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REVIEW

The Antioxidant Functions of Tocopherol and Tocotrienol Homologues in Oils, Fats, and Food Systems

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Abstract This review paper is focused on the relative antioxidant activities of tocopherols and tocotrienols in oils and fats and certain food systems. α-Tocopherol generally showed better antioxidant activity than γ-tocopherol in fats and oils, but at higher concentrations γ-tocopherol was found to be a more active antioxidant. The results of studies on the optimum antioxidant concentrations of tocopherols in oils and fats indicated that the optimal level for α-tocopherol is usually lower than other tocopherols, meaning less α-tocopherol is needed for maximum antioxidant protection. There are comparatively very few studies related to the antioxidant activities of tocotrienols in oils and fats. It has been stated that generally γ-tocotrienol has higher antioxidant effect than α-tocotrienol, and tocotrienols may be better antioxidants than their corresponding tocopherols in certain oils and fats systems. Studies on the antioxidant activity of various tocopherols in food systems are varied and cannot be uniformly evaluated because experiments have generally focused on different foods and used various methods for the detection of antioxidant activities. Depending on the food system, in certain cases tocopherols were better antioxidants than synthetic antioxidants such as butylhydroxy toluene (BHT) or butylhydroxy anisole (BHA). However, in certain other food systems the synthetic antioxidants were more effective to increase the shelf life and the stability of foods than those containing tocopherols.

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Introduction

The objective of this review was to investigate the relative antioxidant activities of tocopherols and tocotrienols in oils and fats and certain food systems as reported in the literature over the past 35 years.

Vitamin E is the collective term for a group of naturally occurring tocopherols and tocotrienols. In 1922 [1], an unknown dietary factor, first called factor X, was discovered, the deficiency of which resulted in fetal death and resorption in laboratory rats. Three years later [2], the name vitamin E was given to this fat-soluble factor X. In 1936 [3], α-tocopherol was isolated from wheat germ oil and the chemical formula ($C_{29}H_{50}O_2$) was established. The following year, the β- and γ-tocopherols were isolated and it was noticed that α-tocopherol had a higher biological activity than β- and γ-tocopherols. In 1938 [4], the chemical structure for α-tocopherol was elucidated. In 1947 [5], the isolation of δ-tocopherol from soybean oil was reported. Several other components of vegetable oils were first thought to be other tocopherols because they were noted to have activity similar to α-tocopherol [5–9]. When the chemical structures of these substances were found to be more unsaturated in their side chain, these tocopherols were named tocotrienols [6, 7]. The first tocotrienols were identified as α-, β-, and γ-tocotrienol and δ-tocotrienol was isolated later and identified from palm oil [6].

Tocopherols and tocotrienols have similar basic chemical structures (Fig. 1) [8]. They are the derivatives of a 6-chromanol ring and the difference between the tocopherol homologues and the tocotrienol homologues is in the

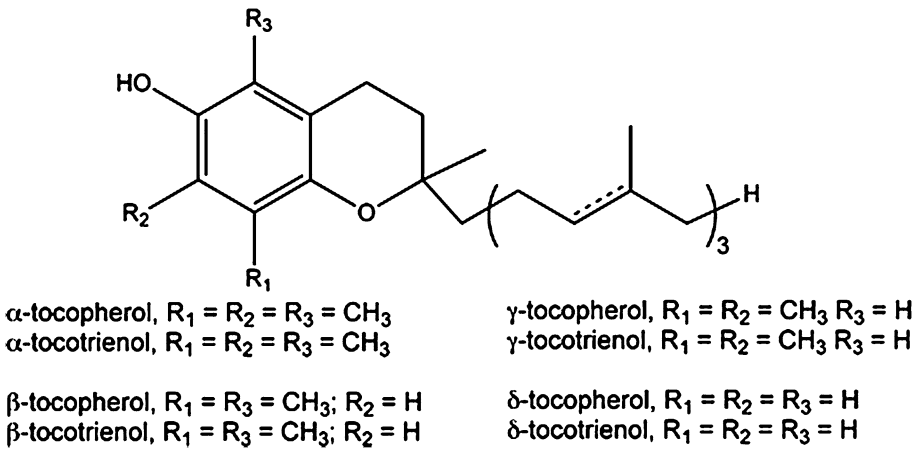

Fig. 1 The chemical structures of tocopherols and tocotrienols

saturation or the unsaturation of their side chain. The tocopherols have a saturated side chain, while the tocotrienols have an unsaturated side chain containing three double bonds. The tocopherol and tocotrienol homologues are named α, β, γ, and δ depending on the position and number of the methyl substitutions on the aromatic side of the chromanol ring.

The tocopherols and tocotrienols are yellow viscous compounds at room temperature; insoluble in water but miscible in aprotic solvents. The tocopherols and tocotrienols are found in whole grains, seeds, nuts, vegetable oils, fruits, green leafy vegetables, meat, fish, milk and egg products [9]. The tocopherols are mainly present in oil seeds, oils, meats and green parts of higher plants, whereas the tocotrienols are mostly found in the germ and bran fraction of certain seeds and cereals. The most abundant natural antioxidants in vegetable oils are the α- and γ-tocopherols.

It is generally agreed that tocopherols and tocotrienols can inhibit lipid oxidation in food lipids and some of the homologues can also do so in biological systems; α-tocopherol has the highest in vivo antioxidant activity for higher animals and humans. The activity of tocopherols in biological systems is beyond the scope of this review paper. A comprehensive review which gives information about recent advances in the knowledge of vitamin E chemistry and biology as well as evidence from clinical and epidemiologic studies on the beneficial effects of supplementation with vitamin E is has recently been published [10].

The antioxidant activities of tocopherols and tocotrienols are due to their abilities to donate their phenolic hydrogen to lipid free radicals and retard the autocatalytic lipid peroxidation processes. Originally the hydrogen donating power was believed to be in the order of $\alpha > \beta > \gamma > \delta$ tocopherol homologues [11]. However, different lipid model systems, varying oxidation conditions, and multiple methods to determine the relative antioxidant activities of the various tocopherol and tocotrienol homologues in vitro have shown differing results. This has led to considerable confusion about the antioxidant activities of tocopherols and tocotrienols in the literature.

Antioxidant Function of Tocopherols in Animal Fats

Numerous studies have compared the antioxidant activities of various tocopherols in vegetable oils and animal fats. Studies have mainly focused on the comparison of the antioxidant activities of α- and γ-tocopherols.

Telegdy and Berndorfer [12] investigated the antioxidative mechanism of α-, β-, γ-, and δ-tocopherol in lard. They found that the relative antioxidant effects of 0.2% tocopherols were α-T > γ-T > β-T > δ-T between 20 and 60 °C, and δ-T > γ-T > α-T > β-T between 80 and 120 °C. Parkhurst et al. [13] determined the oxidative stability (the length of the induction period) of tocopherols in vacuum distilled lard. A sample was placed in a Warburg flask and the individual tocopherols were added in ethanol solution. The concentrations of α-tocopherol were 0, 50, 200, 300 and 650 ppm. The concentrations of γ-tocopherol were 0, 50, 100, 400, 450 and 600 ppm. The concentrations of δ-tocopherol were 0, 25, 100, 250, 300 and 500 ppm. The ethanol from the sample was removed by a vacuum. The flask was attached to the Warburg manometer and placed in an oil bath (97 ± 0.25 °C). They measured the pressure change in the flask during the oxidation and the uptake of molecular oxygen was used to indicate the length of the induction period. The efficiency of antioxidants was found to be as follow: γ-tocopherol > δ-tocopherol > α-tocopherol. Yuki [14] used a continuous water spraying and heating system to compare the thermo stability of a natural tocopherol mixture and

butylated hydroxyanisole (BHA). The rate of decrease of the tocopherol mixture was very small and the induction period of oxidation in the heated oils was very short compared to BHA. Cort [15] also found that at 0.02, 0.05 and 0.2%, DL-γ-tocopherol was a better antioxidant than DL- or D-α-tocopherol in chicken and pork fats. DL-γ-tocopherol was found to be better antioxidant than DL-α-tocopherol in beef fat at 0.02% concentration. In a different experiment, 0.2 g of chicken, pork and beef fats and tocopherols were applied onto thin layers and kept at 45 °C. The peroxide value (PV) was measured daily until PV reached 20 mequiv/kg animal fat. These early studies showed that γ-tocopherol usually exhibited a higher antioxidant effect than α-tocopherol in the protection against oxidation of animal fats used in the experiments.

Ke et al. [16] compared the antioxidative activities of butylhydroxy anisole (BHA), butylhydroxy toluene (BHT), *tert*-butylhydroquinone (TBHQ), α-tocopherol, and tempeh oil in mackerel (fish) skin lipids. Tempeh oil was extracted from tempeh, a fermented soybean product that had previously shown some antioxidant activity. BHA was added into corn oil, BHT and TBHQ were added into propylene glycol, and tempeh oil and α-tocopherol were added directly. In this experiment the weight gain due to molecular oxygen absorption during autoxidation, and PV, thiobarbituric acid reactive substances (TBARS), and free fatty acid content were measured. The relative order of efficiency for preventing oxidation of mackerel skin lipids at 0.02% for all synthetic antioxidants and 0.01% for α-tocopherol and 5% for tempeh oil was: TBHQ > α-tocopherol > tempeh oil > BHA > BHT.

Lampi and Piironen [19] examined how α- and γ-tocopherol affect the oxidation of butter oil triacylglycerols from which tocopherols and most of the other anti- and pro-oxidants had been removed. Tocopherols were added in the range of 2–500 μg/g concentrations to samples. The test samples were oxidized at 40 °C in the dark for 16 days, and the PV, anisidine value (AV), volatile aldehydes and residual tocopherol concentrations were measured every 4 days. PV is a measurement for hydroperoxide concentration, the primary oxidation product of lipids. AV and volatile aldehydes are a measurement of secondary oxidation products. The rate of oxidation during the induction period with added α-tocopherol was less than that with added γ-tocopherol. These investigators did not find prooxidative effect of tocopherols even at 500 μg/g concentration, which was 25 times of the level of the original butter oil.

Kanno et al. [20] investigated the antioxidant effect of tocopherols on the protection of autoxidation in milk fat at 50 °C. The order of antioxidant activity of tocopherol homologues was compared as the time to reach 30 PV mequiv/kg. It was found that: at 0.001% γ-T > β-T > δ-T > α-T, at 0.003% α-T > γ-T > β-T > δ-T, at 0.01% γ-T > δ-T > β-T > α-T, and at concentrations greater than 0.05% δ-T > γ-T > β-T > α-T. α-Tocopherol at 0.003%, which corresponded to the content in original milk fat, was more effective than other tocopherols at the same level and α-tocopherol at other levels. These investigators also observed that all the tocopherols had clearly defined induction periods at the levels less than 0.01%, and no definite induction periods at higher concentrations.

Information on the antioxidant effects of tocopherols and tocotrienols in fish oils is relatively less compared to other animal fats. Hamilton et al. [21] investigated the effects of α-tocopherol, δ-tocopherol, and a mixture of γ- and δ-tocopherols on the oxidative stability and flavor of refined fish oil. Stability was measured in the presence of air at 20 °C from 0 to 6 months by measuring PV and off-flavor formations. The protective effect of tocopherols at 2% concentration was as follows: δ-T > γ-/δ-T > α-T. Kulas and Ackman [22] used purified fish oil triacylglycerols to study the antioxidant properties of α-, γ- and δ-tocopherols. The samples were stored in uncapped glass vials in the dark at 30 °C for 0, 2, 4, 6, 8 and 10 days. The ability to retard the formation of hydroperoxides, measured by the PV, decreased in the order of α-T > γ-T > δ-T at a level for 100 ppm, and a reverse order was observed when the initial concentration was 1,000 ppm. They observed that the reverse of order was due to the changes in concentrations. These investigators also found that all three tocopherols strongly influenced the formation of volatile secondary oxidation products in a concentration-dependant manner. The relative consumption rate was found to be greater for α-tocopherol than for γ-tocopherol. The relative consumption rate for δ-tocopherol was not dependent on the concentration above 500 ppm.

Réblová [23] investigated the effect of temperatures between 80 and 150 °C on the antioxidant activity of α- and γ-tocopherols in lard using the Oxipres apparatus to determine the oxygen consumption. A concentration of 100 mg/kg for both tocopherols was used. The γ-tocopherol showed decreasing antioxidant activity with increasing temperature while the α-tocopherol activity remained constant in the range from 80 to 110 °C, with decreased activity at higher temperature. At 150 °C, both tocopherols were ineffective antioxidants.

Antioxidant Function of Tocopherols in Vegetable Oils

Reinton and Rogstad [17] studied the inhibitory effect of α-tocopherol and γ-tocopherol on the lipoxygenase catalyzed oxidation of linoleic acid. They used gas chromatography to measure the unchanged fatty acid content after 1-, 3-, 5-, 7-, 10-, 12- and 15-min incubation periods at

50 °C, and they also measured the PV and TBARS value. After an incubation time of one-minute, 8% α- and γ-tocopherol did not inhibit the oxidation, while 0.8% α- and γ-tocopherol had inhibitive effects. However, at longer incubation times, both α- and γ-tocopherol at 8% concentration showed very nearly identical inhibitive effects. These investigators found that γ-tocopherol could better inhibit the formation of secondary oxidative products than α-tocopherol. Hudson and Ghavami [18] used ethanolic alkali saponified soybean oil and extracted the unsaponifiable matter by hexane, which were active antioxidants in soybean oil. They analyzed the unsaponifiable matter and found various tocopherols and some of their derivatives, such as α-tocopheryl quinone, α-tocopheryl dimer, and γ-tocopheryl dimer. In this system, at 0.02% concentration γ- and δ-tocopherols were found to be better antioxidants than α-tocopherol. The antioxidant effects of tocopherols were determined by two methods: the FIRA-Astell method and the Rancimat method. The FIRA-Astell method monitored the oxygen absorption continually until its sudden acceleration at the end of the induction period. The Rancimat method monitored the conductivity of a heated sample, through which a stream of air was passed. The results of these two methods were similar to each other. The above two studies showed that γ-tocopherol had better antioxidant effect than α-tocopherol in vegetable oils.

Jung et al. [25] studied the effects of α-, γ-, and δ-tocopherols on chlorophyll b-photosensitized oxidation of purified soybean oil. α-Tocopherol, γ-tocopherol, and δ-tocopherol were added in concentrations of 0, 0.001, 0.002 and 0.004 mol/L to purified soybean oil (0.16 mol/L) in methylene chloride containing 3.3×10^{-9} mol/L chlorophyll b at 25 °C. The oxidation of soybean oil was evaluated by PV and headspace oxygen concentration of the samples. The relative antioxidant effects were found to be α-T > γ-T > δ-T at 0.001 mol/L, α-T ≈ γ-T > δ-T at 0.002 mol/L, and α-T ≈ γ-T ≈ δ-T at 0.004 mol/L indicating an antioxidant concentration dependence of antioxidant activity. Fuster et al. [26] examined the effects of α- and γ-tocopherol (1, 2, 4, 7, 20, 40, 70, 100, 200, 400, 700, 1,000, 1,500 and 2,000 ppm) on the autoxidation of purified sunflower oil triacylglycerols by PV measurement. The test samples were oxidized at 55 °C in a thermostated oven in the dark for 7 days. α-Tocopherol was a better antioxidant than γ-tocopherol at the levels of less than 40 ppm, while γ-tocopherol was better than α-tocopherol at the levels of more than 200 ppm. Both α- and γ-tocopherols had no prooxidant effect at 2,000 ppm. Lampi et al. [27] studied the antioxidant properties of α- and γ-tocopherol (5, 10, 50, 100 and 500 μg/g) in the oxidation of rapeseed oil triacylglycerols at 40 °C in the dark for 16 days. The test samples were analyzed every 4 days for their oxidative status by measuring PV, AV and the volatile aldehydes containing 5–10 carbon atoms. α-Tocopherol was more stable and effective than γ-tocopherol at concentrations less than 50 μg/g, γ-tocopherol was more effective than α-tocopherol at concentrations greater than 100 μg/g.

Yanishlieva et al. [28] developed a kinetic model to study the antioxidative behavior of α- and γ-tocopherols (5, 10, 50, 100, 200, 350, 500, 1,000, and 2,000 ppm) in purified triacylglycerols of sunflower oil and soybean oil at 100 °C. Air was blown through the samples in the dark at a rate of 100 mL/min. In this model, the antioxidant activity on the length of the induction period and the rate of oxidation during the induction period were calculated. α-Tocopherol was better antioxidant than γ-tocopherol at low levels (≤400 ppm in sunflower oil and ≤700 ppm in soybean oil), while γ-tocopherol was a better antioxidant at higher concentrations. They concluded that the decrease of antioxidant effect at high levels of tocopherols was due to their consumption in some side reactions, such as the decomposition of hydroperoxides to generate alkoxyl and hydroxyl radicals, and caused peroxidizing reactions. These more recent studies have shown that at lower concentrations, α-tocopherol was a better antioxidant, and at higher concentrations, γ-tocopherol was better antioxidant protecting the oxidation of vegetable oil triacylglycerols. These studies suggest that the hydrogen radical of α-tocopherol reacted more quickly with the fatty acid chain than the hydrogen radical of γ-tocopherol.

Makinen et al. [29] evaluated the antioxidative effects of α- and γ-tocopherols (at 0, 10, 100, 500 and 1,000 ppm) on the autoxidation of methyl linoleate in open vials at 40 °C for 4 days. Tocopherols were added to the methyl linoleate dissolved ethanol and the solvent was removed by purging the oil with nitrogen. The following oxidation products were found by HPLC analysis: 9-*cis* and 13-*trans*, 13-*cis* and 9-*trans* isomers of fatty acid hydroperoxides, hydroxyl, and ketodiene and other oxidation products. α-Tocopherol was a more effective antioxidant at low concentration (10 ppm) but a less effective antioxidant at higher levels (100–1,000 ppm).

The effectiveness of tocopherols in a low oxygen environment was investigated by Isnardy et al. [30]. The researchers used α-, γ-, and δ-tocopherols in concentrations ranging from 0.1 to 0.25% in purified rapeseed oil triacylglycerols in the presence and absence of the peroxidation catalyst α,α′-asoisobutyronitrile (AIBN). They measured PV, conjugated dienes, AV, hexanal, and IV and found that in the low oxygen environment, none of the tocopherols had an antioxidant effect. Both α- and γ-tocopherols were observed to accelerate hydroperoxide formation. Only the δ-tocopherol had a non-accelerating effect on lipid peroxidation. The researchers felt that these results supported the strength of δ-tocopherol as a potent antioxidant, but not in this particular system.

Antioxidant Function of Tocopherols in Frying Oils and Fried Foods

The effect of thermal oxidative conditions, such as encountered in deep-frying, on tocopherols has also been investigated. Using a variety of oil quality tests including refractive index, free fatty acids, conjugated diene formation, and smoke point, Önal and Ergin [31] studied the effectiveness of the addition of 200 ppm α-tocopherol or ascorbyl palmitate to canola oil which was used to deep fry potatoes. They concluded that the addition of the antioxidants significantly improved the stability of the frying oil and extended the useful life of the oil.

Nogala-Kalucka et al. [32] also studied the effects of deep-frying on antioxidant stability and activity by adding α- and δ-tocopherol to the frying fat Planta, a mixture of partially hydrogenated rapeseed oil and palm oil. The amounts added were 0.01, 0.05, and 0.1% and PV, AV, and hexanal were used as measures of oxidation at 160 °C. The addition of an antioxidant improved the stability of the frying fat, but no concentration-dependent effects were observed. δ-Tocopherol was shown to be more stable than α-tocopherol at the high temperature used in this study.

CheMan et al. [24] studied the effects of TBHQ and α-tocopherol on the change of quality in refined, bleached and deodorized palm olein during deep fat frying (180 °C, 5 h/day for 5 consecutive days). α-Tocopherol was more effective in reducing AV and Totox (Totox = 2PV + AV) value, but TBHQ was more effective in reducing free fatty acid concentrations, polar components and polymer formations, the rates of change in iodine values, and C18: 2 to C16: 0 fatty acid ratio.

Aoyama et al. [33] investigated the oxidative stability of potato chips fried in lard and palm oil containing 0.02 and 0.05% α-, γ- and δ-tocopherols by measuring their PV. For potato chips fried in lard, the order of antioxidant efficiency was: δ-T > γ-T > α-T. None of the tocopherols showed protective effect on the oxidation of potato chips fried in palm oil. Tocopherols in potato chips at 60 °C storage, which were fried in lard, disappeared faster than those fried in palm oil. Rate of disappearance was in the following order: α-T > γ-T > δ-T. In a subsequent experiment, the same investigators [34] observed the antioxidant effects of various tocopherols of palm oil by using potato frying tests. Potato chips were fried for 1, 5, or 10 min in a) fresh palm oil in batch frying, and b) continuous frying in palm oil. Tocopherols were added to the oils in levels of 0, 0.03, 0.05 and 0.07%, and the potato chips were stored for 7–49 days. Addition of tocopherols to fresh palm oil had no effect on autoxidation of the chips, but addition of γ- and δ-tocopherol in the continuous frying test resulted in lower PV in the potato chips after 49 days storage. These effects were more significant with increasing dose and less significant with increasing frying time.

Antioxidant Function of Tocopherols in Emulsions

The activity of antioxidants in emulsions as compared to in bulk oil systems has been characterized by the "polar paradox" which is that polar antioxidants are more effective in nonpolar bulk oils and nonpolar antioxidants are more effective in more polar oil-in-water emulsions. In their study of dispersed systems by Nenadis et al. [35] looked at the effectiveness of BHA, BHT, TBHQ, α-tocopherol, caffeic acid, and Trolox in lecithin liposomes and an oil-in-water emulsion. They found that the low polarity BHA and BHT were most effective in the dispersed system and the a-tocopherol was intermediate in its activity in these systems.

In a further study of emulsions, Chaiyasit et al. [36] investigated the effectiveness of two pairs of polar and nonpolar antioxidants by comparing α- and δ-tocopherol, and BHT and 4-hydroxymethyl-2,6-di-*tert*-butylphenol in both bulk oil and an oil-in-water emulsion. All of the antioxidants were determined to have similar free-radical scavenging capabilities. They found that in bulk menhaden oil, BHT and α-tocopherol were more effective than the more polar 4-hydroxymethyl-2,6-di-*tert*-butylphenol and δ-tocopherol. In the emulsion, δ-tocopherol was the more effective tocopherol, but again BHT was more effective than 4-hydroxymethyl-2,6-di-*tert*-butylphenol. The researchers suggest that particle size may be a contributing factor and not just polarity and surface activity in determining antioxidant activity in bulk oils and emulsions.

Early studies indicated that γ-tocopherol was a better antioxidant than α-tocopherol but more recent studies have indicated that, on the basis of hydroperoxide formation, at lower concentrations α-tocopherol has higher antioxidant activity than γ-tocopherol. At higher concentrations γ-tocopherol was found to be a better antioxidant. This phenomenon may be due to the fact that γ-tocopherol is less effective as a prooxidant than α-tocopherol at higher concentrations. The cited studies are summarized in Table 1.

There are quite a few studies in the literature on the optimum concentrations of tocopherols in vegetable oils and animal fats. Kanno et al. [20] stated that α-tocopherol was contained at the optimal level in milk fat regarding to its antioxidant activity. Khafizov et al. [37] reported that soybean oil contained relatively more tocopherols than the optimum level for protecting oxidation. It was concluded that soybean oil between 500 and 700 ppm tocopherol concentrations has the best antioxidative qualities. Shishkov et al. [38] studied the contents of tocopherols in sunflower oil

Table 1 Comparison of the antioxidant activities of tocopherols in oils and fats

References	Oils or fats	Temperature	Methods	Order of antioxidant activity
[12]	Lard	20–60 °C	–	α-T > γ-T > β-T > δ-T
		80–120 °C	–	δ-T > γ-T > α-T > β-T
[13]	Lard	97 °C	Uptake of O_2	γ-T > α-T
[15]	Chicken, pork, and beef fats	45 °C	PV	γ-T > α-T, 0.02%
[16]	Lipids of mackerel skin	–	Weight gain from O_2 absorption, PV, TBARS, etc.	TBHQ > α-T > BHA > BHT α-T, 0.01%; others, 0.02%
[17]	Linoleic acid	–	GC, PV, TBARS	γ-T > α-T
[18]	Soybean oil	–	FIRA-Astell method, Rancimat method	γ-/δ-T > α-T
[19]	Butter oil triacylglycerols	40 °C/dark	PV, AV, volatile aldehydes	γ-T > α-T
[24]	Palm olein		AV, Totox	α-T > TBHQ
[25]	Soybean oil	25 °C	PV and headspace O_2 depression	α-T > γ-T > δ-T, 0.001 M α-T ≈ γ-T > δ-T, 0.002 M α-T ≈ γ-T ≈ δ-T, 0.004 M
[26]	Sunflower oil triacylglycerols	55 °C	PV	α-T > γ-T, < 40 ppm γ-T > α-T, > 200 ppm
[27]	Rapeseed oil triacylglycerols	40 °C/dark	PV, AV, HPLC	α-T > γ-T, < 50 μg/g γ-T > α-T, > 100 μg/g
[28]	Sunflower oil triacylglycerols	100 °C	HPLC	α-T > γ-T, ≤ 400 ppm γ-T better, higher conc.
	Soybean oil triacylglycerols	100 °C	HPLC	α-T > γ-T, ≤ 700 ppm γ-T better, higher conc.
[20]	Milk fat	50 °C	PV	γ-T > β-T > δ-T > α-T, 0.001% α-T > γ-T > β-T > δ-T, 0.003% γ-T > δ-T > β-T > α-T, 0.01% δ-T > γ-T > β-T > α-T, 0.05%
[21]	Fish oil	20 °C	PV	δ-T > γ-/δ-T > α-T, 2%
[22]	Fish oil triacylglycerols	30 °C/dark	PV, AV	α-T > γ-T > δ-T 100 ppm δ-T > γ-T > α-T 1000 ppm
[29]	Methyl linoleate	40 °C	HPLC	α-T > γ-T, 10 ppm γ-T > α-T, 100-1000 ppm

AV anisidine value, *BHA* butylated hydroxyanisole, *BHT* butylated hydroxytoluene, *GC* gas chromatography, *HPLC* high performance liquid chromatography, *PV* peroxide value, *TBARS* thiobarbituric acid reactive substances, *TBHQ tert*-butyl hydroquinone, *T* tocopherol

after extraction and refining, and their effect on oxidation. They found the optimum levels of tocopherols to inhibit oil oxidation are from 350 to 550 ppm. They found that the antioxidant effect was reduced if the concentrations were either greater or lower than the optimum concentration.

Timmermann and Adams [39] investigated the antioxidant effects of various tocopherols in lard by measuring their induction periods. Significant antioxidant action was observed by adding greater than 50 ppm tocopherols to lard. The antioxidant effect increased as tocopherols concentration increased to 500 ppm, and remained constant to around 2,500 ppm, but the antioxidant effect decreased above 2,500 ppm. Clark et al. [40] studied the antioxidant effectiveness of Covi-ox® T-70 (a commercial tocopherol mixture consisting of 12% α-tocopherol, 1% β-tocopherol, 61% γ-tocopherol and 26% of δ-tocopherol). Addition of 400 ppm Covi-ox® T-70 to vegetable oils such as peanut, cottonseed and hydrogenated soybean oil or animal fats such as milk fat, pork lard and chicken fat increased the stability of these fats measured by the active oxygen method. However, above 400 ppm a plateau in the antioxidant activity was observed, but even above 1,000 ppm concentration of antioxidants no prooxidant effect was observed. However, the addition of Covi-ox® T-70 to vegetable oils produced very small increase in the oils stability, but the addition of Covi-ox® T-70 to animal fats caused a relatively large increase in their stability. The lower increase in stability for oils was probably because plants contain endogenous tocopherols, and the concentrations in most vegetable oils are close to their optimum levels, however, animal fats usually do not contain high concentrations tocopherols.

Jung and Min [41] found the concentrations for α-, γ-, and δ-tocopherols to produce optimum oxidative

stability, for purified soybean oil, in the dark at 55 °C in the levels of 100, 250 and 500 ppm, respectively. It was found that the α-, γ-, and δ-tocopherols had significant prooxidant effect above their optimum concentration. It was also determined that oxidized α-, γ-, and δ-tocopherols had prooxidant effects measured by PV and headspace analysis in purified soybean oil under the same experimental condition. Oxidized α-tocopherol had higher prooxidant effect than oxidized γ- and δ-tocopherol [42].

Yoshida et al. [43] measured the effects of tocopherols on the oxidative stability in vacuum distilled oils such as rapeseed, soybean and palm oils using microwave heating and measuring the PV, AV and carbonyl value which measures the concentrations of secondary oxidation products. Optimum concentration required to produce oxidative stability in the above oils was 100 ppm for α-tocopherol, 150–200 ppm for β- and γ-tocopherols, and 500 ppm for δ-tocopherol. Above 500 ppm none of the tocopherols significantly increased the antioxidant activities of the oils.

Huang et al. [44] evaluated the inhibition of α- and γ-tocopherols on the formation of hydroperoxides in vacuum distilled corn oil and in a 10% oil-in-water system. The optimum concentration for α-tocopherol was 100 ppm in corn oil and 250–500 ppm in oil-in-water emulsion, while the optimum concentration for γ-tocopherol was 250–500 ppm in corn oil. α-Tocopherol showed a prooxidant effect at more than 250 ppm in corn oil and at more than 500 ppm in the oil-in-water emulsion. In another study, the same investigators [45] observed that γ-tocopherol had a prooxidant effect at 5,000 ppm in vacuum distilled corn oil. The antioxidant activity of δ-tocopherol was still active even up to 2,000 ppm concentration in the above systems. The concentrations for maximum antioxidant effects of α- and γ-tocopherol mixture (50% α-tocopherol and 50% γ-tocopherol) and natural mixture tocopherols isolated from soybean (13% α-tocopherol, 64% γ-tocopherol and 21% δ-tocopherol) were found to be 250 and 500 ppm, respectively. The α- and γ-tocopherol mixture (50% α-tocopherol and 50% γ-tocopherol) showed prooxidant effect at 500 ppm and the natural mixture tocopherols isolated from soybean (13% α-tocopherol, 64% γ-tocopherol and 21% δ-tocopherol) showed prooxidant effect at 1,000 ppm. The concentration of α-tocopherol determined in the mixtures whether it acted as an antioxidant or a prooxidant.

Blekas et al. [46] studied the effect of 100, 500, and 1,000 ppm of α-tocopherol in the oxidative stability of purified olive oil. Periodic measurements for PV and absorbance at 232 nm (measuring diene conjugation) were carried out of the oil held at 40 °C in the dark. α-Tocopherol demonstrated antioxidant activity at all the above levels, but the antioxidant effect was greater at 100 ppm than at the higher levels. Evans et al. [47] determined the optimum concentrations of tocopherols to inhibit soybean oil oxidation. Stability was determined by measuring conjugated diene formation rate (conjugated dienes are formed in the fatty acids during autoxidation). The optimum level to produce stability for α-tocopherol was about 100 ppm and for γ-tocopherol was about 300 ppm, and the optimum concentration for the natural tocopherols mixture (5% α-tocopherol, 68% γ-tocopherol and 26% δ-tocopherol) in soybean oil was between 340 and 660 ppm. Individual tocopherols showed prooxidant behavior in oils above their optimal concentrations. The antioxidant activity of α-tocopherol at about 100 ppm was 3–5 times more potent than that of γ-tocopherol at about 300 ppm. Yanishlieva et al. [28] reported that the optimum concentration of α-tocopherol was 200 ppm in soybean oil and 350 ppm in sunflower oil, and that of γ-tocopherol was 500 ppm in soybean oil and 1,000 ppm in sunflower oil at 100 °C in the dark. In general the optimum antioxidant concentration of α-tocopherol for vegetable oils is lower than the other tocopherols (Table 2).

There are a few studies reported in the literature on the order of decomposition of tocopherols during autoxidation of oils and fats. Kajimoto et al. [48] studied the antioxidant activity of α-tocopherol, δ-tocopherol, a mixture of α- and δ-tocopherols and BHA in lard by comparing the heat stability of these antioxidants after heating the lard at 160 °C for an extended period. The time for 75% decomposition of antioxidants was found to be as follow: 1 h for BHA $<$ 2.5 h for α-T $<$ 3.8 h for γ-T and $<$ 4.2 h for a mixture of α-T and γ-T. Ha and Igarashi [49] investigated the formation of oxidation products of tocopherols due to autoxidation of methyl linoleate. They found that α-tocopherol was oxidized first during the autoxidation and γ- or δ-tocopherols oxidized after all of the α-tocopherol was consumed. Yoshida et al. [50, 51] studied the relative stabilities of individual tocopherols in different types of fatty acid esters, vacuum distilled vegetable oils (tocopherols removed) and purified animal fats such as beef tallow and lard, after microwave heating for 0, 4, 8, 12, 16 and 20 min. Tocopherols at 0.25 μmol/g were added to the oils or fats. The order of stability of tocopherols during microwave heating was δ-T $>$ β-T $>$ γ-T $>$ α-T. It was reported that in methyl linoleate and tocopherol stripped vegetable oils (rapeseed oil, soybean oil and palm oil) the antioxidant effect of tocopherols disappeared in the following order: α-T $>$ β-T $=$ γ-T $>$ δ-T. α-Tocopherol was consumed first, followed by β- or γ-tocopherol, and δ-tocopherol was consumed more slowly [44]. This finding is in good agreement with the experiment reported by Kulas and Ackman [22] in fish oils. In general, during the lipid oxidation process, α-tocopherol is oxidized first by donating its hydroxy free radical as an

Table 2 Optimum concentrations of tocopherols in oils and fats

References	Oils or fats	Optimum concentrations
[20]	Milk fat	α-T = original content (0.003%)
[37]	Soybean oil	500–700 ppm of original content
[38]	Sunflower oil	350–550 ppm of original content
[39]	Lard	500–2,500 ppm addition
[40]	Peanut oil	400 mg tocopherols/kg vegetable oils
	Cottonseed oil	
	Soybean oil	
	Milk fat	400 mg tocopherols/kg animal fats
	Pork lard	
	Chicken fat	
[41]	Purified soybean oil	α-T = 100 ppm, γ-T = 250 ppm, δ-T = 500 ppm
[43]	Stripped rapeseed/soybean/palm oils	α-T = 100 ppm, β-/γ-T = 150–200 ppm, δ-T = 500 ppm
[44]	Stripped corn oil and 10% oil-in-water	α-T = 1 00 ppm (corn oil) γ-T = 250–500 ppm (corn oil)
		α-T = 250–500 ppm (oil-in water)
[46]	Purified olive oil	α-T = 100 ppm
[47]	Soybean oil	α-T = 100 ppm, γ-T = 300 ppm
[28]	Soybean oil	α-T = 200 ppm, γ-T = 500 ppm
	Sunflower oil	α-T = 350 ppm, γ-T = 1,000 ppm

T tocopherol

Table 3 The decomposition order of tocopherols in oils and fats

References	Oils or fats	Decomposition order
[48]	Lard	BHA > α-T > γ-T > α-/γ-T
[49]	Methyl linoleate	α-T > γ-/δ-T
[50, 51]	Stripped oils and fats	α-T > γ-T > β-T > δ-T
[43]	Stripped rapeseed/soybean/palm oils	α-T > γ-T = β-T > δ-T

BHA butylhydroxy anisole, *T* tocopherol

antioxidant to stabilize the fatty acid radicals, while undergoing oxidation itself, mostly to α-tocopheryl quinone (Table 3).

Antioxidant Function of Tocopherols in Food Products

The antioxidant function of tocopherols in various foods has been reported by many researchers in various types of food. However, because every experiment focused on a different food, it is challenging to compare the results (Table 4).

Instant ramen, a Japanese dried noodle product, is often fried in lard during production to produce the characteristic flavor. Kuwahara et al. [58] reported that natural vitamin E at levels of 0.01–0.05% prevented the lard oxidation in the noodles very well. Instant ramen noodles manufactured by frying with lard containing 0.03% vitamin E produced better results than the instant ramen noodles manufactured by frying with lard containing synthetic antioxidants such as BHA and BHT, which was measured by the active oxygen method. The above investigators reported another study [59] on the comparison of instant ramen noodles fried with lard containing 0.02 and 0.04% vitamin E and 0.01% BHT. Manufacturing of ramen noodles was carried out on a plant-size scale, and the fried instant ramen noodles were subjected to oxidative stability tests under daylight. Results showed again that in the presence of vitamin E the oxidative stability of ramen noodles was better than in the presence of BHT used in lard for frying. There were no significant differences in antioxidant activity between the lards containing 0.02 and 0.04% vitamin E. Products fried with lard containing vitamin E were also free from unfavorable flavor and color compared to products fried with lard containing BHT. Rho and Seib [60] also compared the shelf life of instant fried noodles with δ-tocopherol, synthetic α-tocopherol, BHA, a mixture of 50% BHA and 50% BHT. In this experiment 200 ppm of the antioxidant was dissolved in 95% ethanol and the solution was added to the frying oil. The frying was conducted at 180 °C. After a single frying, the oxidative stability of fried noodles was determined by the onset of rancidity by sensory evaluation of the oxidation products. The addition of α-tocopherol, δ-tocopherol, BHA and mixture of BHT and

Table 4 Antioxidant Activities of Tocopherols in Food Systems

References	Food system	Methods	Results
[58]	Instant ramen with lard	Active oxygen	Vitamin E (0.03%) > BHA or BHT
[59]	Instant ramen with lard	Preservation test (under sunlight)	Vitamin E (0.02–0.04%), free from unfavorable flavor and color
[60]	Instant fried noodles	Shelf life	α-T: 7 days, δ-T: 9 days, BHA: 11 days, BHA/BHT: 14 days BHA/BHT > BHA > δ-T > α-T
[61]	Margarines	Acid value, PV	Tocopherols = BHA > DL-α-T γ-T
[62]	Pecan kernel	Headspace pentane	Mixed tocopherols had effects, BHA/BHT/TBHQ had not.
[33, 34]	Potato chip fried with lard and palm oil	PV	δ-T > γ-T > α-T (lard), no effects (palm oil).
		Storage at 60 °C	Disappearance rate: α-T > γ-T > δ-T, T (lard) > T (palm oil)
[63]	cookies	loss of T	α-T > δ-T
		storage at 25–60 °C	
[65]	15 edible plant leaves	relationship	coefficient = 0.93 (between α-T/antioxidant effect)
[67]	avocado puree	IV, PV	α-T improved product shelf-life

BHA butylated hydroxyanisole, *BHT* butylated hydroxytoluene, *IV* iodine value, *PV* peroxide value, *TBARS* thiobarbituric acid reactive substances, *TBHQ tert*-butyl hydroquinone, *T* tocopherol, *T3* tocotrienol

BHA prolonged the shelf life of the fried noodles to 7, 9, 11 and 14 days, respectively, at 63 °C. The previously described results of Kuwahara et al. [58, 59] indicated that vitamin E was a better antioxidant than BHA or BHT, however, the study of Rho and Seib showed opposite results, that BHA or a mixture of BHA and BHT had better antioxidant effects than α-tocopherol and δ-tocopherol in fried noodles.

Kanematsu et al. [61] studied the effect of tocopherols, such as synthetic α-tocopherol, mixed natural tocopherol concentrate and BHA, on oxidative stability of margarines by measuring changes in acid value, PV and tocopherol content. As a control, margarine without antioxidants was used. Margarines were stored at 5 or 25 °C for 6 months. Natural mixed tocopherols and BHA was found to have nearly the same antioxidant effect, but the synthetic α-tocopherol showed a slightly lower antioxidant effect.

King [62] determined the effects of antioxidants and modified atmospheres (vacuum and N_2 gas) on the stability of pecan kernels stored at 85 °C for 15 weeks. Chopped pecan kernels were treated with various antioxidants such as α-tocopherol at 0.05%, γ-tocopherol and mixed tocopherols at 0.02 and 0.05%, BHA, BHT and TBHQ at 0.02% sealed in cans with or without headspace modification by vacuum or N_2 flush. α-Tocopherol, γ-tocopherol and mixed tocopherols at 0.05% had significantly protected the color and reduced flavor changes. γ-Tocopherol and mixed tocopherols also reduced the headspace pentane production. BHA, BHT and TBHQ had no effect at all. Using vacuum or N_2 gas flush for preserving the oxidation of pecan kernels was more effective than tocopherol treatment.

Ochi et al. [63] studied the effects of α- and δ-tocopherols on oxidative stability of cookies. Both α- and δ-tocopherol were decreased by 20% during baking. During storage between 25 and 60 °C, the degradation of α-tocopherol was faster than the degradation of δ-tocopherol. But the loss of α- and δ-tocopherols decreased with an increase in added amounts of whole milk powder and egg because they protected the fats from oxidative degradation. Cookies with added α-tocopherol (50 mg/100 g dough) had relatively high PV of their lipid fraction after baking.

Inagaki [64] investigated the antioxidative components in unshu-orange flavedo (the white part in the peel of unshu orange), which inhibited autoxidation of limonene. The antioxidants identified by thin layer and gas–liquid partition chromatography were: 100–160 μg/g α-tocopherol, and 60–70 μg/g γ-tocopherol on fresh weight basis.

Mallet et al. [65] investigated the relationship of antioxidant activity of 15 species edible plant leaves and their α-tocopherol concentrations. Air-dried leaves were ground to a fine power and extracted with hexane. The crude extracts, obtained after drying by vacuum, and were stored under argon at −10 °C. The α-tocopherol contents of various leaves were determined by a gas-chromatographic (GC) method on a fused-silica capillary column with α-tocopherol acetate as an internal standard. Antioxidant activities of leaf extracts were measured by a spectrophotometric method described by Taga et al. [66], which is based on the extent of oxidative losses of β-carotene in a β-carotene-linoleic acid system. The correlation coefficient between the α-tocopherol content and antioxidant activity was 0.93, which suggested that α-tocopherol was the major lipid soluble antioxidant in leaves.

Elez-Martínez et al. [67] studied the ability of α-tocopherol to extend the shelf life of an avocado puree by determining the PV and IV of the stored puree with and without added tocopherol (100 ppm) and sorbic acid, an antimicrobial agent. They found that the α-tocopherol was very effective in extending the shelf-life but sorbic acid had the effect of enhancing oxidation in the avocado puree. Therefore, the best quality product was obtained with the addition of α-tocopherol and sorbic acid and using low oxygen packaging.

Antioxidant Function of Tocotrienols in Oils and Fats

Tocotrienols are free radical scavenging antioxidants, however, only the α-isomer has considerable biological antioxidant activity. It is therefore not surprising that there are relatively very few studies on their antioxidative effects in oils and fats.

Pennock et al. [6] identified all four tocotrienols (α, β, γ, and δ) in 1964. Seher and Ivanov [52] isolated α- and γ-tocotrienols from the unsaponifiable fraction of fennel seed oil, β- and δ-tocotrienols were isolated from the unsaponifiable fraction of raw palm oil by preparative TLC. The antioxidant activities of tocotrienols were studied in lard measured by PV (1.5 mequiv O_2/kg) with the refractometric method of Ivanov. The tocotrienols were found to be more active antioxidants in lard than the corresponding tocopherols at levels of 0.02 and 0.05%. The order of antioxidative activity at 0.02% concentration was found to be: δ-T3 > γ-T3 > β-T3 > α-T3 at 110 °C in the dark.

Yamaoka et al. [53] compared the antioxidative activities of α-tocotrienol, γ-tocotrienols, α-tocopherol and γ-tocopherols in methyl linoleate at 60 °C using the increase of weight gain of oxidized samples due to oxygen incorporation to form peroxide of fatty acids in the samples. The results confirmed that tocotrienols had slightly superior or equal antioxidant activities compared to the corresponding tocopherols in methyl linoleate.

Top et al. [54] investigated the antioxidant activity of vitamin E isolated from palm *Elaeis guineensis* (an African oil palm) in a model system. The model system contained vitamin E-free, refined, bleached, and deodorized palm olein and palm oil methyl ester. Oxidative stability was measured by the Rancimat method. This method measures the stability of fats based on the active oxygen method. Addition of 200–2,000 ppm α-, γ-, or δ-tocotrienol effectively inhibited the oxidation of vitamin E free refined, bleached, and deodorized palm olein. The order of antioxidant activity was: γ-T3 > δ-T3 > α-T3. γ-Tocotrienol had twice the antioxidant activity of α-tocotrienol.

Feng [55] used preparative chromatographic techniques to isolate and purify various tocopherols and various tocotrienols from vegetable oils. Oxidative stability index (OSI), Totox and conjugated diene measurements were used to study the antioxidant activity of purified α-tocopherol, α-tocotrienol, γ-tocopherol and γ-tocotrienol. Corn oil, palm olein and soybean oil were vacuum distilled to remove the tocopherols and tocotrienols and were reconstituted with the individual tocopherol and tocotrienol homologues. Results showed that the order of antioxidant activities measured by the OSI method were in the following order in palm olein: γ-T3 ≥ γ-T > α-T ≈ α-T3 between 100 and 1,000 ppm. Antioxidant activities using 400 ppm tocopherols or tocotrienols measured by Totox and conjugated dienes at 100 °C for 0.5–17 h heat treatment were as follows: in palm olein γ-T3 > γ-T > α-T3 ≥ α-T, in soybean oil γ-T3 > γ-T > α-T3 > α-T and in corn oil γ-T3 > γ-T > α-T ≈ α-T3.

Wagner et al. [56] studied the stabilizing effects of tocotrienols and the corresponding tocopherols in coconut fat during frying. α-, β-, γ-, δ-Tocotrienols and α-, γ-, δ-tocopherols were used in this study. Final concentrations of tocotrienols in coconut fat were 0.01–0.1% and for tocopherols were 0.01–0.5%. Frying was carried out at 160 °C using airflow of 3 L per hour. The relative antioxidant effects of tocotrienols and tocopherols were expressed as the oxidative stability index. It was found that γ- and δ-tocotrienols were more active antioxidants in this medium than their corresponding tocopherols. The order of the antioxidative properties was as follows: α-T ≈ α-T3 < β-T3 < γ-T < γ-T3 < δ-T < δ-T3. In another experiment, the samples were oxidized at 60 °C in the dark up to 120 days and the oxidative changes were expressed as PV and by the formation of conjugated dienes. Both γ- and δ-tocotrienols increased the shelf life of the coconut fat, however, δ-tocotrienol activity was concentration dependant. γ-Tocotrienol did not show concentration dependence in the coconut fat.

The effectiveness of α-tocopherol and α-tocotrienol was compared to the antioxidant effect of a natural plant extract by Romero et al. [57]. An extract from the Rosa mosqueta shell, which is a source of carotenoid pigments, was added to stripped canola oil and the antioxidant activity was determined by Rancimat at 180 °C. The antioxidant activity was compared to α-tocopherol (185 mg/kg) and α-tocotrienol (138 mg/kg). The activity of the tocopherol was greater than the tocotrienol at the given concentrations and the researchers concluded that the natural extract was also a good antioxidant.

In general, in oils and fats, γ-tocotrienol was found to be a better antioxidant than α-tocotrienol, and tocotrienols were found to have higher antioxidant properties than their corresponding tocopherols (Table 5).

Table 5 Comparison of the antioxidant activity of tocotrienols in oils and fats

References	Oils or fats	Temperature	Methods	Order of antioxidant activity
[52]	Lard	110 °C/dark	Refractometric method	δ-T3 > γ-T3 > β-T3 > α-T3 (0.02%)
				Tocotrienols > Tocopherols (0.02 and 0.05%)
[53]	Methyl linoleate	60 °C	Weight gain	Tocotrienols > Tocopherols
[54]	palm methyl ester and palm olein	–	Rancimat method	γ-T3 > δ-T3 > α-T3
[55]	Corn oil	100 °C	Totox, CD	γ-T3 > γ-T > α-T $\approx$ α-T3 (400 ppm)
	Palm olein	100 °C	Totox, CD	γ-T3 > γ-T > α-T3 $\geq$ α-T (400 ppm)
	Soybean oil	100 °C	Totox, CD	γ-T3 > γ-T > α-T3 > α-T (400 ppm)
	Palm olein	–	OSI	γ-T3 $\geq$ γ-T > α-T $\approx$ α-T3 (100-1000 ppm)
[56]	Coconut fat	160 °C	OSI	γ-T3 > γ-T > α-T3 $\approx$ α-T
		60 °C	PV and CD	γ- and δ-T3 increased the shelf life
[57]	Canola oil	180 °C	Rancimat method	α-T > α-T3 > natural extract

CD conjugated dienes, *OSI* oxidative stability index, *PV* peroxide value, *TBARS* thiobarbituric acid reactive substances, *T* tocopherol, *T3* tocotrienol

Summary

Although various studies applied different methodologies to investigate the antioxidant activities of tocopherols in various oils and fats, on the basis of hydroperoxide formation at lower concentrations, α-tocopherol generally showed better antioxidant activity than γ-tocopherol, but at higher concentrations γ-tocopherol was found to be a more active antioxidant. The results of studies on the optimum antioxidant concentrations of tocopherols in oils and fats indicated that the optimal level for α-tocopherol is usually lower than other tocopherols, meaning less α-tocopherol is needed for maximum antioxidant protection. The optimum antioxidant concentrations of the various tocopherols also partly depend on the type of fat system used in an experiment. In addition α-tocopherol is oxidized faster than other tocopherols during lipids oxidation, meaning its hydrogen donating capacity is better than the other isomers. It is also speculated that tocopherols generally are consumed not only by antioxidant reactions but also in other "side reactions" which are not fully understood. α-Tocopherol was found to participate in side reactions other than peroxyl radicals formation more easily than γ-tocopherol.

There are quite a few studies stating that tocopherols, especially the α-isomer, have prooxidant effects at high concentrations. During the prooxidant stage, the lipid hydroperoxides decompose faster and the formed hydroxy free radicals initiate more oxidations in the system. There are comparatively very few studies related to the antioxidant activities of tocotrienols in oils and fats. It has been stated that generally γ-tocotrienol has a higher antioxidant effect than α-tocotrienol, and tocotrienols may be better antioxidants than their corresponding tocopherols in certain oils and fats systems.

Studies on the antioxidant activity of various tocopherols in food systems are varied and cannot be uniformly evaluated. It is because experiments generally have focused on different foods and used various methods for the detection of antioxidant activities. Depending on the food system, in certain cases tocopherols were better antioxidants than synthetic antioxidants such as BHT or BHA. However, in certain other food systems the synthetic antioxidants were more effective to increase the shelf life and the stability of foods than those containing tocopherols. The endogenous antioxidants were more effective than the exogenous antioxidants to improve the quality and shelf life of various meats.

It is proposed by one of the investigators in the literature [68] that understanding the interfacial phenomena is a key to understand the actions of antioxidants in heterogeneous food systems.

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