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Effect of Elevated Temperature on Development of Tocopherolquinones in Oils

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Studies were conducted to determine the formation of tocopherolquinones (TOCQ) in heated sunflower (SUN) and soybean (SBO) oils with and without enrichment with added α-tocopherol (α-TOC). Samples of the heated oils were extracted with acidified hot methanol and analyzed for changes in TOC contents and TOCQ levels by high-performance liquid chromatography (HPLC). In the oils without added α-TOC, the α-TOC in SUN significantly decreased from 829 ppm at 0 h to 183 ppm at 5 h and to 0 ppm by 10 h. In contrast, α-TOCQ increased from 0 ppm at 0 h to 87 ppm at 5 h and 104 ppm at 10 h. The level of α-TOC in SBO decreased from 138 ppm at 0 h to 99 and 98 ppm after 5 and 10 h, respectively, with an increase in α-TOCQ from 0 ppm at 0 h to 29 ppm at 5 h and 53 ppm at 10 h. In the oils with added α-TOC, the α-TOC in the SUN decreased rapidly from 1128 ppm at 0 h to 225 ppm at 5 h and 28 ppm at 10 h; however, the α-TOC in the SBO was 1176 ppm at 0 h, 367 ppm by 5 h, and 242 ppm at 10 h. There was a corresponding increase of α-TOCQ in SUN with added α-TOC from 0 ppm at 0 h, 127 ppm at 5 h, and 164 ppm at 10 h, whereas the α-TOCQ in SBO with added α-TOC changed from 0 ppm initially to 159 ppm by 5 h and 187 ppm at 10 h. As expected, SUN with no added α-TOC formed significantly more α-TOCQ than the SBO. However, SBO with added α-TOC had significantly more α-TOCQ than the SUN with added α-TOC even though the α-TOC levels at 0 h were similar. These results indicate that TOCQs are formed easily from the decomposition of α-TOC and could be potential antioxidants even as α-TOC decomposes.

KEYWORDS: α-Tocopherol; antioxidants; quinones; tocopherols; soybean oil; sunflower oil; tocopherols

INTRODUCTION

Lipid oxidation in heated vegetable oils decreases nutritional quality and produces off flavors and poor quality in fried foods. Modified fatty acid compositions and additives are the primary approaches to inhibit deterioration of frying oils. The current trend away from hydrogenated frying oils in the United States and the move toward oils with fatty acid compositions modified by breeding has increased the need for additional protection of the oil from degradation during frying beyond just modified fatty acids. Although chemical antioxidants such as BHA, BHT, and TBHQ can be added to frying oils, there is increasing interest in naturally occurring compounds to help inhibit oil degradation. Minor constituents naturally present in vegetable oils, such as tocopherols (TOCs), tocotrienols, phenolic compounds, and phytosterols, can act individually or synergistically to protect the oil from deterioration. Of these minor constituents, TOCs are the most potent natural antioxidants. Many studies have been conducted to show the positive effects of TOCs in oils during heating of oils to frying temperature or during frying (*1*−*8*). Previous research has shown that the formation of nonvolatile degradation products in heated oils can be inhibited by TOCs (*1*−*3*, *8*). Barrera-Arellano et al. (*2*) found that a mixture of α-, *β*-, *γ*-, and *δ*-TOCs inhibited polar compound formation better than *δ*-TOC, which, in turn, was better than α-TOC in triolein heated to 180 °C. However, it is well-known that TOCs decrease over time in oils heated to frying temperatures. Recent studies by Warner and coauthors reported that rancid flavor development and hexanal formation (*7*) and nonvolatile decomposition products (*8*) in oils and fried potato chips were inhibited by *γ*-TOC addition. This positive effect continued even after the *γ*-TOC had been depleted in the oil and fried food. This continuing antioxidant effect on the oxidative stability in the oils and fried food may be partly due to the presence of tocopherolquinones (TOCQs) that are formed from the breakdown of TOCs. Research has shown that natural and synthetic quinones such as rosmariquinone, tertiary butylhydroquinone, TOCQ, and ubiquinone have antioxidant properties (*9*, *10*−*13*). In biological systems, the role of α-TOCQ, α-tocopherolhydroquinone, and ubiquinone as antioxidants has gained much attention (*14*−*16*). Recent studies determined that extracts of rosemary, sage, and thyme containing rosmariquinone and carnosol quinone, oxidation products of carnosic acid, exhibited an antioxidant activity comparable to α-TOC (*17*, *18*). Frankel (*19*) reported that oxidation products such as quinones not only maintain their antioxidant activity at high temperatures

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but also exhibit a carryover effect that protects fried food. Few studies, however, have described the isolation and detection of TOC oxidation products in heated vegetable oils, primarily because of problems associated with complex oil matrices. It is also difficult to measure the oxidation products at the low concentrations present in the oil. In addition to low concentrations, other oil constituents can interfere with oxidation reactions and, in turn, the oxidation products formed. To limit interference of other oil constituents, heated model substrates (triolein and tripalmitin) have been used (*20*, *21*). In these studies, α-TOCQ and α-TOCQ epoxides were identified as the major oxidation products formed. Using a more complex substrate of heated maize germ oil enriched with α-TOC, Murkovic et al. (*22*) also identified α-TOCQ and α-TOCQ epoxides as major oxidation products. Our objectives in this study were to determine the decreases in α-, γ-, and δ-TOC in consumer vegetable oils such as soybean (SBO) and sunflower (SUN) oils heated to a frying temperature of 180 °C and to determine the patterns of formation of α-, γ-, and δ-TOCQs. We evaluated the effects of TOC degradation and TOCQ formation in consumer oils that had been supplemented with a high level of vitamin E (α-TOC). In addition, extraction methods were developed to overcome problems with the isolation of oxidation products such as TOCQs in the complex oil matrices.

EXPERIMENTAL PROCEDURES

Materials and Reagents. α-, γ-, and δ-TOC (95% purity) and γ- and δ-TOCQ (97−99% purity) were purchased from Matreya, Inc. (Pleasant Gap, PA). α-TOCQ (95% purity) was purchased from Research Plus, Inc. (Manasquan, NJ). Refined, bleached, and deodorized SUN and SBO oils containing no additives other than citric acid were purchased from commercial sources. High-performance liquid chromatography (HPLC) grade solvents (methanol and acetic acid) were purchased from Fisher Scientific (Fair Lawn, NJ). High-purity water was obtained by a Barnstead (Dubuque, IA) EASYpure UV water purification system.

Enrichment of α-TOC Level. Two hundred grams of SUN was enriched with 300 ppm of α-TOC to achieve a final concentration of 1128 ppm of α-TOC. Two hundred grams of SBO oil was enriched with 1000 ppm of α-TOC to achieve a final concentration of 1176 ppm of α-TOC.

Heating Protocol. Two hundred grams each of SUN and SBO oils with and without added α-TOC was weighed into 500 mL glass crystallizing dishes and was heated to 180 °C (±2 °C). Oil samples (10 mL) were taken at zero time and after 1, 5, 10, 20, 30, and 40 h of heating, then blanketed with nitrogen, and stored at 0 °C until analyses could be performed.

Extraction Protocol. Published procedures (*21*) were modified for more efficient extraction of TOCs and TOCQs. Briefly, duplicate oil samples (2 g) were extracted with acidified (0.05% acetic acid) methanol (3 × 8 mL) heated to 60 °C. Combined methanol extracts were evaporated under a nitrogen stream, dissolved in 1 mL of methanol, and centrifuged. The decanted methanol layer was immediately analyzed by HPLC.

TOC and TOCQ Analysis. Measurement of the TOCQ content in oil required solvent extraction and concentration prior to analysis by reversed phase HPLC. TOC (α, γ, and δ) and TOCQ (α, γ, and δ) contents in zero time oils and in heated oils were analyzed using reversed phase HPLC. Analyses were carried out with Thermo Separations Products (San Jose, CA) SpectraSYSTEM connected via Starrett column splitter (70:30) to a SpectraFOCUS forward optical scanning detector and SpectraSYSTEM FL3000 fluorescence detector in parallel. Duplicate samples were injected onto a MetaChem Technologies, Inc. (Torrance, CA) Inertsil ODS-3 column (5 μm, 250 mm × 4.6 mm i.d.) via a Rheodyne (Cotati, CA) model 7125 injector (50 uL loop). The fluorescence detector was set at 292 nm for excitation and 326 nm for emission. The scanning UV detector was set at 262 nm with scanning from 250 to 275 nm. The mobile phase employed a gradient elution starting from (A) methanol:H_2O (90:10, vol/vol) to (B) 100% MeOH (**Table 1**). The flow rate was 1 mL/min. Quantification of the TOCs and TOCQs was made using external standard calibration.

Table 1. Optimized Time Program for Gradient Chromatography[a]

time (min)	A%	B%
0	100	0
20	15	85
30	10	90
40	0	100
45	100	0

[a] A, 90:10 (v/v) methanol:water; B, 100% methanol.

To determine the efficiency of the MeOH extraction procedure, direct analysis of unextracted zero time oil for α-, γ-, and δ-TOC contents was done by normal phase HPLC and results were compared to reversed phase HPLC analysis of the same oil after extraction and concentration. The normal phase HPLC analysis of TOC (α, γ, and δ) was conducted on a Varian ProStar (Varian Associates, Inc., Walnut Creek, CA) with a model 363 fluorescence detector. The detector was set at 290 nm for excitation and 330 nm for emission. The HPLC was fitted with a 5 μm Varian Inertsil Si column (250 mm × 4.6 mm i.d.). The isocratic solvent system, 0.5% 2-propanol in hexane, was pumped at 0.5 mL/min. Quantification of the TOCs was made using external standard calibration.

Statistical Analysis. The experimental design consisted of four treatment groups (two oil types with two levels of α-TOC) with duplicate measurements taken at seven time intervals from 0 to 40 h of heating. Data were statistically analyzed by analysis of variance, and statistical significance was expressed as $P \leq 0.05$.

RESULTS AND DISCUSSION

Extraction Efficiency. In this study, several methods of isolation of α-TOCQ including various extraction solvents, solvent volumes, saponification, and use of SepPak columns (Waters Corporation, Milford, MA) were tried with limited success (data not shown). The addition of 0.05% acetic acid to hot (60 °C) MeOH provided the best recovery of TOCs. Recovery was determined by comparing the level of TOCs isolated by MeOH/acetic acid extraction and injected onto reversed phase HPLC to the level of TOCs measured by the direct injection of the unextracted vegetable oil onto normal phase HPLC. The α- and γ-TOC recoveries were 50 and 60%, respectively, whereas the δ-TOC recovery was 100%. Other researchers have reported 35% recovery for α-TOC by hot MeOH extraction alone (*21*); however, no literature data are available for γ- or δ-TOC isolation utilizing this method. A possible explanation for the greater efficiency of extraction of the δ-TOC may be due to chemical structure and/or interaction with the extraction solvent. All data presented in figures are for extracted oils.

Identification of Compounds. A reversed phase HPLC chromatogram of standard TOCs and TOCQs utilizing fluorescence and scanning ultraviolet detection in parallel is shown in **Figure 1**. TOCs were identified with fluorescence detection based upon retention times with known standards. TOCQs were detected with a scanning ultraviolet detector and tentatively identified based upon the comparison of their spectra scan characteristics and retention times with those of pure TOCQ standards. An example of a reversed phase HPLC separation of SBO without added α-TOC after 5 h of heating at 180 °C is shown in **Figure 2**. Although α-, γ-, and δ-TOCQ were easily separated in standard mixtures, only α-TOCQ could be identified in the heated oils. This result may be because of either the lack of γ- or δ-TOCQ formed or the extremely low quantities of γ-

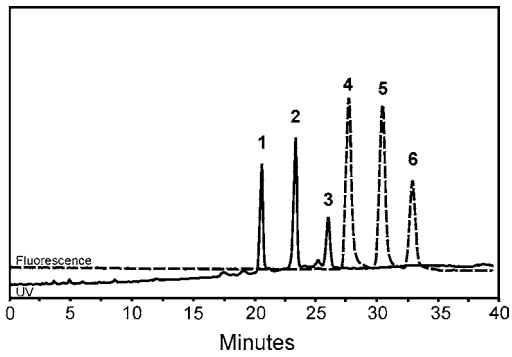

Figure 1. Reversed phase HPLC chromatograms of standard TOCs and standard TOCQs (1, δ-TOCQ; 2, γ-TOCQ; 3, α-TOCQ; 4, δ-TOC; 5, γ-TOC; and 6, α-TOC) using fluorescence and scanning ultraviolet detectors in parallel.

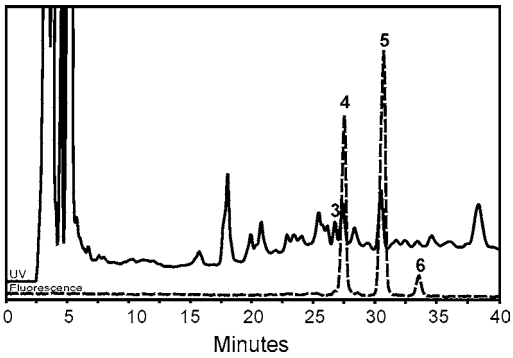

Figure 2. Reversed phase HPLC chromatograms of TOCs and TOCQs in heated SBO without added α-TOC (3, α-TOCQ; 4, δ-TOC; 5, γ-TOC; and 6, α-TOC) using fluorescence and scanning ultraviolet detectors in parallel.

and δ-TOCQ, which were not detectable. In nonbiological systems, research has shown that γ- and δ-TOC are not readily oxidized to their quinone products (*23*), whereas research studies in biological systems suggest that γ-TOC oxidation may preferentially produce dimers instead of quinone oxidation products (*24*).

Loss of α-TOC Levels in Heated Oils. α-TOC concentrations decreased with increased heating time for SUN and SBO oils with and without added α-TOC (**Figure 3**). α-TOC levels decreased at a greater rate initially in the enriched oils. The SUN without added α-TOC decreased slightly (6%) from zero time (829 ppm) to 1 h (779 ppm) followed by a significant 78% decrease at 5 h to 183 ppm and a 100% reduction of α-TOC after 10 h of heating at 180 °C (**Table 2**). In SUN with added α-TOC, the concentration of α-TOC significantly decreased from zero time (1128 ppm) to 21 (887 ppm), 80 (225 ppm), and 98% (28 ppm) after 1, 5, and 10 h, respectively. No α-TOC was detected in the sample heated for 20 h. Although significant decreases in concentrations of α-TOC were seen with increased heating time in the SBO samples, detectable levels of α-TOC remained in SBO with and without added α-TOC longer than in SUN. The SBO without added α-TOC significantly decreased 16% from zero time (138 ppm) to 1 h (116 ppm), followed by a 28% decrease to 99 ppm at both 5 and 10 h. At 20 h, we observed a 79% decrease to 29 ppm and a 93% decrease to 9 ppm at 30 h. In SBO oil with added α-TOC, the initial concentration of 1176 ppm of α-TOC significantly decreased by 31 (814 ppm), 69 (367 ppm), 79 (242 ppm), and 99% (10 ppm) at 1, 5, 10, and 20 h, respectively.

SUN with added α-TOC (1128 ppm total of α-TOC) and SBO with added α-TOC (1176 ppm total of α-TOC) were not

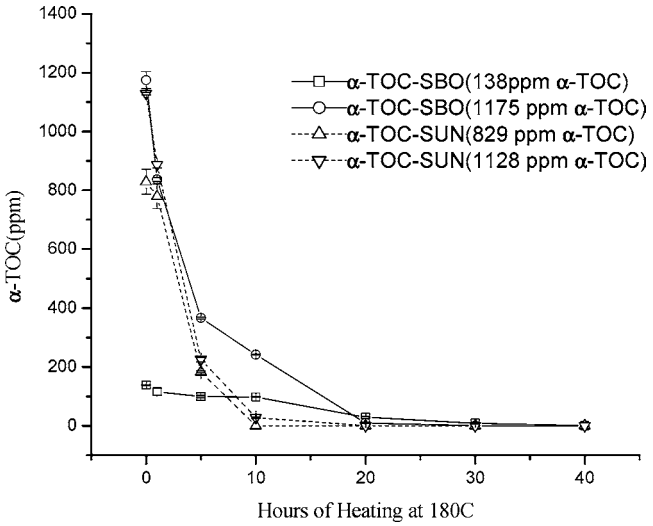

Figure 3. α-TOC (ppm) remaining in SBO and SUN oils with and without added α-TOC after heating for 0, 1, 5, 10, 20, 30, and 40 h at 180 °C. Each data point represents the mean ± the standard error of two determinations.

Table 2. % Decrease of α-TOC in SBO and SUN Oils with and without Added α-TOC after Heating for 0, 1, 5, 10, 20, 30, and 40 h at 180 °C

		hours of heating					
oil	initial α-TOC (ppm)	0	1	5	10	20	30
SBO	138	0	16	28	28	79	93
SBO + α	1176	0	31	69	79	99	100
SUN	829	0	6	78	100	100	100
SUN + α	1128	0	21	80	98	100	100

significantly different in α-TOC concentration at zero time; however, the levels were greater than the levels in SUN (829 ppm) and SBO (138 ppm) with no added TOC. Significant differences in α-TOC levels between all treatments were observed at 5 h in the following order, SBO with α-TOC (367 ppm) > SUN with α-TOC (225 ppm) > SUN (183 ppm) > SBO (99 ppm). At 10 h of heating time, SBO with α-TOC (242 ppm) had significantly more α-TOC than SBO at 98 ppm; however, both were significantly greater than SUN with α-TOC (28 ppm). This relationship between oil types with and without added α-TOC continued through 30 h of heating. After 20 h, SBO had significantly more α-TOC (29 ppm) than SBO with α-TOC (10 ppm). Only SBO had α-TOC (9 ppm) remaining at 30 h. In other studies on heated oils (*2*), researchers found that the α-TOC decreased at a slower rate in those oils without added α-TOC than those with added α-TOC. We found this to be true at most heating times. This may be attributed to other constituents in the oil such as γ- and δ-TOC, which have been shown to have a synergistic effect on inhibition of oxidation of lipids (*19*).

Loss of Other TOCs in Heated Oils. The disappearance of the other TOCs in the heated oils was also monitored (data not shown). In SUN, γ-TOC was 45 ppm at zero time and after 1 h of heating. The γ-TOC concentration in SUN with α-TOC was 43 ppm at zero time and decreased significantly to 7 ppm at 1 h. δ-TOC concentration in SUN was 8 ppm at zero time and increased to 12 ppm at 1 h of heating. This unexpected increase may be because of slight variations in extraction

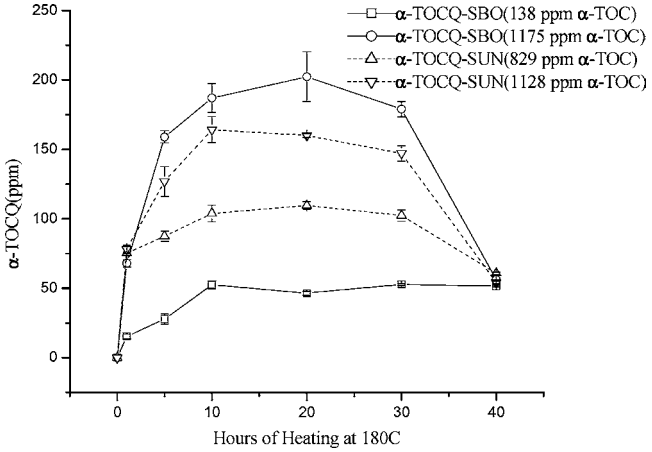

Figure 4. α-TOCQ (ppm) formed in SBO and SUN oils with and without added α-TOC after heating for 0, 1, 5, 10, 20, 30, and 40 h at 180 °C. Each data point represents the mean ± the standard error of two determinations.

efficiency. In SUN with α-TOC, *δ*-TOC levels were 15 ppm at zero time and 7 ppm at 1 h. No *γ*-TOC or *δ*-TOC was detected in SUN or enriched SUN at 5 h.

In SBO, the *γ*-TOC concentration was 1003 ppm at zero time and significantly decreased as follows: 5 (677 ppm), 20 (190 ppm) and 30 h (43 ppm). The *δ*-TOC concentration followed the same trend as *γ*-TOC. In SBO, the *δ*-TOC concentration was 450 ppm at zero time and did not significantly decrease until 20 h when it was 233 ppm, then 157 ppm at 30 h, and 118 ppm at 40 h. The *γ*-TOC concentration in SBO with α-TOC was 846 ppm at zero time and significantly decreased to 692 ppm at 1 h, 281 ppm at 5 h, 101 ppm at 10 h, and 10 ppm at 20 h. It plateaued at 10 ppm until 30 h; however, by 40 h, no *γ*-TOC was detected in the SBO with α-TOC. In SBO with α-TOC, *δ*-TOC was 412 ppm at zero time and then was significantly lower at 1 h to 341 ppm, 242 ppm at 5 h, 75 ppm at 20 h, and 12 ppm at 40 h. Even though the zero time SBO had high concentrations of *γ*- and *δ*-TOC and lost significant amounts during heating, no *γ*- or *δ*-TOCQ were detected in the heated oils. *γ*- and *δ*-TOC are not readily oxidized to their quinone products (*23*) in nonbiological systems. Therefore, we may not have been able to detect TOCQ that might have formed from *γ*- and *δ*-TOC because they may have degraded into different types of compounds than quinones.

α-TOCQ Levels in Heated Oils. The formation of α-TOCQ showed a similar pattern for all oil treatments except for unenriched SBO (**Figure 4**). Significant increases in α-TOCQ levels were observed during the early heating times of 1, 5, and 10 h for all oils, before plateauing at the maximum concentration during midheating times of 20 and 30 h. This was followed by a significant decrease in concentration at 40 h, except in SBO with no enrichment. α-TOCQ significantly increased in SUN from zero time to 1 (75 ppm), 5 (87 ppm), and 10 h (104 ppm), until reaching a plateau at 20 (110 ppm) and 30 h (103 ppm). A significant decrease in concentration occurred at 40 h when the level was 61 ppm. In the SUN with α-TOC, the formation of α-TOCQ significantly increased to 78 ppm after 1 h, 127 ppm at 5 h, and 164 ppm at 10 h. A plateau was reached from 10 to 30 h, followed by a significant decrease in concentration at 40 h to 54 ppm. α-TOCQ significantly increased in SBO from 0 to 10 h with 15 ppm at 1 h, 29 ppm at 5 h, and 53 ppm at 10 h, and then, the concentration remained constant through 40 h. No decrease in α-TOCQ formation was observed as was noted in all other samples possibly because the α-TOCQ had not begun to decompose to other compounds as occurred in the SUN and in the enriched SBO and SUN. In SBO with α-TOC, the formation of α-TOCQ increased significantly at 1 h to 68 ppm and then to 159 ppm by 5 h. A plateau was reached at 10 (187 ppm), 20 (202 ppm), and 30 h (179 ppm) followed by a significant decrease at 40 h to 56 ppm.

At 1 h, SUN with α-TOC and SUN had significantly more α-TOCQ formed than SBO with α-TOC, which was significantly greater than SBO. By 5 h, significant differences between treatments were detected in the following order, SBO with α-TOC > SUN with α-TOC > SUN > SBO. SUN with α-TOC and SBO reached maximum α-TOCQ formation by 10 h, whereas SBO with α-TOC and SUN reached maximum α-TOCQ formation by 20 h, although the differences were not significantly different than the 10 h values. We found that almost all of the α-TOC in SUN with or without added α-TOC had disappeared by 10 h of heating (**Table 2**); however, α-TOCQ concentrations were at their maximum levels at this corresponding time. The α-TOC in SBO with or without added α-TOC did not decrease to zero levels until 20 and 30 h, possibly because of the presence of *γ*- and *δ*-TOC. The maximum α-TOCQ concentration was detected at 20 h for enriched SBO and at 30 h for SBO.

In this study we found that α-, *γ*-, and *δ*-TOC in consumer vegetable oils decreased rapidly when heated at a frying temperature of 180 °C and that these TOCs also decreased in SBO and SUN enriched with vitamin E to a high level but at a faster rate initially than the unenriched oils. An acidified MeOH extraction method isolated oxidation products from the oil, but only α-TOCQ was identified as an oxidation product from α-TOC. No quinones from *γ*- or *δ*-TOC were identified. New data about the pattern of formation and degradation of α-TOCQ were obtained. α-TOCQ increased rapidly in regular or α-TOC-enriched SBO and SUN but at higher amounts in the enriched oils. The levels of α-TOCQ plateaued after 10−20 h of heating and then decreased in all oils except unenriched SBO. The levels of α-TOC that were used in this study effectively showed the patterns of decrease in α-TOC as well as the patterns of increase and then decrease of α-TOCQ. More levels of enrichment between the level in the regular oil and in the highly enriched level would probably not provide new information beyond what is reported here. Because TOCQs may act as antioxidants, these results indicate that frying oils and fried foods could have not only the positive antioxidant effects of TOCs during heating but also the potential antioxidant benefit of α-TOCQ as it is formed from the breakdown of α-TOC. Even unenriched SBO with its naturally low levels of α-TOC developed 53 ppm of α-TOCQ. More research needs to be conducted to determine better methods to detect other oxidation products from TOC degradation and to determine optimum levels of α-TOCQ in frying oils and their carryover effect into fried food.

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