Effects of Individual Tocopherols and Tocopherol Mixtures on the Oxidative Stability of Corn Oil Triglycerides

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This study was aimed at evaluating the effectiveness of individual tocopherols and their mixtures in inhibiting the formation and decomposition of hydroperoxides in bulk corn oil stripped of natural tocopherols. δ-Tocopherol showed an antioxidant activity in the inhibition of both formation and decomposition of hydroperoxides at 2000 ppm or below, and its effectiveness increased with concentration. γ-Tocopherol promoted the formation of hydroperoxides but strongly inhibited their decomposition at 5000 ppm. On the basis of hydroperoxide formation, the concentrations for maximum antioxidant activity of α- and γ-tocopherol mixtures (1:1) and natural soybean tocopherol mixtures (α:γ:δ = 13:64:21) were 250 and 500 ppm, respectively. Prooxidant activity was also observed at a lower concentration with the α- + γ-tocopherol mixture (500 ppm) than with the soybean tocopherol mixture (1000 ppm). However, the inhibition by tocopherol mixtures increased with oxidation time. In contrast to hydroperoxide formation, tocopherol mixtures inhibited hydroperoxide decomposition more effectively at higher concentrations than at lower concentrations. Whether tocopherol mixtures acted as antioxidants or prooxidants depended on the concentration of α-tocopherol in the mixtures. The optimum concentration of tocopherol mixtures to increase the oxidative stability of bulk oils is determined by inhibition of hydroperoxide formation but not by inhibition of hydroperoxide decomposition.

Keywords: *Antioxidants; tocopherols; corn oil; antioxidation; hydroperoxides; hexanal*

INTRODUCTION

Much research has been reported on the antioxidant activities of individual tocopherols in different lipid systems (Bailey et al., 1943; Lee and Ward, 1959; Olcott and van der Veen, 1968; Parkhurst et al., 1968; Cillard and Cillard, 1980; Peers et al., 1981; Burton and Ingold, 1981; Lambelet and Loliger, 1984; Burton et al., 1985; Pryor et al., 1988, 1993; Gottstein and Grosch, 1990; Jung and Min, 1990; Yoshida et al., 1993; Huang et al., 1994). In bulk oil systems, antioxidant activity of tocopherols based on hydroperoxide formation was not improved by elevating tocopherol concentration in vegetable oils stripped of natural tocopherols (Jung and Min, 1990; Yoshida et al., 1993; Huang et al., 1994) or in lard (Parkhurst et al., 1968). Individual tocopherols were reported to have prooxidant activities at high concentrations in purified soybean oil (Jung and Min, 1990). The antioxidant activity of tocopherol mixtures was also investigated in vegetable oils and animal fats (Bailey et al., 1943; Stern et al., 1947; Frankel et al., 1959; Parkhurst et al., 1968). However, no simple relationship was found between tocopherol content and oil stability (Fore et al., 1953; Sturm et al., 1966). In lard, oxidative stability with 250 ppm of γ-tocopherol was not improved by adding more α-tocopherol (150 ppm) and δ-tocopherol (15 ppm) to make up to the content of tocopherols in peanut oil (Parkhurst et al., 1968), and in peanut oil stripped of natural tocopherols, the stability was also not increased by increasing the concentration of natural peanut tocopherols (Bailey et al., 1943). The oxidative stability of soybean oil was increased by decreasing the concentration of tocopherols from 1000–1500 to 400–600 ppm (Frankel et al., 1959) or to 500–1000 ppm (Sherwin, 1978).

In a previous study, the effectiveness of α- and γ-tocopherols was highly dependent on the test system (bulk oil, emulsion), the concentration, the oxidation time, and the method used to determine lipid oxidation (Huang et al., 1994). In stripped corn oil, the optimum concentrations to inhibit hydroperoxide formation were 100 ppm for α-tocopherol and 250–500 ppm for γ-tocopherol. α-Tocopherol showed an initial prooxidant effect at 250 ppm or higher, whereas γ-tocopherol showed no prooxidant activity at 1000 ppm or below. In contrast to hydroperoxide formation, the ability of α- and γ-tocopherols to inhibit the formation of hexanal, a decomposition product of linoleate hydroperoxides, was improved by increasing tocopherol concentration.

Although the evaluation of different tocopherols is important to understand how they affect lipid oxidation individually, tocopherols are always present as mixtures in food systems. How tocopherol mixtures influence the oxidative stability of oils and fats is a practical problem in food systems. Information from the literature is not sufficient to establish the relationship between the composition of tocopherol mixtures and lipid oxidation. In addition, few studies have been reported on the effects of tocopherol mixtures on the decomposition of hydroperoxides to volatile products, which is related to off-flavor formation in oxidized lipids (Frankel, 1982).

This paper presents a study of the relationship between the concentration and composition of tocopherol mixtures and oil stability. Also, antioxidant activity of γ- and δ-tocopherols was examined to extend our previous study on the effectiveness of individual tocopherols in corn oil triglycerides. The effectiveness of various concentrations of δ-tocopherol and tocopherol mixtures and of 5000 ppm of γ-tocopherol was evaluated at different stages of oxidation by measuring both the formation of hydroperoxides (conjugated dienes) and the decomposition of hydroperoxides to volatile products (hexanal) in corn oil.

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MATERIALS AND METHODS

Materials. Corn oil stripped of tocopherols by molecular distillation and γ- and δ-tocopherols were obtained commercially (Eastman Kodak Co., Rochester, NY). Corn oil was found to be free of tocopherols by high-performance liquid chromatography using a fluorescence detector (Handelman et al., 1985), and its peroxide value was below 10. The fatty acid composition of the corn oil as determined by gas chromatography (GC) of the methyl esters was 10.5% 16:0, 2.1% 18:0, 25.5% 18:1, 60.8% 18:2, and 1.1% 18:3. α-Tocopherol was purchased from Sigma Chemical Co. (St. Louis, MO). Soybean mixed tocopherol concentrate (Covi-ox T-90) was a gift from Henkel Corp. (La Grange, IL). Covi-ox T-90 contains 12% α-tocopherol, 1% β-tocopherol, 58% γ-tocopherol, 19% δ-tocopherol, and 10% vegetable oil.

Preparation of Oil Samples. Stripped corn oils containing different amounts of γ- and δ-tocopherols, 1:1 mixtures of α- and γ-tocopherols, or Covi-ox T-90 were prepared by direct addition.

Methods. Oxidations at 60 °C, spectrophotometric measurements of hydroperoxides, and headspace GC determinations of hexanal were carried out according to the same procedures described previously (Frankel et al., 1994). All oxidations and determinations were done in duplicate. Data obtained daily were analyzed by one-way analysis of variance (Steel and Torrie, 1980).

RESULTS

The effects of individual tocopherols and tocopherol mixtures on the oxidative stability of tocopherol-stripped corn oil were evaluated by measuring the formation and decomposition of hydroperoxides at 60 °C. The decomposition of hydroperoxides was determined by measuring the formation of hexanal, one of many important volatile products that has proved to be a useful analytical marker for the routine determination of oxidative decomposition of oxidized $n-6$ PUFAs (Frankel, 1982).

Effect of δ-Tocopherol. *Formation of Hydroperoxides.* In the control oil, the rate of hydroperoxide formation increased rapidly after an induction period of approximately 2 days (Figure 1a). In the presence of 100 and 250 ppm of δ-tocopherol, the rates of hydroperoxide formation increased rapidly after 3 and 5 days, respectively. At higher concentrations, the rate of hydroperoxide formation did not show an induction period and decreased with increasing concentration (Figure 2). The initial rate of hydroperoxide formation (expressed as millimoles per kilogram of oil per day) decreased more between 100 and 1000 ppm than between 1000 and 2000 ppm of δ-tocopherol. Furthermore, the inhibition of hydroperoxide formation by δ-tocopherol increased with oxidation time (Table 1).

Decomposition of Hydroperoxides. In the control oil, hexanal formation increased significantly after 2 days of oxidation (Figure 1b). δ-Tocopherol inhibited hexanal formation at all levels tested. With 100 ppm of δ-tocopherol, the rate of hexanal formation increased after 3 days, and after 5 days, the rate increased more rapidly than did that of the control oil. In the presence of 250 ppm of δ-tocopherol, hexanal formation increased rapidly after 5 days. At higher levels of δ-tocopherol, hexanal formation increased only slightly after 5 days. After 6 days of oxidation, the inhibition of hexanal formation by δ-tocopherol increased with concentration (Table 1).

Effect of α- and γ-Tocopherol Mixtures. *Formation of Hydroperoxides.* In the control oil, the rate of hydroperoxide formation increased sharply after an induction period of about 3 days of oxidation (Figure 3a). In the presence of 1:1 mixtures of α- and γ-tocopherols, the rate of hydroperoxide formation was approximately linear and did not show an induction period during 6 days of oxidation. The rate of hydroperoxide formation increased with increasing tocopherol concentration (Figure 2). Comparing concentrations, α- and γ-tocopherol mixtures (1:1) at 250 ppm inhibited hydroperoxide formation to a greatest extent after 2 days of oxidation, but at higher concentrations, α- and γ-tocopherol mixtures promoted hydroperoxide formation between 1 and 3 days (Figure 3a; Table 1). On day 4, α- and γ-tocopherol mixtures significantly inhibited the formation of hydroperoxide below 3000 ppm (1:1). After 6 days, α- and γ-tocopherol mixtures exhibited an antioxidant activity at all concentrations tested. The inhibition by α- and γ-tocopherol mixtures increased with oxidation time. Pure γ-tocopherol had a prooxidant effect at 5000 ppm on day 2 (Table 1).

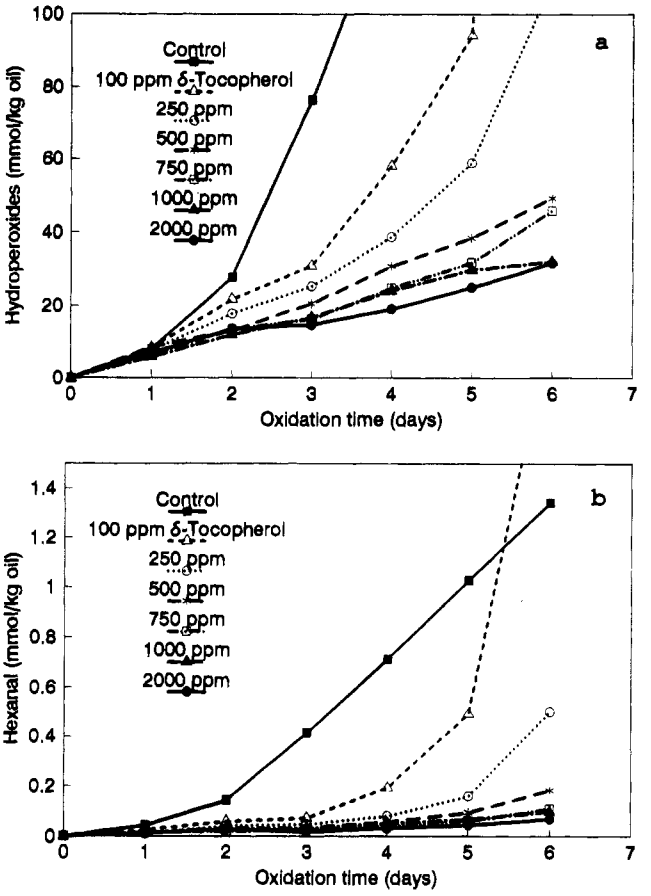

Figure 1. Effect of δ-tocopherol on oxidative stability of tocopherol-stripped corn oil at 60 °C: (a) hydroperoxide formation; (b) hexanal formation.

Decomposition of Hydroperoxides. In the control oil, the rate of hexanal formation increased sharply after 4 days (Figure 3b). With α- and γ-tocopherol mixtures, no hexanal formation was detected until day 6. In contrast to hydroperoxide formation, hexanal formation was inhibited at all α- and γ-tocopherol levels (Table 1). Hexanal formation was highest with 250 ppm of α- and γ-tocopherol mixture after 5 days. No significant difference was observed in hexanal formation between 500 and 3000 ppm. In the presence of 5000 ppm of pure γ-tocopherol, no hexanal formation was detected during oxidation (Table 1).

Effect of Soybean Tocopherol Mixtures. *Formation of Hydroperoxides.* Between 250 and 750 ppm, soybean tocopherol mixtures did not inhibit hydroperoxide formation, and at 1000 ppm or higher they

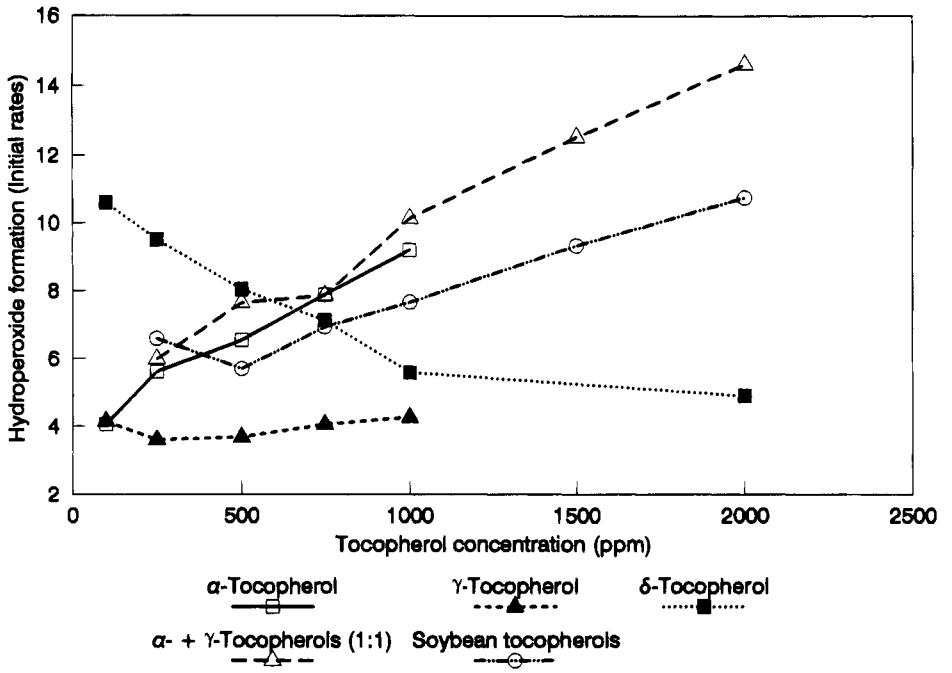

Figure 2. Effect of individual tocopherols and their mixtures on initial rate of hydroperoxide formation in tocopherol-stripped corn oil at 60 °C. The initial rate of hydroperoxide formation was expressed as millimoles per kilogram of oil per day and calculated from the observations before the rate of oxidation increased. The initial rates of hydroperoxide formation in the presence of α- and γ-tocopherols were obtained from the data of Huang et al. (1994).

Table 1. Inhibition of Hydroperoxide Formation and Hexanal by δ- and γ-Tocopherols and Tocopherol Mixtures in Bulk Corn Oil (Percent Mean Inhibition ± SD)[a,b]

sample	hydroperoxides day 2	hydroperoxides day 4	hydroperoxides day 6	hexanal day 6
control δ-tocopherol	0.0 ± 7.5^{d}	0.0 ± 1.7^{f}	0.0 ± 1.3^{d}	0.0 ± 2.6^{d}
100 ppm	21.6 ± 1.8^{c}	56.2 ± 0.3^{e}	−75.2 ± 2.0^{e}	−53.3 ± 6.3^{e}
250 ppm	36.1 ± 0.8^{b}	70.8 ± 0.3^{d}	55.7 ± 0.7^{c}	62.7 ± 1.5^{c}
500 ppm	53.1 ± 2.5^{a}	76.7 ± 0.4^{c}	80.0 ± 0.9^{b}	86.4 ± 1.0^{b}
750 ppm	51.8 ± 3.8^{a}	81.2 ± 1.1^{b}	81.4 ± 1.1^{ab}	91.9 ± 0.1^{ab}
1000 ppm	57.2 ± 0.5^{a}	81.8 ± 0.2^{b}	87.0 ± 0.4^{a}	92.8 ± 0.2^{a}
2000 ppm	51.1 ± 0.3^{a}	85.6 ± 1.5^{a}	87.1 ± 0.4^{a}	94.9 ± 0.1^{a}
control α- + γ-tocopherols	0.0 ± 2.0^{a}	0.0 ± 4.3^{f}	0.0 ± 3.5^{f}	0.0 ± 19.5^{b}
125 + 125 ppm	6.4 ± 1.1^{a}	67.5 ± 0.1^{a}	90.2 ± 0.4^{a}	93.5 ± 0.3^{a}
250 + 250 ppm	−49.0 ± 9.4^{c}	55.2 ± 0.2^{b}	87.6 ± 0.4^{ab}	99.3 ± 0.1^{a}
375 + 375 ppm	−32.9 ± 4.5^{b}	56.3 ± 1.3^{b}	87.4 ± 0.3^{ab}	99.4 ± 0.4^{a}
500 + 500 ppm	−68.5 ± 9.0^{d}	39.4 ± 0.6^{c}	84.0 ± 0.3^{bc}	98.3 ± 0.8^{a}
750 + 750 ppm	−101.3 ± 2.0^{e}	29.2 ± 3.3^{d}	80.2 ± 0.6^{cd}	98.7 ± 0.1^{a}
1000 + 1000 ppm	−120.0 ± 5.4^{f}	19.9 ± 1.1^{e}	76.7 ± 0.5^{d}	98.9 ± 0.2^{a}
1500 + 1500 ppm	−177.9 ± 1.8^{g}	−4.7 ± 0.1^{g}	70.6 ± 0.8^{e}	98.9 ± 0.5^{a}
γ-tocopherol 5000 ppm	−95.4 ± 3.2^{e}	37.2 ± 2.0^{c}	81.3 ± 0.2^{cd}	100.0 ± 0.1^{a}
control soybean tocopherol mixtures	0.0 ± 1.0^{c}	0.0 ± 0.5^{g}	0.0 ± 0.4^{e}	0.0 ± 4.3^{b}
250 ppm	23.8 ± 3.8^{b}	66.2 ± 2.9^{a}	90.6 ± 0.1^{b}	98.4 ± 0.3^{a}
500 ppm	34.7 ± 0.6^{a}	69.1 ± 0.7^{a}	92.1 ± 0.2^{a}	99.4 ± 0.1^{a}
750 ppm	36.2 ± 3.8^{a}	57.6 ± 1.5^{b}	91.2 ± 0.1^{ab}	99.5 ± 0.1^{a}
1000 ppm	2.4 ± 0.2^{c}	50.7 ± 0.4^{c}	89.4 ± 0.1^{b}	100.0 ± 0.1^{a}
1500 ppm	−13.2 ± 0.7^{d}	43.4 ± 0.3^{d}	86.8 ± 0.2^{c}	100.0 ± 0.1^{a}
2000 ppm	−21.1 ± 1.5^{e}	36.5 ± 2.9^{e}	85.3 ± 0.3^{c}	100.0 ± 0.1^{a}
3000 ppm	55.8 ± 3.7^{f}	19.4 ± 2.6^{f}	80.7 ± 0.4^{d}	100.0 ± 0.1^{a}

[a] % inhibition = $[(C - S)/C] \times 100$, where C = hydroperoxide or hexanal formed in control and S = hydroperoxides or hexanal formed in sample. Negative values represent prooxidant activity. SD, standard deviation, $n = 2$. [b] Values within each column followed by the same letter are not significantly different ($p < 0.05$).

promoted hydroperoxide formation on day 1 (Figure 4a). After 1 day, soybean tocopherol mixtures inhibited hydroperoxide formation at 750 ppm or below, and the rate of hydroperoxide formation did not change with time during the oxidation period. The rate of hydroperoxide formation decreased between 250 and 500 ppm and then increased at higher concentrations of tocopherols (Figure 2). After 4 days, hydroperoxide formation was inhibited at all levels of soybean tocopherol mixtures tested, and this inhibition increased with oxidation time (Table 1).

Decomposition of Hydroperoxides. In the control oil, hexanal formation was detected after 2 days of oxidation and increased rapidly after 2 days (Figure 4b). No hexanal formation was detected in the presence of 1000 ppm or higher concentrations of soybean tocopherol

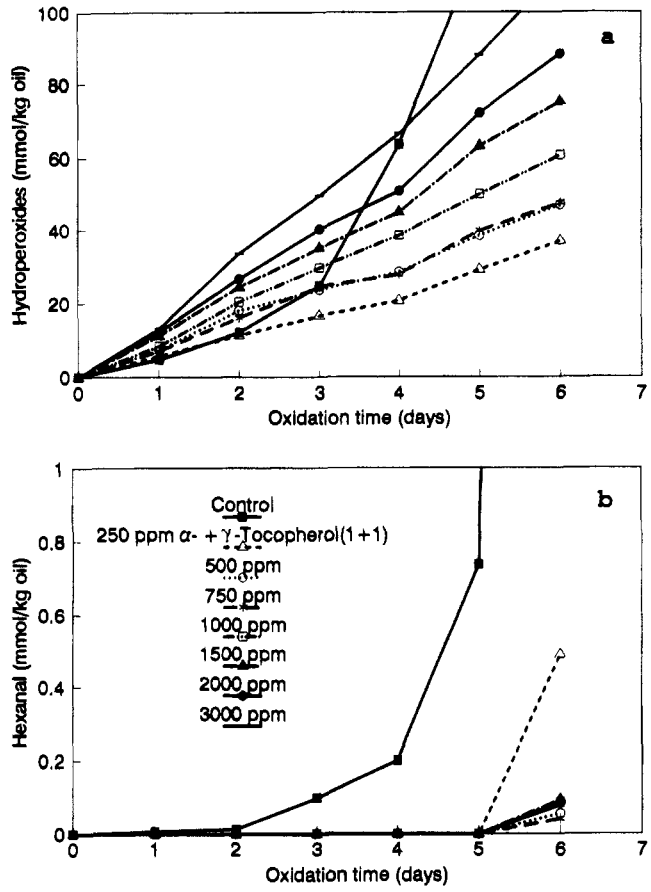

Figure 3. Effect of 1:1 ratio of of α- and γ-tocopherol mixtures on oxidative stability of tocopherol-stripped corn oil at 60 °C: (a) hydroperoxide formation, same legend as (b); (b) hexanal formation.

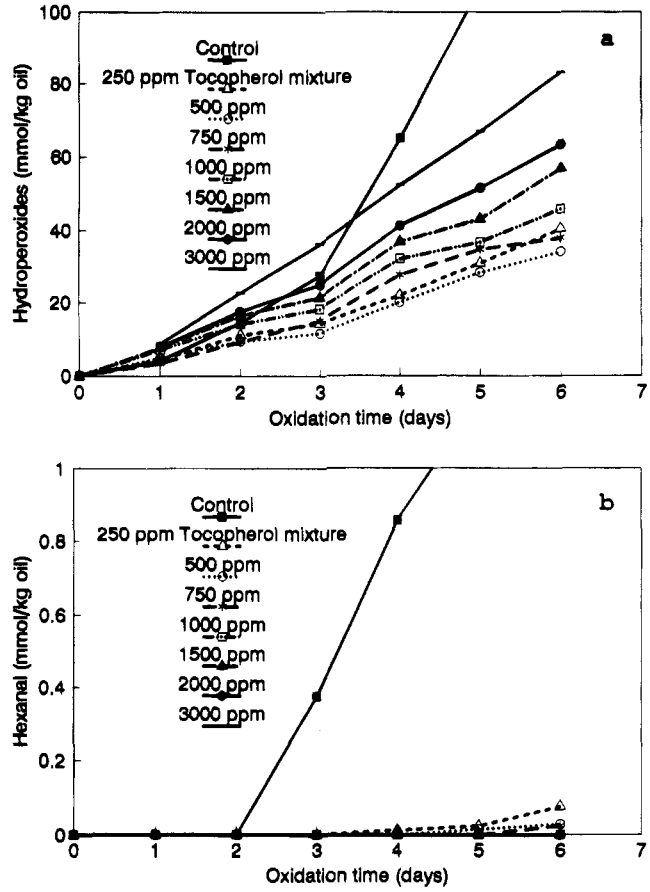

Figure 4. Effect of soybean tocopherol mixtures on oxidative stability of tocopherol-stripped corn oil at 60 °C: (a) hydroperoxide formation; (b) hexanal formation.

mixtures during 6 days of oxidation. No significant difference in inhibition of hexanal formation was observed between 250 and 3000 ppm (Table 1).

DISCUSSION

Previous work showed that α- and γ-tocopherols inhibited hydroperoxide formation in corn oil at optimum concentrations of 100 and 250–500 ppm, respectively (Huang et al., 1994). α-Tocopherol was initially prooxidant at 250 ppm or higher, whereas γ-tocopherol was not a prooxidant at 1000 ppm or below. In the present study, γ-tocopherol showed a prooxidant effect at 5000 ppm of concentration. However, on the basis of hexanal formation, γ-tocopherol inhibited the decomposition of hydroperoxides at 5000 ppm during oxidation. In marked contrast to α- and γ-tocopherols, δ-tocopherol showed antioxidant activity at 2000 ppm or below, on the basis of both the formation and decomposition of hydroperoxides and its activity increased with increasing concentration.

In purified soybean oil, δ-tocopherol was reported to have optimum antioxidant activity at 500 ppm and prooxidant activity at 1000 ppm based on peroxide value (Jung and Min, 1990). In contrast, in the present study, δ-tocopherol more effectively inhibited both hydroperoxide and hexanal formation at higher concentrations. Also, at 1000 ppm, the inhibition of hydroperoxide formation by δ-tocopherol found in this study was better than the inhibition by γ- and α-tocopherols previously reported (Huang et al., 1994), but at 100 ppm, α-tocopherol was more effective than γ- and δ-tocopherols.

Several mechanisms to explain the prooxidant activity of α-tocopherol at higher concentrations were discussed by Huang et al. (1994). Cillard and Cillard (1986) reported that some chelating agents could reduce or nullify the prooxidant effect of α-tocopherol. The presence of trace metals may therefore induce the prooxidant effect of α-tocopherol. Cillard and Cillard (1980) also proposed for this prooxidant effect that the more reactive tocopherol was more easily oxidized by air (α > γ > δ) to enhance the formation of a perhydroxyl radical (•OOH) or other reactive oxygen species ($O_2^{\bullet}$, •OH). Thus, higher concentrations would be required to cause prooxidant effects for γ- and δ-tocopherols at the early stage of oxidation. This effect is supported by the results of Jung and Min (1990) and Huang et al. (1994). Lambelet and Loliger (1984) found that in oxidized chicken fat, α-tocopheroxyl radicals were formed in relatively high concentration but were rapidly destroyed as compared to δ-tocopheroxyl radicals, which were formed in rather low concentration and were destroyed slowly, while γ-tocopheroxyl radicals were intermediate in reactivity. This result suggested that the depletion periods of tocopherols were related to the period during which they remained effective as antioxidant. The rate of disappearance of tocopheroxyl radicals as intermediates was also related to the stability of these tocopheroxyl radicals and the type of products formed. α-Tocopherolquinone, dimers, and trimers were identified as major oxidation products of α-tocopherol (Cillard and Cillard, 1980; Fujitani and Ando, 1984; Gottstein and Grosch, 1990), whereas two types of dimers were detected as individual oxidation products of γ- and δ-tocopherols (Ishikawa, 1982; Fujitani and Ando, 1984; Gottstein and Grosch, 1990).

Gottstein and Grosch (1990) found that the dimers of 2,2,7,8-tetramethyl-6-hydroxychroman, an analog of γ-tocopherol, were effective as antioxidants. They hypothesized that α-tocoquinoperoxyl radical formed from an α-tocopheroxyl radical could promote lipid oxidation by abstracting hydrogen atoms from lipid substrates. These mechanisms could explain why δ- and γ-tocopherols were more effective than α-tocopherol as antioxidants at higher concentrations during autoxidation.

On the basis of hydroperoxide formation, whether tocopherol mixtures acted as antioxidants or prooxidants seemed to depend on the concentration of α-tocopherol in mixtures. When α-tocopherol was below 130 ppm, the mixtures of α- and γ-tocopherol and natural mixtures of soybean tocopherols acted as antioxidants. When α-tocopherol was above 130 ppm, both tocopherol mixtures were prooxidants in the early stage of oxidation. At 750 ppm or below, the concentration effect of soybean tocopherol mixtures on hydroperoxide formation seemed to be determined by γ-tocopherol. δ-Tocopherol seemed to have the least influence on hydroperoxide formation in tocopherol mixtures during oxidation. However, this maximum concentration for soybean tocopherol mixtures in corn oil is in agreement with the result of Frankel et al. (1959), who found an optimum concentration of 400–600 ppm of tocopherols for antioxidant activity in soybean oil. Niki et al. (1986) found that α-tocopherol reacted rapidly with β-, γ-, and and δ-tocopheroxyl radicals to form α-tocopheroxyl radicals and β-, γ-, δ-tocopherols, respectively, and spared γ- and δ-tocopherols to increase the oxidative stability of liposomes. However, in the present study, tocopherol mixtures were not additive or synergistic on hydroperoxide formation.

In contrast to hydroperoxide formation, both tocopherol mixtures strongly inhibited hexanal formation, and this inhibition was more effective at higher concentrations. This study showed therefore that the optimum concentration of tocopherol mixtures to increase the oxidative stability of bulk oils is determined by inhibition of hydroperoxide formation but not by inhibition of hydroperoxide decomposition. In tocopherol mixtures, the consumption of individual tocopherols during oxidation needs to be investigated at different concentrations to better understand the relationship between the amount of individual tocopherols consumed and their prooxidant effect. Although hexanal is an important volatile product of linoleate hydroperoxides derived by β-cleavage of alkoxy radicals, these intermediates produce other nonvolatile secondary products, which include hydroxy, keto, and epoxy compounds (Frankel, 1985; Gardner, 1989). To clarify the mechanism of antioxidant action of individual tocopherols and their mixtures in inhibiting hydroperoxide decomposition, their effects need to be evaluated on the basis of nonvolatile secondary oxidation products as well as hexanal formation.

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