J Am Oil Chem Soc (2009) 86:1199–1207
DOI 10.1007/s11746-009-1461-9

ORIGINAL PAPER

Frying Stability of Purified Mid-Oleic Sunflower Oil Triacylglycerols with Added Pure Tocopherols and Tocopherol Mixtures

Kathleen Warner · Jill Moser

Received: 29 May 2009 / Revised: 28 July 2009 / Accepted: 3 August 2009 / Published online: 22 August 2009

Abstract To determine the effects of the addition of pure tocopherols to triacylglycerols, α, γ, and δ tocopherols were added singly and in various combinations to stripped mid-oleic sunflower oil (SMOSUN). Tortilla chips were fried in the treated oils and then aged at ambient temperature to determine storage stability of the fried food. Frying oils were evaluated for total polar compounds (TPC) as an indicator of oil deterioration, and they were also analyzed for retention of tocopherols. To determine effects of tocopherols on fried-food stability, chips were evaluated for hexanal as an indicator of oxidative stability and for odor characteristics by a trained, experienced analytical sensory panel. Oils extracted from the tortilla chips were also analyzed for residual tocopherols. TPC were highest in the SMOSUN control with no additives followed by the SMOSUN containing only α tocopherol. The SMOSUN oil containing γ tocopherol had the best fry life as indicated by the lowest TPC. Hexanal content and rancid odor intensity were highest in the chips fried in the SMOSUN control and in the SMOSUN containing only α tocopherol. The most stable tortilla chips were fried in SMOSUN containing all three (α, γ, and δ) tocopherols; however, the lowest hexanal levels were measured when γ and δ tocopherols were added at their highest concentrations.

Keywords Fried food · Frying · Mid-oleic sunflower oil · Sensory · Tocopherols

Introduction

Oxidation causes deterioration in oils and oil-containing foods; however, this process can be inhibited by tocopherols, which are well recognized as effective antioxidants both endogenously and as additives. Much of the research on tocopherol efficacy has been done at temperatures of 60 °C or less [1–4]; however, these results may not be the same under frying conditions because studies have shown that temperature can have a significant effect on oxidation with tocopherols [5–7]. For example, Gottstein [6] found that α tocopherol was better than δ tocopherol at 20 °C in lard, but the reverse was noted when the test was conducted at 60 °C. Reblova [7] used the Oxipress apparatus to heat lard at temperatures from 80 to 150 °C and found that α and δ tocopherols had the same activity at 130 °C; however, the activity of δ was two times higher than α at 80 °C. To test the effectiveness of tocopherols in frying oils or model systems, many researchers only heat oils to 180–190 °C without using it for frying food [8–10]. Gamma tocopherol was better than α tocopherol in high oleic acid sunflower triacylglycerols heated to 180 °C [8]; similarly, γ and δ tocopherols were better than α in coconut oil heated to 160 °C [9]. Olive oil enriched with added tocopherols and heated to 120 °C in an OSI apparatus had the best OSI readings when γ tocopherol or a combination of γ and δ tocopherol were used; conversely, the lowest OSI readings were obtained when α tocopherol only was added [10]. Others have conducted studies by frying food to determine the effects of tocopherols in oils [11–15]. In our previous work on effects of tocopherols in frying, we added pure γ tocopherol to

Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by USDA implies no approval of the product to the exclusion of others that may also be suitable.

K. Warner (✉) · J. Moser
National Center for Agricultural Utilization Research,
1815 North University Street, 61604 Peoria, IL, USA
e-mail: kathleen.warner@ars.usda.gov

triolein and found that it significantly inhibited polar compound formation in the oil as well as nonanal formation and rancid odor intensity in aged potato chips when added at either 100 or 400 ppm [14, 15]. The German Society for Fat Research (DGF) recommended at their deep fat frying symposium in 2000 that sensory evaluation should be the primary determinant of quality in frying research [16]. Therefore, in this present study, we included frying of food (tortilla chips) and sensory analysis of the aged chips. Our objectives were to determine the effects of α, γ, and δ tocopherols, added singly and in combinations, on the stability of mid-oleic sunflower oil triacylglycerols during frying and on the shelf life of the food fried in the oil.

Experimental Procedures

Oil and Chemicals

Fully processed mid-oleic sunflower oil (MOSUN) was obtained from a commercial processor with citric acid as the only additive. Tocopherols were purchased from Matreya (Pleasant Gap, PA, USA). All other chemicals and solvents were obtained from Sigma-Aldrich (St. Louis, MO, USA) and were ACS grade or HPLC-grade for solvents. Raw white-corn tortillas were purchased locally.

Oil Stripping by Molecular Distillation

Tocopherols were removed from MOSUN with an ICL-04A short-path thin-film evaporator (Incon Processing, Batavia, IL, USA) attached to an Edwards (Tewksbury, MA, USA) high-vacuum pump and diffusion pump, a Neslab (Thermo Scientific, Newington, NH) model RTE-140 recirculating chiller filled with ethylene glycol and set to 30 °C, a Julabo (Vista, CA, USA) model SE-6 recirculating heated bath filled with Thermal H (Julabo) bath fluid, and an Ika Works (Wilmington, NC) model RW20 digital mechanical overhead stirrer set to 350 rpm. The oil was first degassed by passing it through the evaporator at ~2–3 ml/min under vacuum of 100 mTorr and evaporator temperature of 250 °C. The degassed oil was passed through the evaporator a second time at the same rate and temperature, but under increased vacuum of 1 mTorr. The stripped MOSUN (SMOSUN) was placed in dark glass, screw-cap bottles, sealed with argon in the headspace, and kept frozen at 0 °C until used. The oils were measured for tocopherols, fatty acid composition, and peroxide value.

Tocopherol Addition to Oils

Pure tocopherols were added to the SMOSUN singly and in combinations of α, γ, and/or δ tocopherols for a total concentration of approximately 780–850 ppm, which is a total tocopherol range similar to that in many fully processed sunflower oils. β-tocopherol was not used as an additive because of its naturally low levels in most vegetable oils. A SMOSUN with no added tocopherols was used as a control. Treated oils were placed in screw-cap bottles and argon was added to the headspace. Samples were frozen at 0 °C until frying studies were conducted.

Frying Protocol

Samples (100 g) of SMOSUN with or without added pure tocopherol(s) were weighed into 500-ml Pyrex glass crystallizing dishes (8.5 cm diameter × 7.5 cm height) (Corning Inc. Life Sciences, Lowell, MA, USA). The crystallizing dish was placed on a hot plate with a probe to control temperature at 180 ± 2 °C. Frying protocol included use of the oil for intermittent batch frying of raw tortilla pieces (approximately 3 × 1 cm) with total heating/frying time of 6 h in 1 day. Tortilla pieces were fried in 5-g batches for approximately 1.5 min/batch every 15 min. Tortilla chips were sampled for analysis at the 1, 3, and 6 h frying times; at these three collection times, five 5-g batches of tortilla chips were fried to provide enough samples for analyses. At each sampling time of 1, 3, and 6 h, chips from each treatment were combined and equally divided into three screw-top vials with air in the headspace and were aged in the dark for 0, 2, and 4 months at 25 °C and then frozen at 0 °C until later analyses. No makeup oil was added.

Compositional Analyses of Oils

Fatty acid compositions of the MOSUN before and after stripping were determined in duplicate by capillary gas chromatograph (GC) analysis with a Hewlett-Packard 5890 GC (Wilmington, DE) equipped with a SP2330 column (30 m, 0.20 mm ID, 0.20 micron film thickness) (Supelco, Bellefonte, PA). Column temperature was first held at 190 °C for 5 min, and then was programmed to 230 °C at 20 °C/min. The injector was held at 250 °C and the detector at 260 °C. Fatty acids were identified by comparison with retention times of known standards, and quantification was determined as the percent area of each peak relative to the sum of all peak areas.

Analysis of α, β, γ, and δ tocopherols by normal-phase HPLC was conducted in triplicate using a Varian ProStar (Varian Associates, Walnut Creek, CA, USA) 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 tocopherols was made using external standard calibration. Tocopherols were identified by comparison with retention times of known standards.

Peroxide Value

Oxidation levels of the MOSUN before and after stripping were measured in duplicate for peroxide value (PV) (AOCS method Cd 8-53) [17]. Peroxide values are expressed as milliequivalents (meq) of peroxide per kilogram of oil.

Extraction of Oil from Tortilla Chips

Tortilla chips were extracted with an automated Avanti 2050 Soxtec (Foss, Eden Prairie, MN, USA). Samples of 4–5 g crushed tortilla chips were extracted using 60 ml hexane for 1 h. Argon was used to remove any residual hexane from the extracted oil. Extracted oils were placed in screw-top vials with argon in the headspace and frozen at 0 °C.

Total Polar Compound Analysis

Amounts of polar compounds were analyzed in duplicate by the AOCS column chromatography method Cd 20-91(97) [17].

Volatile Compound Analysis

Volatile compounds were analyzed in triplicate with a purge-and-trap apparatus equipped with a test-tube adapter (Tekmar model 3000, Tekmar-Dohrmann, Cincinnati, OH, USA) coupled with a model 3400 GC and a Saturn model 3 ion trap mass spectrometer (Varian, Walnut Creek, CA, USA). A 50-mg sample was placed in the 1.9 × 7.6 cm test tube and heated at 100 °C for 9 min preheat time. Volatile compounds were trapped on a 30.5-cm Tenax #1 trap, with 10 min sample purge time, 170 °C for 6 min desorbing, 180 °C desorb temperature, 160 °C GC transfer line and valve temperature. Volatile compounds were introduced onto a GC column, DB-1701, 1 μm film thickness, 30 m × 0.32 mm (J & W Scientific, Folsom, CA, USA). The column was programmed at −20 °C for 2 min then heated from −20 to 233 °C at 3 °C/min. Helium flow rate through the column was 2 ml/min with 28 ml/min injector split vent flow. The GC injector was set at 240 °C, and the line to the mass spectrometer was set at 230 °C. The ion trap MS operated in the EI mode with mass scan range 23–400 m/z over 0.8 s. Filament emission current was 25 micro amps, axial modulation was 2.1 V, manifold heater was set at 160 °C, and the filament/multiplier delay was 2.5 min. Compound structural identifications were made both from spectral comparisons with the NIST 92 mass spectrometry library (Varian, Walnut Creek, CA, USA) and from retention-time comparisons with standard compounds.

Odor Evaluation of Tortilla Chips

Tortilla chips were rated for negative odor attributes of stale and rancid by a 10-member trained, analytical, descriptive panel experienced in evaluating fried foods for odor and flavor [18, 19]. Panelists had experience and training in evaluating fresh and aged fried food including tortilla chips with a wide variety of odors and flavors at weak, moderate, and strong intensity levels. Panelists were presented with 0.5 g crushed tortilla chip samples in 28.4-ml (1-oz) plastic souffle cups with snap-on lids (Solo Cup, Urbana, IL, USA). All sensory evaluations were conducted at our research center in a panel room with individual booths, temperature control, and with red lighting to mask color differences between samples [18]. Panelists rated the tortilla chips for stale and rancid odor intensities on a 3-point intensity scale with 0 = no intensity, 1 = weak intensity, 2 = moderate intensity, and 3 = strong intensity. Each panelist received three coded, randomized samples of each fry time (e.g., 1 h) at each storage time (e.g., 2 month) per session.

Statistical Analysis

Data were evaluated by analysis of variance and Duncan's multiple range test when F values were significant [20]. ANOVA was conducted using Microcal Origin 6.0 (Microcal Software, Northampton, MA, USA). Statistical significance was expressed at the $P \leq 0.05$ level unless otherwise indicated.

Results and Discussion

Composition of Stripped and Unstripped Oils

The fatty acid composition of the SMOSUN did not significantly change from the initial MOSUN after molecular distillation with 3.8% 16:0, 3.1% 18:0, 60.1% 18:1, and 33.0% 18:2. All tocopherols were removed in SMOSUN from the original level in the MOSUN with the exception of a few ppm of β tocopherol. Peroxide values were 0.3 meq/kg in the MOSUN and 0.5 meq/kg in the SMOSUN.

Frying-Oil Deterioration

TPC were measured as an indicator of deterioration in the frying oils. Houhoula et al. [21] reported that polar

compounds increased linearly with increasing frying time. We observed similar results in this study (Fig. 1). We plotted the TPC data with the tocopherol additions on the horizontal axis rather than plotting the formation of TPC over time as is most common. We wanted to show graphically how the quantities of TPC differ from one tocopherol addition to another for each frying time.

Initially, all samples had similar TPC levels in the 2.0–2.3% range. At the 1-h sampling time, TPC increased slightly to a range of 2.2–2.8%, and no significant differences were noted among the various combinations of pure tocopherol additions. However, after 3 h of heating/frying, the TPC levels were significantly higher in the SMOSUN control with no additives than in any of the treated samples. Also at this time, the oils with combinations of all three added tocopherols were significantly lower in TPC than the oils with single tocopherols or combinations of two tocopherols. The oils with three added tocopherols increased only slightly at 3 h from the TPC levels at the 1-h sampling time. By 6 h, TPC was significantly higher in the SMOSUN control at 15% than any other sample followed by the oil with 850 ppm α tocopherol at 12.5% TPC. The oil with 830 ppm γ tocopherol had the lowest TPC at 8.9%. All other samples ranged from 9.5 to 11% TPC at 6 h. The results for TPC were not generally correlated with specific homologues added to the oils, except that the oils with no tocopherols or only α tocopherol had the highest TPC and the oil with only γ tocopherol had the lowest TPC after 6 h of heating/frying.

Combining α tocopherol with other tocopherols was effective in improving frying-oil stability compared with α only. That the formation of nonvolatile degradation products can be affected by tocopherols [8, 10, 22] has been shown by other researchers including Barrera-Arellano et al. [22] who reported that a mixture of all four tocopherols inhibited polar compound formation better than δ tocopherol alone, which in turn, was better than α tocopherol only in triolein heated to 180 °C. Our results also agree with those of Lampi et al. [8] who found that γ was better than α in inhibiting frying-oil deterioration.

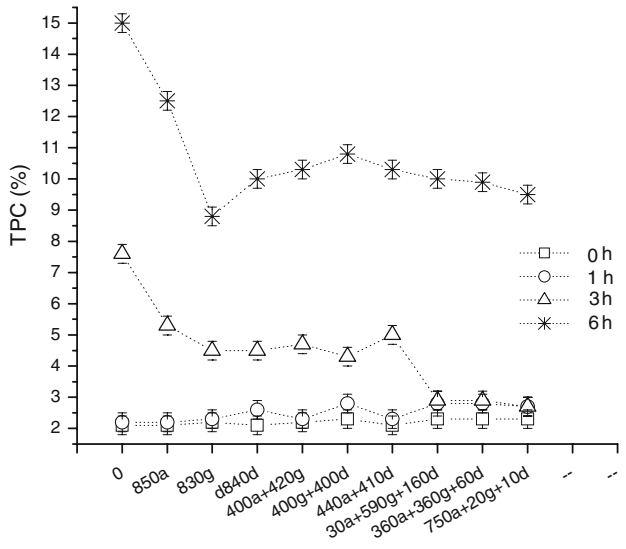

Fig. 1 Total polar compounds (%) in stripped mid-oleic sunflower oils with added pure tocopherols. The oils were used for frying at 180 °C for 0, 1, 3, or 6 h

Tocopherol Retention in Oils and Fried Food

Measurements of the disappearance of tocopherols in oils have been used to determine the effect of antioxidants during frying [11]. In our study, after 1 h of heating/frying, SMOSUN with γ tocopherol lost the most compared to oils with similar concentrations of either α or δ tocopherol (Table 1). This pattern continued at the 3-h sampling time; however, more γ tocopherol than α was retained at 6 h. The oil with δ tocopherol lost the least amount compared to oils with either α or γ tocopherol. When the tocopherols were added in pairs, the loss of α tocopherol was less when it was combined with γ tocopherol than with δ tocopherol. When γ tocopherol was combined with α tocopherol, less was lost than when it was paired with δ tocopherol. Finally, slightly more δ tocopherol was lost when it was combined with α tocopherol than with γ. It appears that α tocopherol is preferentially lost to γ and δ tocopherols during frying; however, γ tocopherol is lost to a greater extent compared to δ tocopherol when only those two tocopherols are in the antioxidant mixture. These results agree with those of Lampi and Kamal-Eldin [8], who found that α tocopherol was lost faster than γ tocopherol from purified high oleic sunflower triacylglycerols heated to frying temperatures.

The ratios of tocopherol homologues in the mixtures of three tocopherols were selected as fairly similar to those concentrations naturally occurring in common oils including soybean (30 α + 590 γ + 160 δ), corn (360 α + 360 γ + 60 δ), and sunflower (750 α + 20 γ + 10 δ) oils. At almost all sampling times of heating/frying, α tocopherol was preferentially lost compared to γ and δ tocopherols, except for the sample containing 30 ppm of α tocopherol at the 3- and 6-h times. Delta tocopherol was retained in the highest concentrations in the oils, except for α when it was added at 30 ppm (6 h time), followed by γ tocopherol, regardless of whether tocopherols were added in pairs and with all three in the mixture. Other researchers have also reported that δ tocopherol was retained at the highest amounts in triacylglycerols heated at frying temperatures [22]. We also found that when a tocopherol homologue was added at a lower concentration, less of that tocopherol was lost than when it was added at moderate to high amounts.

In oils containing only single added tocopherols that were extracted from tortilla chips, increasing amounts of

Table 1 Tocopherol retention (%) in stripped mid-oleic sunflower oil with added pure tocopherols. The oil was used for frying tortilla chips for 1, 3, or 6 h at 180 °C

Tocopherol (ppm)	1 h			3 h			6 h		
	Alpha	Gamma	Delta	Alpha	Gamma	Delta	Alpha	Gamma	Delta
850 α	90			70			25		
830 γ		83			68			37	
840 δ			95			81			43
400 α + 420 γ	71	81		53	64		40	40	
400 γ + 400 δ		63	85		41	74		19	53
440 α + 410 δ	47		79	31		71	10		52
30 α + 590 γ + 160 δ	64	71	90	64	53	79	63	22	61
360 α + 360 γ + 60 δ	77	78	95	56	58	82	32	38	74
750 α + 20 γ + 10 δ	78	87	92	64	80	90	53	62	75

tocopherols were lost as frying time increased similar to what was seen in the frying oils (Table 1); however, additional losses were noted in the aged chips after storage (Table 2). The chips fried in oil with only α tocopherol lost the highest percent of the original amount, followed by chips fried in oil with only γ tocopherol, whereas δ tocopherol was retained at the highest percent. For example, in chips fried in oils used for 6 h and then aged for 4 months, only 1% of α tocopherol was retained, 27% of γ tocopherol was left, and 34% of δ tocopherol remained. The higher retention of γ and δ tocopherols in the oil extracted from chips could help to inhibit oxidation in the tortilla chips during storage. Gordon and Kourimska [12] reported that the stability of rapeseed oil decreased as the tocopherols were consumed during oxidation.

In oils containing two added tocopherols that were extracted from tortilla chips, increasing quantities of tocopherols were lost as frying time and storage time increased (Table 3). Delta tocopherol, both alone and paired with other tocopherols, was the most stable tocopherol in both the 6-h oil and chips fried in 6-h oil and then stored for 4 months. As we determined in the oils during frying, α and γ are mostly lost preferentially to δ tocopherol in the chips during storage.

In chips fried in oils containing three added tocopherols, we noted that when one of these tocopherols was the highest concentration of the three additives, that tocopherol was retained proportionately less than when it was added at the lowest amount (Table 4). For example, δ tocopherol was usually retained at the highest amount compared to α or γ; however, when added at 160 ppm in the mixture, only 34% was retained compared with 74% retention when added at 10 ppm to oil used to fry chips (6-h fry/4-month storage).

Table 2 Tocopherol retention (%) in tortilla chips fried in stripped mid-oleic sunflower oil with added single pure tocopherols for 1, 3, or 6 h at 180 °C and aged for 0, 2, or 4 months at 25 °C

Tocopherol (ppm)	1 h			3 h			6 h		
	Alpha	Gamma	Delta	Alpha	Gamma	Delta	Alpha	Gamma	Delta
0 months at 25 °C									
850 α	60			55			7		
830 γ		75			56			32	
840 δ			89			70			42
2 months at 25 °C									
850 α	47			32			6		
830 γ		74			54			31	
840 δ			89			67			35
4 months at 25 °C									
850 α	46			14			1		
830 γ		71			54			27	
840 δ			78			65			34

Table 3 Tocopherol retention (%) in tortilla chips fried in stripped mid-oleic sunflower oil with two added pure tocopherols for 1, 3, or 6 h at 180 °C and aged for 0, 2, or 4 months at 25 °C

Tocopherol (ppm)	1 h			3 h			6 h		
	Alpha	Gamma	Delta	Alpha	Gamma	Delta	Alpha	Gamma	Delta
0 months at 25 °C									
400 α + 420 γ	66	75		52	56		33	39	
400 γ + 400 δ		49	84		32	73		7	51
440 α + 410 δ	51		82	34		70	8		62
2 months at 25 °C									
400 α + 420 γ	50	58		51	52		14	35	
400 γ + 400 δ		46	84		32	70		2	36
440 α + 410 δ	46		82	24		70	2		48
4 months at 25 °C									
400 α + 420 γ	42	58		42	50		3	24	
400 γ + 400 δ		46	80		20	67		3	38
440 α + 410 δ	21		80	2		68	1		32

Table 4 Tocopherol retention (%) in tortilla chips fried in stripped mid-oleic sunflower oil with three added pure tocopherols for 1, 3, or 6 h at 180 °C and aged for 0, 2, or 4 months at 25 °C

Tocopherol (ppm)	1 h			3 h			6 h		
	Alpha	Gamma	Delta	Alpha	Gamma	Delta	Alpha	Gamma	Delta
0 months at 25 °C									
30 α + 590 γ + 160 δ	48	58	84	35	30	78	23	11	51
360 α + 360 γ + 60 δ	45	69	89	40	35	78	18	34	73
750 α + 20 γ + 10 δ	65	87	92	48	80	83	42	80	83
2 months at 25 °C									
30 α + 590 γ + 160 δ	42	57	84	35	30	78	20	2	34
360 α + 360 γ + 60 δ	44	69	89	20	31	78	10	33	73
750 α + 20 γ + 10 δ	62	87	92	32	80	83	18	80	75
4 months at 25 °C									
30 α + 590 γ + 160 δ	33	47	83	32	30	78	19	2	34
360 α + 360 γ + 60 δ	44	68	88	6	28	78	3	24	72
750 α + 20 γ + 10 δ	33	87	92	10	74	83	8	78	74

Oxidative Stability of Tortilla Chips

Hexanal was used to monitor the oxidation of the aged tortilla chips because it is a major volatile compound formed during the oxidation of linoleic acid, which was measured at 33.1% in the SMOSUN sample. Although oleic acid was the predominant fatty acid at 60.2% in the SMOSUN, this fatty acid does not oxidize as readily as linoleic acid. Frankel reported that linoleic acid oxidizes at a rate 50 times faster than oleic acid [23]. Therefore the oxidation of linoleic acid in the chips as measured by hexanal formation was monitored after aging at 0, 2, and 4 months at 25 °C.

In the unaged (0 months) tortilla chips fried in oils used for 1 h, hexanal levels were low and similar, with a range of 1–4 ppm (Fig. 2a). Chips fried in the SMOSUN control that had been used for 1 h of heating/frying had 4 ppm of hexanal at 0 months. All samples showed slight to moderate increases in hexanal after 2 and 4 months of aging, except for the control. By 2 months, the chips fried in the control had 60 ppm hexanal. Four-month data for the control was not included in the plot (Fig. 2a) because the peak area was over range. Lowest hexanal quantities were measured in the chips fried in oils with all three tocopherols followed by chips fried in oils containing only γ or δ tocopherol or the combination of γ and δ tocopherol.

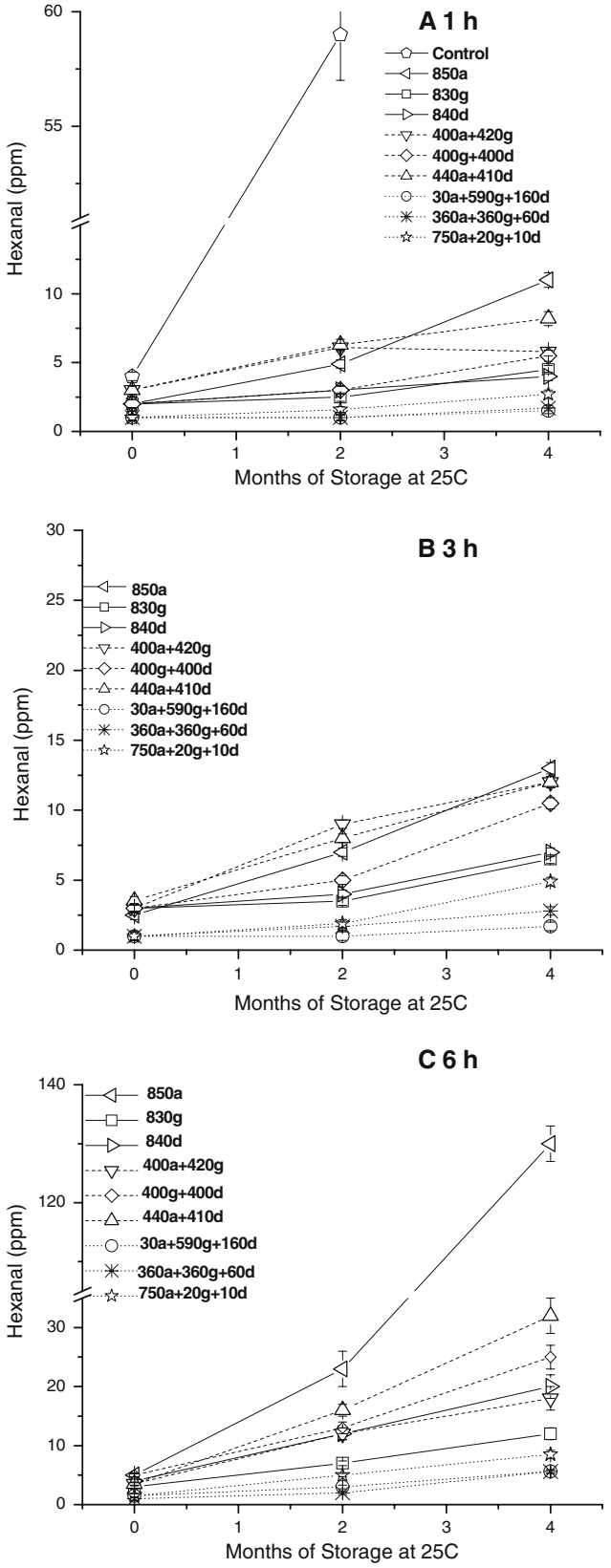

Fig. 2 Hexanal (ppm) in tortilla chips fried in stripped mid-oleic sunflower oils with added pure tocopherols at 180 °C for **a** 1, **b** 3, or **c** 6 h and aged for 0, 2, and 4 months at 25 °C

Chips fried in oils with α tocopherol added alone or in combination with either γ or δ tocopherol had the highest hexanal content after the control. After 4 months of aging, chips prepared in oil with only α tocopherol had the highest quantity of hexanal at 11 ppm.

A similar pattern in hexanal formation was observed in the chips fried in oil used for 3 h (Fig. 2b). The chips prepared in the SMOSUN control had 9 ppm of hexanal at 0 months; however data are not plotted because only one data point would be included. Further testing of hexanal in the SMOSUN control showed extremely high peaks for this volatile compound that were all over range and therefore could not be calculated for ppm levels or plotted. After the control, the next highest hexanal levels were found in chips fried in oil with only α tocopherol and combinations of α–γ and α–δ tocopherols. Lowest hexanal levels were found in chips fried in oil containing all combinations of three tocopherols and in oils with individual γ tocopherol and δ tocopherol.

In chips fried in oils used for 6 h (Fig. 2c), the pattern of hexanal formation was similar to those found at 1-h and 3-h sampling times. No data for the chips fried in the 6-h control are plotted because of high, over-range quantities at 2 and 4 months. The unaged (0 months) chips fried in the 6-h control had 15 ppm of hexanal. Chips fried in oil with only α tocopherol had significantly more hexanal formed after 2 and 4 months of storage than chips fried in the oils with any of the other tocopherols or combinations of tocopherols. By 4 months of storage, hexanal was significantly lower in the chips fried in oils with the combination of high γ (590 ppm), high δ (160 ppm), and low α (30 ppm) tocopherol as well as the combination of moderate γ (360 ppm), moderate δ (60 ppm), and moderate α (360 ppm) tocopherol, followed by the chips fried in oil with high α (750 ppm), low γ (20 ppm), and low δ (10 ppm) tocopherol. The chips fried in the oil with only α tocopherol had the highest hexanal level, except for the control.

These results are similar to those reported in our previous studies on effects of tocopherols on oil stability [3, 4]. We found that stripped soybean oil treated with the tocopherol profile typical of soy (high γ, high δ, and low α) had significantly lower formation of total volatiles when compared to stripped sunflower oil with added pure tocopherols typical of sunflower oil (low γ, low δ, and high α) in storage stability tests at 60 °C [3]. Similarly, in other work, we showed that mid-oleic sunflower oils bred to have high γ and δ tocopherol concentrations had significantly less hexanal formation than mid-oleic sunflower oil with its typical tocopherol profile of low γ and δ [4].

Fried-Food Stability

Sensory analysis of stale and rancid odor intensities was conducted on tortilla chips aged for 0, 2, and 4 months

after sampling at 1, 3, and 6 h of intermittent batch frying. The 0.0–3.0 scale used represented a range of intensity from 0 = no odor, 1 = weak odor intensity, 2 = moderate odor intensity, and 3 = strong odor intensity. Panelists were presented with reference standards of oxidized tortilla chips representative of none, weak, and strong stale and rancid odor intensities. In this study, the intensity levels for stale odor were low for most chip samples (Fig. 3a–c).

Intensity scores for stale odor for the control are not plotted because only the unaged chips fried in the control at the 1-h sampling time were described as moderately stale; all other control samples were described as rancid. In the chips fried in tocopherol-treated oils, the stale intensity range was 0–0.8 for unaged samples to a maximum of 2.3 for some samples aged 4 months. As storage time increased, the intensity levels for stale odor increased gradually from 0 to 4 months, with the exception of the chips fried in oil containing only 850 ppm α tocopherol and used for 6 h of frying (Fig. 3c). That sample, which had the highest intensity of stale odor at 2 months, showed a decrease in stale intensity by 4 months because of a rancid odor that was predominant then. After 4 months of storage, chips with the least stale odor intensity were those that had been fried in oils containing moderate to high concentrations of γ tocopherol.

Data are not plotted for rancid odor intensity because only two products were rated as having rancid odor. First, all chips fried in the SMOSUN control, except the unaged 1 h sample were described as rancid. The control chips fried at the 1-h sampling time and aged 2 months were rated as weak rancid, and the rancid intensity scores increased with increasing oil use and storage time. In the 3-h/2-month sample, the rancid odor intensity was moderate and increased to strong intensity (3.0) in the 6-h/4-month chips. The only other sample to have a rancid odor was fried in the oil with only α tocopherol; the odor was noted as weak intensity (intensity score = 1.1) at the 6-h heating/frying time and after 4 months of storage. No rancid odors were reported in chips fried in any of the other tocopherol-treated oils.

Conclusions

As the frying-oil deterioration increases over time, the foods fried in the more abused oils are more susceptible to oxidation during storage [19, 23]. Therefore, it was not unexpected that the SMOSUN control or oil with only α tocopherol, which had the highest amounts of TPC (Fig. 1), produced chips with the most hexanal at 2 and 4 months of storage (Fig. 2c) and rancid odor intensities. The addition of individual tocopherols or tocopherols added in pairs had

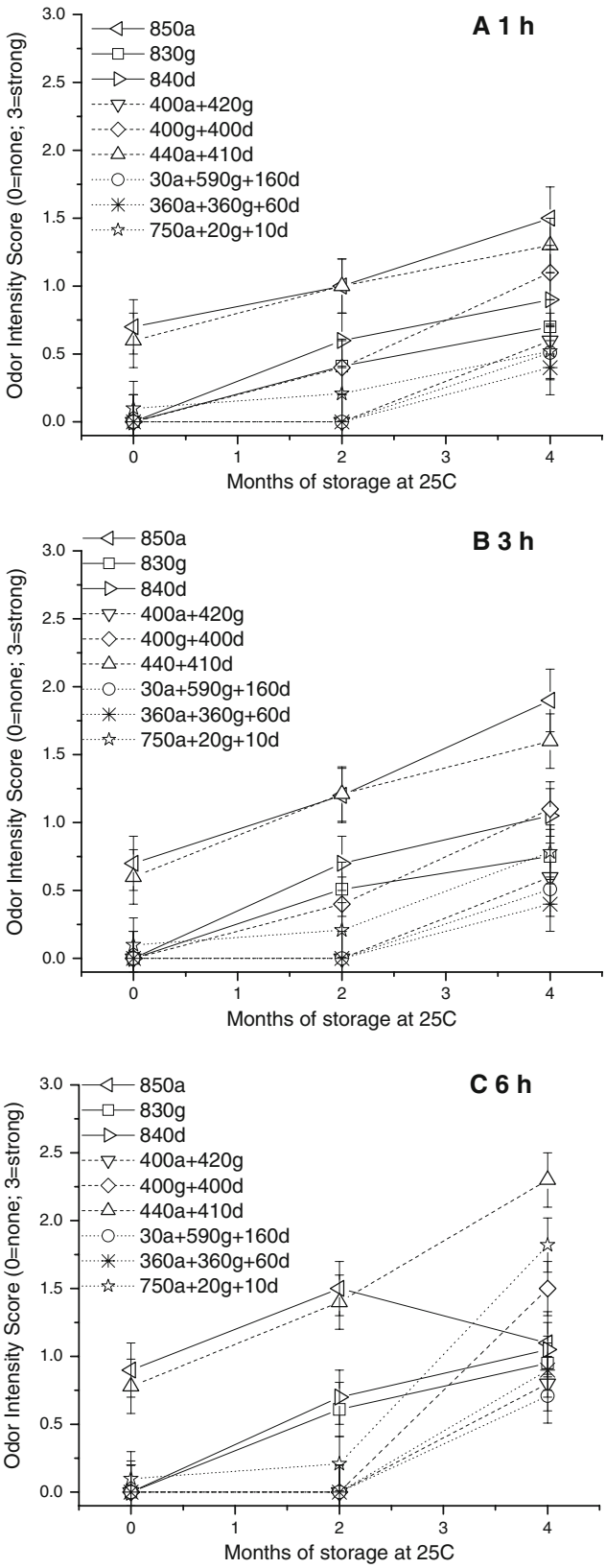

Fig. 3 Stale odor intensity scores for tortilla chips fried in stripped mid-oleic sunflower oils with added pure tocopherols at 180 °C for **a** 1, **b** 3, or **c** 6 h and aged for 0, 2, and 4 months at 25 °C

less of an effect than when all three tocopherols were added together. Of the oils containing all three tocopherols, the two samples containing the higher concentrations of γ and δ tocopherols produced chips with better oxidative stability than when the γ and δ tocopherol amounts were lower with a higher α level. This effect can be attributed in part to the better retention of γ and δ tocopherols in the oils during frying and in the chips during aging.

Acknowledgments The authors acknowledge L. Parrott, W. Rinsch, and C. Novota for technical assistance and the NCAUR sensory panel.

References

1. Frankel EN, Cooney PM, Moser HA, Cowan JC, Evans CD (1959) Effect of antioxidants and metal inactivators in tocopherol-free soybean oil. Fette Seifen Anstrich 61:1036–1039
2. Huang SW, Frankel EN, German JB (1995) Effects of individual tocopherols and tocopherol mixtures on the oxidative stability of corn oil triglycerides. J Agric Food Chem 43:2345–2350
3. Warner K (2005) Effects of the flavor and oxidative stability of stripped soybean and sunflower oils with added pure tocopherols. J Agric Food Chem 53:9906–9910
4. Warner K, Miller J, Demurin Y (2008) Oxidative stability of crude mid-oleic sunflower oils from seeds with high gamma and delta tocopherol levels. J Am Oil Chem 85:529–533
5. Lea CH, Ward RJ (1959) Relative activities of the seven tocopherols. J Sci Food Agric 10:537–548
6. Gottstein T, Grosch W (1990) Model study of different antioxidant properties of alpha and gamma tocopherol in fats. Fat Sci Tech 92:139–143
7. Reblova Z (2006) The effect of temperature on the antioxidant activity of tocopherols. Eur J Lipid Sci Technol 108:858–863
8. Lampi A, Kamal-Eldin A (1998) Effect of alpha and gamma tocopherols on thermal polymerization of purified high-oleic sunflower triacylglycerols. J Am Oil Chem Soc 75:1699–1703
9. Wagner KH, Wotruba F, Elmadfa I (2001) Antioxidative potential of tocotrienols and tocopherols in coconut fat at different oxidation temperatures. Eur J Lipid Sci Technol 103:746–751
10. Wagner KH, Elmadfa I (2000) Effect of tocopherols and their mixtures on the oxidative stability of olive oil and linseed oil under heating. Eur J Lipid Sci Technol 102:624–629
11. Gordon MH, Kourimska L (1995) Effect of antioxidants on losses of tocopherols during deep fat frying. Food Chem 52:175–177
12. Gordon MH, Kourimska L (1995) The effects of antioxidants on changes in oils during heating and deep fat frying. J Sci Food Agric 68:347–353
13. Normand L, Eskin NAM, Przybylski R (2001) Effect of tocopherols on the frying stability of regular and modified canola oils. J Am Oil Chem Soc 78:369–373
14. Warner K, Neff WE, Eller FJ (2003) Enhancing quality and oxidative stability of aged fried food with gamma-tocopherol. J Agric Food Chem 51:623–627
15. Neff WE, Warner K, Eller FJ (2003) Effect of gamma-tocopherol on formation of nonvolatile lipid degradation products during frying of potato chips in triolein. J Am Oil Chem Soc 80:801–806
16. Deutsche Gesellschaft für Fettwissenschaft [DGF] (German Society for Fat Research) (2000) 3rd international symposium on deep-fat frying. http://www.dgfett.de/material/recomm.htm
17. AOCS (1998) Official methods and recommended practices of the American Oil Chemists' Society, 5th ed. Champaign
18. Warner K (1995) Sensory evaluation of oils and fat-containing foods. In: Warner K, Eskin NAM (eds) Methods to assess quality and stability of oils and fat-containing foods. AOCS Press, Champaign, pp 49–75
19. Warner K, Gupta M (2005) Potato chip quality and frying oil stability of high oleic acid soybean oil. J Food Sci 70:395–400
20. Snedecor GW (1956) Statistical methods, 5th ed. Iowa State University Press, Ames
21. Houhoula DP, Oreopoulou V, Tzia C (2003) The effect of process time and temperature on the accumulation of polar compounds in cottonseed oil during deep-fat frying. J Sci Food Agric 83:314–319
22. Barrera-Arellano D, Ruiz-Mendez V, Ruiz GM, Dobarganes C (1999) Loss of tocopherols and formation of degradation compounds in triacylglycerol model systems heated at high temperature. J Sci Food Agric 79:1923–1928
23. Frankel EN (2005) Antioxidants. In: Lipid oxidation, 2nd ed. Oily Press, Bridgwater, pp 15–24