

Review Article

Natural antioxidants as stabilizers of frying oils*

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Frying is a very complex process and the applied conditions often overwhelm most endogenous and added antioxidants. Synthetic antioxidants such as butylated hydroxytoluene (BHT), butylated hydroxyanisole (BHA), and *tert*-butylhydroquinone (TBHQ) are often added to processed oils to retard oxidative degradation during storage and frying; however, beside their poor performance under frying conditions, consumers' acceptance of synthetic antioxidants remains negative due to their perceived detrimental effect on human health. Consequently, there is a growing interest in the search for effective natural antioxidants for frying applications, notably, from phenolic components of common spices and herbs. The present study provides an overview of the literature on natural antioxidants, sources, and their performance under frying conditions.

Practical applications: Sources and performance of natural antioxidants during frying were reviewed. Despite abundance of data on the radical scavenging activity and antioxidant potency of some natural antioxidants under storage conditions, there is still a dearth of information on their activity during frying. This study revealed a number of under-exploited sources of natural antioxidants that could be used to improve the stability of frying oils.

Keywords: Endogenous minor components / Frying / Natural antioxidants / Phenolic extracts

Received: November 4, 2013 / Revised: January 2, 2014 / Accepted: February 3, 2014

DOI: 10.1002/ejlt.201300267

1 Introduction

Deep fat frying is the process of cooking foods by immersing them in edible fat or oil at a temperature above the boiling point of water, usually 150–200°C. Although an ancient food preparation technique, frying has grown exponentially over the last 50 years, and the consumption of fried food continues to grow even in the midst of various campaigns against dietary fat consumption. Indeed, frying is a very effective way of cooking food, delivering products with desirable sensory properties such as a golden crust, crispy texture, and unique fried food flavors within a reasonably short amount of time. During repeated frying, such as is happening in commercial frying operations, the oil is continuously used at elevated

temperature, often topped-up with fresh oil regularly. The elevated temperature, continuous exposure to oxygen, coupled with the presence of water from the food result in a series of chemical reactions with consequent degradation of the frying oil and food components. More than 500 different chemical compounds have been detected as a result of the complex reactions occurring during frying [1], and a number of these compounds can compromise the sensory attributes, shelf-life, and safety of fried foods.

The presence of antioxidants in frying oils can extend both the fry-life of the oils and the shelf-life of the fried products. Simply put, antioxidants are compounds possessing the ability to inhibit oxidation when present in food or biological systems at comparatively lower concentrations to the substrates [2]. Depending on the structural features of the antioxidative compounds, the mechanism of action may include: scavenging free radicals; chelating prooxidant metal ions; quenching singlet oxygen; inactivating sensitizers; creating oxygen barrier, and; decomposing or removing lipid degradation products, among others. Whereas radical

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Abbreviations: BHT, butylated hydroxytoluene; MRP, Maillard reaction products; TBHQ, *tert*-butylhydroquinone; TPC, total polar components

*This paper is part of a Special Issue on deep frying which can be accessed online at <http://onlinelibrary.wiley.com/doi/10.1002/ejlt.v116.6/issuetoc>

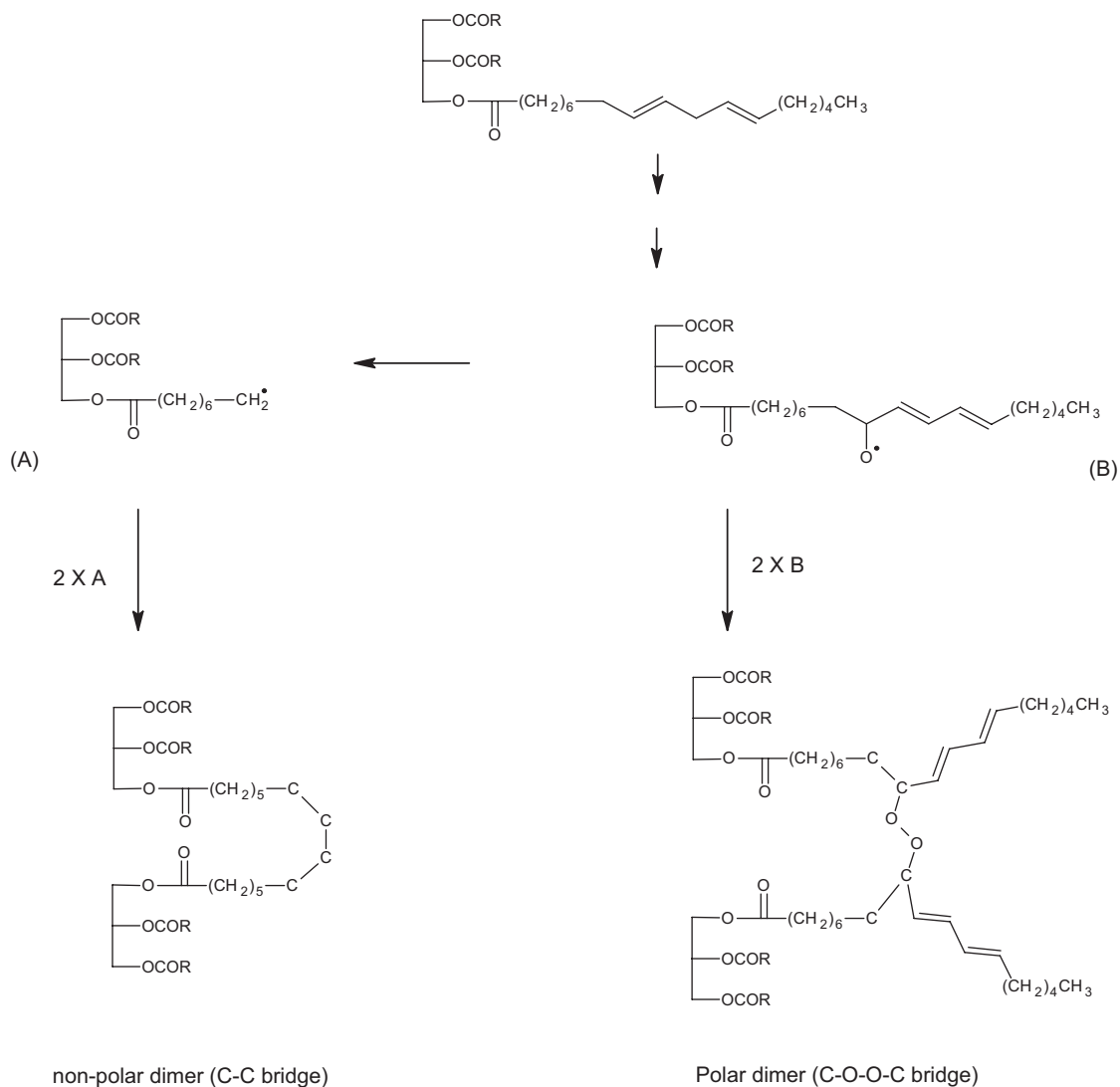


Figure 1. Radical mechanism for the formation of polar and non-polar dimers.

scavenging is generally considered as the predominant antioxidant mechanism in biological systems and under ambient and storage conditions (Fig. 1), it is becoming increasingly evident that radical-mediated deterioration may be relatively less significant under frying conditions [3–5]. In a typical frying operation, with the oxygen supply being rather limited by solubility and steam blanketing from food, a non-radical, acid-catalyzed di- and polymerization of unsaturated fatty acid (Fig. 2) has been suggested to predominate [3–5]. The implication of this is that lipid antioxidants, which operate almost exclusively by radical scavenging mechanism, may perform poorly during actual frying operation despite excellent activity under storage conditions. Based on the later mechanism (Fig. 2), compounds such as phytosterols and sesamol, which can undergo acid-catalyzed decomposition reaction with activation energy lower than that of TAG

dimerization, are effective polymerization inhibitor even though they exhibit negligible radical scavenging activity [5]. Further study is, however, required to verify whether the acid-catalyzed conversion of sterols such as β -sitosterol to steradienes is the principal antioxidant mechanism or the radical scavenging activity of the produced steradienes. According to Winkler and Warner [6], the presence of at least two double bonds is a pre-requisite for phytosterol antioxidant activity. Similarly, additional study is required as to whether the acid-catalyzed decomposition of sesamol is indeed the protective mechanism or the excellent radical scavenging activity of sesamol, its degradation product.

Antioxidants can further be classified into natural, synthetic, or semi-synthetic (chemically modified natural antioxidants), based on source; and the natural antioxidants can be endogenous, exogenous, or generated in situ.

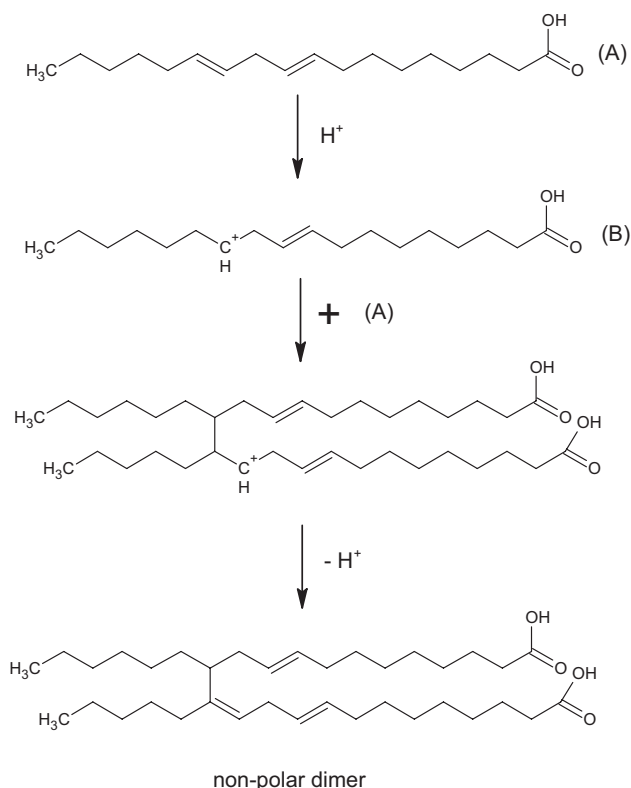


Figure 2. Acid-catalyzed non-radical mechanism for the formation of non-polar dimer [3].

Endogenous antioxidants such as tocopherols, phytosterols, carotenoids, and phospholipids (Table 1) are part of the unsaponifiable components of fats and oils, representing about 5% of the total lipid composition [7]. The antioxidant performance of these endogenous minor components in vegetable oils and fats under storage and frying conditions has been adequately reviewed [8–10]. Suffice to say, however, that due to some inherent shortcomings (e.g., weak antioxidant activity, poor thermal stability, and loss during processing) of the endogenous antioxidants, a number of synthetic antioxidants including butylated hydroxytoluene

Table 1. Common antioxidative endogenous minor components in edible oils

Class of compounds	Examples
Hydrocarbons	Squalene
Phytosterols	β -Sitosterol, stigmasterol
Tocochromanols	α -, β -, γ -, δ -Tocopherol/tocotrienols
Phenolic compounds	Phenolic acids, flavonoids, and isoflavonoids
Carotenoids	Carotenes, xanthophylls
Phospholipids	Phosphatidylcholine, phosphatidylethanolamine

(BHT), butylated hydroxyanisole (BHA), and *tert*-butylhydroxyquinone (TBHQ) are often added to improve thermooxidative stability of fats/oils. Unfortunately, the use of these common synthetic antioxidants has been limited due to their failure to meet performance expectations, especially under frying conditions, and their perceived detrimental effect on human health [11]. Thus, the search for effective exogenous antioxidants from natural sources to stabilize frying oils remains an ongoing story, the recent trends being the application of phenolic extracts from various parts of plants.

In this review, literature reports on the performance of applied natural antioxidants in vegetable oils/fats under frying conditions are summarized. Potential sources, challenges, and limitations of natural antioxidants for frying applications are also enumerated.

2 Natural antioxidants

2.1 Endogenous

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 (Table 1). As previously mentioned, the capacity of these endogenous minor components to protect oils/fats under frying conditions has been adequately reviewed [8–10] and will only be briefly mentioned in the present study.

The most important and often studied endogenous antioxidants are the tocopherols and tocotrienols, collectively referred to as tocochromanols (Fig. 3). It has been reported that lipid peroxy radicals react with tocopherols much faster (10^4 – 10^9 $M^{-1} s^{-1}$) than with lipids (10 – 60 $M^{-1} s^{-1}$) [12], making them an excellent peroxy radicals scavengers and chain breakers. Rossi et al. [13] reported a very strong positive correlation between the radical scavenging capacity of different refined oils and the total content of tocochromanols. Although endogenous tocochromanols are the oils' first line of defense against oxidative deterioration, they are, however, thermally unstable and offered limited protection during frying [8].

Phytosterols are the major constituents of unsaponifiables present in edible oils [14], β -sitosterol, campesterol, stigmasterol, Δ^5 -avenasterol, and brassicasterol (Fig. 4) being the most common. Whereas they offer no protection under oxidative and storage conditions, phytosterols have been reported to improve the frying stability of oils [15–18]. Older literatures indicated that phytosterol's antioxidant activity is restricted to those with ethylidene side chain configuration, such as avenasterol, fucosterol, vernosterol, and citrostadienol [15–17]; however, it is becoming more evident that alternative mechanisms may be involved in phytosterol antioxidant activity considering recent reports on the excellent anti-polymerization potency of β -sitosterol and other phytosterols devoid of ethylidene side chain [5, 6, 19].

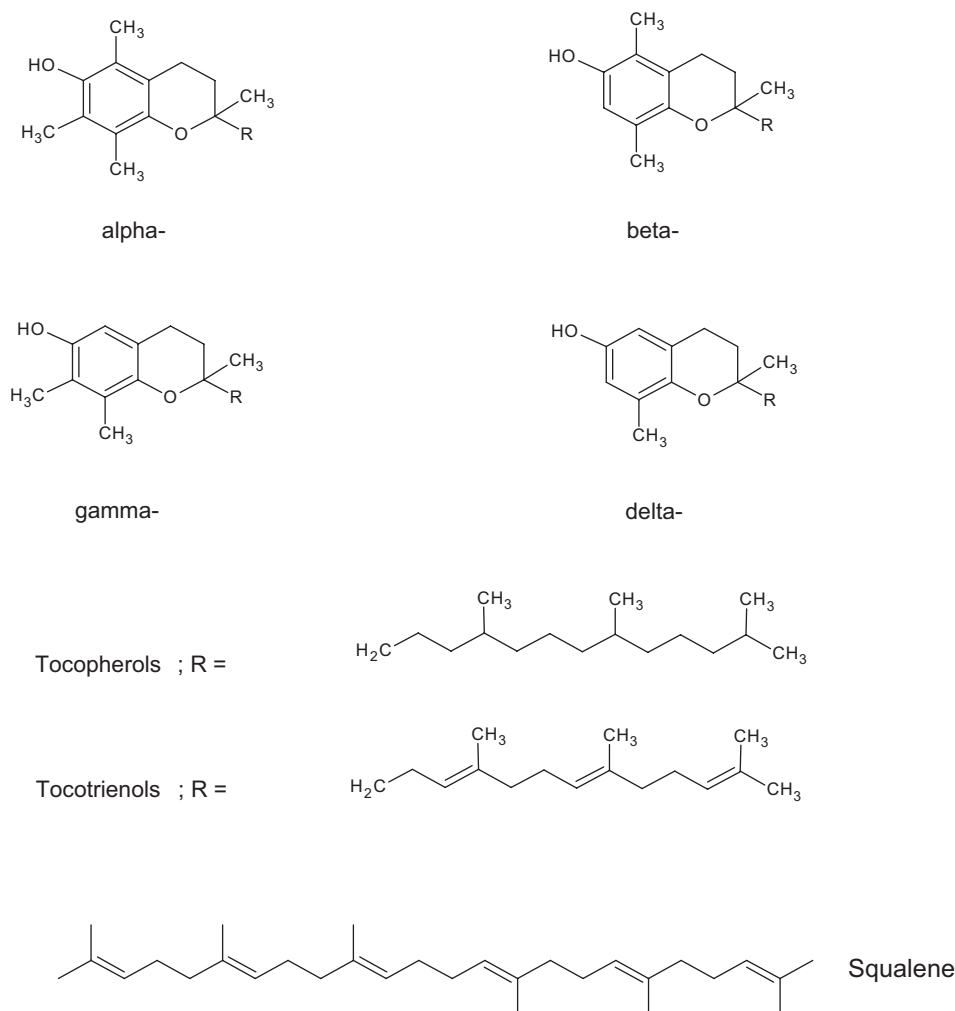


Figure 3. Tocochromanols and squalene Δ^5 -avenasterol.

Acid-catalyzed conversion of sterols into steradienes at frying temperature has been suggested as a possible mechanism [5, 18].

Squalene (Fig. 3) 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. While the antioxidant activity of squalene under storage and oxidative conditions remain controversial, it is generally agreed that squalene inhibits thermooxidative degradation of oils under frying conditions [3, 15, 20, 21] even though all available data were in a model heated oil rather than in actual frying experiments.

A mixture of steryl ferulates (Fig. 5) found in rice bran oil (γ -oryzanol) or corn fiber oil have also been shown to protect frying oils against thermooxidative degradation [3, 5, 22, 23]. According to Winkler-Moser et al. [23], steryl ferulates from corn oil offered superior performance compared to the mixture isolated from rice bran oil; highlighting structural

differences between the two groups of steryl ferulates, which resulted in differential interaction with endogenous tocopherols. Although, the antioxidant activity of steryl ferulates is attributed to the radical scavenging activity of the ferulic acid moiety [24], other important mechanism may also be involved during frying of food, including: (i) A competitive acid-catalyzed hydrolysis of the ferulate ester bond, which may limit the degradative TAG dimerization reaction (Fig. 2) and (ii) sequential release of secondary antioxidants (ferulic acid and sterols) through hydrolysis which, in combination with higher thermal stability, may extend the activity period of steryl ferulates.

Sesamin, sesamol, sesaminol, and sesamolol (Fig. 6) are lignan compounds naturally present in sesame oil, and have been implicated in the oil's high stability [25, 26]. Sesamolol is considered the precursor of sesamol, sesaminol, and sesamol through a series of acid-catalyzed hydrolytic and intermolecular transformations [27]. According to

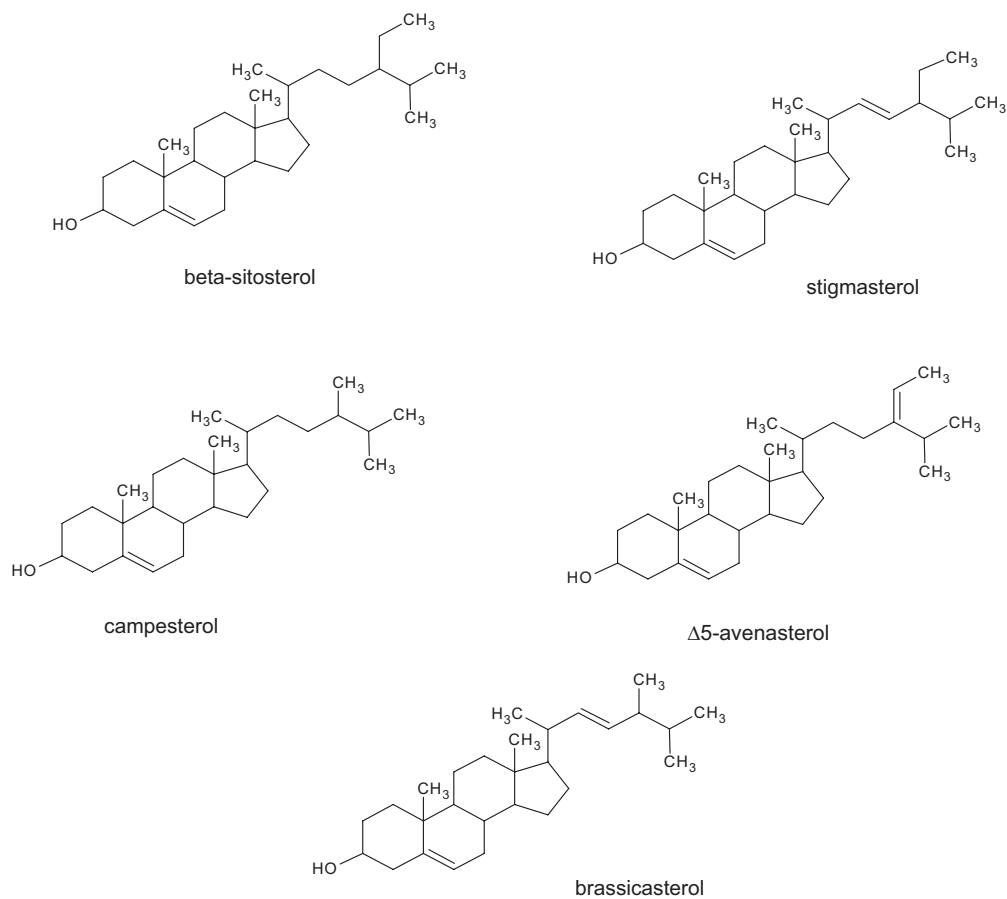


Figure 4. Common phytosterols present in frying oils.

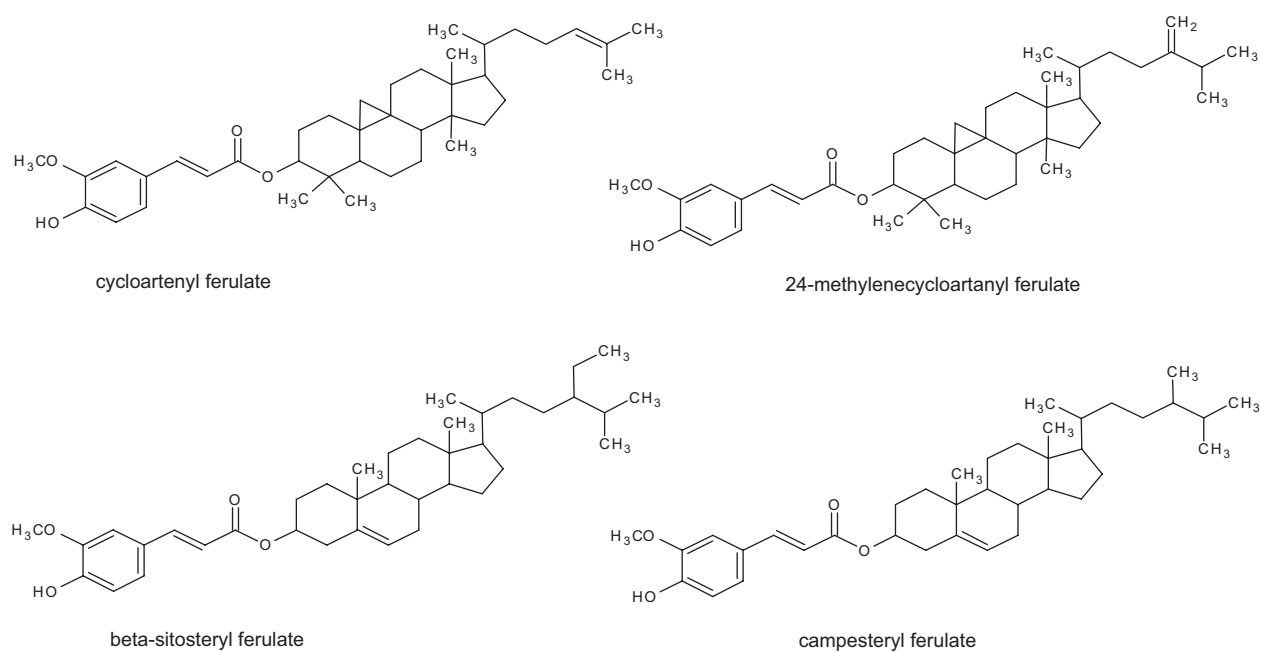


Figure 5. Common steryl ferulates.

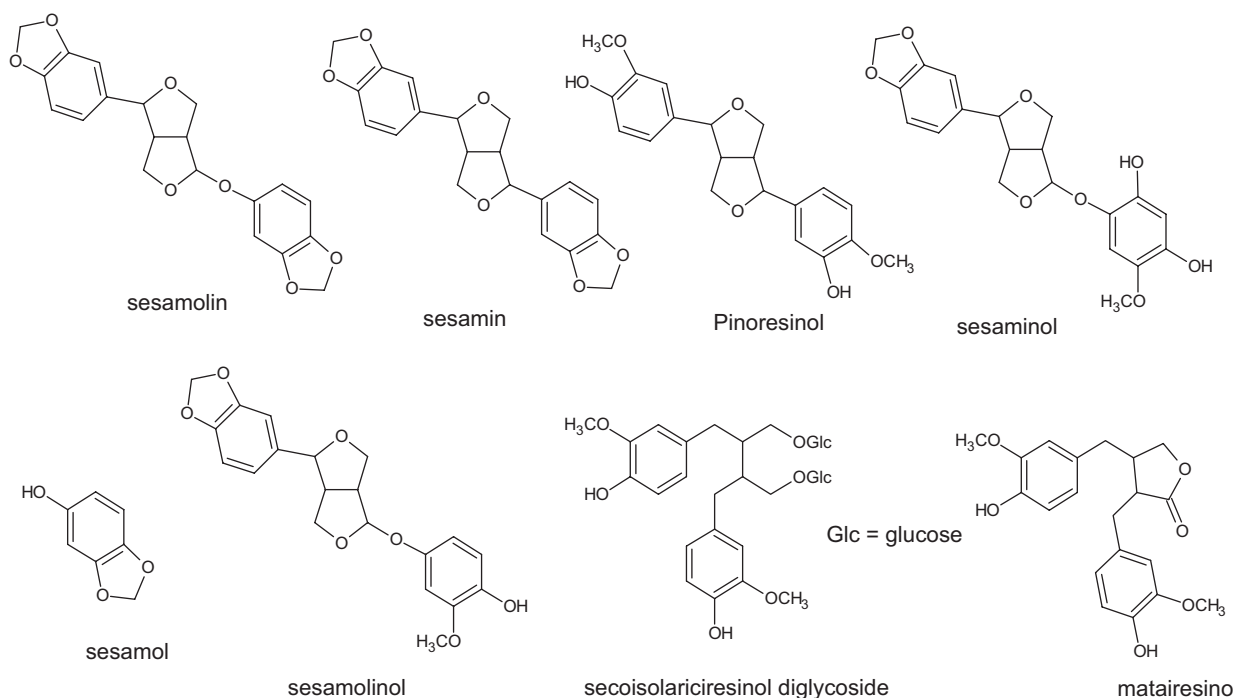


Figure 6. Sesamol and some antioxidant lignans from sesame and flax oils.

Kochhar and Gertz [5] and based on the non-radical mechanism of frying oil degradation (Fig. 2), this acid-catalyzed decomposition of sesamol, with activation energy lower than that of TAG dimerization, may be the major factor for the frying stability of sesame oil. On the other hand, sesamol and sesaminol, the degradative products of sesamol are excellent radical scavengers and evidently contributed to the overall stability of the oil [28, 29]. A recent study on sesamol and a variety of lignans (nordihydroguaiaretic acid, pinoresinol, secoisolariciresinol, enterodiol, piperonyl alcohol, and sesamin) suggested sesamol as the most promising natural alternative to synthetic antioxidant for frying application [30]. Unfortunately, the application of sesamol for frying application is hampered by its high volatility and poor thermal stability; this problem was partly circumvented by adding the sesamol in batches during the frying process [31].

2.2 Exogeneous

Whereas common vegetable oil endogenous antioxidative compounds, such as the tocopherols, inhibit oxidative deterioration during storage, they are markedly less effective under the more stringent frying conditions [8]. The ineffectiveness of endogenous antioxidants during frying are related to: (i) poor thermal stability resulting in premature decomposition; (ii) high volatility resulting in evaporative losses; (iii) insufficient concentrations consequent to losses from refining and other processing steps; (iv) lack of proper

antioxidant synergist; and (v) insufficient potency, for instance, due to a narrow antioxidant reaction mechanism, which in most cases is limited to radical scavenging or chain-breaking mechanism.

To improve the frying performance of vegetable oils and fats, external fortification is imperative, and a number of (semi)synthetic and natural antioxidants has been developed and utilized for such purpose. Potential sources and applications of exogenous natural antioxidants for enhancing frying performance of oils/fats are discussed below.

2.2.1 Natural antioxidants from vegetable oils with unique endogeneous antioxidants

Individual vegetable oils are naturally endowed with their own unique constituents and compositions of endogenous antioxidants, and the effectiveness of these endogenous antioxidants can change depending on the nature of the substrates [10]. Thus, certain vegetable oils containing antioxidants other than tocopherols, such as, virgin olive, sesame, rice, wheat, and oat oils, have been added to other oils/fats for improved frying stability [32].

Olive contains several classes of antioxidative phenolic compounds, namely; phenolic acids (hydroxybenzoic and hydroxycinnamic acid derivatives), phenylethyl alcohols (tyrosol and hydroxytyrosol), flavonoids (apigenin, luteolin), lignans (pinoresinol and acetoxy pinoresinol), and secoiridoids (elenolic acid) [33, 34]. These components are largely

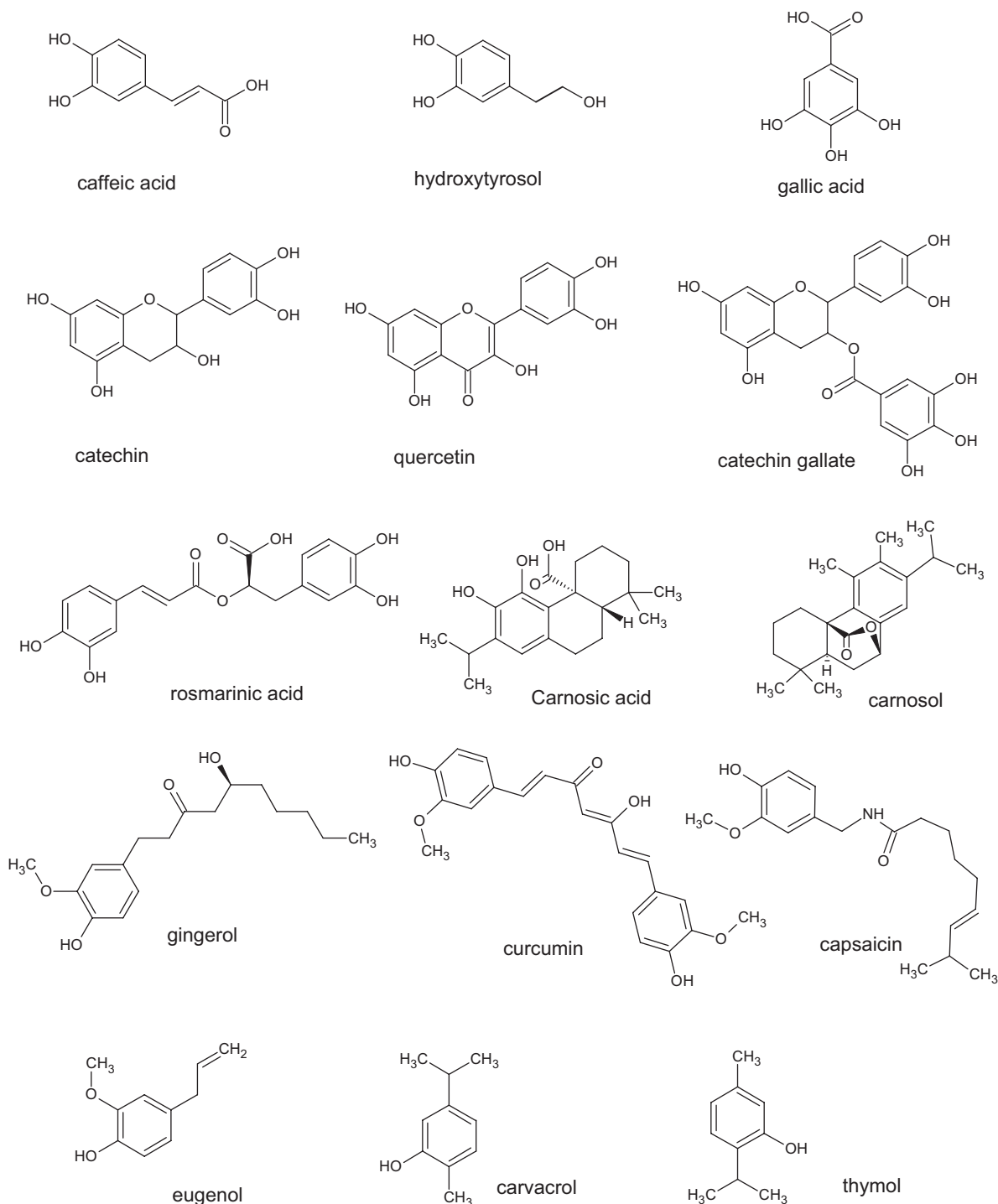


Figure 7. Representative antioxidative compounds in natural phenolic extracts.

retained in virgin olive oil and are partly responsible for the improved frying stability reported for the oil and its blends with conventional oils such as canola and sunflower oils [35–39]. Similarly, due to the higher antioxidant activity and thermal stability of sesame lignans, conventional oils such as

canola, soybean, and sunflower are blended with sesame oil to improve their frying stability [40–45]. For instance, Farhoosh and Kenari [43], Alireza et al. [44], and Serjouie et al. [45] attributed the improved frying stability of blends of sesame and canola oils over pure canola oil to the activity of sesame oil

lignans. Similarly, Chung et al. [40, 41] ascribed the superior frying performance of a blend of soybean and sesame oils over unblended soybean oil to the presence of sesame oil lignans. Indeed, the purified lignans (sesamin, sesamol, and sesaminol) isolated from sesame seed oil significantly improved the frying stability of soybean oil, lard, and methyl linoleate [28–30, 46, 47]. Supplementing refined rapeseed oil with up to 20% wheat germ oil or sesame oil improved the frying stability of the rapeseed oil [48]. The commercial product, Good-fry[®] oil, reportedly exhibiting high frying stability was composed primarily of high-oleic sunflower oil

delicately blended with a small portion of ‘dedicated’ refined sesame oil and specially produced rice bran oil [49].

2.2.2 Natural antioxidants from agricultural and processing by-products

A number of agricultural and food processing by-products contain high concentration of antioxidative compounds, mainly phenolics, that can be used to improve the stability of frying oils and fats (Table 2). Olive leaves are agricultural waste obtained from annual pruning of olive trees. According

Table 2. Studies evaluating phenolic extracts under frying conditions

Refs.	Sources	Fat/oil substrate	Conditions
[54]	Olive leaf, hazelnut leaf, hazelnut green leafy cover	Canola oil	Frying of dough patties at 180°C
[130]	Andea mashua (<i>Tropaeolum tuberosum</i>)	Soybean oil	Frying of potatoes at 175°C
[192]	Oregano	Soybean	Heating of oil at 180°C
[59]	Grape seed	Sunflower oil	Heating at 180°C
[131]	Inca munã (<i>clinopodium bolivianum</i>) leaves	Soybean oil	Frying of potatoes at 180°C
[154]	Rosemary	Sunflower	Heating of oil at 180°C
[193]	<i>Majorana syriaca</i>	Corn oil	Frying of potato at 185°C
[194]	Thyme flower	Corn oil	Frying of potato at 180°C
[129]	Pompozia fruits	Sunflower oil	Frying of French fries 180°C
[53]	Olive waste cake	Sunflower oil	Heating of oil at 180°C
[195]	Mulberry leaves	Rice bran oil	Heating at 180°C
[150]	Apple, blueberry, mangosteen, dragon fruits	Peanut oil	Potatoes immersed in fruit extracts and then fried at 170°C
[196]	Denatured carob fiber (Exxenterol [®])	Sunflower oil	Heating at 180°C
[156]	<i>Curcuma longa</i> (turmeric) leaf	Palm olein	Frying of French fries at 180°C
[157]	<i>Murraya koenigii</i> leaf	Palm olein	Frying of French fries at 180°C
[134]	Rooibos tea	Soybean oil	Rancimat at 120, 140, 160 and 180°C
[51]	Olive leaf	Sunflower, olive, and palm oils	Pan-frying at 175°C for 6 min
[132]	<i>Pandanus amaryllifolius</i> leaf	Palm olein	Frying of French fries at 180°C
[153]	Bamboo, green tea leaves	Vegetable oil	Mixed with wheat flour prior to dough preparation, bread stick deep-fried at 180°C
[197]	Greek sage and summer savory	Virgin olive, refined olive, sunflower and commercial blend of oils	Heating at 180°C
[167]	Black tea, garlic bulb, onion skin	Corn oil	Heating at 140°C
[198]	Black tea leaves	Corn oil	Frying of potato at 180°C
[199]	Oregano	Cottonseed	Frying of potato at 185°C
[126]	Oleoresin rosemary, sage	Palm olein	Frying of potato at 180°C
[57]	Citrus hystrix peel	Palm olein	Frying of fish crackers at 180°C
[124]	Rosemary	Rapeseed	Frying of potato chips at 180°C
[58]	Mung bean hull	Soybean	Heating at 180°C
[201]	Cassia essential oil	Rapeseed, soybean, sunflower, peanut, palm oil	Frying of precooked beef at 130, 150, and 190°C
[128]	Coriander oleoresin, coriander essential oil	Clarified butterfat (ghee)	Frying of wet cotton at 180°C
[200]	Rosemary	Olive and sunflower	Frying of potatoes at 180°C
[202]	Rosemary	Soybean	Heating of oil at 180°C
[133]	Spinach	Soybean	Flour dough fortified with spinach powder and deep fried at 160°C
[56]	Old tea leaves	Rapeseed	Frying of potatoes at 180°C
[203]	Green tea, green coffee	Lard	Frying of fortified donuts at 180°C
[50]	Olive leaves	Sunflower	Heating at 180°C

to the study by Farag et al. [50], addition of crude juice pressed from olive leaves to sunflower oil remarkably increased the thermooxidative stability of the oil during intermittent heating at 180°C for 5 h per day for five consecutive days as measured by total polar components (TPC), polymer formation, acid value, thiobarbituric acid test, and peroxide value. According to the authors, crude olive leaf juice at 800 µg total phenols per gram of oil was superior to BHT at its legal limit (200 µg g⁻¹). In a related study, Chiou et al. [51] reported significant frying stability and retention of endogenous tocopherols during domestic frying of sunflower, olive, and refined palm oils fortified with methanol extract of olive tree leaves. Addition of phenolic extracts from spray-dried olive mill waste water to a blend of rapeseed (60%), sunflower (38%), and grape seed (2%) oils resulted in improved frying stability and a lower accumulation of acrylamide in prepared French fries [52]. The frying stability of sunflower oil increased significantly in the presence of ethanolic extract of olive waste cake added at 100–600 µg/g during intermittent heating at 180°C for 4 h per day for five consecutive days [53]. Contrary to the previous studies on olive leaves extracts [50, 51], Aydeniz and Yilmaz [54] observed no protective effect for olive leaf aqueous ethanolic extract during an intermittent frying of dough patties at 180°C in canola oil for 5 h per day for 7 days, based on the formation of TPC, conjugated dienoic acids, and turbidity of the frying oil. The observed difference may be related to the lower phenolic concentration (~160 µg gallic acid equivalent per gram of oil) used in the study. The authors, however, reported a significant antioxidant and antipolymerization activities (about 60% decrease in TPC) for hazelnut green leafy cover, another agro-by-product [54].

Tea, derived from *Camellia sinensis* L., is one of the most widely consumed beverages in the world [55]. For tea production, young shoots, mainly the first two to four leaves and a bud are typically selected, whereas old tea leaves, which are not used in tea manufacture, are considered as agricultural waste [56]. The methanolic extract of this agricultural waste was reported to significantly protect rapeseed oil against thermooxidative deterioration in the course of frying 12 consecutive batches of potato crisps over a period of 3 days (5 min per batch) at 180°C, as measured by the formation of polar components and the *p*-anisidine value [56]. The efficiency of the old tea leaves extract was at least similar to that of rosemary extract at similar concentration of 0.1% [56].

In the study by Jamilah et al. [57], ethanolic extract of citrus peel was added to refined, bleached, and deodorized palm olein at 0.2% concentration and used to fry fish crackers at 180°C for 5 h per day for 4 consecutive days. Analyses of peroxide value, totox value, iodine value, viscosity, and linoleic:palmitic acids ratio indicated strong antioxidant and antipolymerization effects of the citrus peel extract [57]. In a similar study, Duh et al. [58] reported that the methanolic extract of mung bean hulls offered better protection for

soybean oil EFA than BHT at equivalent concentration (100 µg/g) during heating at frying temperature (180°C) for 2 h, based on the linolenic:palmitic acids ratio. A concentration-dependent inhibition of thermooxidative deterioration was also observed for the ethanolic extracts of grape seeds recovered from grape pomace during microwave and convective heating of sunflower oil at frying temperature [59]. Although extracts from a number of related agricultural wastes such as apple pomace, peanut skin, apple peel, peach peel, banana peel, potato peel, rice hull, buckwheat hull, almond hull, cocoa hull, lentil hull, pistachio hull, and corn cob have been shown to demonstrate good radical scavenging activity and delay oxidation of edible oil under oxidative conditions, they are yet to be evaluated for frying application [60–78]. Generally, these agro-industrial by-products harbor more phenolic antioxidants than their primary products [79–84].

Edible oil processing steps such as degumming, refining, bleaching, and deodorization often result in significant removal of some endogenous minor components possessing promising antioxidant/antipolymerization potentials [85]. A number of technologies are available or emerging for economical recovery, reprocessing, and purification of these by-products, which can then be applied for extending performance of frying oils. Lecithin, comprising primarily of phosphatides such as phosphatidylcholine (PC), phosphatidylethanolamine (PE), phosphatidylserine (PS), phosphatidylinositol (PI), and phosphatidic acid (PA) is one of such products. The addition of 0.1% soy lecithin remarkably decreased the formation of lipid hydroperoxides and polymers during frying in olive oil at 170°C [86]. The thermooxidative stability of salmon oil heated at 180°C was significantly improved in the presence of a phospholipid fraction isolated from bluefish [87]. In a recent study, the performance of PC and PE was evaluated during a model frying of formulated food comprising of gelatinized starch, glucose and silica (4:1:1) in canola oil TAG at 185°C [88]. At a concentration of 0.05%, neither PC nor PE offered any protection to canola oil TAG. However, at higher concentrations (0.1 and 0.2%), 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 application of phospholipids as frying oil antioxidants is limited by their reported adverse effects on color and foaming of oils [89]; however, according to Kourimska et al. [86], 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. The observed antioxidant activity of phospholipids has been attributed to: (i) their synergistic activity with phenolic antioxidants such as tocopherols [90–97]; (ii) the ability of the phosphate group to chelate prooxidant metals [98, 99]; (iii) the formation of nonenzymatic browning reaction products between amino phospholipids and sugar or lipid oxidation products [100–104]; and

(iv) the ability of phospholipids to form an oxygen barrier between the oil and air interface [105, 106].

Deodorization is a processing step during the production of commercial edible oil in which steam is passed through the oil at very low pressure and relatively high temperatures. Under these conditions, significant amounts of oil's endogenous minor components are also removed from the oil, along with other volatile impurities, and are concentrated in the deodorizer distillate as by-products [85, 107]. In a study by Abdalla [108], unsaponifiable residues extracted from olive oil deodorizer distillate were added to sunflower oil at different concentrations, up to 1%, and the oil was used for frying potatoes at 180°C for 8 h per day for 10 days. The author reported a concentration-dependent increase in antioxidant and antipolymerization activity of the distillate with an up to 60% increase in frying performance of fortified sunflower oil as measured by anisidine value, peroxide value, iodine value, and TPC formation. The protective effect observed for the deodorizer distillate was attributed to the presence of squalene, avenasterol, and tocopherols in the mixture [108]. Due to the high level of impurities, such as PAH and other oxidized volatiles formed during bleaching, the application of deodorizer distillate as frying antioxidants requires prior purification.

During the extraction of oil from the oilseed, phenolic compounds are mostly retained in the meal due to their relatively poor lipophilic nature, compared to other antioxidants like the tocopherols and phytosterols. Innovative extraction methods are available or being developed for economic recovery of these phenolic antioxidants toward their applications in functional foods and nutraceuticals [109–114]. Whereas the antioxidant activity of extracts from deoiled meal/cake has been evaluated in bulk oil and oil-in-water emulsion under oxidative and storage conditions [115–117], there is a dearth of information on the utilization of this by-products for frying applications. De Leonardis et al. [118] described the extraction of a powdery antioxidant product, consisting of 58% caffeic acid, from partially defatted sunflower seed shells, but the effectiveness as antioxidant in edible oils was only evaluated under Rancimat condition at 130°C and 20 L/h air flow.

2.2.3 Natural antioxidants from herbs and spices, berries, and other vegetal sources

Spices and herbs such as rosemary, oregano, savory, marjoram, sage, thyme, basil, clove, cinnamon, nutmeg, turmeric, cumin, pepper, and garlic have long been recognized as important sources of potent antioxidants [119–123]. Active compounds present in most common spices and herbs include phenolic mono- and diterpenes (e.g., carnosic acid, carnosol, rosmarinol, rosmadial, cavacrol, and thymol), phenolic acids and derivatives (e.g., rosmarinic, caffeic, gallic, ferulic, and protocatechuic), gingerol-related compounds (e.g., gingerol and shogaol) diarylheptanoids (e.g.,

curcumin, cassamunin A, B, C), phenolic amides (e.g., capsaicin and capsaicinol), and flavonoids (e.g., quercetin, luteolin, apigenin, kaempferol, and isoharmnetin) (Fig. 7). Whereas reports abound on the antioxidant activity of extracts and components from various spices and herbs in edible oils under ambient and storage conditions, investigations on their effectiveness during frying have received relatively less attentions (Table 2).

In general, extracts from different parts of spices, herbs, and fruits studied so far indicated their efficacy in inhibiting thermooxidative degradation and extending the fry-life of vegetable oils (Table 2). For instance, commercial extract of rosemary added at 0.1% concentration significantly inhibited dimer formation and tocopherol degradation in rapeseed oil during intermittent frying of potato chips at 162°C [124]. Commercially obtained oleoresin rosemary and sage extracts at 0.04% markedly improved the frying performance of refined, bleached, and deodorized palm olein, based on wet and FTIR spectrometry measurements of peroxide value, iodine value, and free fatty acid content of the oils after extended frying at 180°C for 5 consecutive days [125]. The study by Che Man and Jaswir [126] revealed a synergistic interaction among rosemary extract, sage extract, and citric acid that resulted in a significant stability of palm olein and improved sensory scores of the fried food during extended frying of potato at 180°C for 6 days. According to Yanishlieva et al. [127], thermal degradation of sunflower oil TAG was significantly inhibited in the presence of summer savory ethanolic extract; the time to reach 73% unchanged TAG (~27% TPC) increased by up to 14 h in the presence of the extract during heating in an oven at 180°C for 8 h per day for 7 days. In a recent study, Patel et al. [128] reported a significant improvement in stability of clarified butterfat (Indian ghee) fortified with 0.5% commercial steam distilled coriander extract and oleoresin in a model frying of wet cotton balls at 180°C. The steam distilled extract reportedly exhibited better performance than the oleoresin based on the determination of conjugated dienes, thiobarbituric acid value, and the Rancimat at 120°C of the fried oils [128]. A recent data by Gertz and Matthaues (personal communication) also indicates a reduced effectiveness of rosemary extract at elevated temperature and a dependency on preparation method.

Apart from the more frequently studied common spices and herbs, a number of vegetal sources including fruits and berries also present viable sources for frying antioxidants. Freeze-dried, expelled juice from pompozia fruit (*Syzygium cumini*; Myrtaceae) added at 0.12% offered significantly better protection than BHT against thermooxidative deterioration of sunflower oil during continuous frying of frozen French fries at 180°C for 12 h [129]. According to Betalleluz-Pallardel et al. [130] ethyl acetate extract from the Andean mashua (*Tropaeolum tuberosum*; Tropaeolaceae) tuber at 200 µg phenolic equivalent/gram improved the stability of soybean oil during frying at 175°C, based on the levels of

conjugated dienes, conjugated trienes, free fatty acids, and total polar compounds formed at the end of the 4-h frying period. Ethyl acetate extract of Inca munã (*Clinopodium bolivianum*; Lamiaceae) leaves at 600 µg phenolic equivalent/gram exhibited significantly better antioxidant and antipolymerization activity than TBHQ (200 µg/g) during frying of potatoes in soybean oil at 180°C for 4.5 h as measured by the formation of conjugated dienes, conjugated trienes, anisidine value, and total polar compounds [131]. *Pandanus amaryllifolius* (Pandanaeae) leaves ethanolic extract was added to palm olein (10 kg) at 0.2% concentration; the oil was used for frying 14 batches at 200 g per batch of French fries for 2.5 min per batch at 30 min interval for 8 h daily [132]. At the end of the 5 days of frying, the level of total polar compounds was reduced by about 35% and oligomer formation by 47% in the presence of the extract [132]. The addition of freeze-dried spinach (*Spinacia oleracea*; Amaranthaceae) powder in flour dough significantly decreased formation of polar compounds in soybean oil during frying at 160°C for 20 h, and reduced the accumulation of conjugated dienes and aldehydes in the lipid of the fried dough during storage [133]. The extracts from rooibos tea and green tea also improved the thermo-oxidative stability of edible oils at frying temperatures [134].

Apple and berries, such as strawberry, elderberry, chokecherry, blueberry, gooseberry, cranberry, and grape contain significant amounts of phenolic antioxidants and a number of underutilized wild and ornamental species have been extensively characterized [135–141]. Presently, the literature reports on the effectiveness of extracts from these natural phenolic sources as antioxidants for frying applications are rather scanty [59, 142–144]. In the recent study by Sun-Waterhouse et al. [144], apple phenolic extract at a concentration of 300 µg/g was incorporated into batters that were subsequently used in the preparation of deep-fried potato fritters. The level of peroxide value, anisidine value and free fatty acids in the extracted oil from the fritters indicated that the phenolic extract significantly inhibited thermooxidative deterioration of the canola oil used for the frying [144]. We recently reported on the effectiveness of the phenolic extracts from some Canadian small fruits, namely, wood's rose, hawthorn, chokecherry, crabapple, and rowanberry in inhibiting thermooxidative and polymerization reactions in canola and sunflower oils during frying at 180°C for up to 2 days [145–147]. Thermooxidative degradation in rapeseed oil was reduced by up to 30% in the presence of phenolic extracts from rowanberry and crabapple (500 µg gallic acid equivalent/g of oil) during frying at 180°C for 8 h per day for 2 days, based on the anisidine value and accumulation of TPC and di- and polymerized triacylglycerols (DPTG) [145]. In a similar study, the rate of TPC formation was 2.07, 2.70, and 2.67% per hour for samples fortified with phenolic extract from wood's rose hip with seed, BHT, and the control rapeseed oil, respectively, indicating a significant inhibition of thermooxidative degradation in the presence of the phenolic extract [146].

Besides extending the usage life of the frying oils, natural phenolic extracts effectively inhibited the formation and accumulation of toxic thermooxidative degradation products in the fried foods. For instance, apple, elderberry, blueberry, grape, and cherry extracts mixed with ground beef prior to pan-frying at 175–210°C improved stability and inhibited the formation of toxic heterocyclic amines [148–150]. Marination of beef patties in an oil-based marinade containing grape seed and rosemary extracts prior to frying resulted in up to 90% decrease in the level of individual carcinogenic heterocyclic amines [151]. An 83% decrease in acrylamide level was reported when potatoes were immersed in rosemary extract (1 g/kg potatoes) for up to 1 h prior to frying at 180°C for 4 min [152]. Similarly, bamboo (0.1%) and green tea (0.01%) extracts mixed with wheat flour for the preparation of deep-fried bread stick inhibited acrylamide formation by more than 70% [153]. Formation of *trans* fat in sunflower oil during heating at 180°C for 120 h was also significantly inhibited in the presence of 0.1% rosemary extract [154]. Although relatively less reported, available data indicated that the addition of plants extracts to frying oil did not negatively affect the sensory attributes of the fried products [126, 134, 155–158], lending credence to their utilization as antioxidants for frying applications. Further studies are needed for most extracts, however, in order to establish optimum concentrations for antioxidative performance without compromising consumers' acceptance of fortified oils and the fried products.

The polyphenolic constituents of antioxidative plant extracts are more thermally stable than the common synthetic and endogenous antioxidants (tocochromanols, BHT, BHA, and TBHQ), which are easily degraded and evaporated during frying [159–164]. According to Cordeiro et al. [160], rosemary extract showed excellent stability at frying temperature with only 6% mass loss at 190°C, attributable to moisture and solvent loss. This relatively higher thermal stability suggests that phenolic constituents of applied extracts can survive the stringent conditions of frying and be transferred into the fried food where they can continue to offer protection during storage (carry-through effect). Furthermore, whereas the efficacy of many conventional antioxidants including tocopherols and BHT dramatically decrease at frying temperatures, the effectiveness of polyphenolic compounds (active constituents of antioxidative extracts) appear to improve with temperature as indicated by a number of studies, which may be related to thermally enhanced dissolution. For instance, whereas mixed tocopherol was more effective than rooibos tea phenolic extract at protecting antioxidant-free soybean oil at 120 and 140°C, the polyphenolic extract was significantly more effective at 160 and 180°C [134]. Similarly, whereas lavender and thyme incorporated in sunflower oil showed no effect at 25°C, they dramatically increased stability at 150, 180, and 200°C, based on analyses of free fatty acids, peroxide value, and viscosity [165]. Elhamirad and

Zamanipour [166] evaluated the temperature-dependent antioxidant activity of α -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 α -tocopherol with the difference being 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 48 h [167]. Nevertheless, the poor dispersal of extracts in oils coupled with the hydrophilic nature of their phenolic constituents is a major drawback to their applications in frying oils. Research into novel methods for effective dissolution of extracts in oils, including chemo(enzymatic) lipophilization of the phenolic constituents, are rigorously being pursued, and a number of excellent reviews on the topic are available in the literature [168–173].

2.3 In situ, secondary antioxidants

The inherent presence of various potential catalysts such as water, acid, alkali, and metal ions in oils and food, and the high operational temperature (>160°C) provides a unique environment for a host of chemical reactions, both destructive and constructive, during frying. Thermal decomposition of endogenous and exogenous antioxidants can result in secondary antioxidants with potent antioxidative potential [27, 174, 175]. For instance, thermal degradation of sesamol yielded sesamol, a very potent lipid antioxidant [27], and the major components of the thermal degradation of quercetin glycoside at 180°C was quercetin, another antioxidative polyphenol [175]. Besides this antioxidant degradation phenomenon, there is also the possibility of composing new, in situ secondary antioxidants as a consequence of some physico-chemical reactions involving antioxidants, food materials (starch and protein), and lipid degradation products during frying. 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, a secondary antioxidant [176]. Indeed, the influence of components' molar ratios and other conditions necessary for such in situ synthesis requires further investigations. For instance, according to Nasibullin et al. [177], depending on the molar ratio, a stable, hydrogen bond-mediated complex can be formed between quercetin and phospholipids by mixing at RT. This knowledge was recently applied by Ramadan [178] 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 15 days.

Formation of Maillard reaction products (MRP) is another example of heat-induced in situ generation of antioxidants during frying. Their formation, nutritional, biological, and antioxidant activities have been extensively reviewed [179–187]. Their formation involves reactions 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 PE can react, via their amine group, with aldehydic moiety of lipid oxidation products during frying to generate MRP analogous compounds with potent antioxidant activity [100–104]. In a recent study, the products isolated from a model heating of amino acids (glycine, lysine, and 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 [188]. According to Vhangani and Van-Wyk [189], the antioxidant activity of MRP 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 MRP will offer improved antioxidant performance at frying temperatures. Wagner et al. [190] reported that the water-soluble and water-insoluble fractions of MRP formed by a glucose-glycine model was effective at delaying hydroperoxides formation (by up to 23% at 60°C) in corn oil at 0.5% concentration, but not at 0.01 and 0.1%. According to the authors, however, this high concentration (0.5%) may not be practicable for the food industry due to color changes [190]. No activity was observed for the MRP when the storage temperature was increased to 200°C, based on the peroxide value analysis [190]. In the recent study by Miyagi [191], the oxidative stability of deep-fried peanut was significantly improved by extending the frying time up to 30 min at 150°C to allow the formation of sufficient level of MRP. Apart from their radical scavenging activity, it is conceivable that the formation of MRP through reactions involving lipid oxidation-derived aldehydic compounds will extend the fry life of oils through removal of these prominent secondary lipid oxidation products. According to Wagner et al. [190], the 4-OH-3(2*H*)-furanones formed in the reaction between glucose and glycine could generate tocopherol from tocopheryl radicals, with potential to enhancing oil stability.

3 Conclusions

In response to growing consumers' interest in "natural" products, the search for effective natural alternatives to synthetic antioxidants is intensifying. Whereas common vegetable oil endogenous antioxidative compounds such as

the tocopherols can inhibit oxidative deterioration during storage, they are markedly less effective under the more stringent frying conditions. The ineffectiveness of endogenous antioxidants during frying are related to: (i) poor thermal stability resulting in premature decomposition; (ii) high volatility resulting in evaporative losses; (iii) insufficient concentrations consequent to losses from refining and other processing steps; (iv) lack of proper antioxidant synergist; and (v) a narrow antioxidant reaction mechanism, which in most cases is limited to radical scavenging or chain-breaking mechanism. Phenolic extracts from: traditional spices and herbs; wild/ornamental edible fruits, and other vegetal sources; and agricultural and processing by-products are promising sources for natural antioxidants for frying application. Despite abundant data on the antioxidant activity of phenolic extracts from these natural sources, there is still a dearth of information on their activity in edible oils under frying conditions. Blending of frying oils with vegetable oils containing unique endogenous antioxidants (e.g., virgin olive, sesame, rice, wheat, and oat oils), and manipulation of frying conditions and constituents in order to generate active in situ secondary antioxidants during frying may offer additional opportunity for enhancing performance of frying oils with natural antioxidants. Whereas the effectiveness of natural antioxidants in frying oil may not be in doubt, their commercial application is undoubtedly without some challenges, considering: (i) possible inconsistency in activity arising from (a) genetic, climatic, and geographical variations in phenolic constituents of the vegetal source and (b) extraction and preparation method; (ii) possible negative impact of extract's inherent color and flavor on the sensory attributes of the frying oils and foods; (iii) possible co-extraction/contamination with some toxic or allergenic compounds, (iv) poor lipophilic nature of antioxidative phenolic constituents of extracts; and (v) significantly lower market prices of available synthetic antioxidants compared to the natural alternatives.

The complex interaction involving oxygen, water, and components from food and the frying oil, initiated by high temperature, over an extended period of time, makes frying a unique process quite difficult to simulate. Consequently, the activity and performance of antioxidants observed in a model system and under storage/oxidative conditions may be at variance to what is observed during frying, calling for the needs to examine antioxidative materials using actual frying experiments. The effect of applied phenolic extracts and other natural antioxidants on sensory attributes of fried food is of paramount importance, after all, consumers' acceptance is the ultimate judge of oil's frying performance.

The financial support of the Alexander von Humboldt Foundation is highly appreciated.

The author has declared no conflict of interest.

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