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Lipid Oxidation and Stability of Tocopherols and Phospholipids in Soy-added Fried Products During Storage in the Dark

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Abstract Lipid oxidation and contents of tocopherols and phospholipids (PL) in soy-added fried products during storage in the dark were studied. Flour dough containing soy flour at 0, 10, 20, and 30% on a weight basis was fried in corn oil at 180°C for 2.5 min. The fried products were stored at 60°C for 11 days in the dark. Lipid oxidation of the fried products was evaluated by conjugated dienoic acid (CDA) and *p*-anisidine values (PAV). Tocopherols and PL were determined by high performance liquid chromatography (HPLC). CDA contents and PAV of the fried products were increased during storage, and addition of soy flour improved lipid oxidative stability of the fried products, which was partly related to increased amount of tocopherols and PL in the soy-added fried products. Tocopherols and PL were degraded during the dark storage of the fried products. Soy flour addition to the dough did not affect the rate of tocopherols degradation during storage of the fried products; however, PL degradation was higher in the soy-added fried products. Residual amounts of α-tocopherol and phosphatidylinositol showed high correlations with the lipid oxidation of the fried products during storage in the dark.

Keywords: lipid oxidation, tocopherol, phospholipid, soy-added fried product, storage

Introduction

Frying produces many peroxy and alkyl radicals as well as oxidized compounds in oil, and the oil containing the radicals and oxidized compounds is absorbed into the foods during frying (1,2). The oil absorbed during frying and originally present in the foods undergoes oxidation during storage, and the lipid oxidation is affected by composition of the fried foods and storage conditions (3). Composition of fried foods is dependent on food materials as well as frying oil. Wheat flour is one of the most used food materials to make fried snacks, and some food materials besides wheat flour are added to improve nutritional, sensory, and physicochemical quality of the fried foods. Addition of dried spinach and carrot, egg yolk, or red ginseng extracts to wheat flour dough improved the lipid oxidative stability of the fried dough during storage in the dark by decreasing conjugated dienoic acid formation and/or p-anisidine or thiobarbituric acid values (4-7).

Soy flour addition improves texture and nutrition of fried noodles and bread (8,9). Soy flour contains high amount of phospholipids (PL) and tocopherols as well as carbohydrate, protein, and lipid (10,11). Tocopherols are well-known antioxidants by free radical scavenging and singlet oxygen quenching (12,13). PL acts as antioxidants and prooxidants; it decreases autoxidation of oil by chelating metals (14), and accelerates the oxidation by decreasing surface tension of the oil to increase oxygen diffusion to the oil (15).

Consumer concerns on health and food texture have led to introduction of many soy-added products to the market. Yoon and Choe (11) reported that soy flour in wheat flour

dough increased corn oil oxidation during frying of the dough. However, there was no report on the effects of soy flour addition to the dough on the oxidative stability of the fried products during storage. In spite of high significance of lipid oxidative stability in soy-added fried foods during handling and storage, related studies are hardly found. Therefore, this study was performed to determine (1) how soy flour addition in making dough affects lipid oxidation of the fried products during storage in the dark, and (2) how much tocopherols and PL are related with the lipid oxidation of the fried products in the dark.

Materials and Methods

Materials and chemicals Full-fat soy flour, wheat flour, and refined, bleached, and deodorized corn oil were products of Natural Product, Inc. (Iowa Cty, IA, USA), Daehan Flour Mills Co., Ltd. (Incheon, Korea), and CJ Co. (Seoul, Korea), respectively. Wheat flour (1 kg) contained tocopherols (16 mg) and phospholipids (PL, 3.6 g), and the amount of tocopherols and PL in soy flour (1 kg) were 415 mg and 10.9 g, respectively, as determined by high performance liquid chromatography (HPLC). Corn oil (1 kg) contained tocopherols at 1,000.1 mg/ kg oil, but no PL was detected. Fatty acid composition of the corn oil was palmitic (13.2%), stearic (2.2%), oleic (34.0%), linoleic (50.5%), and linolenic (0.1%) acids, as determined by gas chromatography (GC). Isooctane, isopropanol, n-hexane, acetonitrile, methanol, and phosphoric acid of HPLC grade were purchased from J.T. Baker, Inc. (Phillipsburg, NJ, USA). p-Anisidine, 14% BF₃-methanol, standard mixture of phosphatidylinositol (PI), lysophosphatidylcholine (LPC), phosphatidylethanolamine (PE), and phosphatidylcholine (PC), and methyl esters of standard fatty acid (palmitic, stearic, oleic, linoleic, and linolenic acid) were purchased from Sigma-Aldrich (St. Louis, MO, USA). All other chemicals were of analytical grade.

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Preparation and storage of fried products Fried products were prepared by frying dough pieces in corn oil at 180° C for 2.5 min, according to the method of Yoon and Choe (11). The dough pieces ($2 \times 2 \times 0.1$ cm) were prepared by mixing distilled water (35 g) with mixture (100 g) of full fat soy flour and wheat flour, followed by sheeting and cutting the dough. The weight ratios of soy flour to wheat flour in the mixture were 0:100, 10:90, 20:80, and 30:70.

Fried products were put into 460-mL glass bottles, 80 g in each bottle, and the bottles were capped, wrapped with aluminum foil, and then placed in an incubator (Model D1-3375, 700 W; Dong Yang Science, Gyeonggi, Korea) at 60°C for 11 days. All samples were prepared in duplicate. The bottles were taken out after 2, 5, 8, and 11 day storage for analyses.

Analysis of fatty acid composition and lipid oxidation of the fried products during storage Fatty acid composition of the fried products was analyzed by GC (11) after lipid extraction by the Folch method (16). The lipid was esterified with 14% BF₃-methanol solution and then injected into a Younglin M600D GC (Younglin Co., Seoul, Korea) equipped with a SupelcowaxTM capillary column (30 m×0.53 mm, 0.5-µm thick: Bellefonte, PA, USA) and a flame ionization detector. Temperatures of the oven, injector, and detector were 200, 270, and 280°C, respectively. Nitrogen flow rate was 5 mL/min, and the split ratio was 33:1. Each fatty acid in the chromatograms was identified by comparing retention times of standard fatty acid methyl esters, and their relative concentration was determined based on the electronic units of peak areas.

Degree of lipid oxidation of the fried products was evaluated by combination of conjugated dienoic acid (CDA) contents and *p*-anisidine values (PAV) by AOCS method Ti la-64 and Cd 18-90 (17), respectively, after lipid extraction from fried products by the Folch method.

Determination of tocopherols and phospholipids in the **fried products** Tocopherols and PL in the fried products were determined by HPLC as described by Yoon and Choe (11), after the lipid extraction by the Folch method. An instrument for tocopherols determination was a Younglin SP 930D HPLC (Younglin Co.) equipped with a μ-porasil column (3.9×300 mm; Waters, Milford, MA, USA) and a fluorescence detector set at 294 nm for the excitation and 330 nm for the emission. The lipid (20 μ L) dissolved in nhexane was passed through a polytetrafluoroethylene membrane filter (0.2 μm×24 mm; National Scientific Co., Lawrenceville, NJ, USA) and injected into the instrument. The elution solvent was 0.2% isopropanol in *n*-hexane at 1.5 mL/min. Each tocopherol content was determined from the respective calibration curves of standard tocopherol isomers.

PL of the fried products was determined by HPLC according to the method of Balazs *et al.* (18) with some modification as described by Yoon and Choe (11) after the lipid extraction by the Folch method. The lipid was dissolved in 5 mL of chloroform, loaded onto silica Seppak cartridge ($125 \times 80 \ \mu m$; Waters), and then eluted with 5 mL of chloroform, acetone, and methanol, in series. Only methanol fraction was taken, and methanol was completely removed using a rotary evaporator (N-N; Rikakikai Co.,

Ltd., Tokyo, Japan). The residue was dissolved in chloroform and injected into a Younglin SP 930D HPLC equipped with a Cosmosil 5SL-II column (4.6×250 mm, i.d. 5-µm; Nacalai Tesque, Kyoto, Japan) and a ultraviolet (UV) detector set at 205 nm. The eluting solvent was a mixture of acetonitrile, methanol, and phosphoric acid (130:5:1.5, v/v/v) at 1.0 mL/min. Concentration of PL was determined from the calibration curve of standard PL.

Statistical analysis Data were presented as mean± standard deviation (SD) of 2 replicates and analyzed with the analysis of variance (ANOVA) procedure and Duncan's multiple-range test at 5% significance level (SAS Version 8.2, SAS Inst. Inc., Cary, NC, USA).

Results and Discussion

Lipid oxidation of sov-added fried products during storage in the dark Lipids of the fried products consisted of palmitic (12-13%), stearic (2-3%), oleic (32-34%), linoleic (50-51%), and linolenic (<0.1%) acids (Table 1), which was very similar to fatty acid composition of the frying oil. Fatty acid composition of the corn oil was palmitic (13.2%), stearic (2.2%), oleic (34.0%), linoleic (50.5%), and linolenic (0.1%) acids. There was no difference in fatty acid compositions among the fried products having different amount of soy flour before storage, because the lipid of fried products was mostly from frying oil, as shown in other studies (3,5,19,20). The fried products showed little change in fatty acid compositions with storage time regardless of soy flour addition, suggesting that soy flour addition to the dough did not affect fatty acid composition of the fried products during storage.

Lipid oxidation of the fried products during storage at 60°C in the dark is shown in Table 2 and 3. CDA contents of the fried products before storage were not significantly different among the fried products having different amount of soy flour (Table 2), and increased with storage time due to lipid oxidation of the fried products. It is very well-known that the oxidation transforms some of nonconjugated linoleic acid to more stable conjugated dienes. Increase in CDA contents of the fried products became more significant with storage time increase, and the addition of soy flour to the dough tended to delay the time for a significant increase in CDA contents in the fried products during the dark storage. The soy-added fried products at 30% did not show a significant increase in CDA contents until 11 day storage. This clearly shows that the addition of soy flour to dough significantly decreased CDA formation in the fried products during storage in the dark.

PAV, an indicator for secondary oxidation products of lipids (21), was not very different among the fried products before storage (Table 3). This suggests that soy flour addition to dough exerted little effect on the contents of secondary oxidation products in the fried products. As storage time increased, PAV was increased due to the increase in decomposition of the primary oxidation products in the fried products by lipid oxidation. The fried product without soy flour showed a faster increase in PAV at an earlier storage time than those with soy flour; PAV of the fried product without soy flour showed a significant increase on the 5th day of the storage. This indicates that

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Table 1. Fatty acid compositions of soy-added fried products during storage at 60°C in the dark

Addition level of	Storage time of	Relative content (%)				
soy flour to the dough (%)	fried products (day)	C16:0	C18:0	C18:1	C18:2	C18:3
	0	13.1±0.16	2.4±0.02	33.8±0.10	50.6±0.24	0.08±0.01
	1	13.0 ± 0.07	2.4 ± 0.00	33.8 ± 0.15	50.7 ± 0.20	0.06 ± 0.01
0	2	13.0 ± 0.02	2.4 ± 0.07	33.9 ± 0.27	50.6 ± 0.28	$0.07 {\pm} 0.01$
U	5	13.0 ± 0.04	2.4 ± 0.00	33.9 ± 0.01	50.6 ± 0.02	0.09 ± 0.01
	8	12.9 ± 0.03	2.4 ± 0.05	34.1 ± 0.10	50.6±0.16	$0.07 {\pm} 0.01$
	11	13.1 ± 0.13	2.4 ± 0.04	34.0 ± 0.00	50.4 ± 0.05	0.09 ± 0.00
	0	12.9±0.18	2.4±0.01	33.2±0.02	50.6±0.10	0.08±0.01
	1	13.0 ± 0.11	2.4 ± 0.18	33.3±0.12	50.8 ± 0.14	0.08 ± 0.00
10	2	13.0 ± 0.00	2.3 ± 0.10	33.4 ± 0.28	50.7 ± 0.45	$0.07 {\pm} 0.01$
10	5	13.0 ± 0.08	2.3 ± 0.04	33.4 ± 0.18	50.8 ± 0.18	$0.08 {\pm} 0.01$
	8	13.0 ± 0.02	2.3 ± 0.04	33.6 ± 0.13	51.0 ± 0.11	$0.07 {\pm} 0.01$
	11	13.0 ± 0.20	2.4 ± 0.02	33.8 ± 0.10	50.8 ± 0.09	0.07 ± 0.00
	0	13.0±0.25	2.4±0.02	33.3±0.09	51.2±0.13	0.08±0.01
	1	13.1 ± 0.29	2.5 ± 0.09	33.2 ± 0.31	50.6 ± 0.31	$0.08 {\pm} 0.01$
20	2	12.9 ± 0.05	2.5 ± 0.04	33.5 ± 0.27	50.5 ± 0.37	$0.08 {\pm} 0.01$
20	5	13.0 ± 0.09	2.5 ± 0.07	33.4 ± 0.48	50.5 ± 0.03	$0.08 {\pm} 0.01$
	8	12.8 ± 0.30	2.4 ± 0.03	33.3 ± 0.21	50.9±0.16	0.07 ± 0.01
	11	13.0 ± 0.11	2.5 ± 0.04	33.2 ± 0.08	50.7 ± 0.52	0.07 ± 0.00
30	0	12.9±0.02	2.6±0.04	32.4±0.03	50.4±0.07	0.09±0.06
	1	13.2 ± 0.05	2.7 ± 0.12	33.3 ± 0.10	50.7 ± 0.03	0.08 ± 0.02
	2	13.1 ± 0.21	2.7 ± 0.03	32.9 ± 0.50	50.4 ± 0.42	$0.08 {\pm} 0.01$
30	5	13.1 ± 0.03	2.6 ± 0.06	33.0 ± 0.26	50.5 ± 0.66	0.09 ± 0.01
	8	13.1 ± 0.30	2.5±0.01	32.8 ± 0.12	50.8 ± 0.65	$0.08 {\pm} 0.01$
	11	13.1±0.23	2.5±0.12	32.7±0.20	51.0±0.42	0.08 ± 0.00

Table 2. Effects of soy flour addition to the dough on the conjugated dienoic acid contents (%) of the fried products during storage at 60° C in the dark

Storage time of fried	Addition level of soy flour to the flour dough (%)				
products (day)	0	10	20	30	
0	$0.33 \pm 0.00^{defg1)}$	$0.30\pm0.01^{\rm fg}$	0.29±0.01g	0.33 ± 0.02^{defg}	
2	$0.34{\pm}0.00^{\rm defg}$	0.29 ± 0.00^{g}	$0.31 \pm 0.02^{\rm efg}$	$0.34{\pm}0.06^{\rm defg}$	
5	0.38 ± 0.00^{cde}	$0.35{\pm}0.08^{\rm defg}$	$0.36 {\pm} 0.01^{\rm defg}$	$0.33{\pm}0.01^{\rm defg}$	
8	0.44 ± 0.03^{c}	0.39 ± 0.04^{cd}	$0.37{\pm}0.00^{\rm cdefg}$	0.37 ± 0.01^{cdef}	
11	$0.73{\pm}0.07^a$	0.58 ± 0.00^{b}	0.53 ± 0.02^{b}	$0.38 {\pm} 0.00^{cde}$	

¹⁾Different letters mean significant differences among samples at α =0.05.

Table 3. Effects of soy flour addition to the dough on the p-anisidine value of the fried products during storage at 60° C in the dark

Storage time of fried	Addition level of soy flour to the flour dough (%)				
products (day)	0	10	20	30	
0	21.04±0.85 ^{f1)}	24.15±0.72 ^{cd}	22.78±0.33 ^{def}	21.70±0.08 ^{ef}	
2	22.53 ± 1.74^{def}	24.23 ± 0.10^{cd}	$22.93 \pm 0.74^{\text{def}}$	22.55 ± 1.48^{def}	
5	26.01 ± 0.24^{bc}	23.95 ± 1.33^{cd}	23.06 ± 0.32^{def}	22.96 ± 1.33^{def}	
8	27.72 ± 0.24^a	25.57 ± 0.46^{bc}	23.56 ± 0.76^{cde}	23.30 ± 0.90^{de}	
11	28.25 ± 0.45^a	$26.72{\pm}0.29^{ab}$	23.66 ± 0.36^{cde}	23.66 ± 0.15^{cde}	

¹⁾Different letters mean significant differences among samples at α =0.05.

soy flour addition to the dough decreased decomposition of the primary oxidation products of lipids in the fried products. Soy flour added to dough improved lipid oxidative stability of the fried products during storage in the dark by decreasing CDA values and PAV of the lipid, and thus soy

Table 4. Tocopherol contents (mg/kg of product) of soy-added fried products during storage at 60°C in the dark

Addition level of soy	Storage time of fried	Tocopherols				
flour to the dough (%)	products (day)	α	γ	δ	Total	
	0	26.4±1.33 ^{de1)} (100.0) ²⁾	160.7±0.90 ^{ab} (100.0)	2.2±0.20 ^{cd} (100.0)	189.3±2.43 ^{de} (100.0)	
0	5	24.3±0.36 ^{ef} (92.0)	156.9±7.98 ^{bcd} (97.6)	$2.3\pm0.36^{\text{cd}}$ (104.5)	$183.6 \pm 7.98^{ef} $ (97.0)	
	11	14.1 ± 1.63^{g} (53.4)	141.6±7.18 ^e (88.1)	0.8±0.19 ^e (36.4)	$156.1 \pm 8.62^{\text{hi}} \\ (82.5)$	
	0	29.8±1.56 ^{cd} (100.0)	167.5±3.51 ^{ab} (100.0)	3.4±0.15 ^{bc} (100.0)	200.6±2.11 ^{bcd} (100.0)	
10	5	30.2±0.64° (101.3)	159.7 ± 11.36^{abc} (95.3)	3.0±0.23 ^{bcd} (88.2)	192.9±10.49 ^{cde} (96.2)	
	11	$21.7\pm0.33^{\mathrm{f}}$ (72.8)	$144.4 \pm 7.97^{\text{de}} \\ (86.2)$	2.1 ± 0.12^{d} (61.8)	$168.1 \pm 7.76^{gh} \\ (83.8)$	
	0	37.8±0.62 ^{ab} (100.0)	166.3±2.11 ^{ab} (100.0)	5.4±0.34 ^a (100.0)	211.1±1.15 ^{ab} (100.0)	
20	5	34.7±0.88 ^b (91.8)	164.3 ± 4.03^{ab} (98.8)	3.7±1.32 ^b (68.5)	202.7±6.22 ^{bcd} (96.1)	
	11	21.7±4.11 ^f (57.4)	146.3±1.80 ^{cde} (88.0)	2.4±0.03 ^{cd} (44.4)	$170.5 \pm 5.93^{\rm fg} \\ (80.8)$	
30	0	40.0±0.28 ^a (100.0)	172.5±3.89 ^a (100.0)	6.2±1.06 ^a (100.0)	218.8±0.86 ^a (100.0)	
	5	35.6±1.32 ^b (89.0)	165.8±3.24 ^{ab} (96.1)	3.9 ± 0.19^{b} (62.9)	$205.2\pm6.93^{\text{abc}}$ (93.8)	
	11	29.3±0.11 ^{cd} (73.3)	119.5±6.85 ^f (69.3)	2.3±0.01 ^{cd} (37.1)	$151.1 \pm 4.18^{i} $ (69.1)	

¹⁾Different letters mean significant differences among samples in the same column at α =0.05.

²⁾Relativity (%) based on the values before storage.

flour was an antioxidant in the fried products in the dark.

Tocopherols and phospholipids contents of soy-added fried products during storage in the dark Changes in tocopherol contents of the fried products during storage at 60°C in the dark are shown in Table 4. Before storage, total concentration of tocopherols in the fried products ranged from 189.3 to 218.8 mg/kg, with a tendency of higher amount in the fried products to which higher amount of soy flour was added. This was due to presence of tocopherols at higher concentration in soy flour (415 mg/kg) than in wheat flour (16 mg/kg), thus the products with higher amount of soy flour should have more tocopherols. Tocopherol isomers in the fried products were α -, δ -, and γ -tocopherols, with the highest amount of γ -tocopherol and the lowest in δ -tocopherol. Youn and Choe (11) reported that y-tocopherol was the most present tocopherol isomer in soy flour, wheat flour, and corn oil.

Contents of tocopherols in the fried products were decreased during storage in the dark, indicating their degradation. Lee and Choe (10) reported degradation of tocopherols in full fat soy flour during storage in the dark. Yanishlieva *et al.* (22) reported that degradation of tocopherols was due to their participation in decomposition of lipid hydroperoxides and peroxidizing reactions. Tocopherol degradation in the fried products during storage could affect the oxidative stability of the fried products lipids since tocopherols are good free radical scavengers. Tocopherols donate hydrogen to peroxy and alkyl radicals of lipid (23)

to make them less reactive nonradical species, and become a tocopheryl radical. The tocopheryl radical is more stable than peroxy and alkyl radicals of lipid and the rate of free radical-mediated lipid autoxidation is decreased (24). There was no clear difference in the degree of tocopherols degradation among fried products having different amount of soy flour (Table 4). γ-Tocopherol in the fried products tended to show a lower degradation than α - or δ tocopherol during storage in the dark, as shown in Yanishlieva et al. (22). This suggests higher antioxidant activity of α -tocopherol than that of γ -tocopherol in the lipid oxidation of the fried products in the dark since antioxidizing action of tocopherols results in their degradation; the higher the antioxidizing action, the higher the degradation. Degradation of tocopherols is possibly related to the bond dissociation energy of phenolic hydrogen in the structure; the bond dissociation energy between hydrogen and oxygen of γ -tocopherol is higher than that of α -tocopherol (25). Thus α -tocopherol could give hydrogen to the lipid peroxy radicals of the fried products more easily than γ -tocopherol, resulting in higher degradation. Concentration dependence of antioxidant activity by tocopherols was also reported; α-tocopherol was more effective than γ -tocopherol at low concetration (26,27).

Changes in PL contents of soy-added fried products during storage at 60°C in the dark are shown in Table 5. PL contents of the fried products ranged from 1,958.1 to 2,801.5 mg/kg before storage, and the more the soy flour was added to the dough, the higher the PL content in the

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Table 5. Phospholipid contents (mg/kg of product) of soy-added fried products during storage at 60°C in the dark

Addition level of	Storage time of	Phospholipid ¹⁾				
soy flour to the dough (%)	fried products (day)	PI	LPC	PE	PC	Total
	0	35.5±0.94 ^{b2)} (100.0) ³⁾	1837.5±21.80° (100.0)	72.2±0.79° (100.0)	12.8±0.48 ^h (100.0)	1958.1±24.01 ^d (100.0)
0	5	33.5±0.19 ^b (94.4)	1622.0±106.17 ^{ed} (88.3)	64.2±3.99 ^{cd} (88.9)	11.6±0.76 ^h (90.6)	1731.4±111.12 ^{de} (88.4)
	11	22.7±0.61° (63.9)	1536.3±42.34 ^{ef} (83.6)	60.7±1.62 ^{ef} (84.1)	12.1±1.00 ^h (94.5)	1631.8±45.56 ^{fg} (83.3)
	0	44.4±2.21 ^{de} (100.0)	2145.4±28.45 ^b (100.0)	83.8±1.05 ^b (100.0)	30.7±0.67 ^f (100.0)	2304.3±32.38° (100.0)
10	5	31.1±0.11 ^e (70.0)	1424.4±98.56 ^{de} (66.4)	60.4±1.54 ^{de} (72.1)	23.4±0.21 ^g (76.2)	1539.3±100.43 ^{ef} (66.8)
	11	24.7±0.11 ^{de} (55.6)	1511.6±80.95 ^{ef} (70.5)	56.3±2.24 ^{ef} (67.2)	22.2±0.33 ^g (72.3)	1614.3±83.63 ^{fg} (70.1)
20	0	46.7±0.21 ^a (100.0)	2388.8±203.00 ^a (100.0)	92.8±7.62 ^a (100.0)	89.0±7.60 ^b (100.0)	2617.3±218.43 ^b (100.0)
	5	28.3 ± 0.84^{d} (60.6)	1813.7±55.07° (75.9)	71.2±2.06° (76.7)	38.8±4.60 ^d (43.6)	1952.0±62.57 ^d (74.6)
	11	24.7±0.21 ^{de} (52.9)	$1003.5 \pm 13.79^{g} $ (42.0)	$40.7 \pm 0.52^{g} $ (43.9)	39.0±0.35 ^e (43.8)	$1107.8 \pm 14.86^{\rm h} \\ (42.3)$
30	0	49.2±0.28 ^a (100.0)	2549.1±115.99 ^a (100.0)	98.9±4.38 ^a (100.0)	104.2±1.14 ^a (100.0)	2801.5±121.79 ^a (100.0)
	5	39.7±1.92 ^{de} (80.7)	1592.3±13.96 ^{de} (62.5)	62.9±0.51 ^{de} (63.6)	86.1±3.11 ^b (82.6)	1780.9±19.49 ^{de} (63.6)
	11	24.5±1.99 ^{de} (49.8)	1277.6±112.92 ^f (50.1)	51.0±4.25 ^f (51.6)	71.5±1.92° (68.6)	1424.6±121.08 ^g (50.9)

¹⁾PI, standard mixture of phosphatidylinositol; LPC, lysophosphatidylcholine; PE, phosphatidylethanolamine; PC, phosphatidylcholine.

²⁾Different letters mean significant differences among samples in the same column at $\alpha = 0.05$.

fried products, as was expected. Soy flour contained 3 times more PL (10.9 g/kg) than wheat flour (3.6 g/kg). LPC was the most abundant PL in the fried products. Addition of soy flour to the dough showed the biggest increase in PC content in the fried products. This was due to high content of PC in soy flour than wheat flour; the soy flour contains 5.67 times more PC than wheat flour (11). PL contents of the fried products were decreased by the dark storage, indicating their degradation. Keller and Kinsella (28) reported degradation of PL in the ground beef via oxidation. PL is susceptible to oxidation due to highly unsaturated fatty acids in the structure (29). Lambelet et al. (30) suggested formation of nitroxides from PL via reaction with peroxy radicals and then with oxygen. Degradation of PL during storage was higher in the fried products to which soy flour was added. Higher than 80% of total PL was remained after 11 day storage in the fried products without soy, however, only 40-70% of total PL was left in the soyadded fried products after the same period of storage. There was no consistent tendency in PL contents change among the fried products having 10, 20, or 30% soy flour. This might be due to different reaction behavior between soy PL and wheat PL, partly related with fatty acid composition difference between them. Soy PL contains higher amount of unsaturated fatty acids than wheat PL (31,32), possibly resulting in higher PL oxidation and lower retention of PL in the soy-added fried products. PC tended to be degraded more slowly than PE, suggesting its lower antioxidant

activity than PE. Khan and Shahidi (33) reported higher antioxidant activity of PE than PC.

Relationship between lipid oxidation and residual amounts of tocopherols and phospholipids in the fried products during storage Table 6 and 7 show regressions between lipid oxidation parameters and residual amounts of tocopherols and between lipid oxidation parameters and residual amounts of PL, respectively, during 11 day storage of the fried products in the dark. Slopes of the regression lines between tocopherol contents and CDA contents or PAV were all negative values although the correlation (r) between them was not very high (Table 6). This indicates

Table 6. Slope of the regression equation between contents of tocopherols and lipid oxidation (conjugated dienoic acid contents, CDA and p-anisidine value, PAV) of the fried products during storage at 60°C for 11 day in the dark

Tocopherol	Oxidation parameters ¹⁾			
Тосорпетот	CDA	PAV		
α-	-0.04159 (0.8182)	-0.19804 (0.7130)		
γ-	-0.00427 (0.4907)	-0.05953 (0.4387)		
δ-	-0.05741 (0.6545)	-0.79315 (0.5803)		
Total	-0.00413 (0.6733)	-0.05693 (0.5953)		

¹⁾CDA or PAV=a×tocopherol contents (mg/ kg product)+b; Number in parenthesis is a correlation coefficient of the regression line.

³⁾Relativity (%) based on the values before storage.

Table 7. Slope of the regression equation between phospholipid (PL) contents and lipid oxidation (conjugated dienoic acid contents, CDA and p-anisidine value, PAV) of the fried products during storage at 60°C for 11 day in the dark

PI.	Oxidation parameters ¹⁾			
FL	CDA	PAV		
Phosphatidylinositol	-0.01025 (0.7045)	-0.12281 (0.5416)		
Lysophosphatidylcholine	-0.00017 (0.5714)	-0.00195 (0.4186)		
Phopsphatidy lethanolamine	-0.00455 (0.5724)	-0.05186 (0.4185)		
Phosphatidylcholine	-0.00190 (0.4631)	-0.03356 (0.5239)		
Total	-0.00016 (0.5872)	-0.00189 (0.4428)		

¹⁾CDA or PAV=a×PL contents (mg/ kg product)+b; Number in parenthesis is a correlation coefficient of the regression line.

that lipid oxidation tended to be higher in the fried products having lower amounts of tocopherols as was expected. Tocopherol can slow down the decomposition of hydroperoxides (13,27) as well as scavenge lipid peroxy radicals. Among tocopherol isomers, α -tocopherol showed the highest correlation with the lipid oxidation parameters of the fried products during storage in the dark.

CDA contents and PAV of the fried products also showed a negative relationship with their PL contents. Lipid oxidation was lower in the fried products with higher amounts of PL including PI, LPC, PE, and PC, suggesting that PL decrease the lipid oxidation of the fried products and act as antioxidant. High oxidative stability of egg yolkadded fried products during storage in the dark was suggested to be partly due to PL (7). Koidis and Boskou (15) reported that PL decreased the lipid oxidation by chelating prooxidative metals. Among PL, PI showed the highest correlation with the lipid oxidation parameters of the fried products during storage in the dark. There was a tendency that absolute values of the slopes in the regression lines between residual amounts of tocopherols and CDA or PAV were higher than that between residual amounts of PL and CDA or PAV contents. This suggests that tocopherol exert higher effects on the lipid oxidation of the fried products than PL during storage in the dark.

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