# Effect of γ-Tocopherol on Formation of Nonvolatile Lipid Degradation Products During Frying of Potato Chips in Triolein

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**ABSTRACT:** Formation of undesirable odors and flavors during food processing operations is an important problem for the food industry. To determine the effect of  $\gamma$ -tocopherol on these negative attributes of fried food, we fried potato chips in triolein with 0, 100, or 400 ppm  $\gamma$ -tocopherol. Triolein extracted from potato chips was sampled for residual  $\gamma$ -tocopherol and nonvolatile degradation products after the chips were aged. RP-HPLC coupled to atmospheric pressure chemical ionization MS and sizeexclusion chromatography was used to analyze samples for degradation products in the triolein absorbed in potato chips as well as the fryer triolein. MS results showed that  $\gamma$ -tocopherol reduced the production of nonvolatile degradation products in the triolein absorbed by the potato chips and in the triolein in the fryer. Fryer oil samples and extracted potato chip oils with 400 ppm γ-tocopherol had a significantly lower production of degradation compounds than did samples with 100 ppm  $\gamma$ -tocopherol. Both fryer oils and potato chips containing 100 ppm  $\gamma$ -tocopherol had significantly fewer nonvolatile degradation products than did the samples without  $\gamma$ -tocopherol. These nonvolatile compounds are known precursors of negative odors and flavor compounds produced during the frying and aging of foods.

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**KEY WORDS:** Fryer oil, frying, mass spectrometry, nonvolatile degradation products, potato chips,  $\gamma$ -tocopherol, tocopherol, triolein.

Stability of vegetable oils in frying foods has long been a concern of food processors in regard to potential health effects to consumers. The actual health effect of degradation products produced from oils during the frying process is controversial. Although current research indicates that oils used under good commercial frying practice are fairly benign with respect to toxicity, concern exists in regard to some of the degradation products consumed in large quantities (1). It is believed that degradation products, such as polymers and DAG, are harmless but that some of the degradation products, including aldehydo-glycerides (also called core aldehydes) and some unsaturated aldehydes produced from oxidized monomeric products, may be nutritionally harmful (1). Studies have been conducted on how the use of antioxidants, such as tocopherols, retards the production of degradation products during frying. One recent study indicated that the effect of tocopherols present in canola oils may be more important than the FA

composition on the stability of these oils during frying (2). Further work indicated that oils with high y-tocopherol content, such as high-oleic soybean oil, were more stable to polymer formation during frying than oils with high  $\alpha$ -tocopherol levels, such as high-oleic sunflower oil (3). To better understand the effect of tocopherols on frying oil stability, model oil systems, such as pure TAG (triolein, trilinolein, and their blends), have been studied (4). These researchers found an inverse relationship between the amount of FA unsaturation and tocopherol degradation in heated triolein and trilinolein. Their model systems avoided the influence of naturally occurring minor compounds in vegetable oils that might have an antioxidant or pro-oxidant effect or interfere with uncovering the actual effect that specific tocopherols may have on oil stability. Therefore, there is a need to investigate the effects of tocopherols such as  $\gamma$ -tocopherol on vegetable oils purified of minor compounds or on pure TAG such as triolein. Previously, we studied the effect of model systems of pure triolein and trilinolein on the production of negative odors, such as fruity and plastic (5), and of positive odors, such as deep-fried food (6). Further, we studied the identification by MS of nonvolatile products produced in triolein heated at frying temperatures (7). Our work, however, did not investigate the role of minor oil compounds, such as tocopherols, in the quality and stability of frying oils as measured by the formation of nonvolatile degradation compounds. In fact, there is little information available on the effect of tocopherols on production of nonvolatile compounds during frying. Such information is needed because nonvolatile compounds are precursors of odor and flavor volatile compounds (5,6) and potentially toxic compounds (1) in oils. In this work, we investigated the effects of  $\gamma$ -tocopherol (8) on the production of nonvolatile compounds in both potato chips and frying oil.

# **EXPERIMENTAL PROCEDURES**

*Materials and reagents.* Triolein (99+% purity) was purchased from Nu-Chek-Prep, Inc. (Elysian, MN). TAG was checked for non-TAG products by PV (AOCS method Cd 8-523) (9), polar component analysis (AOCS method Cd 20-91) (9), and detection of oligomers, MAG, DAG, and FFA by size-exclusion (SEC) HPLC (5). FA purity was checked by GC (5) of the transmethylated TAG, and TAG purity was checked by RP-HPLC (5). Triolein was used without further purification. The standards for soybean oil oligomers (dimer, trimer, tetramer,

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etc.) were isolated from heated soybean oil (7). The standard oleic series of triolein, diolein, monoolein, and oleic acid was obtained from Nu-Chek-Prep, Inc.  $\gamma$ -Tocopherol (99.4% pure) was purchased from Matreya, Inc. (Pleasant Gap, PA). Purity of the  $\gamma$ -tocopherol standard was established by a normal-phase HPLC procedure used for TAG analysis (5), and the standard was used without further purification. The HPLC solvents, acetonitrile (ACN) from EM Science (Gibbstown, NJ) and dichloromethane (DCM) from Fisher Scientific (Fair Lawn, NJ), were HPLC grade and were used without further purification. Idaho Russet potatoes were purchased locally.

Frying protocol. Thirty grams each of triolein with 0, 100, or 400 ppm  $\gamma$ -tocopherol were weighed into 100-mL Pyrex<sup>TM</sup> beakers. Beakers were placed in a thermostatically controlled silicone oil bath and heated to 190°C. Potatoes were peeled, then cut into pieces approximately  $3 \times 0.5 \times 1$  cm and rinsed three times in cold water. Potato chips were air-dried, then fried in 3-g batches for approximately 3.5-4 min/batch. One batch was fried every 10 min for a total of approximately 24 min of frying for every hour of oil use. Oil samples were taken at zero-time and after 1, 3, and 6 h of frying, then blanketed with argon and stored at -15°C until analyses could be performed. Potato chips sampled at 1, 3, and 6 h after frying were stored for 0, 2, or 4 d at 60°C in sealed vials. After the 1- and 3-h oil samples were taken, 3 g of zero-time triolein with the appropriate  $\gamma$ -tocopherol addition was added to replenish the level of oil in the fryer; however, the makeup oil was not intended to restore the oil to the original level of  $\gamma$ -tocopherol. The frying experiment was duplicated.

Extraction of oil from potato chips. Supercritical fluid extractions (SFE) were performed with an ISCO Model 3560 SFE (ISCO Corp., Lincoln, NE) apparatus. Potato chip samples were mixed with approximately 2 g LECO-Dry (LECO Corp., St. Joseph, MI) and subsequently added to the extraction cell containing a glass-fiber filter disk (18-mm diameter) on the bottom. Additional LECO-Dry was added to nearly fill the extraction cell, and a second glass-fiber filter was placed on top. The supercritical extractions were performed with carbon dioxide at 10,000 psi and 70°C at a flow rate of 2 mL/min for 45 min after an initial 1 min static hold. The variable restrictor was held at 70°C, and extracts were collected in 20mL precooled (0°C) and pressurized vials. Five milliliters of methylene chloride was added to the collection vial prior to starting the extraction, and 3 mL of methylene chloride was used to rinse the restrictor after the extraction. The solvent was removed under a gentle stream of nitrogen at room temperature, and samples were subsequently stored under nitrogen at -70°C. SFE-grade CO<sub>2</sub> (Air Products and Chemicals Inc., Allentown, PA) was used for all extractions. Average weight recovery of oil from the chips was 48.0%.

*Total polar compound analysis.* Amounts of polar compounds were analyzed in duplicate by AOCS column chromatography method Cd 20-91 (9).

 $\gamma$ -Tocopherol analysis.  $\gamma$ -Tocopherol levels in triolein from the fryers and in oil extracted from the potato chips were determined by HPLC. The polar phase HPLC column system included two 5-µm particle size ultra silica HPLC columns (25 × 0.49 cm) (Phenomenex, Torrance, CA). The isocratic solvent system, 2% 2-propanol in hexane, was pumped at 0.5 mL/min. Sample size was 10 µL of 50 mg solute/mL mobile solvent, and samples were injected in triplicate. The fluorescence detector was a Varian programmable unit model ProStar 363 (excitation wavelength set at 298 nm and emission wavelength set at 345 nm with a gain at 6) (Varian Associates, Inc., Walnut Creek, CA). Data output from the fluorescence detector was processed by a Star Chromatography Workstation with version 4.0 software (Varian Associates, Inc.). A linear standard curve of areas for  $\gamma$ -tocopherol standards from concentrations of 0.6–500 ppm was obtained to calculate ppm.

Nonvolatile compound analysis. Levels of polymeric, monomeric, DAG, MAG, and FFA components of triolein were obtained by SEC in triplicate. The SEC of triolein was performed with three  $30 \times 7.5$ -cm, 5-µm particle size, PLgel columns (PL Separation Sciences/Polymer Laboratories Ltd., Shropshire, United Kingdom) in series. One column each of 500, 100, and 50 Å was used. DCM at 0.5 mL/min was used as the isocratic solvent for SEC. The ELSD for SEC was a Sedex Model 75, Sedone (Altontville, France). The drift tube was set at 40°C and gas flow at a pressure of 2.0 bar. The photomultiplier gain was ×4 and high-purity N<sub>2</sub> was used as the nebulizer gas. SEC chromatogram peak identification was in reference to a standard of soybean oil oligomers (dimer, trimer, tetramer, etc.) and to a standard oleic series of tri-, di-, mono-olein, and oleic acid (Nu-Chek-Prep, Inc.).

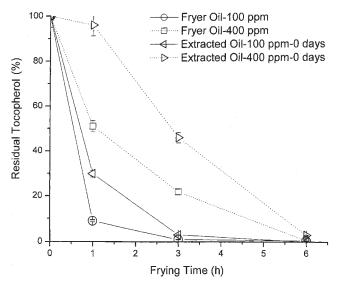
In the fryer oil samples, the triolein monomer measured by SEC contained oxidized triolein monomer products in addition to unreacted triolein, so it was necessary to know types and amounts of monomeric triolein oxidation products produced during frying. Therefore, specific triolein degradation products were analyzed by RP-HPLC to identify not only monomeric but also higher-M.W. degradation products (7). The HPLC system used for semiquantification of the triolein products was RP-HPLC performed with a Thermo-Separation Products (Schaumburg, IL) Model SP 8800 ternary solvent system with two RP-HPLC columns placed in series (5). The columns, packed with bonded silyl ODS (Inertsil ODS-80A; Keystone Scientific, Bellefonte Park, PA) were 25 cm × 4.6 mm i.d. with 5-µm packing particle size. The gradient elution was 80 ACN/20 DCM (%/%) to 20 ACN/80 DCM after 100 min. The flow rate was 0.5 mL/min throughout. The sample size (75 µg) injected was 15 µL of 50 mg solute/mL DCM. The ELSD was operated as stated for SEC. HPLC chromatogram peaks for degradation products were identified based on earlier analyses of heated triolein by RP-HPLC coupled with an atmospheric pressure chemical ionization mass spectrometer (RP-HPLC/APCI-MS) (7). Data output from the ELSD were processed or integrated by a Star Chromatography Workstation with version 4.0 software (Varian Associates, Inc.). Amounts of products were expressed in chromatogram peak area counts because suitable standards were not available for detector calibration. Results were semiquantitative because most of the analyses were of mixtures of components with various functional groups, which gave different detector responses. All analyses of nonvolatile compounds were analyzed in triplicate.

Statistical analysis. We conducted statistical analyses of triplicate determinations of tocopherol levels and tocopherol degradation products from the two frying trials. ANOVA were performed with Excel software (Microsoft Corp., Redmond, WA). Significant differences were expressed as  $P \leq 0.05$  unless indicated otherwise.

## **RESULTS AND DISCUSSION**

Purity and quality of triolein and  $\gamma$ -tocopherol. Initial analyses of the purity of the triolein by SEC showed no FFA, trimer, dimer, or DAG. FA purity of the triolein showed 100% oleic acid. The triolein contained 0.3% total polar compounds and 0.8 meq/kg PV.  $\gamma$ -Tocopherol purity was 99+%.

*Y*-Tocopherol levels in fryer triolein and in extracted potato chips. In triolein sampled from the fryers,  $\gamma$ -tocopherol decreased with increasing frying time for both the 100- and 400ppm samples (Fig. 1). However, for the sample with 100 ppm γ-tocopherol only 9% was left after 1 h of frying, but 51% was left in the sample with 400 ppm  $\gamma$ -tocopherol. After 3 h of frying, only 1 and 22% remained in the triolein with 100 or 400 ppm  $\gamma$ -tocopherol, respectively. After 6 h of frying, only 0.5 and 0.6% of the original starting levels of 100 and 400 ppm  $\gamma$ to copherol remained in the fryer oils. The decreases in  $\gamma$ tocopherol in the extracted potato chips showed a trend similar to that of the fryer oils. For example, after 1 h of frying, 30% of the  $\gamma$ -tocopherol remained in potato chips fried in triolein with 100 ppm  $\gamma$ -tocopherol (Fig. 1). After 3 h of frying, 3% of the original tocopherol level remained, and after 6 h frying, no tocopherol remained. Potato chips fried in triolein with 400 ppm had 96%  $\gamma$ -tocopherol remaining after 1 h frying, 46% after 3 h, and 3% after 6 h. The method of sampling potato chips and fryer oils is a possible explanation for the dif-



**FIG. 1.** Loss of  $\gamma$ -tocopherol in triolein and extracted potato chip oil originally containing 100 or 400 ppm  $\gamma$ -tocopherol.

ferences in the amounts of residual tocopherol, because the potato chip samples were collected over a 30-min period, whereas the fryer oil was collected at the end of each frying period. Also, the steam surrounding the potato chip in the fryer may have prevented loss of  $\gamma$ -tocopherol. Later in this paper, we discuss the finding that the lower amounts of nonvolatile degradation products found in the extracted oil as compared with the fryer oil could be an effect of the higher tocopherol levels in the extracted oil. Also, extracted oil from the potato chips fried in triolein with 0 ppm  $\gamma$ -tocopherol oil had lower contents of degradation products than did the fryer oil. Data for residual  $\gamma$ -tocopherol content of the potato chips aged for 2 and 4 d at 60°C are not shown, because few differences were noted between the contents of the zero-time and aged potato chips. This lack of differences could be because storage conditions were not severe enough.

Oligometric and monometric degradation products.  $\gamma$ -Tocopherol had a significant effect in inhibiting the formation of degradation products, especially dimers, in the fryer oil (Table 1). At all three oil sampling times, the addition of 100 or 400 ppm  $\gamma$ -tocopherol significantly limited the production of dimers. The use of 400 ppm  $\gamma$ -tocopherol prevented any trimers from forming in the fryer oil. Monomers decreased with increasing tocopherol level. Based on previous results with triolein heated at 190°C with steam (5-7), it is doubtful that FFA and MAG were present, because they were probably steam-distilled from the fryer oil during frying. The percentage of nonvolatile degradation products in the extracted potato chips followed a pattern similar to that of the fryer oils with a few exceptions (Table 2). The greatest effect of the tocopherol additions was on the production of dimers with the increasing levels of  $\gamma$ -tocopherol causing decreasing levels of dimers. The only exception to this trend was the 6-h sample of extracted oil originally containing 100 ppm  $\gamma$ -tocopherol, which had an unusually high amount of dimers. This excep-

#### TABLE 1

Area Percentage of Nonvolatile Degradation Products<sup>a</sup> in Triolein with 0-, 100-, or 400-ppm  $\gamma$ -Tocopherol and Used for Frying Potato Chips for 0, 1, 3, or 6 h (analyzed by size-exclusion chromatography)

	γ-Tocopherol	Hours of frying						
Products	(ppm)	0	1	3	6			
Trimer	0	0 <sup>a</sup>	0.1 <sup>a</sup>	0.5 <sup>a</sup>	0.6 <sup>a</sup>			
	100	0 <sup>a</sup>	0 <sup>a</sup>	0.1 <sup>a</sup>	0.3 <sup>a</sup>			
	400	0 <sup>a</sup>	0 <sup>a</sup>	$0^{a}$	0 <sup>a</sup>			
Dimer	0	0 <sup>a</sup>	3.1 <sup>a</sup>	5.1 <sup>a</sup>	6.2 <sup>a</sup>			
	100	0 <sup>a</sup>	0.2 <sup>b</sup>	2.2 <sup>b</sup>	4.7 <sup>b</sup>			
	400	0 <sup>a</sup>	0.1 <sup>b</sup>	0.5 <sup>c</sup>	0.8 <sup>c</sup>			
Monomer	0	100 <sup>a</sup>	94.6 <sup>a</sup>	92.1 <sup>a</sup>	90.7 <sup>a</sup>			
	100	100 <sup>a</sup>	98.6 <sup>b</sup>	96.8 <sup>b</sup>	94.3 <sup>b</sup>			
	400	100 <sup>a</sup>	99.1 <sup>b</sup>	99.6 <sup>c</sup>	98.3 <sup>c</sup>			
DAG	0	0	2.2	2.5	2.5			
	100	0	1.2	0.9	0.7			
	400	0	0.8	0.9	0.8			

<sup>a</sup>Within each product type, values with letters in common at each frying time are not significantly different ( $P \le 0.05$ ). DAG results were semiquantitative at <2%; therefore, no statistical analyses were conducted.

#### TABLE 2

Area Percentage of Nonvolatile Degradation Products<sup>a</sup> in Extracted Potato Chips Fried in Triolein with 0, 100, or 400 ppm γ-Tocopherol and Used for Frying for 0, 1, 3, or 6 h (analyzed by size-exclusion chromatography)

	Storage	γ-Tocopherol	Frying (h)		(h)	
Products	(d)	(ppm)	0	1	3	6
Trimer	0	0 100 400	0 <sup>a</sup> 0 <sup>a</sup> 0 <sup>a</sup>	0.1 <sup>a</sup> 0.1 <sup>a</sup> 0 <sup>a</sup>	0.4 <sup>a</sup> 0.3 <sup>a</sup> 0 <sup>a</sup>	0.2 <sup>a</sup> 0.6 <sup>b</sup> 0.1 <sup>a</sup>
	2	0 100 400	0 <sup>a</sup> 0 <sup>a</sup> 0 <sup>a</sup>	0.1 <sup>a</sup> 0 <sup>a</sup> 0 <sup>a</sup>	0.4 <sup>a</sup> 0.2 <sup>a</sup> 0 <sup>a</sup>	0.5 <sup>a</sup> 0.4 <sup>a</sup> 0.1 <sup>a</sup>
	4	0 100 400	0.0 <sup>a</sup> 0.0 <sup>a</sup> 0.0 <sup>a</sup>	0.2 <sup>a</sup> 0.0 <sup>a</sup> 0.0 <sup>a</sup>	0.4 <sup>a</sup> 0.2 <sup>a</sup> 0.0 <sup>a</sup>	0.5 <sup>a</sup> 0.8 <sup>b</sup> 0.1 <sup>a</sup>
Dimer	0	0 100 400	0.0 <sup>a</sup> 0.0 <sup>a</sup> 0.0 <sup>a</sup>	2.7 <sup>a</sup> 1.1 <sup>b</sup> 0.2 <sup>c</sup>	5.7 <sup>a</sup> 4.2 <sup>b</sup> 0.6 <sup>c</sup>	5.0 <sup>a</sup> 8.2 <sup>b</sup> 3.3 <sup>c</sup>
	2	0 100 400	0.0 <sup>a</sup> 0.0 <sup>a</sup> 0.0 <sup>a</sup>	2.2 <sup>a</sup> 0.7 <sup>b</sup> 0.3 <sup>c</sup>	6.4 <sup>a</sup> 3.9 <sup>b</sup> 0.9 <sup>c</sup>	10.7 <sup>a</sup> 8.1 <sup>b</sup> 2.6 <sup>c</sup>
	4	0 100 400	0.0 <sup>a</sup> 0.0 <sup>a</sup> 0.0 <sup>a</sup>	2.9 <sup>a</sup> 0.8 <sup>b</sup> 0.3 <sup>c</sup>	6.0 <sup>a</sup> 4.2 <sup>b</sup> 1.0 <sup>c</sup>	10.6 <sup>a</sup> 10.2 <sup>a</sup> 3.5 <sup>b</sup>
Monomer	0	0 100 400	100.0 <sup>a</sup> 100.0 <sup>a</sup> 100.0 <sup>a</sup>	96.3 <sup>a</sup> 97.7 <sup>b</sup> 98.6 <sup>c</sup>	93.1 <sup>a</sup> 93.8 <sup>a</sup> 98.0 <sup>b</sup>	93.8 <sup>a</sup> 89.6 <sup>b</sup> 95.1 <sup>c</sup>
	2	0 100 400	100.0 <sup>a</sup> 100.0 <sup>a</sup> 100.0 <sup>a</sup>	95.6 <sup>a</sup> 98.9 <sup>b</sup> 97.0 <sup>c</sup>	91.2 <sup>a</sup> 94.3 <sup>b</sup> 97.6 <sup>c</sup>	86.4 <sup>a</sup> 89.1 <sup>b</sup> 96.4 <sup>c</sup>
	4	0 100 400	100.0 <sup>a</sup> 100.0 <sup>a</sup> 100.0 <sup>a</sup>	94.9 <sup>a</sup> 97.6 <sup>b</sup> 97.7 <sup>b</sup>	90.9 <sup>a</sup> 93.8 <sup>b</sup> 96.6 <sup>c</sup>	85.9 <sup>a</sup> 87.1 <sup>b</sup> 95.2 <sup>c</sup>
DAG	0	0 100 400	0.0 0.0 0.0	0.9 1.1 1.2	0.8 1.6 1.4	1.0 1.5 1.5
	2	0 100 400	0.0 0.0 0.0	2.2 0.5 2.7	2.0 1.7 1.6	2.4 2.4 0.8
	4	0 100 400	0.0 0.0 0.0	2.1 1.7 2.0	2.7 1.8 2.4	3.0 1.9 1.2

<sup>a</sup>Within each product type at each storage time, values with a letter in common at each frying time are not significantly different ( $P \le 0.05$ ). DAG results were semiquantitative at <2%; therefore, no statistical analyses were conducted.

tion was also found in the trimer and monomer levels in the 6-h, 100-ppm sample. The reason for this exceptional result is not clear. The levels of dimers in the extracted oils from aged potato chips did not vary much over 0, 2, or 4 d of storage, with the exception of the 6-h, 0-ppm  $\gamma$ -tocopherol sample. Because of partial resolution between monomers and DAG, the DAG in the fryer oils (Table 1) and in the extracted oils (Table 2) could not be quantified accurately at 2% or less.

*Polar component analysis.* Polar compound formation in the fryer oils showed a significant decrease in the percentage of polar compounds with increasing  $\gamma$ -tocopherol concentration

#### TABLE 3

Percentage of Polar Compounds<sup>a</sup> in Triolein with 0, 100, or 400 ppm γ-Tocopherol and Used for Frying Potato Chips for 0, 1, 3, or 6 h

γ-Tocopherol		Hours	of frying	
(ppm)	0	1	3	6
0	0.3 <sup>a</sup>	9.1 <sup>a</sup>	16.4 <sup>a</sup>	28.1 <sup>a</sup>
100	0.6 <sup>a</sup>	4.2 <sup>b</sup>	12.6 <sup>b</sup>	26.5 <sup>b</sup>
400	0.7 <sup>a</sup>	2.2 <sup>c</sup>	3.9 <sup>c</sup>	11.5 <sup>c</sup>

<sup>a</sup>Within each column, values with a letter in common at each frying time are not significantly different ( $P \le 0.05$ ).

(Table 3). Other researchers have found similar significant effects in heated oil with added  $\alpha$ - and  $\delta$ -tocopherols; however, no frying of food or other components was done (4). Oils with 400 ppm of  $\gamma$ -tocopherol showed significantly less polar compound formation than did the 100-ppm sample, which in turn produced less polar compound formation than samples with no  $\gamma$ -tocopherol. The effects of the low levels of residual  $\gamma$ -tocopherol in the 100-ppm fryer oil at 3 h (Fig. 1) are evident in the polar compound level at this time. Polar compounds in the 3-h, 100-ppm sample were 12.6%, which was significantly higher than the 3-h, 400-ppm fryer oil that still had 22% residual  $\gamma$ -tocopherol.

Identification of degradation compounds. Compounds detected in fryer oils and in the oil extracted from potato chips were the same as those previously identified by RP-HPLC/ APCI-MS in heated triolein and reported in detail by Byrdwell and Neff (7). These compounds eluted by RP-HPLC in the following order: core DAG or diolein aldehydes (DAG with one FA chain cleaved), DAG (diolein), core TAG triolein monomeric aldehydes (TAG oxidation products with one FA chain cleaved), TAG hydroperoxides, TAG keto compounds, TAG epoxides with the epoxy group adjacent to a double bond, TAG epoxides with the epoxy group across the original double-bond carbons, unreacted triolein, higher-M.W. TAG with chain addition of one or more FA, TAG dimer with an oxidized FA chain, and nonpolar TAG dimer. In unfractionated triolein, RP-HPLC within the sensitivity limit of the ELSD was useful for identifying and quantifying the above triolein degradation products. Core aldehydes were the respective diolein and triolein, which had lost a terminal chain of triolein hydroperoxy FA (7). Chain-addition products were those diolein and triolein molecules that had trapped the terminal chains. Dimers were two trioleins connected by a carbon-carbon single bond (7). Polar dimer compounds had one of the two triolein molecules containing a polar functional group (7). Because RP-HPLC peaks have been identified by MS and by retention times, it was possible to obtain the quantity of each triolein degradation product as an area count when RP-HPLC was connected to ELSD. Although area counts were only semiquantitative, because no internal or external standard was used during HPLC analysis, they did indicate changes in the amounts of degradation products with fry and storage times and tocopherol levels. In almost all cases, the amounts of nonvolatile compounds formed in the fryer oils (Table 4) and in the extracted oils (Table 5) decreased as the  $\gamma$ -tocopherol levels increased. This effect was observed in the oil extracted

TABLE 4Area Counts/0.25 mg Oil for Nonvolatile Decomposition Products <sup>a</sup> and Used for Frying for 0, 1, 3, or 6 h (analyzed by RP-HPLC)	in Triolein with 0, 100, or 400 ppm γ-Tocopherol
I	Decomposition products

	Decomposition products									
Fry time (h)	γ-Tocopherol (ppm)	Diolein core aldehydes	Diolein	Diolein chain addition products	Triolein core aldehydes	Triolein monohydro- peroxides	Keto + epoxy triolein	Epoxystearic triolein	Triolein chain addition products	
1	0	791 <sup>a</sup>	1,119 <sup>a</sup>	259 <sup>a</sup>	2,675 <sup>a</sup>	8,165 <sup>a</sup>	4,005 <sup>a</sup>	13,999 <sup>a</sup>	1,138 <sup>a</sup>	
	100	0 <sup>b</sup>	0 <sup>b</sup>	0 <sup>b</sup>	547 <sup>b</sup>	1,566 <sup>b</sup>	789 <sup>b</sup>	2,601 <sup>b</sup>	433 <sup>b</sup>	
	400	0 <sup>b</sup>	0 <sup>b</sup>	0 <sup>b</sup>	0 <sup>c</sup>	0 <sup>c</sup>	0 <sup>c</sup>	0 <sup>c</sup>	0c	
3	0	1,537 <sup>a</sup>	2,268 <sup>a</sup>	765 <sup>a</sup>	3,425 <sup>a</sup>	20,753 <sup>a</sup>	12,569 <sup>a</sup>	35,647 <sup>a</sup>	3,130 <sup>a</sup>	
	100	766 <sup>b</sup>	528 <sup>b</sup>	234 <sup>b</sup>	1,270 <sup>b</sup>	4,693 <sup>b</sup>	3,090 <sup>b</sup>	7,516 <sup>b</sup>	1,804 <sup>b</sup>	
	400	203 <sup>c</sup>	628 <sup>b</sup>	187 <sup>b</sup>	588 <sup>c</sup>	2,483 <sup>c</sup>	1,718 <sup>c</sup>	3,550 <sup>c</sup>	1,020 <sup>c</sup>	
6	0	3,928 <sup>a</sup>	3,481 <sup>a</sup>	1,388 <sup>a</sup>	7,472 <sup>a</sup>	58,193 <sup>a</sup>	31,263 <sup>a</sup>	89,357 <sup>a</sup>	11,793 <sup>a</sup>	
	100	2,306 <sup>b</sup>	3,002 <sup>b</sup>	857 <sup>b</sup>	3,197 <sup>b</sup>	23,336 <sup>b</sup>	19,755 <sup>b</sup>	35,773 <sup>b</sup>	949 <sup>b</sup>	
	400	569 <sup>c</sup>	352 <sup>c</sup>	198 <sup>c</sup>	1,169 <sup>c</sup>	4,776 <sup>c</sup>	2,467 <sup>c</sup>	6,545 <sup>c</sup>	320 <sup>c</sup>	

<sup>a</sup>Within each fry time, values with a letter in common for each decomposition product are not significantly different ( $P \le 0.05$ ).

## TABLE 5 Area Counts per 0.25 mg Oil for Nonvolatile Decomposition Products<sup>a</sup> in Extracted Potato Chips Fried in Triolein with 0, 100, or 400 ppm $\gamma$ -Tocopherol and Used for Frying for 0, 1, 3, or 6 h and Aged for 0, 2, or 4 d at 60°C (analyzed by RP-HPLC)

			Decomposition products (area counts per 0.25 mg oil)									
Fry time (h)	Storage (d)	γ-Tocopherol (ppm)	Diolein core aldehydes	Diolein	Diolein chain- addition products	Triolein aldehydro- glycerides	Triolein monohydro- peroxides	Keto + epoxy triolein	Epoxystearic triolein	Triolein chain- addition products	Polar dimer	Nonpolar dimer
1	0	0 100 400	0 <sup>a</sup> 0 <sup>a</sup> 0 <sup>a</sup>	1,268 <sup>a</sup> 0 <sup>b</sup> 0 <sup>b</sup>	0 <sup>a</sup> 0 <sup>a</sup> 0 <sup>a</sup>	1,848 <sup>a</sup> 970 <sup>b</sup> 0 <sup>c</sup>	5,578 <sup>a</sup> 820 <sup>b</sup> 0 <sup>c</sup>	2,959 <sup>a</sup> 671 <sup>b</sup> 0 <sup>c</sup>	11,386 <sup>a</sup> 1,931 <sup>b</sup> 0 <sup>c</sup>	0 <sup>a</sup> 0 <sup>a</sup> 0 <sup>a</sup>	1,433 <sup>a</sup> 888 <sup>b</sup> 0 <sup>c</sup>	3,985 <sup>a</sup> 1,756 <sup>b</sup> 0 <sup>c</sup>
	2	0 100 400	0 <sup>a</sup> 0 <sup>a</sup> 0 <sup>a</sup>	0 <sup>a</sup> 0 <sup>a</sup> 0 <sup>a</sup>	0 <sup>a</sup> 0 <sup>a</sup> 0 <sup>a</sup>	21,122 <sup>a</sup> 0 <sup>b</sup> 0 <sup>b</sup>	4,470 <sup>a</sup> 0 <sup>b</sup> 0 <sup>b</sup>	2,343 <sup>a</sup> 0 <sup>b</sup> 0 <sup>c</sup>	14,668 <sup>a</sup> 633 <sup>b</sup> 0 <sup>c</sup>	0 <sup>a</sup> 0 <sup>a</sup> 0 <sup>a</sup>	1,634 <sup>a</sup> 0 <sup>b</sup> 0 <sup>b</sup>	2,809 <sup>a</sup> 0 <sup>b</sup> 0 <sup>b</sup>
	4	0 100 400	0 <sup>a</sup> 0 <sup>a</sup> 0 <sup>a</sup>	733 <sup>a</sup> 274 <sup>b</sup> 0 <sup>c</sup>	0 <sup>a</sup> 0 <sup>a</sup> 0 <sup>a</sup>	89,145 <sup>a</sup> 709 <sup>b</sup> 0 <sup>c</sup>	5,341 <sup>a</sup> 1,048 <sup>b</sup> 0 <sup>c</sup>	2,191 <sup>a</sup> 589 <sup>b</sup> 0 <sup>c</sup>	23,757 <sup>a</sup> 0 <sup>b</sup> 0 <sup>b</sup>	0 <sup>a</sup> 0 <sup>a</sup> 0 <sup>a</sup>	0 <sup>a</sup> 0 <sup>a</sup> 0 <sup>a</sup>	3,642 <sup>a</sup> 0 <sup>b</sup> 0 <sup>b</sup>
3	0	0 100 400	766 <sup>a</sup> 0 <sup>b</sup> 0 <sup>b</sup>	1,324 <sup>a</sup> 0 <sup>b</sup> 0 <sup>b</sup>	478 <sup>a</sup> 0 <sup>b</sup> 0 <sup>b</sup>	2,834 <sup>a</sup> 1,022 <sup>b</sup> 881 <sup>c</sup>	14,397 <sup>a</sup> 10,200 <sup>b</sup> 0 <sup>c</sup>	7,719 <sup>a</sup> 878 <sup>b</sup> 515 <sup>c</sup>	25,085 <sup>a</sup> 2,489 <sup>b</sup> 638 <sup>c</sup>	0 <sup>a</sup> 0 <sup>a</sup> 0 <sup>a</sup>	9,754 <sup>a</sup> 330 <sup>b</sup> 0 <sup>c</sup>	21,354 <sup>a</sup> 1,351 <sup>b</sup> 0 <sup>c</sup>
	2	0 100 400	1,564 <sup>a</sup> 0 <sup>b</sup> 0 <sup>b</sup>	0 <sup>a</sup> 0 <sup>a</sup> 0 <sup>a</sup>	0 <sup>a</sup> 0 <sup>a</sup> 0 <sup>a</sup>	25,103 <sup>a</sup> 651 <sup>b</sup> 0 <sup>c</sup>	25,331 <sup>a</sup> 2,554 <sup>b</sup> 1,664 <sup>c</sup>	2,559 <sup>a</sup> 1,419 <sup>b</sup> 795 <sup>c</sup>	15,455 <sup>a</sup> 4,459 <sup>b</sup> 803 <sup>c</sup>	0 <sup>a</sup> 0 <sup>a</sup> 0 <sup>a</sup>	2,889 <sup>a</sup> 0 <sup>b</sup> 0 <sup>b</sup>	4,429 <sup>a</sup> 0 <sup>b</sup> 0 <sup>b</sup>
	4	0 100 400	2,365 <sup>a</sup> 0 <sup>b</sup> 0 <sup>b</sup>	1,488 <sup>a</sup> 370 <sup>b</sup> 0 <sup>c</sup>	767 <sup>a</sup> 0 <sup>b</sup> 0 <sup>b</sup>	120,562 <sup>a</sup> 10,548 <sup>b</sup> 542 <sup>c</sup>	14,895 <sup>a</sup> 3,859 <sup>b</sup> 710 <sup>c</sup>	6,585 <sup>a</sup> 1,843 <sup>b</sup> 1,321 <sup>c</sup>	49,693 <sup>a</sup> 9,318 <sup>b</sup> 1,616 <sup>c</sup>	0 <sup>a</sup> 0 <sup>a</sup> 0 <sup>a</sup>	4,758 <sup>a</sup> 2,026 <sup>b</sup> 0 <sup>c</sup>	10,427 <sup>a</sup> 2,812 <sup>b</sup> 0 <sup>c</sup>
6	0	0 100 400	4,769 <sup>a</sup> 1,296 <sup>b</sup> 0 <sup>c</sup>	2,233 <sup>a</sup> 1,331 <sup>b</sup> 554 <sup>c</sup>	3,853 <sup>a</sup> 654 <sup>b</sup> 0 <sup>c</sup>	2,921 <sup>a</sup> 1,978 <sup>b</sup> 964 <sup>c</sup>	23,765 <sup>a</sup> 12,555 <sup>b</sup> 4,175 <sup>c</sup>	11,639 <sup>a</sup> 6,527 <sup>b</sup> 2,906 <sup>c</sup>	40,695 <sup>a</sup> 23,473 <sup>b</sup> 6,643 <sup>c</sup>	3,118 <sup>a</sup> 2,036 <sup>a</sup> 0 <sup>c</sup>	11,037 <sup>a</sup> 6,237 <sup>b</sup> 2,665 <sup>c</sup>	28,747 <sup>a</sup> 10,911 <sup>b</sup> 2,748 <sup>c</sup>
	2	0 100 400	4,392 <sup>a</sup> 1,518 <sup>b</sup> 0 <sup>c</sup>	1,433 <sup>a</sup> 1,083 <sup>a</sup> 0 <sup>c</sup>	8,142 <sup>a</sup> 919 <sup>b</sup> 0 <sup>c</sup>	54,343 <sup>a</sup> 15,906 <sup>b</sup> 3,147 <sup>c</sup>	35,093 <sup>a</sup> 12,026 <sup>b</sup> 3,037 <sup>c</sup>	17,646 <sup>a</sup> 5,792 <sup>b</sup> 1,647 <sup>c</sup>	83,410 <sup>a</sup> 29,202 <sup>b</sup> 6,375 <sup>c</sup>	3,199 <sup>a</sup> 1,469 <sup>b</sup> 0 <sup>c</sup>	18,557 <sup>a</sup> 6,506 <sup>b</sup> 1,050 <sup>c</sup>	28,233 <sup>a</sup> 9,136 <sup>b</sup> 1,625 <sup>b</sup>
	4	0 100 400	2,597 <sup>a</sup> 0 <sup>b</sup> 0 <sup>b</sup>	16,970 <sup>a</sup> 6,901 <sup>b</sup> 661 <sup>c</sup>	3,850 <sup>a</sup> 0 <sup>b</sup> 0 <sup>b</sup>	14,659 <sup>a</sup> 59,601 <sup>b</sup> 918 <sup>c</sup>	15,881 <sup>a</sup> 13,961 <sup>b</sup> 5,495 <sup>c</sup>	15,623 <sup>a</sup> 7,228 <sup>b</sup> 3,562 <sup>c</sup>	134,919 <sup>a</sup> 41,030 <sup>b</sup> 8,585 <sup>c</sup>	0 <sup>a</sup> 0 <sup>a</sup> 0 <sup>a</sup>	5,659 <sup>a</sup> 5,485 <sup>b</sup> 3,830 <sup>c</sup>	15,418 <sup>a</sup> 7,390 <sup>b</sup> 3,829 <sup>c</sup>

<sup>a</sup>Within each fry time at each storage day, values with a letter in common for each decomposition product are not significantly different ( $P \le 0.05$ ).

from the potato chips, not only at 0, 1, 3, and 6 h of oil use but also for storage times of 2 and 4 d at 60°C. Although  $\gamma$ -tocopherol at 400 ppm had a greater antioxidant effect than at 100

ppm, the lower level was effective in reducing degradation products in the fryer oil as well as in oil extracted from the potato chips. Even samples with very low tocopherol levels (Fig. 1), such as the oils from potato chips fried at the 6-h time with either 100 or 400 ppm  $\gamma$ -tocopherol and aged 4 d, showed an inhibitory effect in reducing degradation products compared with the oil without  $\gamma$ -tocopherol.

Degradation products in fryer oils decreased in the following order: epoxystearoylglycerol > triolein hydroperoxides > nonpolar dimer (Table 4). Polar dimers and epoxy plus ketotriolein occurred in low amounts. Chain-addition compounds were found in the least amounts. The same degradation-product identification profile occurred for degradation products in extracted oils (Table 5). However, because the extracted oils had more tocopherol than the fryer oils, the extracted oils had fewer degradation products. For both fryer oil and oil extracted from potato chips, the data showed a reduction of triolein monohydroperoxides and nonpolar dimers with heating time and with increased tocopherol level. Thus, these data showed benefits of  $\gamma$ -tocopherol in reducing decomposition products. These compounds, such as potentially harmful core aldehydes (1) that may be deleterious to the flavor and odor of frying oils (5,6), were reduced at all frying times and storage times with increased  $\gamma$ -tocopherol levels. This reduction occurred in both the fryer oil and in the oil extracted from potato chips.

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## REFERENCES

- Billek, G., Health Aspects of Thermoxidized Oils and Fats, *Eur. J. Lipid Sci. Technol.* 102:587–593 (2000).
- Normand, L., N.A.M. Eskin, and R. Przybylski, Effect of Tocopherols on the Frying Stability of Regular and Modified Canola Oils, J. Am. Oil Chem. Soc. 78:369–373 (2001).
- Lampi, A.-M., and A. Kamal-Eldin, Effect of α- and γ-Tocopherols on Thermal Polymerization of Purified High-Oleic Sunflower Triacylglycerols, *Ibid.* 75:1699–1703 (2001).
- Barrera-Arellano, D., V. Ruiz-Mendez, G.M. Ruiz, and C. Dobarganes, Loss of Tocopherols and Formation of Degradation Compounds in Triacylglycerol Model Systems Heated at High Temperature, J. Sci. Food Agric. 79:1923–1928 (1999).
- Neff, W.E., K. Warner, and W.C. Byrdwell, Odor Significance of Undesirable Degradation Compounds in Heated Triolein and Trilinolein, J. Am. Oil Chem. Soc. 77:1303–1313 (2000).
- Warner, K., W.E. Neff, W.C. Byrdwell, and H.W. Gardner, Effect of Oleic and Linoleic Acids on the Production of Deep-Fried Odor in Heated Triolein and Trilinolein, *J. Agric. Food Chem.* 49:899–905 (2001).
- Byrdwell, W.C., and W.E. Neff, Non-volatile Products of Triolein Produced at Frying Temperatures Characterized Using Liquid Chromatography with Online Mass Spectrometric Detection, J. Chromatog. A 852:417–432 (1999).
- Kamal-Eldin, A., and L.-A. Appelqvist, The Chemistry and Antioxidant Properties of Tocopherols and Tocotrienols, *Lipids* 31:671–701 (1996).
- 9. AOCS, Official Methods and Recommended Practices of the American Oil Chemists' Society, 5th edn., edited by D. Firestone, AOCS Press, Champaign, 1998.

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