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Oxidation of Corn Oils with Spiked Tocols

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Abstract Stripped corn oils with added tocopherols and tocotrienols, at concentrations between 100 and 5,000 ppm, were used to evaluate antioxidant activity of these tocol compounds. The formation of lipid hydroperoxides, measured as peroxide value (PV), was accelerated at 60 °C in the dark for 5 days. Resistance to oxidation as induction period (IP) was also measured using an oxidative stability instrument (OSI) at 100 °C. For PV inhibition, the oils containing α-tocols exhibited decreasing effectiveness with increasing concentration. At day five, samples with 100 ppm α-tocols had the lowest PVs of about 40 mequiv/kg and samples containing 5,000 ppm had the highest values, ranging from 150 to 200 mequiv/kg. At concentrations above 700 ppm of α-tocols, there was an inversion of antioxidative properties as α-tocols promoted lipid oxidation. The opposite concentration effect was observed with δ-tocols and γ-tocotrienol (T3) for which antioxidant effectiveness increased with concentration. OSI-IP hour at 100 °C increased with increasing tocol concentrations for all tocol homologs, although with diminishing effectiveness at greater than 700 ppm. The α-tocols were less effective in extending the IP (~9 h at 5,000 ppm) than the δ-tocols and γ-T3 (13–14 h at 5,000 ppm). Therefore, the antioxidant or prooxidant activities of different tocols are different and the outcomes are different depending on the evaluation methods used.

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Introduction

Tocopherols and tocotrienols have long been recognized for their antioxidative properties in both food systems and in vivo. Although structurally similar to tocopherols, tocotrienols have not been as well characterized in either biological systems or food products and oils as for tocopherols. A number of preliminary findings of unique biological functions of tocotrienol homologues have spurred research on the healthful or nutritive effects of these compounds [1, 2]. Still, very little research has been performed on the antioxidative effects of individual tocotrienol homologues and their corresponding tocopherols in foods and edible oils [2].

Tocols at high concentrations, however, may act as prooxidants as demonstrated by others previously [3]. As little as 250 ppm of α-tocopherol has been reported as having prooxidative effects in the formation of lipid hydroperoxides [4]. In tocotrienol-spiked coconut fat at 60 °C, the addition of α- and β- tocotrienols at 100, 500 and 1,000 ppm increased fat oxidation as measured by peroxide value (PV) compared to the control, and this prooxidant effect was dose dependent [5]. However, both γ- and δ-tocotrienols had an opposite effect and they reduced lipid hydroperoxide formation, although the effect was not dose dependent [5].

In our previous study [6] on genetically modified corn with 18-fold increase in tocotrienol content (from 300 to 5,400 ppm in oil), we anticipated possible prooxidant effects because of the extremely high concentration of tocols. Crude oils extracted from control and transformed

corn were studied for the formation of lipid hydroperoxides (PV) at 60 °C over 9 days and the induction period (IP) was measured using an oxidative stability instrument. The oil with high tocol concentration did not show oxidation acceleration compared to the control, and the crude oil with elevated tocotrienol even had a longer IP than the control crude oil.

Because of the disagreement between our oil testing results and literature information, we need to test tocols at very high levels in a model system to examine the degree of protection or promotion of oil oxidation by various types of tocols. Since most oils of natural sources of tocols contain various proportions or concentrations of the eight compounds that comprise the tocol group, a model system of corn oil stripped of endogenous tocols and then spiked with different concentrations of individual tocotrienols or tocopherols needs to be used for this study. It was expected that the oxidative or antioxidative contribution of individual tocol homologues will be more clearly delineated in a model system than in a natural product. A model system helps eliminate and reduce the complexity of food systems, such as emulsions and extensive processing that may have other contributing factors that affect lipid oxidation.

Because of the lack of information in the literature of the oxidative implications of the very high concentrations of tocotrienols in oils now available in products of genetic modification, we proposed to examine the effect of high tocol concentration as seen in the oils extracted from our genetically modified corn on lipid oxidation.

Materials and Methods

Materials

Stripped corn oil was purchased from Dyets Inc. (Bethlehem, PA) and it had a total residual tocol content of less than 10 ppm. α-, γ- and δ-tocotrienol were obtained from Davos Life Sciences, PTE Ltd. (Singapore). α- and δ-tocopherol were purchased from MP Biomedicals, LLC (Solon, OH). Acetic acid, chloroform, potassium iodide, sodium thiosulfate, and potato starch were all purchased through VWR International, LLC (West Chester, PA).

Sample Preparation

Stripped corn oil was spiked directly with individual tocotrienols (T3) (α-, γ- and δ-types) and tocopherols (α- and δ-types) to achieve the desired concentrations of 100, 250, 700, 2,000 and 5,000 ppm of each tocol. Non-spiked, stripped corn oil was used as the control for these 25 samples. Since our initial study objective was to determine the effect of only T3 on oil oxidation, we only added two tocopherols (α and δ) for comparison, assuming that the other main tocopherol (γ), when compared with γ-T3, should behave in a similar manner as the difference between the α- and α-T3 and δ and δ-T3 pairs.

Accelerated Oxidation Treatment

For primary oxidation as measured by PV, three sets of 1-mL aliquots of the bulk samples and controls (day 0), were each placed in 1.8-mL amber vials for each of the 5 days of accelerated oxidation. Seventy-five vials (5 treatments × 5 samplings × 3 replicates) were removed from a 60 °C oven each day at the same time over five subsequent days.

Resistance to oxidation as induction period (IP) or conductance of secondary products of oxidation was measured in triplicates for each of the 25 samples and controls using the oxidative stability instrument.

Fatty Acid Composition

The fatty acid composition for the major fatty acids of the stripped corn oil was determined by GC using a ZB-wax column (Phenomenex, Torrance, CA) at 220 °C. About 50 uL of oil was diluted in 1 mL hexane and transmethylated with trimethylsulfonium hydroxide [7, 8].

Primary Lipid Oxidation Products Determined by Peroxide Value

Samples oxidized at 60 °C in the dark over 5 days were analyzed for lipid hydroperoxides by using the AOCS Cd 8–53 method adapted by Crowe and White [9]. Three replicate samples from each day, and tocol type and concentrations were analyzed.

Resistance to Oxidation as IP Determined by an Oxidative Stability Instrument (OSI)

Five gram of each sample was analyzed in triplicate by using an ADM OSI unit (Omnion, Rockland, MA). The samples and controls were analyzed at 100 °C with air flow rate of 110 mL/min. Both the IP in hours and the actual plots of conductivity with time were recorded.

Statistical Analysis

All experiments were conducted with triplicate treatments unless otherwise noted. Data analyses were done by using Microsoft Office Excel 2003 (Microsoft Corporation, Redmond, WA). One-way analysis of variance (ANOVA) was used and least significant difference was calculated at $P = 0.05$ ($LSD_{0.05}$).

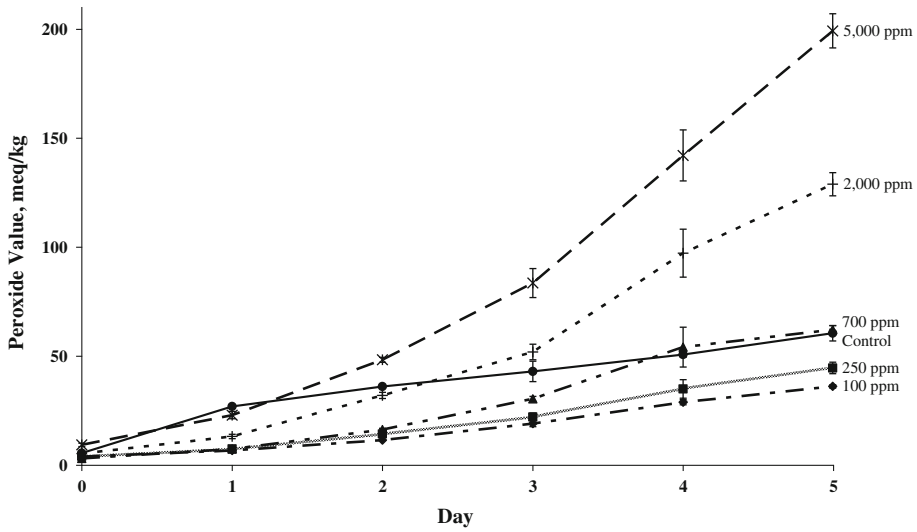

Fig. 1 Lipid hydroperoxide value of corn oil at 60 °C with added α-tocotrienol compared with a stripped corn oil control

Table 1 Change in average daily peroxide value (Δ-PV/day) ± standard deviation over 5 days in stripped corn oil with added tocols at 60 °C in the dark

Concentration (ppm)	α-Toco	α-T3	δ-Toco	δ-T3	γ-T3
100	6.89 ± 0.17^{e}	6.73 ± 0.02^{e}	5.34 ± 0.08^{a}	7.26 ± 0.52^{a}	5.43 ± 0.58^{b}
250	8.87 ± 0.09^{d}	8.37 ± 0.70^{d}	4.98 ± 0.14^{c}	6.88 ± 0.24^{b}	$5.01 \pm 0.33^{c,d}$
700	13.51 ± 0.10^{c}	12.85 ± 0.64^{c}	5.21 ± 0.10^{b}	6.42 ± 0.46^{c}	4.73 ± 0.56^{d}
2,000	20.68 ± 0.59^{b}	25.43 ± 1.02^{b}	4.02 ± 0.08^{e}	5.48 ± 0.46^{d}	7.26 ± 0.43^{a}
5,000	30.28 ± 0.81^{a}	38.35 ± 2.04^{a}	4.63 ± 0.05^{d}	5.36 ± 0.38^{d}	$5.25 \pm 0.08^{b,c}$
$LSD_{0.05}$	0.37	0.90	0.08	0.34	0.36

Stripped control had 10.09 ± 0.35 Δ-PV/day oxidation rate

Values not sharing a common superscript in each column are significantly different ($P < 0.05$)

Toco tocopherol, *T3* tocotrienol

Results and Discussion

Fatty Acid Composition

The major fatty acids as molar percentage of total of the control corn oil were palmitic (10.4%), stearic (1.9%), oleic (28.3%), linoleic (57.3%) and linolenic (0.9%) acids. This was a typical profile for corn oil and well within the expected range [10]. Because of the higher degree of unsaturation, corn oil is more prone to oxidation than other oils such as coconut, lard or hydrogenated fats [5, 11, 12], but less prone to oxidation than other oils with higher concentrations of polyunsaturated fatty acids, such as fish oils [13]. Although the fatty acid composition of oil is usually the main determinant of oxidative stability, stability of oils can be enhanced by elevated amounts of endogenous antioxidants or with the addition of natural or synthetic antioxidants [14]. The starting fatty acid composition was the same for all samples in this experiment, so this variable did not influence the differential oxidative stability observed.

Oxidative Stability as Measured by PV

The rate of lipid oxidation was calculated as the change of the PV over 5 days. These changes were unusually linear during the 5 days of sampling. A representative graph showing the PVs of the control and oils with five concentrations of added α-tocotrienol is shown in Fig. 1. The R^2 of PV over time (day) linear line was 0.965 for 100 ppm α-tocotrienol-spiked oil, 0.953 for 250 ppm, 0.934 for 700 ppm, 0.934 for 2,000 ppm, and 0.939 for the 5,000 ppm spiked oil. The R^2 for the control linear line was 0.941. Unlike typical RBD oils in which lipid hydroperoxides slowly build up and then rapidly increase after the induction period in a nearly exponential manner, the rate of PV increase was relatively linear across the 5 days. When making plots of ln (PV) versus time (day), the linearity (R^2) decreased for some samples.

The rate of hydroperoxide development per day for the stripped corn oil with added tocols as measured by PV (mequiv/kg) is given in Table 1. The change in PV demonstrates the effects of both tocol concentration and the

degree of methylation or unsaturation of the tocols. All tocols at the lower two tocol concentrations (100 and 250 ppm) were significantly better at inhibiting hydroperoxide formation compared to the stripped control oil with no added tocols. The α-forms of both tocopherol and tocotrienol exhibited better antioxidant properties at 100 ppm than at any of the higher concentrations. The antioxidative effects diminished at concentrations above 100 ppm. At concentrations of 700 ppm and above, the α-tocols promoted lipid hydroperoxide formation compared with the control and thus they acted as prooxidants under the test conditions. The daily rate of PV development was highest (38.35 mequiv/kg/day) for 5,000 ppm α-T3 followed by 5,000 ppm α-tocopherol (30.28 mequiv/kg/day).

However, oils spiked with δ-tocopherol, δ-T3 and γ-T3 showed trends different than the α-tocols, as these tocols did not promote lipid oxidation at increasing concentrations. For most of the δ-tocols and γ-T3 spiked oils, the oils with the highest concentrations are seemingly the most stable oils, even though the improvement is not practically significant.

These results are very similar to those of Wagner and others [5]. We tested at concentrations much higher than theirs of 1,000 ppm, nonetheless, even at the extremely high concentration of 2,000 and 5,000 ppm, δ-tocols and γ-T3 did not promote lipid oxidation.

The prooxidant effects of α-tocopherol at high concentrations had been noted before by Frankel [14] and Warner [15]. Recently, the prooxidant properties of α-tocotrienol have also been reported in lard and coconut fat [5, 11]. The PV of lard with 1,000 ppm α-tocotrienol exceeded the PV of the control at day 6 [11]. The optimum concentration for preventing the formation of hydroperoxides was reported to be 100 ppm α-tocotrienol [5]. In coconut fat, the α-tocotrienol reduced the stability of the fat as measured by PV at three spiked concentrations, 100, 500 and 1,000 ppm [5], a result slightly different from ours with α-tocols. This may be because of the different oxidizability of base lipids used for oxidation.

For our results, the decreased protection of oils from the formation of primary oxidation products was well correlated with tocol concentration over the range 100 to 5,000 ppm for both α-tocols, with R^2 of 0.95 and 0.96 for α-tocopherol and α-tocotrienol, respectively. The opposite effect was observed for δ-tocotrienol. Although less well correlated ($R^2 = 0.73$), the higher δ-T3 concentrations improved oil stability. There was little correlation between the concentrations of δ-tocopherol or γ-tocotrienol and oil stability, indicating higher concentrations do not give better protection, neither do they lead to the promotion of lipid oxidation.

The α-tocols, at higher concentrations, acting as prooxidants in this model oil system may be explained. Since the α-tocols have lower bond energies for the cleavage of phenolic OH, it would be predicted that they have the highest antioxidant activity [16]. Thus, α-tocols would form free radicals preferentially over the other tocol homologues found in a mixture. Since the model system lacks any additional antioxidants that could act synergistically, there are no other mechanisms for free radical transfer other than the fatty acids. Although tocols are believed to act by reducing free radical propagation, at higher concentrations the α-tocols or the excess tocol free radicals appear to initiate or catalyze lipid oxidation or continue to propagate oxidation [14]. Similar effects for α-tocopherol were reported in a purified rapeseed triacylglycerol system at 40 °C under low oxygen environment [17]. There is also increased chance of direct interaction at the oil–air interface at higher α-tocols concentrations, leading to increased oxidation [14].

Disagreement Between the Model System Evaluation and Corn Oil with Elevated Tocotrienols

Table 2 shows the differences in corn oil oxidation rates between the oil extracted from the genetically modified corn and oils that were spiked with similar levels of these major tocotrienols individually. Compared to the oil from the control corn (unmodified), the modified oil had much elevated concentrations of tocols, however, it did not have an elevated rate of oxidation as measured by PV (Table 2),

Table 2 Composition and stability of oils from tocol enriched corn and with spiked tocols

	Oil from modified corn	Oil from non-modified corn
Tocol composition[a] (ppm)		
α-Toco	185	373
α-T3	690	187
γ-Toco	565	647
γ-T3	4,051	108
δ-Toco	60	23
δ-T3	618	7
Lipid oxidation[a]		
PV change/day	8.5	9.2
OSI-IP (h)	13.8	9.9
PV change/day	Spiked corn oil	
Control (no tocol addition)	10.1	
α-T3, 700 ppm	12.9	
δ-T3, 700 ppm	6.4	
γ-T3, 5000 ppm	5.3	

[a] Data for comparison are from Dolde and Wang (2011). The fatty acid composition of the two corn oils is the same

Toco tocopherol, *T3* tocotrienol

nor by OSI. In spiked corn oil, as shown in Table 1 and summarized in Table 2, α-T3 acted as a prooxidant at 700 ppm, and δ- and γ-T3 (at 700 and 5,000 ppm individually) both acted as antioxidants. The combined effect of δ- and γ-T3 may have negated α-T3's prooxidant effect on the stability of the oil with elevated tocotrienol (8.5 mequiv/kg PV change/day, and 13.8 OSI hour), and made the oil more stable overall compared to control oil (9.2 mequiv/kg PV change/day, and 9.9 OSI hour), as shown in Table 2.

Oxidative Stability as Measured by OSI

Resistance to oxidation was evaluated by using the OSI at 100 °C. The IP is the time, in hours, at the tangent of the conductivity slope as determined by the instrument. The OSI hours are presented in Table 3. Unlike measuring of primary oxidation products, there were no apparent prooxidant effects of the tocols compared to the stripped control in this experiment. Across all tocol additions, IP duration increased with increasing tocol concentration. There was, however, diminished effectiveness with higher concentrations as shown in Table 3. As with PV, the α-tocols were less effective at increasing the resistance to oxidation than the other tocols assayed. Because this analysis is secondary to hydroperoxide formation and is a degradation measurement, the higher PV formation observed in the first experiment explains the lower IP with the α-tocols. This experiment shows that increased tocol concentration inhibited formation of secondary oxidation products from hydroperoxides. The oil with 5,000 ppm δ-tocopherol added exhibited the longest induction period at 14.05 h, extending the IP by over 9 h compared to the control oil (IP of 4.82 h). Therefore, based on IP and the use of our concentration levels, the optimum or most effective antioxidant concentration was 700 ppm for the α-tocols and 2,000 ppm for the other tocols. Slightly different optimum levels may be obtained if more concentration levels within the same range were used to optimize the experiment.

Comparing the antioxidant activities of tocopherols and tocotrienols, they did not show great differences. In some cases the oxidation rate of oils with tocotrienols seemed slightly higher than those with tocopherols (Tables 1, 3). Using individual tocotrienols from palm oil distillate, Yamaoka and others [18] determined weight gain of methyl linoleate spiked with 200 and 500 ppm α-tocols and 500 ppm γ-tocols to determine rates of oxidation. They found that the IP, as rate of O_2 uptake and subsequent weight gain of the tocotrienol spiked oils, was equal to or greater than the same tocopherol homologue at the same concentration. These are slightly different from our results. However, their results on α-tocols at 200 or 500 ppm are very similar to ours as discussed in the previous section.

Figure 2 shows the conductivity change during 100 °C oxidation of oils with the highest and lowest tocols concentrations. All tocols at high concentration levels had extended IP, however, these curves had different shapes. For α-tocols, the inflection point of the curve and the rate of oxidation after this point were very similar for the high and low concentration samples. However, for δ-tocols, the rate of conductivity change after the inflection point seemed much slower at high tocol concentration than that at low tocol concentration. The higher δ-tocol concentration not only extended IP, but seemed to also have additional protective effect after the oil had reached IP.

The results of oxidation evaluation at two different temperature conditions demonstrate that any claim of prooxidant or antioxidant effect is not only dependent on concentration used, but also the temperature or evaluation method used. Under high temperature, 100 °C and may be higher, all tocols and at all concentrations tested in our study are antioxidants. However, at milder temperature conditions, the antioxidative properties of tocols change. Wagner and others [5] also showed the increased OSI-IP of tocotrienol-spiked coconut fat at 160 °C as tocotrienol

Table 3 OSI induction period ± standard deviation (h) at 100 °C for stripped corn oil spiked with individual tocols at various concentrations

Treatment	α-Toco	α-T3	δ-Toco	δ-T3	γ-T3
Control	4.82 ± 0.41^{d}	4.82 ± 0.41^{e}	4.82 ± 0.41^{f}	4.82 ± 0.41^{f}	4.82 ± 0.41^{e}
100 ppm	$5.93 \pm 0.08^{c,d}$	6.58 ± 0.24^{d}	6.45 ± 0.09^{e}	6.17 ± 0.10^{e}	7.32 ± 0.19^{d}
250 ppm	$6.93 \pm 0.08^{b,c}$	$7.34 \pm 0.57^{c,d}$	8.18 ± 0.58^{d}	7.28 ± 0.18^{d}	8.72 ± 0.08^{c}
700 ppm	$8.15 \pm 0.33^{a,b}$	$8.05 \pm 0.71^{b,c}$	10.23 ± 0.46^{c}	8.60 ± 0.30^{c}	10.82 ± 0.43^{b}
2,000 ppm	8.60 ± 1.35^{a}	$8.91 \pm 0.85^{a,b}$	12.85 ± 0.70^{b}	11.42 ± 0.65^{b}	13.28 ± 1.02^{a}
5,000 ppm	9.30 ± 1.34^{a}	9.40 ± 1.12^{a}	14.05 ± 0.98^{a}	12.95 ± 0.30^{a}	13.95 ± 0.36^{a}
$LSD_{0.05}$	1.29	1.03	0.91	0.61	0.98

Values not sharing a common superscript in each column are significantly different ($P < 0.05$)

Toco tocopherol, *T3* tocotrienol

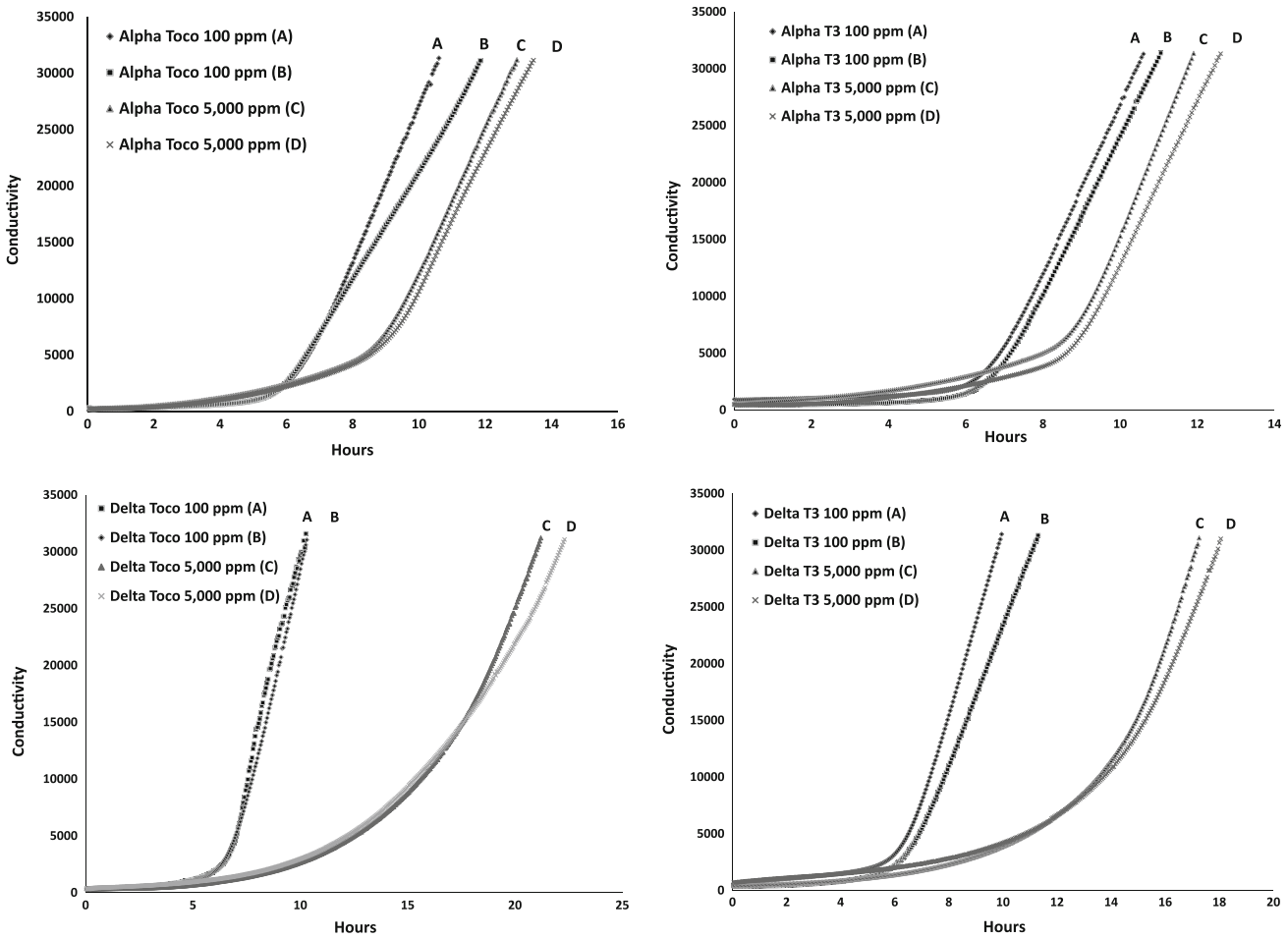

Fig. 2 OSI profiles showing that δ-tocols at high concentration let to more gradual change in conductivity than at that at low concentration. The two replicate measurements (*A*/*B* and *C*/*D*) for each treatments are shown

concentrations increased up to 1,000 ppm, a result different from that at lower oxidation temperature. Therefore, the efficacy of antioxidants should always be specified with testing and application conditions. When these tocols are present in non-homogeneous food systems, such as in emulsion or with the presence of various co-factors for oxidation, their efficacies will be more difficult to be generalized.

Although individual oxidation kinetics vary with type of tocols, the matrix in which they are placed, other compounds in the matrix, and the environmental conditions [14], the mechanisms of oxidation do not suggest synergistic effects for different tocol compositions [19, 20]. This does not preclude the sparing effect of individual tocols, specifically α-tocopherol, which is more rapidly degraded than γ- and δ-tocopherol in a mixed tocol matrix [21]. A preliminary evaluation of possible synergy for two different tocotrienol mixtures in stripped corn oil was performed in duplicate. The ratio of the first mixture was 1:1:1 α-, γ- and δ-tocotrienols at total concentrations of 100, 700 and 5,000 ppm, and the second mixture was 31% α-, 1.9% β-, 45.8% γ- and 21.3% δ-tocotrienol at 250 and 2,000 ppm total concentrations. The IPs of the oils was determined using OSI. Mean IPs were 6.6, 9.5 and 12.0 h for the first experiment and 8.1 and 11.0 h for the second experiment. There was little indication of synergy when these values were compared against the IPs of the individual tocotrienols. If calculated from the data for individual tocols to form a similar mixture, IPs would be 6.7, 9.2, and 12.1 h for the first experiment and 7.7 and 11.6 h for the second experiment. Therefore, no further formal investigation on synergy was performed.

Conclusion

The addition of lower concentrations (100 and 250 ppm) of individual tocotrienols and tocopherols to corn oil stripped of natural tocols provided stabilization to the oil, as indicated by both reduced hydroperoxide formation and

extended IP. As concentration increased, the effectiveness of the tocols as antioxidants diminished. The α-homologues provided less protection against lipid oxidation than the δ-homologues or γ-tocopherol and they actually promoted hydroperoxide formation at concentrations of and above 700 ppm. This prooxidant effect increased with concentrations up to the experiment limit of 5,000 ppm. Increasing the concentration of the δ-homologues or γ-tocopherol above 700 ppm in the oil had little effect on oil stability. We also demonstrated that the oxidation evaluation method used has a significant impact on defining tocols and possibly other compounds as prooxidants or antioxidants.

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