lipophilized products from lipase-catalyzed transesterification of triolein with cinnamic and ferulic acid. *Lipid* **44**: 145–152.
- Choo, W-S., Birch, E. J., and Stewart, I. (2009). Radical scavenging activity of lipophilized products from transesterification of flaxseed oil with cinnamic acid or ferulic acid. *Lipid* **44**: 807–815.
- Chotimarkorn, C., and Silalai, N. (2008). Addition of rice bran oil to soybean oil during frying increases the oxidative stability of the fried dough from rice flour during storage. *Food Res. Int.* **41**: 308–317.
- Chu, Y-H. (1991). A comparative study of analytical methods for evaluation of soybean oil quality. *J. Am. Oil Chem. Soc.* **68**: 379–384
- Collins, F. W., Fielder, D. A., Sarr, A. B., Redmond, M. J., and Attilio, D. (2002). Process for the

- isolation, recovery and purification of non-polar extractives. *US Patent* 6495140.
- Corsini, M. S., Silva, M. G., and Jorge, N. (2009). Loss in tocopherols and oxidative stability during the frying of frozen cassava chips. *Grasas y Aceites* **60**: 77–81.
- David L. Compton, D. L., Laszlo, J. A., and Evans, K.O. (2012). Antioxidant properties of feruloyl glycerol derivatives. *Ind. Crop Prod.* **36**: 217–221.
- Decker, E. A., Warner, K., Richards, M. P., and Shahidi, F. (2005). Measuring antioxidant effectiveness in food. *J. Agric. Food Chem.* **53**: 4303–4310.
- Dessi, M. A., Deiana, M., Day, B. W., Rosa, A., Banni, S., and Corongiu, F. P. (2002). Oxidative stability of polyunsaturated fatty acids: Effect of squalene. *Eur. J. Lipid Sci. Technol.* **104**: 506–512.
- Dobarganes, M. C., Marquez-Ruiz, G., and Velasco, J. (2000). Interaction between fat and food during deep-frying. *Eur. J. Lipid Sci. Technol.* **102**: 521–528.
- Dong, A., Lee, J., and Shin, H. S. (2011). Influence of natural food ingredients on the formation of heterocyclic amines in fried beef patties and chicken breasts. *Food Sci. Biotechnol.* **20**: 359–365.
- Drusch, S., Groß, N., and Schwarz, K. (2008). Efficient stabilization of bulk fish oil rich in long-chain polyunsaturated fatty acids. *Eur. J. Lipid Sci. Technol.* **110**: 351–359.
- Dutta, P. C., and Appelqvist, L. Å. (1996). Sterols and sterol oxides in the potato products, and sterols in the vegetable oils used for industrial frying operations. *Grasas y Aceites.* **47**: 38–47.
- Dutta, P. C. (1997). Studies on phytosterol oxides. II: Contents in some vegetable oils and in French fries prepared in these oils. *J. Am. Oil Chem. Soc.* **74**: 659–666.

Dziedzic, S. Z., and Hudson, B. J. F. (1984). Phosphatidylethanolamine as a synergist for primary

antioxidants in edible oils. *J. Am. Oil Chem. Soc.* **61**: 1042–1045.

Echavarria, A. P., Pagan, J., and Ibarz, A. (2012). Melanoidins formed by Maillard reaction in food and their biological activity. *Food Eng. Rev.* **4**: 203 – 223.

Edge, R., Land, E. J., McGarvey, D., Mulroy, L., and Truscott, T.G. (1998). Relative one-electron reduction potentials of carotenoid radical cations and the interactions of carotenoids with the vitamin E radical cation. *J. Am. Chem. Soc.* **120**: 4087–4090.

Fakourelis, N., Lee, E. C., and Min, D. B. (1987). Effects of chlorophyll and beta-carotene on the oxidation stability of olive oil. *J. Food Sci.* **52**: 234–235.

Fang, N. B., Yu, S. G., and Badger, T. M. (2003). Characterization of triterpene alcohol and sterol ferulates in rice bran using LC-MS/MS. *J. Agric. Food Chem.* **51**: 3260–3267.

Farhoosh, R., and Kenari, R. E. (2009). Anti-rancidity effects of sesame and rice bran oils on canola oil during deep frying. *J. Am. Oil Chem. Soc.* **86**: 539–544.

Fernandez-Bolanos, J. G., Lopez, O., Fernandez-Bolanos, J., and Rodriguez-Gutierrez, G. (2008).

Hydroxytyrosol and derivatives: Isolation, synthesis, and biological properties. *Curr. Org. Chem.* **12**: 442–463.

Figueroa-Espinoza, M. C., and Villeneuve, P. (2005). Phenolic acids enzymatic lipophilization. *J. Agric. Food Chem.* **53**: 2779–2787.

Filip, S., Hribar, J., and Vidrih, R. (2011). Influence of natural antioxidants on the formation

- of trans fatty-acid isomers during heat treatment of sunflower oil. *Eur. J. Lipid. Sci. Technol.* **113**: 224–230.
- Frankel, E. N. (2007). Antioxidants in food and biology. Facts and fiction, Oily Press Lipid Library, Volume 20, Oily Press, Bridgwater, England.
- Fritsch, C. W. (1981). Measurements of frying fat deterioration: A brief review. *J. Am. Oil Chem. Soc.* **58**: 272–274.
- Fu, J., Cheng, K., Zhang, Z., Fang, R., and Zhu H. (2010). Synthesis, structure and structure-activity relationship analysis of caffeic acid amides as potential antimicrobials. *Eur. J. Med. Chem.* **45**: 2638–2643.
- Fusakawa, R., Kanda, A., and Hara, S. (2009). Anti-oxidative effects of rooibos tea extract on autoxidation and thermal oxidation of lipids. *J. Oleo Sci.* **58**: 275–283.
- Gertz, C., Klostermann, S., and Kochhar, P. S. (2000). Testing and comparing stability of vegetable oils and fats at frying temperature. *Eur. J. Lipid Sci. Technol.* **102**: 543–551.
- Ghavami, M., and Morton, I. D. (1984). Effect of heating at deep-fat frying temperature on the sterol content of soya bean oil. *J. Sci. Food Agric.* **35**: 569–572.
- Gordon, M. H., and Kourimska, L. (1995a). Effect of antioxidants on losses of tocopherols during deep-fat frying. *Food Chem.* **52**: 175–177.
- Gordon, M. H., and Kourimska, L. (1995b). The effects of antioxidants on changes in oils during heating and deep frying. *J. Sci. Food Agric.* **68**: 347–353.
- Gordon, M. H., and Magos, P. (1983). The effect of sterols on the oxidation of edible oils. *Food Chem.* **10**: 141–147.

- Gulcin, I. (2012). Antioxidant activity of food constituents. An overview. *Arch. Toxicol.* **86**: 345–391.
- Hamdi, N., Puerta, M. C., and Valerga, P. (2008). Synthesis, structure, antimicrobial and antioxidant investigations of dicoumarol and related compounds. *Eur. J. Med. Chem.* **43**: 2541–2548.
- Hemalatha, S., and Ghafoorunissa. (2007). Sesame lignans enhance the thermal stability of edible vegetable oils. *Food Chem.* **105**: 1076–1085.
- Hidalgo, F. J., Zamora, R., Alaiz, M., Maza, M.P., Millan, F., and Vioque, E. (1990). Nonenzymatic browning reactions of phospholipids. *Fett. Wiss. Technol.* **92**: 185–188.
- Hidalgo, F. J., and Zamora, R. (2000). The role of lipids in nonenzymatic browning. *Grasas y Aceites* **51**: 35 – 49.
- Hidalgo, F. J., Nogales, F., and Zamora, R. 2005. Changes produced in the antioxidative activity of phospholipids as a consequence of their oxidation. *J. Agric Food Chem.* **53**: 659–662.
- Hidalgo, F. J., León, M. M., and Zamora, R. (2006). Antioxidative activity of amino phospholipids and phospholipid/amino acid mixtures in edible oils as determined by the rancimat method. *J. Agric Food Chem.* **54**: 5461–5467.
- Hidalgo, F. J., León, M. M., and Zamora, R. (2007). Effect of tocopherols in the antioxidative activity of oxidized lipid-amine reaction products. *J. Agric Food Chem.* **55**: 4436–4442.
- Hosseinian, F. S. Muir, A. D., Westcott, N. D., and Krol, E. S. (2006). Antioxidant capacity of flaxseed lignans in two model systems. *J. Am. Oil Chem. Soc.* **83**: 835–840.
- Houhoula, D. P., Oreopoulou, V., and Tzia, C. (2004). Antioxidant efficiency of oregano in

- frying and storage of fried products. *Eur. J. Lipid Sci. Technol.* **106**: 746–751.
- Huang, D., Ou, B., and Prior, R. L. (2005). The chemistry behind antioxidant capacity assays. *J. Agric. Food Chem.* **53**: 1841–1856.
- Husain, S. R., Terao, J., and Matsushita, S. (1984). Comparison of phosphatidylcholine and phosphatidylethanolamine affecting the browning reaction of heated oil. **In**: Amino–Carbonyl Reactions in Food and Biological Systems, pp. 301–309. Fugimaki, M., Namiki, M. and Kato, H., Eds., Elsevier, New York.
- Hwang, H-S., Winkler-Moser, J. K., and Liu, S. X. (2012). Structural effect of lignans and sesamol on polymerization of soybean oil at frying temperature. *J. Am. Oil Chem. Soc.* **89**: 1067–1076.
- Jamilah, B., Che Man, Y. B., and Ching, T. L. (1998). Antioxidant activity of citrus hystrix peel extract in RBD palm olein during frying of fish crackers. *J. Food Lipids* **5**: 149–157.
- Jaswir, I., Che Man, Y. B., and Kitts, D. D. (2000). Use of natural antioxidants in refined palm olein during repeated deep-fat frying. *Food Res. Int.* **33**: 501–508.
- Jennings, B. H., and Akoh, C. C. (2009). Effectiveness of natural versus synthetic antioxidants in a rice oil-based structured lipid. *Food Chem.* **114**: 1456–1461.
- Jiang, G., Lin, S., Wen, L., Jiang, Y., Zhao, M., Chen, F., Prasad, N., Duan, X., and Yang, B. (2013). Identification of a novel phenolic compound in litchi (*Litchi chinensis* sonn.) pericarp and bioactivity evaluation. *Food Chem.* **136**: 563 – 568.
- Johnson, F. C., and Chichester, C. O. (1971). A Critical review of the safety of phenolic antioxidants in foods. *Crit. Rev. Food Technol.* **2:3**: 267–304.
- Jorge, N., Márquez-Ruiz, G., Martín-Polvillo, M., Ruiz-Méndez M. V., and Dobarganes M. C.

- (1996). Influence of dimethylpolysiloxane addition to frying oils: Performance of sunflower oil in discontinuous and continuous laboratory frying. *Grasas y Aceites* **47**: 20–25.
- Juárez, M. D., Osawa, C. C., Acuña, M. E., Sammán, N., and Gonçalves, L. A. G. (2011). Degradation in soybean oil, sunflower oil and partially hydrogenated fats after food frying, monitored by conventional and unconventional methods. *Food Control* **22**: 1920–1927.
- Judde, A., Villeneuve, P., Rossignol-Castera, A., and Guillou, A. L. (2003). Antioxidant effect of soy lecithins on vegetable oil stability and their synergism with tocopherols. *J. Am. Oil. Chem. Soc.* **80**: 1209–1215.
- Jung, M. Y., and Min, D. B. (1992). Effects of oxidized  $\alpha$ -,  $\gamma$ -, and  $\delta$ -tocopherols on the oxidative stability of purified soybean oil. *Food Chem.* **43**: 183–187.
- Jung, Y-S., Kang, T-S., Yoon, J-H., Joe, B-Y., Lim, H-J., Seong, C-M., Park, W-K., Kong, J-Y., Cho J., and Park, N-S. (2002). Synthesis and evaluation of 4-hydroxyphenylacetic acid amides and 4-hydroxycinnamamides as antioxidants. *Bioorg. Med. Chem. Lett.* **12**: 2599–2602.
- Kalantzakis, G., and Blekas, G. (2006). Effect of Greek sage and summer savory extracts on vegetable oil thermal stability. *Eur. J. Lipid Sci. Technol.* **108**: 842–847.
- Kalogianni, E. P., Karastogiannidou, C. K., and Karapantsios, T. D. (2010). Effect of potato presence on the degradation of extra virgin olive oil during frying. *Int. J. Food Sci. Technol.* **45**: 765–775.



- Kamal-Eldin, A., and Appelqvist, L-A. (1996). The chemistry and antioxidant properties of tocopherols and tocotrienols. *Lipids* **31**: 671–701.
- Kanjilal, S., Shanker, K. S., Rao, K. S., Reddy, K. K., Rao, B. V. S. K., Kumar, K. B. S. Kantam, M. L., and Prasad, R. B. N. (2008). Chemo-enzymatic synthesis of lipophilic ferulates and their evaluation for antioxidant and antimicrobial activities. *Eur. J. Lipid Sci. Technol.* **110** : 1175–1182.
- Karoui, I. J., Dhifi, W., Jemia, M. B., and Marzouk, B. (2011). Thermal stability of corn oil flavoured with *Thymus capitatus* under heating and deep-frying conditions. *J. Sci. Food Agric.* **91**: 927–933.
- Kato, H. (1973). Antioxidative activity of amino-carbonyl reaction products. *J. Food Hyg. Soc. Jpn.* **14**: 343 – 351.
- Katsoura, M. H., Polydera, A. C., Tsironis, L. D., Maria P., Petraki, M. P., Rajačić, K. S., Tselepis, A. D., and Stamatis, H. (2009). Efficient enzymatic preparation of hydroxycinnamates in ionic liquids enhances their antioxidant effect on lipoproteins oxidative modification. *New Biotechnol.* **26**: 83–91.
- Khan, M. A., and Shahidi, F. (2000). Tocopherols and phospholipids enhance the oxidative stability of borage and evening primrose triacylglycerols. *J. Food Lipids* **7**: 143–150.
- Khan, M. A., and Shahidi, F. (2001). Effects of natural and synthetic antioxidants on the oxidative stability of borage and evening primrose triacylglycerols. *Food Chem.* **75**: 431–437.
- Kim, H., and Choe, E. (2008). Effects of egg yolk powder addition to the flour dough on the

- lipid oxidation development during frying. *LWT-Food Sci. Technol.* **41**: 845–853.
- Kim M. C., and Pratt, D. E. (1992). Thermal-degradation of phenolic antioxidants. *ACS Symposium Series* **507**: 200–218.
- Kim, M. A., Matoba, T., and Hasegawa, K. (1988). Relationship between the triacylglycerol composition and foaming of mixed coconut oil under deep-fat frying. *Agric. Biol. Chem.* **52**: 693–699.
- King, M. F., Boyd, L. C., and Sheldon, B. W. (1992). Effects of phospholipids on lipid oxidation of a salmon oil model system. *J. Am. Oil Chem. Soc.* **69**: 237–242.
- Kochhar, S. P. (2001). The Composition of Frying Oil. **In**: *Frying: Improving Quality*, pp. 87–114. Rossell, J. B., Ed., Woodhead, Cambridge, England,
- Kochhar, S. P., and Gertz, C. (2004). New theoretical and practical aspects of the frying process. *Eur. J. Lipid Sci. Technol.* **106**: 722–727.
- Koga, T., and Terao, J. (1994). Phospholipids increase radical-scavenging activity of vitamin E in a bulk oil model system. *J. Agric. Food Chem.* **43**: 1450–1454.
- Koga, T., and Terao, J. (1995). Antioxidant activity of a novel phosphatidyl derivative of vitamin E in lard and its model system. *J. Agric. Food Chem.* **42**: 1291–1294.
- Koga, T., Nagao, A., Terao, J., Sawada, K., and Mukai, K. (1994). Synthesis of a phosphatidyl derivative of vitamin E and its antioxidant activity in phospholipid bilayers. *Lipids*, **29**: 83–89.
- Kourimska, L., Pokorny, J., and Réblová, Z. (1994). Phospholipids as inhibitors of oxidation during food storage and frying. *Prehrambeno-technol. biotechnol. rev.* **32**: 91–94.

- Krinsky, N. I., and Yeum, K. J. (2003). Carotenoid-radical interactions. *Biochem. Biophys. Res. Commun.* **305**: 754–760.
- Lambelet, P. F., Saucy, B., and Loliger, J. (1994). Radical exchange reaction between vitamin E, vitamin C, and phospholipids in autooxidized polyunsaturated lipids. *Free Rad. Res.* **20**: 1–10.
- Lampi, A. M., and Kamal-Eldin, A. (1998). Effect of  $\alpha$ - and  $\gamma$ -tocopherols on thermal polymerization of purified high-oleic sunflower triacylglycerols. *J. Am. Oil Chem. Soc.* **75**: 1699–1703.
- Lampi, A. M., Kemmo, S., Mäkelä, A., Heikkinen, S., and Piironen, V. (2009). Distribution of monomeric, dimeric, and polymeric products of stigmasteryl during thermo-oxidation. *Eur. J. Lipid Sci. Technol.* **111**: 1027–1034.
- Larsen, E., Abendroth, J., Partali, V., Schulz, B., Sliwka, H. R., and Quartey, E. G. K. (1998). Combination of vitamin E with a carotenoid:  $\alpha$ -tocopherol and trolox linked to beta-apo-8'-carotenoic acid. *Chem. Eur. J.* **4**: 113–117.
- Lee, E. C., and Min, D. B. (1988). Quenching mechanism of beta-carotene on the chlorophyll-sensitized photooxidation of soybean oil. *J. Food Sci.* **53**: 1894–1895.
- Lee, J. Ozcelik, B., and Min, D. B. (2003). Electron donation mechanisms of  $\beta$ -carotene as a free radical scavenger. *J. Food Sci.* **68**: 861–865.
- Lee, J., Kim, M., and Choe, E. (2007). Antioxidant activity of lignan compounds extracted from roasted sesame oil on the oxidation of sunflower oil. *Food Sci. Biotechnol.* **16**: 981–987.
- Lee, J., Lee, Y., and Choe, E. (2008). Effects of sesamol, sesamin, and sesamolin extracted from

- roasted sesame oil on the thermal oxidation of methyl linoleate. *LWT-Food Sci. Technol.* **41**: 1871–1875.
- Lee, K.G., and Shibamoto, T. (2002). Toxicology and antioxidant activities of non-enzymatic browning reaction products: Review. *Food Rev. Int.* **18**: 151 – 175.
- Lengyel, J. Jan Rimarčík, J., Vagánek, A., Fedor, J., Lukeš, V., and Klein, E. (2012). Oxidation of sterols: Energetics of C–H and O–H bond cleavage. *Food Chem.* **133**: 1435–1440.
- Li, W. (1996). Phytosterol and tocopherol changes in modified canola oils during frying and storage of fried products. M.Sc. Thesis, University of Manitoba, Canada.
- LoNostro, P., Capuzzi, G., Pinelli, P., Mulinacci, N., Romani, A., and Vincieri, F. F. (2000). Self-assembling and antioxidant activity of some vitamin C derivatives. *Colloid Surf. A-Physicochem. Eng. Asp.* **167**: 83–93.
- Lorentz, C., Dulac, A., Pencreac'h, G., Ergon, F., Richomme, P., and Sultani-Vigneron, S. (2010). Lipase-catalyzed synthesis of two new antioxidants: 4-O- and 3-O-palmitoyl chlorogenic acids. *Biotechnol. Lett.* **32**: 1955–1960.
- Magalhaes, L. M., Segundo, M. A., Reis, S., and Lima, J. L. F. C. (2008). Methodological aspects about in vitro evaluation of antioxidant properties. *Anal. Chim. Acta* **613**: 1–19.
- Maguire, L. Konoplyannikov, M., Ford, A., Maguire, A. R., and O'Brien, N. M. (2003). comparison of the cytotoxic effects of  $\beta$ -sitosterol oxides and a cholesterol oxide, 7 $\beta$ -hydroxycholesterol, in cultured mammalian cells. *Br. J. Nutr.* **90**: 767–775.

- Malecka, M. (1991). The effect of squalene on the heat stability of rapeseed oil and model lipids. *Nahrung* **35**: 541–542.
- Malecka, M. (1994). The effect of squalene on the thermostability of rapeseed oil. *Nahrung* **38**: 135–140.
- Manfredini, S., Vertuani, S., Manfredi, B., Rossoni, G., Calviello, G., and Palozza, P. (2000). Novel antioxidant agents deriving from molecular combinations of vitamins C and E analogues: 3,4-dihydroxy-5(R)-[2(R,S)-(6-hydroxy-2,5,7,8-tetramethyl-chroman-2(R,S)-yl-methyl)-[1,3]dioxolan-4(S)-yl]-5H-furan-2-one and 3-O-octadecyl derivatives. *Bioorg. Med. Chem.* **8**: 2791–2801.
- Manzocco, L., Calligaris, S., Mastrocola, D., Nicoli, M. C., and Leric1, C. R. (2001). Review of non-enzymatic browning and antioxidant capacity in processed foods. *Trends Food Sci. Technol.* **11**: 340 – 346.
- Marmesat, S., Velasco, J., Ruiz-Mendez, M. V., Fernandez-Martinez, J. M., and Dobarganes, M. C. (2008). Thermostability of genetically modified sunflower oils differing in fatty acid and tocopherol compositions. *Eur. J. Lipid Sci. Technol.* **110**: 776–782.
- Marmesat, S., Morales, A., Velasco, J., and Dobarganes, M. C. (2010). Action and fate of natural and synthetic antioxidants during frying. *Grasas y Aceites* **61**: 333–340.
- Mateos, R. Dominguez, M. M., Espartero, J. L., and Cert, A. (2003). Antioxidant effect of phenolic compounds,  $\alpha$ -tocopherol, and other minor components in virgin olive oil. *J. Agric. Food Chem.* **51**: 7170–7175.
- Matsuo, T., Kobayashi, T., Kimura, Y., Hosoda, A., Taniguchi, H., and Adachi, S. (2008).

- Continuous synthesis of glyceryl ferulate using immobilized *Candida antarctica* lipase. *J Oleo Sci.* **57**: 375–380.
- Matthäus, B. (2006). Utilization of high-oleic rapeseed oil for deep-fat frying of French fries compared to other commonly used edible oils. *Eur J Lipid Sci Technol.* **108**: 200–211.
- Messina, V., Biolatto, A., Descalzo, A., Sancho, A., Baby, R., and Walsøe de Reca, N. (2009). Effect of pan-frying in extra-virgin olive oil on odour profile, volatile compounds and vitamins. *Int. J. Food Sci. Technol.* **44**: 552–559.
- Mezouari, S., and Eichner, K. (2007). Evaluation of the stability of blends of sunflower and rice bran oil. *Eur. J. Lipid Sci. Technol.* **109**: 531–535.
- Miller, A. and Engel, K.H. (2006). Content of  $\gamma$ -oryzanol and composition of steryl ferulates in brown rice (*Oryza sativa* L.) of European origin. *J. Agric. Food Chem.* **54**: 8127–8133.
- Miller, N. J., Sampson, J., Candeias, L. P., Bramley, P. M., and RiceEvans, C. A. (1996). Antioxidant activities of carotenes and xanthophylls. *FEBS Lett.* **384**: 240–242.
- Miyagawa, K., Hirai, K., and Takezoe, R. (1991). Tocopherol and fluorescence levels in deep-frying oil and their measurement for oil assessment. *J. Am. Oil Chem. Soc.* **68**: 163–166.
- Monu, E. (2007). Phytosterol antioxidant activity and effects on shelf life of fluid milk and yoghurt quality. M.Sc. Thesis, University of Manitoba, Canada.
- Moon, J. K., and Shibamoto, T. (2009). Antioxidant assays for plant and food components. *J. Agric Food Chem.* **57**: 1655 – 1666.
- Morisaki, K., and Ozaki, S. (1996). Design of novel hybrid vitamin C derivatives: Thermal stability and biological activity. *Chem. Pharm. Bull.* **44**: 1647–1655.

- Moure, A., Cruz, J. M., Franco, D., Domínguez, J. M., Sineiro, J., Domínguez, H., Núñez, M. J., and Parajo, J. C. (2001). Natural antioxidants from residual sources. *Food Chem.* **72**: 145 – 171.
- Murkovic, M., Wiltschko, B., and Pfannhauser, W. 1997. Formation of alpha-tocopherolquinone and alpha-tocopherolquinone epoxides in plant oil. *Fett-Lipid.* **99**: 165–169.
- Naalsund, T., Malterud, K. E., Partali, V., and Sliwka, H. R. (2001). Synthesis of a triantioxidant compound: Combination of beta-apo-8'-carotenoic acid, selenacapyloic acid and trolox in a triglyceride. *Chem. Phys. Lipids* **112**: 59–65.
- Nakayama, S., Manabe, A., Suzuki, J., Sakamoto, K., and Inagaki, T. (1987). Comparative effects of two forms of gamma-oryzanol in different sterol compositions on hyperlipidemia induced by cholesterol diet in rats. *Jpn. J. pharmacol.* **44**: 135–143.
- Namiki, M. (1988). Chemistry of Maillard reactions: recent studies on the browning reaction mechanism and the development of antioxidants and mutagens. *Adv. Food Res.* **32**: 115 – 184.
- Namiki, N. (1995). The chemistry and physiological functions of sesame. *Food Rev. Int.* **11**: 281–329.
- Nasibullin, R. S., Nikitina, T. I., Afanas'eva, Y. G., Nasibullin, T. R., and Spirikhin, L. V. (2001). Complex of 3,5,7,3',4'-pentahydroxyflavonol with phosphatidylcholine. *Pharm Chem. J.* **36**: 33–36.
- Navas, P. B., Carrasquero-Durán, A., and Flores, I. (2006). Effect of black tea, garlic and onion

- on corn oil stability and fatty acid composition under accelerated oxidation. *Int. J. Food Sci. Technol.* **41**: 243–247.
- Naz, S., Siddiqi, R., Sheikh, H., and Sayeed, S. A. (2005). Deterioration of olive, corn and soybean oils due to air, light, heat and deep-frying. *Food Res. Int.* **38**: 127–134.
- Neff, W. E., and El-Agaimy, M. A. (1996). Effect of linoleic acid position in triacylglycerols on their oxidative stability. *Food Sci. Technol-LEB.* **29**: 772–775.
- Neff, W. E., Selke, E., Mounts, T. L., Rinsch, W., Frankel, E. N., and Zeitoun, M. A. M. (1992). Effect of triacylglycerol composition and structures on oxidative stability of selected soybean germplasm. *J. Am. Oil Chem. Soc.* **69**: 111–118.
- Neff, W. E., Mounts, T. L., Rinsch, W. M., Konishi, H., and El-Agaimy, M. A. (1994). Oxidative stability of purified canola oil triacylglycerols with altered fatty-acid compositions as affected by triacylglycerol composition and structure. *J. Am. Oil Chem. Soc.* **71**: 1101–1109.
- Neff, W. E., Warner, K., and Eller, F. (2003). Effect of  $\gamma$ -tocopherol on formation of nonvolatile lipid degradation products during frying of potato chips in triolein. *J. Am. Oil Chem. Soc.* **80**: 801–806.
- Nenadis, N., Zafiropoulou, I., and Tsimidou, M. (2003). Commonly used food antioxidants: A comparative study in dispersed systems. *Food Chem.* **82**: 403–407.
- Nichols, J. A., and Kaliyar, S. K. (2010). Skin photoprotection by natural polyphenols: Anti-inflammatory, antioxidant, and DNA repair mechanisms. *Arch. Dermatol. Res.* **302**: 71–83.



- Nogala-Kalucka, M., Korczak, J., Elmada, I., and Wagner, K. H. (2005). Effect of  $\alpha$ - and  $\delta$ -tocopherol on the oxidative stability of a mixed hydrogenated fats under frying conditions. *Eur. Food Res. Technol.* **221**: 291–297.
- Nor, F. M., Mohamed, S., Nor Aini Idris, N. A., and Ismail, R. (2008). Antioxidative properties of *Pandanus amaryllifolius* leaf extracts in accelerated oxidation and deep frying studies. *Food Chem.* **110**: 319–327.
- Nor, F. M., Mohamed, S., Nor Aini Idris, N. A., and Ismail, R. (2009a). Antioxidative properties of *Curcuma longa* leaf extracts in accelerated oxidation and deep frying studies. *J. Am. Oil Chem. Soc.* **86**: 141–147.
- Nor, F. M., Mohamed, S., Nor Aini Idris, N. A., and Ismail, R. (2009b). Antioxidative properties of *Murraya koenigii* leaf extracts in accelerated oxidation and deep frying studies. *Int. J. Food Sci. Nutr.* **60**: 1–11.
- Normand, L., Eskin, N. A. M., and Przybylski, R. (2001). Effect of tocopherols on the frying stability of regular and modified canola oils. *J. Am. Oil Chem. Soc.* **78**: 369–373.
- Nyaradzo, T. L., Chigorimbo-Murefu, Sergio Riva, S., and Burton, S. G. (2009). Lipase-catalysed synthesis of esters of ferulic acid with natural compounds and evaluation of their antioxidant properties. *J. Mol. Catal. B: Enzym.* **56**: 277–282.
- Nyström, L., Achrenius, T., Lampi, A. M., Moreau, R. A., and Piironen, V. (2007). A Comparison of the antioxidant properties of steryl ferulates with tocopherol at high temperature. *Food Chem.* **101**: 947–954.
- Oehrl, L. L., Hansen, A. P., Rohrer, C. A., Fenner, G. P., and Boyd, L. C. (2001). Oxidation of phytosterols in a test food system. *J. Am. Oil Chem. Soc.* **78**: 1073–1078.

- Palozza, P., and Krinsky, N. I. (1992). Antioxidant effects of carotenoids in vitro and in vivo: An overview. *Methods Enzymol.* **213**: 403–420.
- Palozza, P., Piccione, E. R., Avanzi, L., Ventuani, S., Calviello, G., and Manfredini, S. (2002). Design, synthesis, and antioxidant activity of FeAOX-6, a novel agent deriving from a molecular combination of the chromanyl and polyisoprenyl moieties. *Free Radical Bio. Med.* **33**: 1724–1735.
- Pandey, K. B., and Rizvi, S. I. (2009). Plants polyphenols as dietary antioxidants in human health and disease. *Oximed.* **2**: 270–278.
- Parrado, J. Miramontes, E., Jover, M., Marquez, J. C., Angeles Mejias, M., Collantes De Teran, L., Absi, E., and Bautista, J. (2003). Prevention of brain protein and lipid oxidation elicited by a water-soluble oryzanol enzymatic extract derived from rice bran. *Eur. J. Nutr.* **42**: 307–314.
- Peled, M., Gutfinger, T., and Letan, A. (1975). Effect of water and BHT on stability of cottonseed oil during frying. *J. Sci. Food Agric.* **26**: 1655–1666.
- Perron, N. R., and Brumaghim, J. L. (2009). A Review of the antioxidant mechanisms of polyphenol compounds related to iron binding. *Cell Biochem. Biophy.* **53**: 75–100.
- Petukhov, I, Malcolmson, L. J., Przybylski, R., and Armstrong, L. (1999). Frying performance of genetically modified canola oils. *J. Am. Oil Chem. Soc.* **76**: 627–632.
- Piironen, V., Lindsay, D. G., Miettinen, T. A., Toivo, J., and Lampi, A. M. (2000). Plant sterols, biosynthesis, biological function, and their importance to human nutrition. *J. Sci. Food Agric.* **80**: 939–966.

- Poiana, M-A. (2012). Enhancing oxidative stability of sunflower oil during convective and microwave heating using grape seed extract. *Int. J. Mol. Sci.* **13**: 9240 – 9259.
- Pokorny, J., Luan, N. T., and Janicek, G. (1973). Non-enzymatic browning VII. Reaction of some tocopherol oxidation products with protein. *Z. Lebensm. Unters. Forsch.* **152**: 65–70.
- Pokorny, J. (1981). Browning from lipid-protein interactions. *Prog. Food Nutr. Sci.* **5**: 421–428
- Pokorny, J., Réblová, Z., Ranny, M., Kanova, J., Panek, J., and Davidek, J. (1992). Natural lecithins and phosphorylated acylglycerols as inhibitors of autoxidation of fats and oils. *Nahrung* **36**: 461–465.
- Pokorny, J. (2007). Are natural antioxidants better - and safer - than synthetic antioxidants? *Eur. J. Lipid Sci. Technol.* **109**: 629–642.
- Porter, W. L. (1980). Recent Trends in Food Applications of Antioxidants. **In**: Autoxidation in Food and Biological Systems, pp. 295–365. Simic, M. G., and Karel, M., Eds., Plenum Press, New York,
- Procida, G., Cichelli, A., Compagnone, D., Maggio, R.M., Cerretani, L., and Carlo, M. D. (2009). Influence of chemical composition of olive oil on the development of volatile compounds during frying. *Eur. Food Res. Technol.* **230**: 217–229.
- Psomiadou, E., and Tsimidou, M. (1999). On the role of squalene in olive oil stability. *J. Agric Food Chem.* **47**: 4025–4032.
- Psomiadou, E., and Tsimidou, M. (2002a). Stability of virgin olive oil. 1. Autoxidation studies. *J. Agric Food Chem.* **50**: 716–721.

- Psomiadou, E., and Tsimidou, M. (2002b). Stability of virgin olive oil. 2. Photo-oxidation studies. *J. Agric Food Chem.* **50**: 722–727.
- Raederstorff, D. (2009). Antioxidant activity of olive polyphenols in humans: A review. *Int. J. Vitam. Nutr. Res.* **79**: 152–165.
- Rajan, P., Vedernikova, I., Cos, P., Berghe, V. D., Augustyns, K., and Haemers, A. (2001). Synthesis and evaluation of caffeic acid amides as antioxidants. *Bioorg. Med. Chem. Lett.* **11**: 215–217.
- Ramadan, M. F. (2012). Antioxidant characteristics of phenolipids (quercetin-enriched lecithin) in lipid matrix. *Ind. Crops Prod.* **36**: 363–369.
- Ramadan, M. F. (2008). Quercetin increases antioxidant activity of soy lecithin in a triolein model system. *LWT Food Sci. Technol.* **41**: 581–587.
- Rao, M. K. G., and Achaya, K. T. (1968). Antioxidant activity of squalene. *J. Am. Oil Chem. Soc.* **45**: 296–296.
- Reddy, K. K., Shanker, K. S., Ravinder, T., Prasad, R. B. N., and Kanjilal, S. (2010). Chemo-enzymatic synthesis and evaluation of novel structured phenolic lipids as potential lipophilic antioxidants. *Eur. J. Lipid Sci. Technol.* **112**: 600–608.
- Reddy, K. K., Ravinder, T., and Kanjilal, S. (2012). Synthesis and evaluation of antioxidant and antifungal activities of novel ricinoleate-based lipoconjugates of phenolic acids. *Food Chem.* **134**: 2201–2207.
- Rennick, K. A. and Warner, K. (2006). Effect of elevated temperature on development of tocopherolquinones in oils. *J. Agric. Food Chem.* **54**: 2188–2192.

Rietjens, I. M. C. M., Boersma, M. G., de Haan, L., Spenkelink, B., Awad, H. M., Cnubben, N.

H. P., van Zanden, J. J., van der Woude, H., Alink, G. M., and Koeman, J.H. 2002. The prooxidant chemistry of the natural antioxidants vitamin C, vitamin, E, carotenoids and flavonoids. *Environ. Toxicol. Pharmacol.* **11**: 321–333.

Romero, N., Robert, P., Masson, L., Ortiz, J., Gonzalez, K., Tapia, K., and Dobaganes, C. (2007).

Effect of  $\alpha$ -tocopherol,  $\alpha$ -tocotrienol and rosa mosqueta shell extract on the performance of antioxidant-stripped canola oil (brassica sp.) at high temperature. *Food Chem.* **104**: 383–389.

Rossi, M., Alamprese, C., and Ratti, S. (2007). Tocopherols and tocotrienols as free radical-scavengers in refined vegetable oils and their stability during deep-fat frying. *Food Chem.* **102**: 812–817.

Roy, L. G., Arabshahi-Delouee, S., and Urooj, A. (2010). Antioxidant efficacy of mulberry (*Morus indica* L.) leaves extract and powder in edible oil. *Int. J. Food Prop.* **13**: 1–9.

Rudzińska, M., Przybylski, R., and Wąsowicz, E. (2009). Products formed during thermo-oxidative degradation of phytosterols. *J. Am. Oil Chem. Soc.* **86**: 651–662.

Rudzińska, M., Przybylski, R., Zhao, Y. Y., and Curtis, J. M. (2010). Sitosterol thermo-oxidative degradation leads to the formation of dimers, trimers and oligomers: A study using combined size exclusion chromatography/mass spectrometry. *Lipids* **45**, 549 – 558.

Ryan, E., Chopra, J. McCarthy, F. O., Maguire, A. R., and O'Brien, N. M. (2005). Qualitative and

quantitative comparison of the cytotoxic and apoptotic potential of phytosterol oxidation products with their corresponding cholesterol oxidation products.

*Br. J. Nutr.* **94**: 443–451.

Ryan, E., McCarthy, F. O., Maguire, A. R. and O'Brien, N. M. (2009). Phytosterol oxidation products: Their formation, occurrence, and biological effects. *Food Rev. Int.* **25**: 157–174.

Sabally, K., Karboune, S., St-Louis, R., and Kermasha, S. (2006). Lipase-catalyzed transesterification of trilinolein or trilinolenin with selected phenolic acids. *J. Am. Oil Chem. Soc.* **83**: 101–107.

Sánchez-Muniz, F., Botega, D. Z., di Lorenzo, L., Marmesat, S., Bastida, S., Pérez-Olleros, L., and Ruiz-Roso, B. (2007). A non-extractable condensed-tannins fiber reduces thermal oxidation in oils at frying temperature. *Eur. J. Lipid Sci. Technol.* **109**: 1218–1225.

Schieber, A., Stintzing, F. C., and Carle, R. (2001). By-products of plant food processing as a source of functional compounds – recent developments. *Trends Food Sci. Technol.* **12**: 401–413.

Schroeder, M. T., Becker, E. M., and Skibsted, L. H. (2006). Molecular mechanism of antioxidant synergism of tocotrienols and carotenoids in palm oil. *J. Agric. Food Chem.* **54**: 3445–3452.

Seppanen, C. M., Song, Q., and Csallany, A. S. (2010). The Antioxidant functions of tocopherol and tocotrienol homologues in oils, fats, and food system. *J. Am. Oil Chem. Soc.* **87**: 469–481.

Serrano, J., Puupponen-Pimiä, R., Dauer, A., Auri, A.M., and Saura-Calixto, F. (2009). Tannins:

- current knowledge of food sources, intake, bioavailability and biological effects. *Mol. Nutr. Food Res.* **53**: S310-S329.
- Shahidi, F., and Naczki, M. (1995). Food Phenolics: Sources, Chemistry, Effects, Applications. Technomic, Lancaster, PA.
- Shahidi, F., and Wanasundara, J. P. K. (1992). Phenolic Antioxidants. *Crit. Rev. Food Sci. Nutr.* **32**, 67–103.
- Shahidi, F., and Wanasundara, U.N. (1999). Effects of processing and squalene on composition and oxidative stability of seal blubber oil. *J. Food Lipids* **6**: 159–172.
- Shi, J., Nawaz, H., Pohorly, J., Mittal, G., Kakuda, Y., and Jiang, Y. M. (2005). Extraction of polyphenolics from plant material for functional foods - engineering and technology. *Food Rev. Int.* **21**: 139–166.
- Shin, H. S., Strasburg, G. M., and Ustunol, Z. (2003). Influence of different unifloral honeys on heterocyclic aromatic amine formation and overall mutagenicity in fried ground-beef patties. *J. Food Sci.* **68**: 810–815.
- Simonne, A. H., and Eitenmiller, R. R. (1998). Retention of vitamin E and added retinyl palmitate in selected vegetable oils during deep-fat frying and in fried breaded products. *J. Agric. Food Chem.* **46**: 5273-5277.
- Sims, R., Fioriti, J., and Kanuk, M. (1972). Sterol additives as polymerization inhibitors for frying oils. *J. Am. Oil Chem. Soc.* **49**: 298–301.
- Singh, A. (2013). Sitosterol as an antioxidant in frying oils. *Food Chem.* **137**: 62 – 67.
- Singh, S., and Singh, R. P. (2008). In Vitro methods of assay of antioxidants: An overview. *Food Rev. Int.* **24**: 392–415.

- Song, Q. X., Wei, D. Z., Zhou, W. Y., Xu, W. Q., and Yang, S. L. (2004). Enzymatic synthesis and antioxidant properties of L-ascorbyl oleate and L-ascorbyl linoleate. *Biotechnol. Lett.* **26**: 1777–1780.
- Soupas, L., Juntunen, L., Lampi, A. M., and Piironen, V. (2004). Effects of sterol structure, temperature, and lipid medium on phytosterol oxidation. *J. Agric. Food Chem.* **52**: 6845–6491.
- Soupas, L., Huikko, L., Lampi, A. M., and Piironen, V. (2005). Esterification affects phytosterol oxidation. *Eur. J. Lipid Sci. Technol.* **107**: 107–118.
- Steel, C.J., Dobarganes, M. C., and Barrera-Arellano, D. (2005). The influence of natural tocopherols during thermal oxidation of refined and partially hydrogenated soybean oils. *Grasas y Aceites* **56**: 46–52.
- Struijs, K. Lampi, A. M., Ollilainen, V., and Piironen, V. (2010). Dimer formation during the thermo-oxidation of stigmasterol. *Eur. J. Lipid Sci. Technol.* **231**: 853–863.
- Sun, S., Shan, L., Liu, Y., Jin, Q., Song, Y., and Wang, X. (2009). Solvent-free enzymatic synthesis of feruloylated diacylglycerols and kinetic study. *J. Mol. Catal. B: Enzym.* **57**: 104–108.
- Tabee, E., Azadmard-Damirchi, S., Jägerstad, M., and Dutta, P. C. (2008). Effects of  $\alpha$ -tocopherol on oxidative stability and phytosterol oxidation during heating in some regular and high-oleic vegetable oils. *J. Am. Oil Chem. Soc.* **85**: 857–867.
- Tan, Z., and Shahidi, F. (2011). Chemoenzymatic synthesis of phytosteryl ferulates and evaluation of their antioxidant activity. *J. Agric. Food Chem.* **59**: 12375–12383.
- Torres de Pinedo, A., Peñalver, P., Pérez-Victoria, I., Rondón, D., and Morales J. C. (2007).



Synthesis of new phenolic fatty acid esters and their evaluation as lipophilic antioxidants in an oil matrix. *Food Chem.* **105**: 657–665.

Torres, P., Kunamneni, A., Ballesteros, A., and Plou, F. J. (2008). Enzymatic modification for ascorbic acid and alpha-tocopherol to enhance their stability in food and nutritional applications. *Open Food Sci. J.* **2**: 1–9.

Touré, A., and Xueming, X. (2010). Flaxseed lignans: source, biosynthesis, metabolism, antioxidant activity, bio-active components, and health benefits. *Compr. Rev. Food Sci. F.* **9**: 261–269.

Tsaknis, J., Lalas, S., and Protopapa, E. (2002). Effectiveness of the antioxidants BHA and BHT in selected vegetable oils during intermittent heating. *Grasas y Aceites* **53**: 199–205.

Tsen, S. Y., Ameri, F., and Smith, J. S. (2006). Effects of rosemary extracts on the reduction of heterocyclic amines in beef patties. *J. Food Sci.* **71**: C469–C473.

Valenzuela, A., and Nieto, S. (1996). Synthetic and natural antioxidants: food quality protectors. *Grasas y Aceites* **47**: 186–196.

Valls, J., Millan, S., Marti, M. P., Borrás, E., and Arola, L. (2009). Advanced separation methods of food anthocyanins, isoflavones and flavanols. *J. Chromatogr. A* **43**: 7143–7172.

Verleyen, T., Verhe, R., Huyghebaert, A. Dewettinck, K., and Greyt, W. D. (2001). Identification

of  $\alpha$ -tocopherol oxidation products in triolein at elevated temperatures. *J. Agric. Food Chem.* **49**: 1508–1511.

Viskupicova, J., Ondrejovic, M., and Sturdik, E. (2009). The potential and practical applications of acylated flavonoids. *Pharmazie* **64**: 355–360.

- Voisin-Chiret, A. S., Bazin, M. A., Lancelot, J. C., and Rault, S. (2007). Synthesis of new L-ascorbic ferulic acid hybrids. *Molecules* **12**: 2533–2545.
- Wanasundara, P. K. J. P. D., Shahidi, F., and Shukla, V. K. S. (1997). Endogenous antioxidants from oilseeds and edible oils. *Food Res. Int.* **13**: 225 – 292.
- Wang, A., Zhang, F., Huang, L., Yin, X., Li, H., Wang, Q., Zeng, Z., and Xie, T. (2010). New progress in biocatalysis and biotransformation of flavonoids. *J. Med. Plants Res.* **4**: 847–856.
- Warner, K., and Moser, J. (2009). Frying stability of purified mid-oleic sunflower oil triacylglycerols with added pure tocopherols and tocopherol mixtures. *J. Am. Oil Chem. Soc.* **86**: 1199–1207.
- Warner, K. (2004). Chemical and Physical Reactions in Oil During Frying. **In:** Frying Technology and Practices, pp. 77–90. Gupta, M. K., Warner, K., and White, P.J., Eds., Champaign, Illinois,
- Weitkamp, P., Vosmann, K., and Weber, N. (2006). Highly efficient preparation of lipophilic hydroxycinnamates by solvent-free lipase-catalyzed transesterification. *J. Agric. Food Chem.* **54**: 7062–7068.
- Weng, X. C., and Gordon, M. H. (1993). Antioxidant synergy between phosphatidyl ethanolamine and alpha-tocopherylquinone. *Food Chem.* **48**: 165–168.
- White, P. J., and Armstrong, L. S. (1986). Effect of selected oat sterols on the deterioration of heated soybean oil. *J. Am. Oil Chem. Soc.* **63**: 525–529.
- Winkler, J. K., and Warner, K. (2008a). The Effect of phytosterol concentration on oxidative stability and thermal polymerization of heated oils. *Eur. J. Lipid Sci. Technol.* **110**: 455–

464.

Winkler, J. K., and Warner, K. (2008b). Effect of phytosterol structure on thermal polymerization

of soybean oil. *Eur. J. Lipid Sci. Technol.* **110**: 1068–1077.

Winkler-Moser, J. K., Rennick, K. A., Palmquist, D. A., Berhow, M. A., and Vaughn, S. F.

(2012). Comparison of the impact of  $\gamma$ -oryzanol and corn steryl ferulates on the polymerization of soybean oil during frying. *J Am. Oil Chem. Soc.* **89**: 243–252.

Woodall, A. A., Lee, S. W. M., Weesie, R. J., Jackson, M. J., and Britton, G. (1997). Oxidation of carotenoids by free radicals: relationship between structure and reactivity. *Biochim. Biophys. Acta* **1336**: 33–42.

Xia, E. Q., Deng, G. F., Guo, Y. J., and Li, H. B. (2010). Biological activities of polyphenols from grapes. *Int. J. Mol. Sci.* **11**: 622–646.

Xu, Z., and Godber, J. S. (1999). Purification and identification of components of  $\gamma$ -oryzanol in rice bran oil. *J. Agric. Food Chem.* **47**: 2724–2728.

Yamaguchi, N. (1969). Effect of the products of browning reaction from reducing sugars and amino acids on the stability of fats and oils. *J. Jpn. Oil Chem. Soc.* **18**: 111 – 117.

Yang, Z., Guo, Z., and Xu, X. (2012). Enzymatic lipophilisation of phenolic acids through esterification with fatty alcohols in organic solvents. *Food Chem.* **132**: 1311–1315.

Yanishlieva, N. V., and Marinova, E. M. (2001). Stabilisation of edible oils with natural antioxidants. *Eur. J. Lipid Sci. Technol.* **103**: 752–767.

Yanishlieva, N. V., Raneva, V. G., and Marinova, E. M. (2001).  $\beta$ -Carotene in sunflower oil oxidation. *Grasas y Aceites* **52**: 10–16.

Yao, L. H., Jiang, Y. M., Shi, J. Tomas-Barberan, F. A., Datta, N., Singanusong, R., and Chen, S.

S. (2004). Flavonoids in food and their health benefits. *Plant Foods Hum. Nutr.* **59**: 113–122.

Yeo, J. D., Jeong, M. K., Park, C. U., and Lee, J. (2010). Comparing antioxidant effectiveness of natural and synthetic free radical scavengers in thermally-oxidized lard using DPPH method. *J. Food Sci.* **75**: C258–C262.

Yeo, J., Park, J., and Lee, J. (2011). Evaluation of antioxidant capacity of sesamol and free radical scavengers at different heating temperatures. *Eur. J. Lipid Sci. Technol.* **113**: 910–915.

Yoo, K. M., Kim, D. O., and Lee, C. Y. (2007). Evaluation of different methods antioxidant measurement. *Food Sci. Biotechnol.* **16**: 177–182.

Yoshida, H., Tatsumi, M., and Kajimoto, G. (1991). Relationship between oxidative stability of vitamin-E and production of fatty-acids in oils during microwave-heating. *J. Am. Oil Chem. Soc.* **68**: 566–568.

Yoshida, H. (1994). Composition and quality characteristics of sesame seed (*Sesamum indicum*) oil roasted at different temperatures in electric oven. *J. Sci. Food Agric.* **65**: 331–336.

Yuki, E., and Ishikawa, Y. (1976). Tocopherol contents of 9 vegetable frying oils, and their changes under simulated deep-fat frying conditions. *J. Am. Oil Chem. Soc.* **53**: 673–676.

Zamora, R., León, M. M., and Hidalgo, F. J. (2011). Free radical-scavenging activity of nonenzymatically-browned phospholipids produced in the reaction between

- phosphatidylethanolamine and ribose in hydrophobic media. *Food Chem.* **124**: 1490–1495.
- Zeb, A., and Murkovic, M. (2010). Characterization of the effects of  $\beta$ -carotene on the thermal oxidation of triacylglycerols using HPLC-ESI-MS. *Eur. J. Lipid Sci. Technol.* **112**: 1218–1228.
- Zhang, Y., and Zhang, Y. (2007). Study on reduction of acrylamide in fried bread sticks by addition of antioxidant of bamboo leaves and extract of green tea. *Asia Pac. J. Clin. Nutr.* **16**: 131–136.
- Zhang, C. X., Wu, H., and Weng X. C. (2004). Two novel synthetic antioxidants for deep frying oils. *Food Chem.* **84**: 219–222
- Zheng, Y., Branfort-White, C., Wu, X-M., Wu, C-Y., Xie, J-G., Quan, J., and Zhu, L-M. (2010). Enzymatic synthesis of novel feruloylated lipids and their evaluation as antioxidants. *J. Am. Oil Chem. Soc.* **87**: 305–311.
- Zhong, Y., and Shahidi, F. (2011). Lipophilized epigallocatechin gallate (EGCG) derivatives as novel antioxidants. *J. Agric. Food Chem.* **59**: 6526–6533.
- Zhong, Y., and Shahidi, F. (2012). Lipophilised epigallocatechin gallate (EGCG) derivatives and their antioxidant potential in food and biological systems. *Food Chem.* **131**: 22–30.
- Zhong, Y., Ma, C-M., and Shahidi, F. (2012). Antioxidant and antiviral activities of lipophilic epigallocatechin gallate (EGCG) derivatives. *J. Funct. Foods* **4**: 87 – 93.

Legends for Table

- Table 1: Studies on the relative stability of  $\alpha$ - and  $\gamma$ -tocopherols under frying condition
- Table 2: Studies on the antioxidant activity of plant extracts under frying condition
- Table 3: Studies on (chemo)enzymatic modifications of simple phenolic compounds

Legends for Figures

- Figure 1. Type of antioxidants and respective point of antioxidant activity
- Figure 2. Structures of tocochromanols
- Figure 3. Common phytosterols
- Figure 4. Formation of tertiary free radical at C24 of the sterol containing ethylidene configuration in the side chain
- Figure 5. Representative components of  $\gamma$ -oryzanol
- Figure 6. Antioxidant lignan compounds from sesame and flaxseed oils
- Figure 7. Some phenolic and polyphenolic antioxidants
- Figure 8. Common synthetic antioxidants
- Figure 9. Synthetic antioxidants derived from structural modifications of natural antioxidants

Table 1

References	Study	Conclusions
Al-Khusaibi et al. (2012)	Frying of potato chips in a blend of palm olein:canola oil (1:1) at 185°C (7h/day; total of 114 batches/28h) in an 8L capacity fryer	(a) In the blend with 186 µg/g of $\alpha$ - and 186 µg/g of $\gamma$ -tocopherol, $\alpha$ - degradation was slower (186-57) than in $\gamma$ - (186 – 98). (b) In canola oil, no significant difference with $\alpha$ - from 237 – 161, and $\gamma$ - from 246 – 155 µg/g. (c) In palm olein, at 7h, $\gamma$ - was more stable (110 – 96) than $\alpha$ - (101-29), however, at 14, 21 and 28h, 16, 11, and 9 µg/g of $\alpha$ -, respectively were detected, but no $\gamma$ - was detected at these times.
Juárez et al. (2011)	Frying of potatoes, <i>milanesas</i> , and <i>churros</i> in soybean, sunflower and partially hydrogenated oil at 180°C for 7h/day for 2 days in a 3.5L capacity aluminum fryer.	(a) In soybean, $\alpha$ - was more stable with 67% loss (from 149 – 49.1) and $\gamma$ -, 69% loss from 468 – 145 µg/g (b) In partially hydrogenated mixture of vegetable oil, $\alpha$ - was more stable (17% loss; 101 – 84) and $\gamma$ - 66% loss (626 – 210)
Bansal et al. (2010)	Frying of French fries and chicken nuggets in RBD palm olein at 180-185°C (6h/day for 4 days) in an 8L capacity fryer. The control oil was heated under the same conditions without any food fried it	(a) In the heated control, $\alpha$ - was more stable, decreasing from 250 to 50 µg/g at the end of 20 cycle of frying cf to $\gamma$ -, 100 – 10 (b) During frying of both French fries, $\alpha$ - was more stable with a loss of ~40% after 40 cycles and total loss of $\gamma$ - during the same period. (c) During frying of Chicken $\alpha$ - was more stable, ~64% loss cf to ~80% loss of $\gamma$ -
Warner and Moser (2009)	Frying of tortilla chips in	(a) Added singly at ~850 µg/g, $\gamma$ was more

	<p>purified mid-oleic sunflower oil fortified with different combination of tocopherols at 180°C (6h/d for 1 day) in a 500 mL pyrex glass crystallizing dishes</p>	<p>stable after 6h (37 vs 35% retention)            (b) Added together in equal amounts (400 µg/g, each), no difference in stability after 6h (40% retention, each) although γ- was more stable at lower frying time ≤3h)            (c) Added together in equal amounts (360 µg/g, each) in the presence of 60 µg/g δ-, no difference in stability at 1h and 3h, but more γ- was retained after 6h (38 vs 32%).            (d) With higher amount of γ (30 α + 590 γ), α- was more stable (63 vs 22% retention) after 6h            (e) With higher amount of α (750 vs 20) γ- was more stable (62 vs 53% retention)</p>
Aladedunye and Przybylski (2009a)	<p>Frying of French fries in canola oil at 185°C (7h/d for 7 days) under atmospheric condition, carbon dioxide blanketing, and vacuum</p>	<p>(a) Under standard frying condition, α- was more stable than γ- (37 vs 44 ug/g/d degradation rate)            (b) Under carbon dioxide blanketing, α- was more stable than γ- (7 vs 15 ug/g/d degradation rate)            (c) Under vacuum α- was more stable than γ- (2 vs 4 ug/g/d degradation rate)            Initial tocopherols in the oil was 317 α- and 353 γ-</p>
Messina et al. (2009)	<p>Heating of two varieties of extra virgin olive oil at 180°C for 1h</p>	<p>(a) in all varieties of extra virgin olive oil, γ-tocopherol was more stable (~40 – 11 µg/g and 11 – 3 µg/g) compared to α- (165 – 20 µg/g and 120 – 9 µg/g)</p>
Aladedunye and Przybylski (2009b)	<p>Frying of French fries in canola oil at 185 and 215°C (7h/d for 7 days)</p>	<p>(a) at 185°C, α- (from 214 – 93 µg/g) more stable than γ- (347 – 115 µg/g)            (b) at 215°C, γ- (347 – 55 µg/g) more stable</p>



than  $\alpha$ - (214 – 10  $\mu\text{g/g}$ ) at the end of the 3<sup>rd</sup> day. All tocopherol were lost at the end of the 6<sup>th</sup> day at 215°C

Corsini et al. (2009)  
Data reprocessed by  
regression analysis

Frying of cassava chips in  
refined cottonseed oil at 180°C  
(5h/d for 5 days)

The initial content of  $\alpha$ - and  $\gamma$ - were 432 and 286  $\mu\text{g/g}$ , respectively.  $\gamma$ - was more stable with loss of 2.5  $\mu\text{g/g/d}$  compared to  $\alpha$ - at 3.7  $\mu\text{g/g/d}$ .

Marmesat et al. (2008)

Heating of genetically  
modified sunflower oil at  
180°C for up to 25h using a  
Rancimat

(a)  $\gamma$ - in modified sunflower oil containing only  $\gamma$  was more stable (808 – 241  $\mu\text{g/g}$ ) than  $\alpha$ - in sunflower oil containing only  $\alpha$ - isomer (826 – 28  $\mu\text{g/g}$ )  
(b)  $\gamma$ - was more stable (403 – 235 than  $\alpha$ - (420 – 152) in a 50:50 mixture of both sunflower oils after 10h of heating.

Rossi et al. (2007)  
 $\gamma$ -tocopherol was not  
detected  
in the oil

Frying of potatoes in palm oil  
at 175°C for 18h (6 h/d)

$\alpha$ -tocotrienol was more stable (259 – 199  $\mu\text{g/g}$ ) than  $\gamma$ -tocotrienol (438 – 75  $\mu\text{g/g}$ )

Matthäus (2006)

Frying of French fries in  
Higholeic/low linolenic canola  
and partially hydrogenated  
canola oils at 175°C (6h/d,  
12d)

$\alpha$ -tocopherol was more stable than  $\gamma$ -tocopherol

Steel et al. (2005)

Heating of refined soybean and  
partially hydrogenated soybean  
at 180°C for 10h in a Rancimat

$\alpha$ - was more stable than  $\gamma$ - for soybean oils with IV 130, 115, and 95. Residual  $\gamma$ - were 27, 17, and 12 for soybean 130, 115, and 95, respectively. The corresponding  $\alpha$ - contents

		were ~38, 27, and 18 µg/g. The initial tocopherol ranged from 200-218, α- and 841 – 931 µg/g, γ-
Barrerra-Arellano et al. (2002)	Heating of palm olein, olive, sunflower, rapeseed and soybean oils at 180°C for 10h in a Rancimat	(a) In all natural oils γ-tocopherol was more stable (b) In stripped palm and soybean oils supplemented with 250 µg/g each of α- and γ-, the γ-isomer was slightly more stable
Normand et al. (2001)	Frying of French fries in regular, hydrogenated, low linoleic, and high linolenic canola oil at 175°C (12h/d; 6d)	In all oils, α-tocopherol was more stable
Barrerra-Arellano et al. (1999)	Heating of tocopherol fortified triolein, trilinolein and their 1:1 mixture at 180°C for 10h in a Rancimat	α-tocopherol was less stable than γ-tocopherol
Simonne and Eitenmiller (1998) No γ-tocopherol was detected in the palm olein	Frying of wet cotton-balls in soybean, corn and palm olein at 185°C (10h/d for 3d)	(a) In soybean oil, α- was more stable (79 – 7 µg/g) than γ- (474 – 9 µg/g) (b) In corn oil, α- was more stable (123 – 93 µg/g) than γ- (585 – 206 µg/g)
Lampi and Kamal-Eldin (1998)	Heating of rapeseed oil, sunflower oil, and tocopherol fortified high-oleic sunflower oil at 180°C in an oven for up to 24h	In all oils, γ-tocopherol was more stable than α-
Li (1996)	Frying of French fries in regular, hydrogenated, low	In all oils, α-tocopherol was more stable

	linoleic, and high linolenic canola oil at 180°C (8h/d; 5d)	
Gordon and Kourimska (1995a)	Frying of potato chips in rapeseed oil at 162°C for 6d (12 batches/d)	$\gamma$ - was more stable ( $t_{1/2}$ , 7-8 frying operations) than $\alpha$ - ( $t_{1/2}$ , 4-5 frying operations).
Miyagawa et al (1991)	Frying of French fries, with and without coating, in a mixture of soybean and canola oils at 180°C (32 frying operation; 17min/frying operation)	(a) $\alpha$ - was more stable (83% retention) than $\gamma$ - (50% retention) during tempura-frying (b) $\alpha$ - was more stable (48% retention) than $\gamma$ - (25% retention) during frying without coating.
Yuki and Ishikawa (1976)	Heating of soybean, canola, rice bran, corn, cottonseed, and safflower oil at 180°C with continuous water spraying and gentle agitation of oil for 10h	$\alpha$ -tocopherol was more stable in all oils

Table 2

References	Polyphenolic sources	Fat/oil substrate	Conditions	Conclusions
Aydeniz and Yilmaz (2012)	Olive leaf, hazelnut leaf, hazelnut green leafy cover	Canola oil	Frying of dough patties at 180°C (~5h/d; 7d)	Only hazelnut green leafy cover extract at 200µg/g phenolic equivalence (PE) significantly inhibited thermooxidation as measured by TPC
Betalleluz-Pallardel et al (2012)	Andea mashua ( <i>Tropaeolum tuberosum</i> )	Soybean oil	Frying of batches of potatoes at 175°C for 4h	Extract at 200µg/g PE significantly inhibited thermooxidation as measured by CD, CT, FFA, and TPC
Aranha and Jorge (2012)	Oregano	Soybean	Heating of oil at 180°C for 20h	Extract at 3000µg/g significantly inhibited thermooxidation as measured by TPC
Poiana (2012)	Grape seed	Sunflower oil	Heating at 180°C for up to 4h	Extract at 600-800µg/g significantly inhibited thermooxidation as measured by PV, AnV, totox value, K232 and 268
Chirinos et al. (2011)	Inca munã ( <i>clinopodium bolivianum</i> ) leaves	Soybean oil	Frying of batches of potatoes at 180°C for 4.5h	Extract at 600µg/g PE significantly inhibited thermooxidation as measured by CD, CT, AnV, and TPC

Filip et al. (2011)	Rosemary	Sunflower	Heating of oil at 180°C for 120h	Extract at 1000µg/g significantly inhibited trans fatty acid formation
Al-Bandak and Oreopoulou (2011)	<i>Majorana syriaca</i>	Corn oil	Frying of potato at 185°C for up to 16h	Extract at 500µg/g significantly inhibited thermooxidation as measured by TPC and CD
Karoui et al. (2011)	Thyme flower	Corn oil	Frying of 1 batch of potato at 180°C; and Racimat of the fried oil at 120°C	Extract at 12.5% significantly increased Induction time of fresh and fried oil
Dong et al. (2011)	Korean bramble		Ground beef mixed with extracts and pan-frying of patties at 230°C for 8 min, each side	Extract significantly inhibited the formation of heterocyclic amines
Ali (2010)	Pomposia fruits	Sunflower oil	Frying of French fries every 30 min for 12h at 180°C	Extract at 800 and 1000µg/g inhibited degradation as measured by AV, PV, TBARs, and polymer formation
Abd-ElGhany et al. (2010)	Olive waste cake	Sunflower oil	Heating of oil at 180°C (4h/d; 5d)	Extract at 200-600µg/g significantly inhibited thermooxidation as measured by PV, FFA, IV, TPC and oxFA
Roy et al. (2010)	Mulberry leaves	Rice bran	Heating at 180°C	Extract at 200µg/g inhibited

		oil	for 1h	thermooxidation as measured by PV
Cheng et al. (2010)	Apple, blueberry, mangosteen, dragon fruits	Peanut oil	Potatoes immersed in fruit extracts and then fried at 170°C for 5 min	Apple and its proanthocyanidins fractions significantly inhibited acrylamide formation at 0,05 and 0,1%
Botega et al. (2009)	Denatured carob fiber (Exxenterol®)	Sunflower oil	Heated up to 16h at 180°C	Significantly inhibited thermooxidation especially at 50µg/g as measured by polar materials formation
Nor et al. (2009a)	<i>Curcuma longa</i> (turmeric) leaf	Palm olein	Frying of French fries at 180°C (8h/d; 5d)	Inhibited thermooxidation at 0,2% as measured by FFA, PV, and AnV
Nor et al. (2009b)	<i>Murraya koenigii</i> leaf	Palm olein	Frying of French fries at 180°C (8h/d; 5d)	Inhibited thermooxidation at 0,2% as measured by FFA, PV, and AnV
Fukasawa et al. (2009)	Rooibos tea	Soybean oil	Rancimat at 120, 140, 160 and 180°C	Extract effectively increased the induction time especially at 160 and 180°C
Chiou et al. (2009)	Olive leaf	Sunflower, olive, and palm oils	Rancimat at 110°C, and pan-frying at 175°C for 6 min	Higher DPPH and induction time; positive protection factor and tocopherol retention

Nor et al. (2008)	<i>Pandanus amaryllifolius</i> leaf	Palm olein	Frying of French fries at 180°C (8h/d; 5d)	Inhibited thermooxidation at 0.2% as measured by FFA, PV, AnV and oligomer formation
Abdalla et al. (2007)	Mango seed Kernel	Sunflower oil	Oil was extracted from potato chips fried at 180°C for 7 min, hourly (8h/d; 7d)	Extract significantly inhibited oxidation as measured by PV, AV, and FFA
Cheng et al. (2007)	Apple, elderberry, grape seed, pineapple		Ground beef mixed with extracts and pan-frying of patties at 210°C for 6 min, each side	All extracts, especially apple and grape seed, significantly inhibited the formation of total heterocyclic amine
Zhang and Zhang (2007)	Bamboo, green tea leaves	Vegetable oil	Mixed with wheat flour prior to dough preparation, bread stick deep-fried at 180°C	green tea (100 µg/g) and bamboo (1000 µg/g) inhibited acrylamide formation by more than 72%
Sanchez-Muniz et al. (2007)	Denatured carob fiber (Exxenterol®)	Olive, sunflower oils	Heating at 180°C for 36h	Significantly inhibited polar materials and oligomer formation
Kalantzakis and Blekas (2006)	Greek sage and summer savory	Virgin olive, refined olive, sunflower and	Heating at 180°C for 10h	Extract at 3000µg/g significantly inhibited thermooxidation as measured by TPC and AnV

		commercial blend of oils		
Tsen et al. (2006)	Rosemary		Powder/extract mixed with ground beef and patties pan-fried at 191°C for 5min, each side or 204°C, 7.5min each side	Extracts effectively inhibited total heterocyclic amine formation
Navas et al. (2006)	Black tea, garlic bulb, onion skin	Corn oil	Heating at 140°C for 48h	Reduced PV, but no significant effect when measured by percentage of non-eluted fatty acid fraction
Naz et al. (2005)	Black tea leaves	Corn oil	Frying of potato at 180°C for 90 min	Inhibited thermooxidation as measured by PV and AnV
Houhoula et al. (2004)	Oregano	Cottonseed	Frying of potato at 185°C for up to 12h	Powder/extract inhibited thermooxidation as measured by CD, TPC, AnV and oligomer formation
Shin et al. (2003)	Buckwheat, clover, sage		Mixed with ground beef and patties pan-fried at 225°C for 10min, each side	Formation of total heterocyclic amines effectively inhibited
Che Man and Jaswir	Oleoresin rosemary,	Palm olein	Frying of potato at	Extract at 0.40% significantly



(2000)	sage		180°C (~5h/d; 6d)	inhibited thermooxidation as measured by PV, FFA, IV, AnV, and polymer content
Britt et al. (1998)	Tart cherry		Mixed with ground beef and patties pan-fried at 175°C for 8min, each side	Inhibited heterocyclic amine formation; cholesterol oxide formation in the oil; and TBARs
Jamilah et al. (1998)	Citrus hystrix peel	Palm olein	Frying of fish crackers at 180°C (5h/d; 4d)	Extract inhibited thermooxidative degradation as measured by PV, AnV, totox value, FFA, and viscosity
Gordon and Kourimska (1995b)	Rosemary	Rapeseed	Frying of potato chips at 180°C (2 batches/d, 10 min each; 6days)	Extract significantly inhibited dimers formation

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Table 3

Reference	Study	Antioxidant assay	Results
Compton et al. (2012)	Enzymatic esterification of ethyl ferulate with glycerol and soybean oil mono and diacylglycerols	a. DPPH b. AAPH (peroxidation of $\gamma$ -linolenic acid)	Similar activity as controls (ferulic acid in DPPH and ethyl ferulate in AAPH)
Yang et al. (2012)	Enzymatic esterification of ferulic, caffeic and dihydrocaffeic acids with C4 – C18 straight chain fatty alcohol	Not evaluated	-
Tan and Shahidi (2011)	Chemoenzymatic synthesis of phytosteryl ferulate	a. TBARs b. ORAC	Better than ferulic and the vinyl ferulate intermediate in both tests
Reddy et al. (2010)	Chemoenzymatic synthesis of structured TAG bearing ferulic acid at Sn-1/3 position	a. DPPH b. Rancimat at 110°C c. Autoxidation of linoleic acid	No difference in DPPH compared to ferulic acid Improved activity under Rancimat and linoleic acid assay
Zheng et al. (2010)	Enzymatic esterification of ferulic acid and tributyrin	a. $\text{OH}^\cdot$ $\text{O}_2^\cdot$ , DPPH scavenging b. Autoxidation of linoleic acid c. Reducing power	Better than ferulic acid under all assays
Choo et al. (2009)	Enzymatic esterification of cinnamic and ferulic acids with flaxseed oil	DPPH	Ferulic acid derivative had lower activity than ferulic acid; Cinnamic acid derivative had higher activity than cinnamic acid

Sun et al. (2009)	Enzymatic synthesis of feruloylated diacyl glycerols by esterification of glyceryl ferulate and oleic acid	Not evaluated	-
Katsoura et al. (2009)	Enzymatic esterification of several hydroxycinnamic acids with various C2-C8 aliphatic alcohol in ionic liquid	Inhibition of LDL, HDL, and total serum	Improved antioxidant activity towards the oxidation of LDL, HDL, and total serum Ferulic acid derivative had lower activity than ferulic acid; Cinnamic acid derivative had higher activity than cinnamic acid
Choo and Birch (2009)	Enzymatic esterification of triolein with cinnamic and ferulic acids	DPPH	
Nyaradzo et al. (2009)	Enzymatic esterification of ferulic acid with hydroxyl steroids and p-arbutin	a. ABTS b. DPPH c. LDL oxidation	Better activity than the ferulic acid precursor
Kanjilal et al. (2008)	Chemoenzymatic synthesis of structured TAG bearing ferulic acid	DPPH	Weaker than BHT (not compared with ferulic acid)
Matsuo et al. (2008)	Enzymatic condensation of ferulic acid and glycerol	Not evaluated	-
Torres de Pinedo et al. (2007)	Enzymatic esterification of different classes of phenolic acid and fatty acid alcohols	a. ABTS b. Rancimat at 120°C	Good antioxidant activity (not compared with phenolic acids; but compared with ascorbyl palmitate and $\alpha$ -tocopherol)
Sabally et al. (2006)	Enzymatic esterification of dihydrocaffeic acid and ferulic acid with	DPPH	Reduced radical scavenging compared to the

	trilinolein and trilinolenin		respective phenolic acid
Weltkamp et al. (2006)	Enzymatic esterification of hydroxycinnamic acids and fatty alcohols	Not evaluated	-

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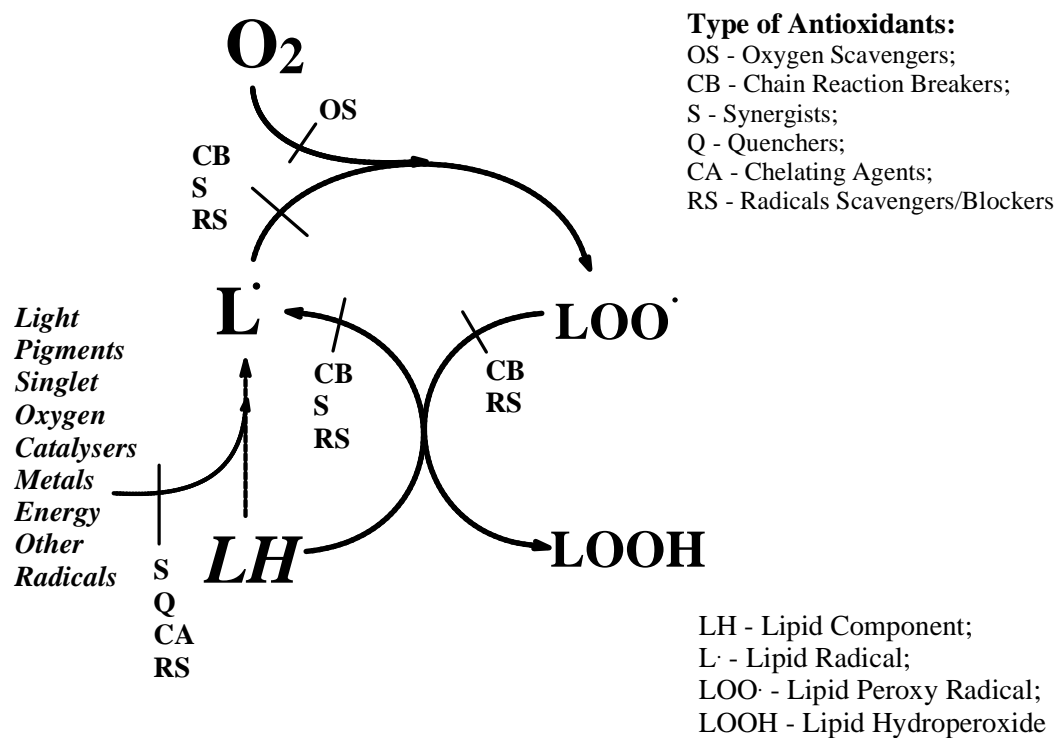
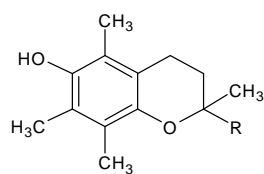
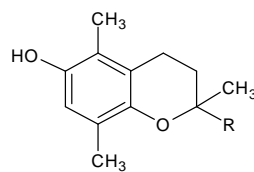


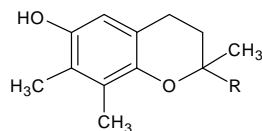
Figure 1



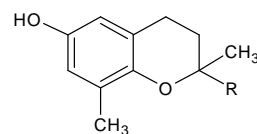
alpha-



beta-

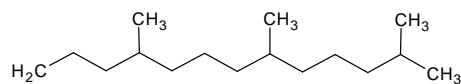


gamma-



delta-

Tocopherols ; R =



Tocotrienols ; R =

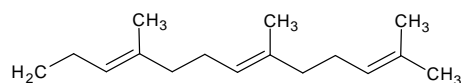


Figure 2

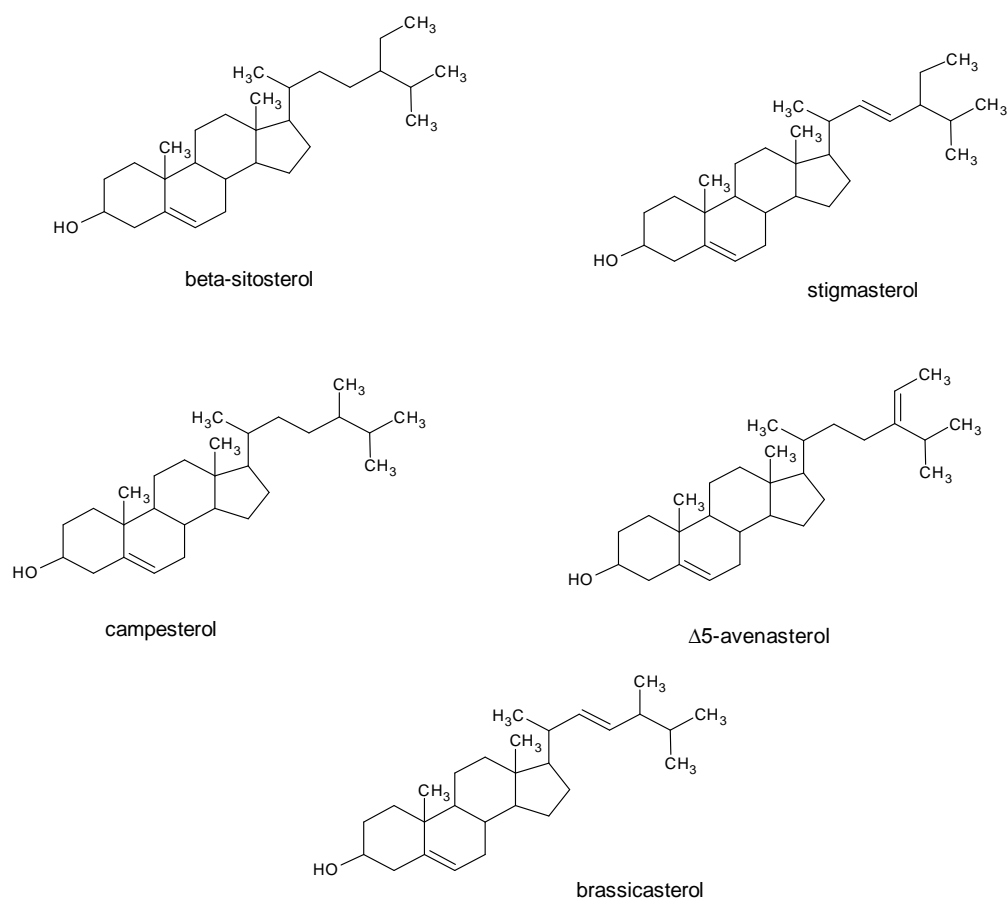


Figure 3

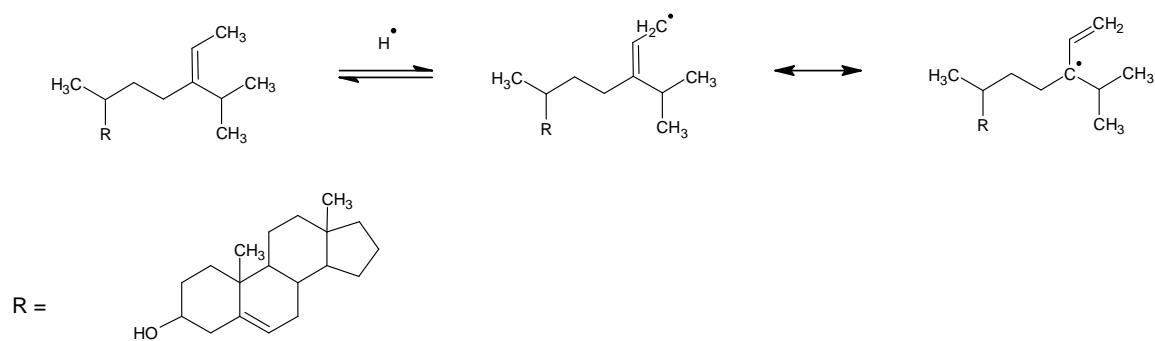


Figure 4

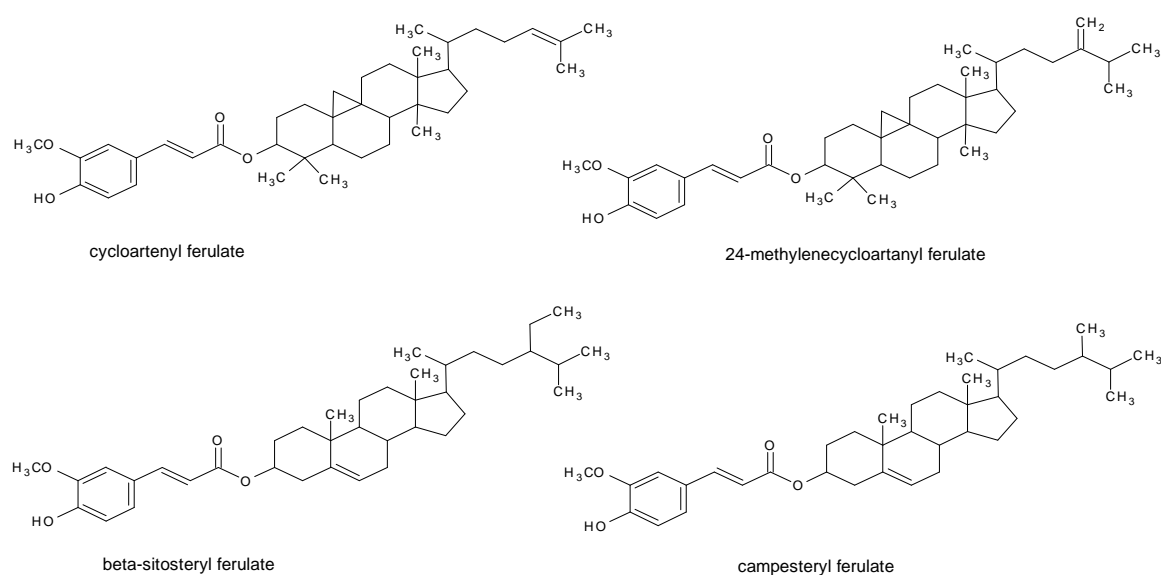


Figure 5



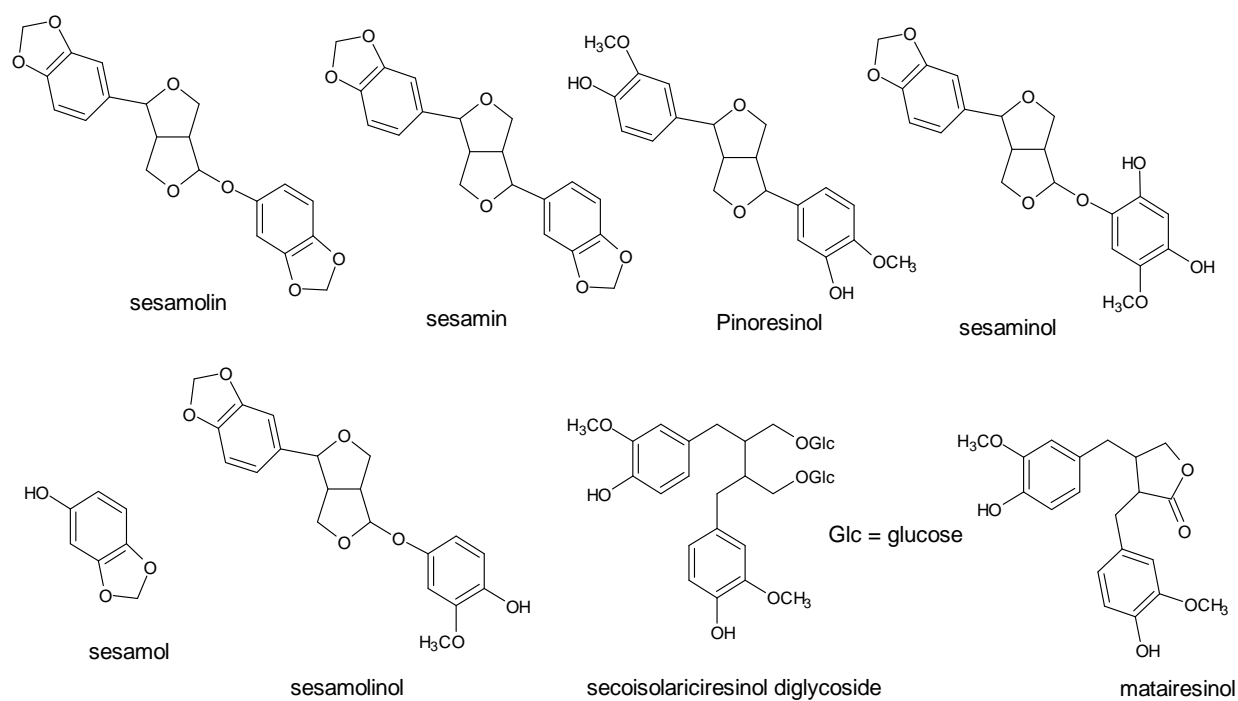


Figure 6

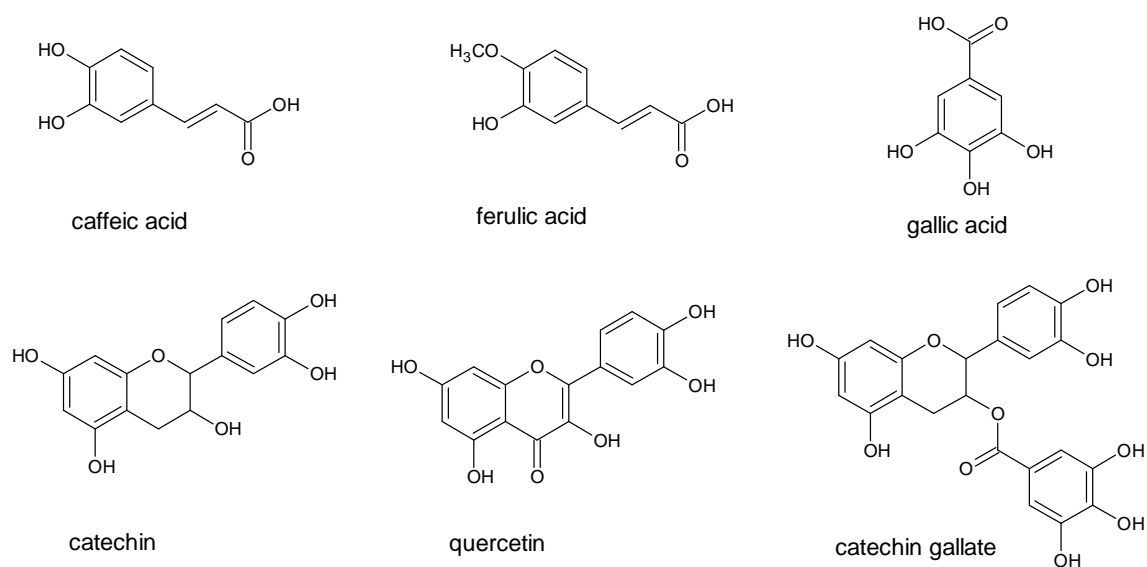
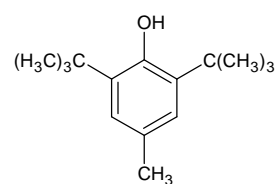
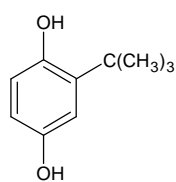


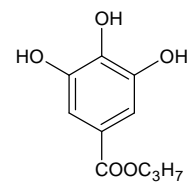
Figure 7



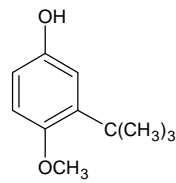
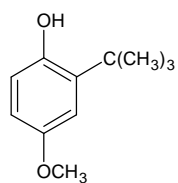
butylated hydroxytoluene (BHT)



tert-butylhydroquinone (TBHQ)



propyl gallate (PG)



butylated hydroxyanisole (BHA)

Figure 8

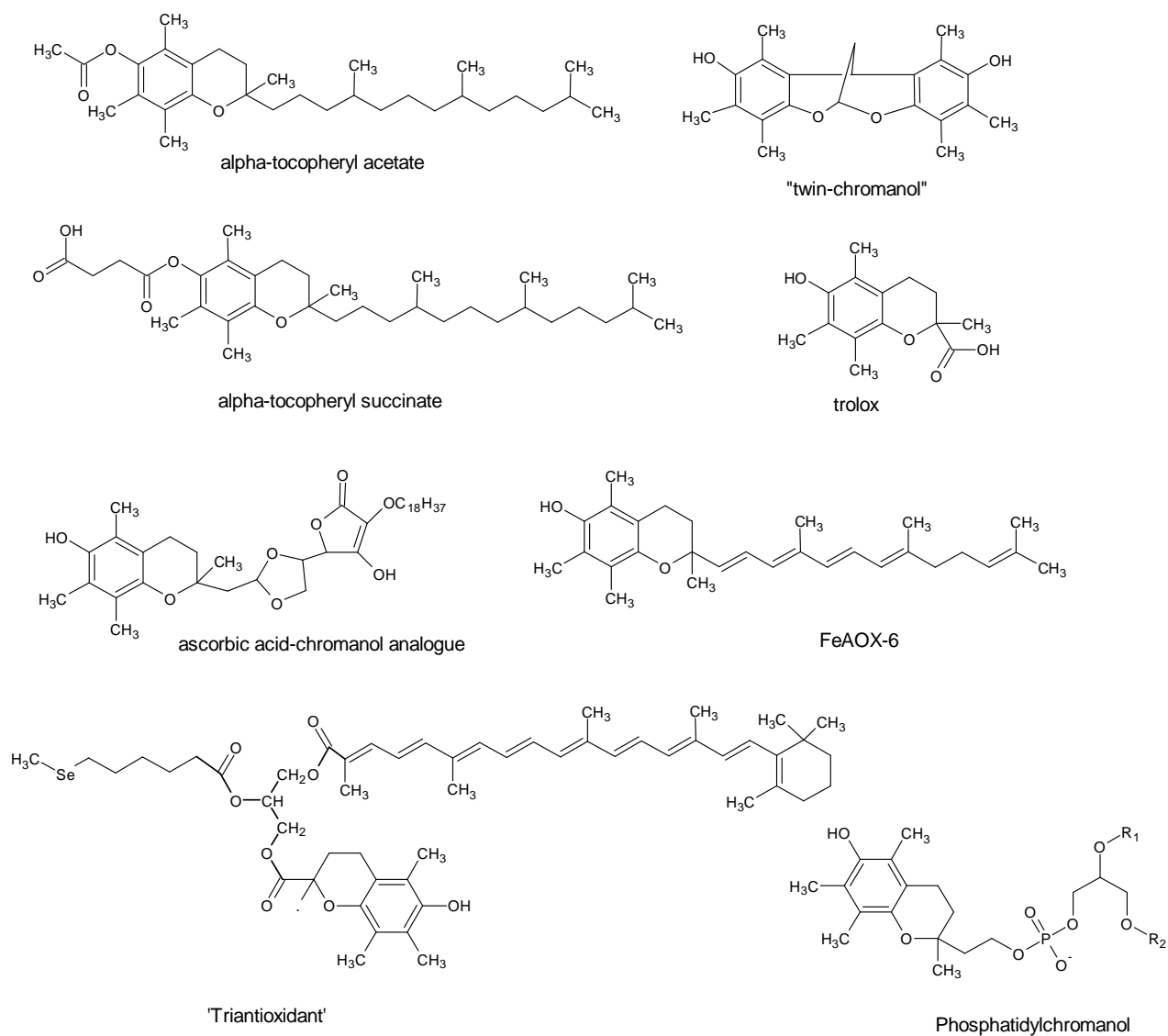


Figure 9