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Antioxidant Activity of Lignan Compounds Extracted from Roasted Sesame Oil on the Oxidation of Sunflower Oil

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Abstract Effects of lignan compounds (sesamol, sesamin, and sesamolin) extracted from roasted sesame oil on the autoxidation at 60°C for 7 days and thermal oxidation at 180°C for 10 hr of sunflower oil were studied by determining conjugated dienoic acid (CDA) contents, *p*-anisidine values (PAV), and fatty acid composition. Contents of lignan compounds during the oxidations were also monitored. α-Tocopherol was used as a reference antioxidant. Addition of lignan compounds decreased CDA contents and PAV of the oils during oxidation at 60°C or heating at 180°C, which indicated that sesame oil lignans lowered the autoxidation and thermal oxidation of sunflower oil. Sesamol was the most effective in decreasing CDA formation and hydroperoxide decomposition in the auto- and thermo-oxidation of oil, and its antioxidant activity was significantly higher than that of α-tocopherol. Sesamol, sesamin, and sesamolin added to sunflower oil were degraded during the oxidations of oils, with the fastest degradation of sesamol. Degradation of sesamin and sesamolin during the oxidations of the oil were lower than that of α-tocopherol. The results strongly indicate that the oxidative stability of sunflower oil can be improved by the addition of sesamol, sesamin, or sesamolin extracted from roasted sesame oil.

Keywords: antioxidant, autoxidation, thermal oxidation, lignan compound, roasted sesame oil

Introduction

Oxidative stability of oil can be improved by addition of natural or synthetic antioxidants such as tocopherol and butylated hydroxyanisole. Possible adverse health effects and volatilization at high temperature of synthetic antioxidants (1) have caused their decrease in consumer acceptability or industrial use. This in turn has brought many interests and researches on naturally present antioxidants such as tocopherol in soybean oil, carotenoids in carrot, and lignan compounds in sesame oil (2-4).

Sesame (*Sesamum indicum* L.) seed and sesame oil have been used as confectionary and medicinal ingredients as well as seasoning in the Orient. Sesame oil consists of mainly triacylglycerols but also contain minor compounds such as phospholipids, tocopherols, sterols, and lignan compounds (5-7). Lignan compounds in sesame oil include sesamol (33-40 mg%), sesamin (433-649 mg%), and sesamolin (168-349 mg%) as shown in Fig. 1, and the oil processing condition affects their contents as well as the chemical properties (8-11). Roasting of sesame seeds and bleaching cause degradation of phenol acetal in sesamolin to form sesamol and sesamin (10, 11). Sesame oil is highly resistant to the oxidation due to lignan compounds and tocopherols; sesame oil stored at 60°C in the dark showed lower peroxide and conjugated dienoic acid formation than soybean oil (12). Addition of sesame oil to soybean oil improved the oxidative stability of soybean oil during heating and frying at 160°C (13, 14).

In spite of many studies on high resistance of sesame oil itself to the oxidation, few studies have been reported on the extension of sesamol, sesamin, and sesamolin extracted from roasted sesame oil as antioxidants in other oils. This study was performed to study the effects of sesamol, sesamin, and sesamolin extracted from roasted sesame oil on the oxidation of tocopherol-stripped sunflower oil to investigate their plausibility as natural-grade antioxidants in frying oils. Stability of lignan compounds was also determined.

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Material and Methods

Food materials and chemicals Roasted sesame oil and RBD (refined, bleached, and deodorized) sunflower oil were obtained by CJ Co. (Seoul, Korea). Alumina (type WN-3, neutral) for column chromatography, sesamol, α-tocopherol, standard fatty acid (palmitic, stearic, oleic, linoleic, and linolenic acids) methyl esters, and *p*-anisidine were purchased from Sigma-Aldrich Chemical Co. (St. Louis, MO, USA). Silica gel (Kiesel gel 60, 70-230 mesh) and isooctane were products of Merck Co. (Darmstadt,

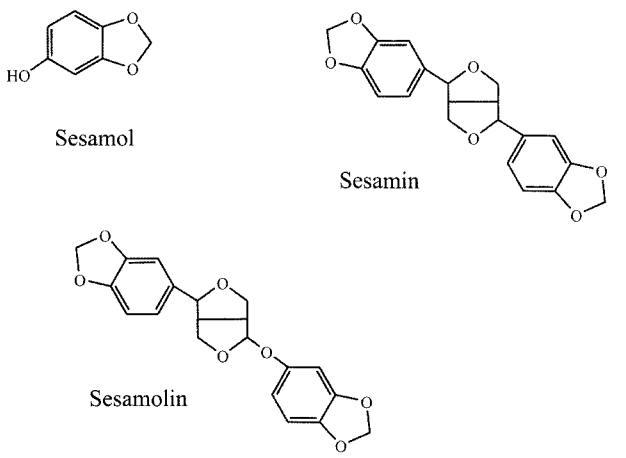

Fig. 1. Chemical structures of sesamol, sesamin, and sesamolin.

Germany) and Junsei Chemical Co. (Tokyo, Japan), respectively. *n*-Hexane, methanol, isopropanol, and water in HPLC grade were purchased from J.T. Baker (Philipsburg, NJ, USA). All other chemicals were of reagent grade.

Sample preparation Sesamol, sesamin, and sesamolin were extracted and isolated from roasted sesame oil and identified with a method of Lee and Choe (15). To exclude the possible effects of tocopherols in RBD sunflower oil on the oil oxidation, tocopherols were stripped from sunflower oil by alumina column chromatography with a method of Yanishlieva *et al.* (16). RBD sunflower oil (100 g) was dissolved in *n*-hexane (1,000 mL), and then applied to 3 glass columns (3×30 cm) in series, which were packed with activated alumina. Hexane in the eluant was completely removed by using a rotary evaporator at 40°C to obtain tocopherol-stripped sunflower oil (TSSO). Characteristics of resulting TSSO were evaluated by conjugated dienoic acid (CDA) content and *p*-anisidine value (PAV) by AOCS method (17) Ti 1a-64 and Cd 18-90, respectively, fatty acid composition by GC, and tocopherol contents by HPLC. TSSO was put into a glass bottle covered with an aluminum foil, and the bottle was tightly sealed with a teflon-coated septum and aluminum cap and placed in a −20°C freezer after nitrogen flushing.

Samples for autoxidation were prepared by mixing TSSO (5 g) with sesamol, sesamin, or sesamolin at 0 and 200 ppm in serum bottles. The bottles were capped with aluminum crimp seals with an open center to allow the air pass through the bottles. The bottles were placed in a 60°C incubator for 7 days in the dark. Thermal oxidation of TSSO was studied with TSSO added with sesamol, sesamin, or sesamolin at 0 and 1,000 ppm in a serum bottle. The bottles were covered with aluminum seals with an open center, and then heated in an 180°C oven for 10 hr. TSSO without lignan compounds nor α-tocopherol was prepared as control samples. α-Tocopherol was used as a reference antioxidant, and the reference samples were prepared with TSSO added with the same concentration of α-tocopherol as that of lignan compound.

Analysis of the oil oxidation The oxidation of TSSO was evaluated by measuring CDA contents and PAV by AOCS method (17) Ti 1a-64 and Cd 18-90, respectively. Fatty acid composition of TSSO during oxidation was determined by gas chromatography with a Younglin M600D gas chromatograph (Younglin Co., Seoul, Korea) equipped with a Supelcowax capillary column (30 m×0.53 mm, 1.0 μm thick; Bellefonte, PA, USA) and a flame ionization detector after esterification of oil with 14% BF_3-methanol solution (18). The oven, injector, and detector temperatures were 200, 270, and 280°C, respectively. Nitrogen flow rate was 5 mL/min, and the split ratio was 33:1.

Determination of lignan compounds and α-tocopherol in oils Changes in lignan compounds concentration in TSSO during oxidation were analyzed by HPLC (19). The oil was dissolved in methanol and injected into a Younglin SP930D HPLC equipped with a C_{18} symmetry reverse column (4.6×150 mm; i.d. 5 μm; Waters, Milford, MA, USA) and a UV detector set at 288 nm. The eluting solvent was a mixture of methanol and water (70:30, v/v) at a flow rate of 1.0 mL/min. Concentrations of lignan compounds in the oils were determined from the calibration curves of purified sesamol (Peak area = 96.618 × concentration − 216.02, R^2; 0.9996), sesamin (Peak area = 63.946 × concentration + 118.61, R^2; 0.9999), and sesamolin (Peak area = 44.171 × concentration − 128.31, R^2; 0.9999). α-Tocopherol was analyzed by HPLC (10) with a μ-porasil column (3.9 × 300 mm; Waters). The eluting solvent was 0.5% isopropanol in *n*-hexane. Wavelengths of a fluorescence detector were 300 nm for the excitation and 338 nm for the emission. α-Tocopherol was quantified from the calibration curve of standard α-tocopherol (Peak area = 30.209 × concentration + 84.244, R^2; 0.9994).

Statistical analysis All the experimental treatments were done in duplicate. Duncan's multiple range test, regression analysis, and one-way ANOVA at a 5% level of significance were used to analyze the data.

Results and Discussion

Characteristics of tocopherol-stripped sunflower oil RBD sunflower oil and TSSO did not show any significant difference in CDA contents (0.78±0.01 and 0.80±0.01%, respectively) and PAV (4.15±0.00 and 4.15 ±0.01, respectively). Fatty acid compositions of both oils were statistically same; palmitic (6.5±0.3%), stearic (3.4± 0.2%), oleic (30.3±0.4%), linoleic (59.0±1.0%), and linolenic acid (0.9±0.0%). RBD sunflower oil contained α-tocopherol (513.9±3.1 ppm), β-tocopherol (6.7±0.8 ppm), and γ-tocopherol (2.4±0.3 ppm). However, TSSO did not contain any detectable amounts of tocopherols.

Effects of lignan compounds extracted from roasted sesame oil on the autoxidation of tocopherol-stripped sunflower oil Effects of added lignan compounds or α-tocopherol on the CDA content and PAV of TSSO during autoxidation at 60°C for 7 days are shown in Fig. 2. CDA contents and PAV of control oils increased from 0.80 to 4.93% and from 4.15 to 461.45 after 7 day autoxidation, respectively. This is due to the transformation of nonconjugated double bonds to more stable conjugated forms (20) and decomposition of the oil hydroperoxides to low molecular compounds such as aldehydes (21) during the autoxidation. TSSO added with sesamol, sesamin, or sesamolin showed significantly ($p<0.05$) lower CDA contents and PAV than control oil during the autoxidation. CDA contents and PAV of sesamol-added TSSO were 1.00% and 23.23, respectively, after 7 day autoxidation, which indicates that the addition of sesamol to TSSO decreased the autoxidation of TSSO by slowing down CDA formation and hydroperoxide decomposition. Sesamol can break a free radical chain reaction of lipid autoxidation by donating hydrogen to peroxy and alkoxy radicals of lipids (22). Sesamin and sesamolin also acted as antioxidants in the autoxidation of TSSO although their antioxidant activities were lower than that of sesamol. It was reported that antioxidant activity of sesamol was higher than that of sesamin or sesamolin in the autoxidation of linoleic acid (15, 23). Sesamin showed lower antioxidant activity than sesamolin, possibly due to the absence of phenolic hydroxy

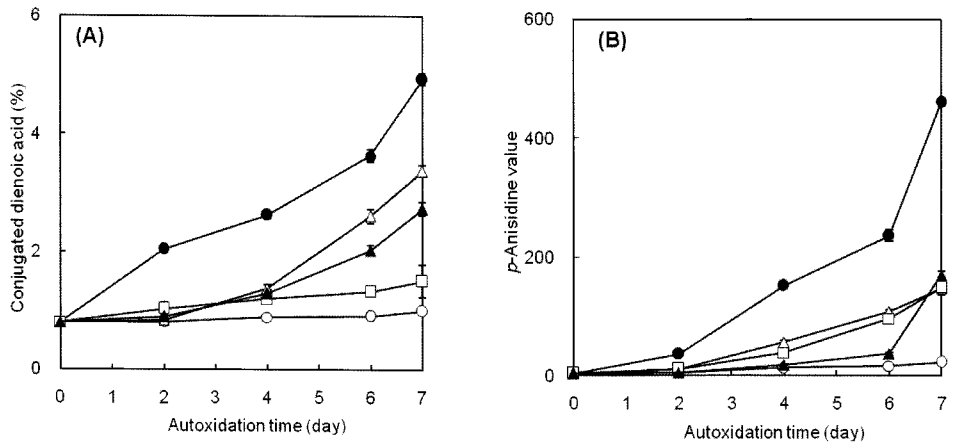

Fig. 2. Effects of lignan compounds (200 ppm) on conjugated dienoic acid content (A) and *p*-anisidine value (B) of tocopherol-stripped sunflower oil during autoxidation at 60°C.
(●, control without any additive; ○, sesamol; △, sesamin; □, sesamolin; ▲, α-tocopherol)

group in the structure (2, 24). The antioxidant activity of sesamol in the autoxidation of TSSO was significantly higher ($p<0.05$) than that of α-tocopherol, which was a similar result to other study (15).

Fatty acid composition changes of TSSO during autoxidation at 60°C are shown in Table 1. As the autoxidation time increased, relative contents of palmitic, stearic, and oleic acids in TSSO increased, and those of linoleic and linolenic acids decreased. Increases in saturated or less unsaturated fatty acids and decrease of polyunsaturated

Table 1. Effects of lignan compounds or α-tocopherol (200 ppm) on fatty acid composition in tocopherol-stripped sunflower oil during autoxidation at 60°C

Additive	Oxidation time (day)	Relative concentration (%)					U/S[1)]
		$C_{16:0}$	$C_{18:0}$	$C_{18:1}$	$C_{18:2}$	$C_{18:3}$	
None	0	6.5±0.1	3.4±0.2	30.3±0.2	58.9±0.4	0.9±0.1	9.1
	2	7.2±0.4	3.7±0.0	32.9±0.1	55.6±0.3	0.7±0.0	8.2
	4	8.4±0.1	3.9±0.5	34.3±0.3	52.9±0.7	0.5±0.0	7.1
	6	10.3±0.6	4.4±0.1	39.0±0.2	45.8±0.3	0.4±0.0	5.8
	7	10.5±0.6	5.0±0.7	40.3±0.4	44.2±0.1	0.1±0.0	5.5
Sesamol	0	6.5±0.1	3.4±0.2	30.3±0.2	58.9±0.4	0.9±0.1	9.1
	2	6.6±0.2	3.5±0.1	31.8±0.0	57.2±0.1	0.8±0.0	8.9
	4	6.8±0.0	4.2±0.0	32.2±0.2	56.2±0.2	0.7±0.0	8.1
	6	6.9±0.5	4.2±0.2	32.4±0.2	55.9±0.1	0.6±0.1	8.0
	7	7.1±0.0	4.3±0.0	32.1±0.3	56.1±0.2	0.4±0.1	7.8
Sesamin	0	6.5±0.1	3.4±0.2	30.3±0.2	58.9±0.4	0.9±0.1	9.1
	2	7.5±0.1	4.0±0.1	34.9±0.3	54.7±0.4	0.8±0.0	7.7
	4	8.1±0.6	4.3±0.1	35.1±0.2	52.0±0.8	0.7±0.1	7.1
	6	10.0±0.2	4.2±0.3	38.2±0.3	47.1±0.4	0.5±0.6	6.1
	7	10.3±0.1	4.3±0.1	39.3±0.4	45.6±0.6	0.5±0.5	5.8
Sesamolin	0	6.5±0.1	3.4±0.2	30.3±0.2	58.9±0.4	0.9±0.1	9.1
	2	7.4±0.2	3.8±0.4	31.8±0.2	56.2±1.3	0.8±0.0	7.9
	4	8.5±0.1	3.8±0.1	33.6±0.1	53.5±0.3	0.7±0.1	7.2
	6	9.5±0.3	4.8±0.4	39.3±0.3	45.9±0.5	0.5±0.1	6.0
	7	10.7±0.3	4.2±0.1	39.8±0.3	44.9±0.5	0.5±0.0	5.7
α-Tocopherol	0	6.5±0.1	3.4±0.2	30.3±0.2	58.9±0.4	0.9±0.1	9.1
	2	6.8±0.1	3.8±0.0	31.3±0.2	57.3±0.4	0.8±0.1	8.4
	4	6.9±0.0	4.0±0.2	31.5±0.4	56.9±0.6	0.7±0.0	8.2
	6	7.1±0.3	4.0±0.2	33.0±0.5	55.4±0.5	0.4±0.0	8.0
	7	7.6±1.0	4.2±0.3	34.6±0.3	53.3±0.5	0.3±0.0	7.5

[1)]Content ratio of unsaturated fatty acids to saturated fatty acids.

fatty acids are commonly observed during the autoxidation of oil (4, 14, 25). Content ratio of unsaturated fatty acids to saturated fatty acids (U/S ratio) in control samples decreased from 9.1 to 5.5 after 7 day autoxidation, whereas less change was observed in sesamol-, sesamin-, or sesamolin-added TSSO during the autoxidation. Table 2 shows regression analyses between U/S ratios and the autoxidation time. Sesamol-added TSSO showed the significantly lowest rate ('a' value in the regression equation) in U/S ratio decrease. U/S ratio decreasing rate of sesamol-added TSSO was lower than that of α-tocopherol. Although there was no significant difference in the rates of U/S ratio decrease with the oxidation time between control oil and sesamin- or sesamolin-added TSSO, the tendency of low value in sesamin- or sesamolin-added TSSO was shown. The results confirmed that the addition of lignan compounds decreased the autoxidation of TSSO, and the antioxidant activity of sesamol was superior to that of α-tocopherol in the autoxidation of sunflower oil.

Table 2. Regression analysis between content ratio of unsaturated fatty acid to saturated fatty acid (U/S ratio) and time in the autoxidation of tocopherol-stripped sunflower oil

Additive	Regression parameters[1)]		
	a	b	R^2
None	-0.54[a 2)]	9.19	0.9932
Sesamol	-0.19[b]	9.11	0.9339
Sesamin	-0.46[a]	8.88	0.9780
Sesamolin	-0.49[a]	9.02	0.9944
α-Tocopherol	-0.20[b]	9.00	0.9480

[1)]U/S ratio = a × autoxidation time (day) + b, R^2; correlation coefficient.
[2)]Different letters mean significant differences in the degradation rate at α = 0.05.

Changes in lignan compounds contents during autoxidation of tocopherol-stripped sunflower oil Table 3 shows contents of sesamol sesamin, sesamolin, and α-tocopherol and their regression with respect to time during the autoxidation of TSSO. Contents of sesamol, sesamin, sesamolin, and α-tocopherol decreased during the autoxidation of TSSO. Lignan compounds and α-tocopherol donate phenolic hydrogen to radicals and change into semiquinone radicals which may produce quinone by reaction with other radicals (26). Degradation rate of sesamol (14.3 ppm/day), sesamin (9.5 ppm/day), or sesamolin (13.9 ppm/day) tended to be lower than that of α-tocopherol (16.1 ppm/day). This result is in agreement with other study in the autoxidation of methyl linoleate (15). Sesamol showed the highest degradation rate among lignan compounds followed by sesamolin and sesamin. Kikugawa *et al.* (27) reported that sesamol was more susceptible to degradation than sesamolin, and Shahidi *et al.* (9) reported faster degradation of sesamolin than sesamin during storage of sesame oil at 60°C. Higher degradation of sesamol than that of sesamin or sesamolin was thought to be partly related with its higher antioxidant activity than that of sesamin or sesamolin.

Effects of lignan compounds extracted from roasted

Table 3. Contents of lignan compounds added to tocopherol-stripped sunflower oil and regression analysis between lignan compounds retention (ppm) and oxidation time (day) during autoxidation at 60°C for 7 day in the dark

Additive	Storage time (day)	Contents (ppm)	Relative retention (%)	Regression parameters[1)]		
				a	b	R^2
Sesamol	0	200.0±3.1	100.0	-14.3[a2)]	202.8	0.9936
	2	179.3±2.1	89.7			
	4	143.0±1.3	71.5			
	6	118.2±2.8	59.1			
	7	101.6±2.7	50.8			
Sesamin	0	200.0±2.2	100.0	-9.5[b]	204.0	0.9815
	2	190.1±3.6	95.1			
	4	166.6±3.0	83.3			
	6	149.1±0.8	74.5			
	7	134.5±6.4	67.3			
Sesamolin	0	200.0±1.1	100.0	-13.9[a]	207.2	0.9757
	2	188.8±5.9	94.4			
	4	153.8±5.6	76.9			
	6	120.3±4.2	60.2			
	7	109.0 ±6.4	54.5			
α-Tocopherol	0	200.0±4.7	100.0	-16.1[a]	203.8	0.9927
	2	177.4±2.6	88.7			
	4	137.7±3.1	68.8			
	6	109.4±2.3	54.7			
	7	88.5±1.9	44.3			

[1)]Lignan compound retention (ppm) = a × autoxidation time (day) + b, R^2; correlation coefficient.
[2)]Different letters mean significant differences in the degradation rate at α = 0.05.

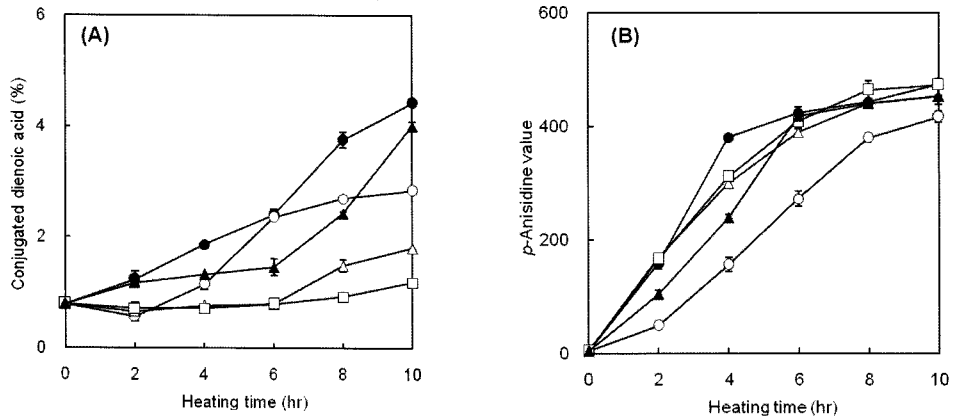

Fig. 3. Effects of lignan compounds (1,000 ppm) on conjugated dienoic acid content (A) and *p*-anisidine value (B) of tocopherol-stripped sunflower oil during heating at 180°C in the dark.
(●, control without any additive; ○, sesamol; △, sesamin; □, sesamolin; ▲, α-tocopherol)

Table 4. Effects of lignan compounds or α-tocopherol (1,000 ppm) on fatty acid composition of tocopherol-stripped sunflower oil during heating at 180°C for 10 hr in the dark

Additive	Oxidation time (hr)	Relative concentration (%)					P/L[1)]
		$C_{16:0}$	$C_{18:0}$	$C_{18:1}$	$C_{18:2}$	$C_{18:3}$	
None	0	6.5±0.2	3.4±0.2	30.3±0.2	58.9±0.9	0.9±0.0	0.11
	2	6.8±0.4	4.2±0.0	32.6±0.2	55.7±0.4	0.6±0.2	0.12
	4	7.9±0.0	4.5±0.2	34.1±0.9	53.1±1.2	0.5±0.1	0.15
	6	8.4±0.2	4.7±0.2	35.6±0.5	50.9±0.5	0.4±0.0	0.17
	8	9.2±0.4	5.0±0.1	36.8±0.2	48.7±0.7	0.4±0.0	0.19
	10	9.9±0.2	5.3±0.1	38.6±0.3	46.0±0.5	0.3±0.0	0.22
Sesamol	0	6.5±0.2	3.4±0.2	30.3±0.2	58.9±0.9	0.9±0.0	0.11
	2	7.0±0.5	3.8±0.4	32.1±0.7	54.5±1.3	0.7±0.2	0.13
	4	7.6±0.3	4.4±0.8	33.5±2.0	54.0±0.1	0.6±0.2	0.14
	6	7.8±0.2	4.3±0.7	34.1±1.8	53.4±2.7	0.4±0.1	0.15
	8	8.3±0.5	4.3±0.3	35.2±1.3	51.9±1.9	0.3±0.2	0.16
	10	8.9±0.7	4.3±0.3	35.7±0.8	50.9±1.7	0.2±0.1	0.17
Sesamin	0	6.5±0.2	3.4±0.2	30.3±0.2	58.9±0.9	0.9±0.0	0.11
	2	7.6±0.5	4.1±0.2	32.3±0.3	55.5±0.3	0.5±0.3	0.14
	4	8.2±0.4	4.3±0.3	33.8±0.8	53.3±1.0	0.4±0.1	0.15
	6	8.0±0.9	4.4±0.7	34.5±0.4	51.1±1.5	0.3±0.3	0.16
	8	8.8±0.8	4.8±0.4	36.5±0.9	49.7±0.8	0.2±0.2	0.18
	10	9.7±0.5	4.4±0.2	37.1±0.5	48.5±0.7	0.3±0.2	0.20
Sesamolin	0	6.5±0.2	3.4±0.2	30.3±0.2	58.9±0.9	0.9±0.0	0.11
	2	6.8±0.4	4.1±0.3	32.5±0.6	55.3±0.9	0.7±0.3	0.12
	4	8.1±0.1	4.9±0.3	34.0±0.9	53.5±1.5	0.5±0.2	0.15
	6	8.6±0.8	4.9±0.4	36.0±0.7	51.0±0.5	0.4±0.1	0.17
	8	8.8±0.9	5.2±0.3	37.2±0.7	48.5±0.9	0.4±0.2	0.18
	10	9.4±0.9	5.9±0.8	38.6±2.9	45.7±1.6	0.4±0.0	0.21
α-Tocopherol	0	6.5±0.2	3.4±0.2	30.3±0.2	58.9±0.9	0.9±0.0	0.11
	2	7.4±0.4	4.1±0.0	32.1±0.4	55.7±0.4	0.6±0.1	0.13
	4	7.8±0.3	4.8±0.7	34.4±2.1	53.4±2.8	0.6±0.2	0.15
	6	7.9±0.5	4.6±0.3	35.3±0.8	51.9±0.9	0.4±0.1	0.15
	8	8.8±0.4	4.4±0.2	35.4±0.5	51.0±0.3	0.4±0.1	0.17
	10	9.8±0.4	5.0±0.5	37.7±0.8	47.3±1.7	0.3±0.2	0.21

[1)]Content ratio of palmitic acid to linoleic acid.

sesame oil on the thermal oxidation of tocopherol-stripped sunflower oil Figure 3 shows CDA contents and PAV changes in TSSO affected by 1,000 ppm sesamol, sesamin, and sesamolin during heating at 180°C for 10 hr in the dark. As the heating time increased from 0 to 4, 8, and 10 hr, CDA contents of the control TSSO increased from 0.80 to 1.87, 3.76, and 4.42%, respectively. PAV of the control increased from 4.15 to 474.23 after 10 hr heating. This was due to formation of conjugated lipids and decomposition of lipid hydroperoxides during heating of TSSO. Addition of sesamol, sesamin, and sesamolin lowered CDA formation in TSSO during heating. TSSO added with sesamolin showed the lowest CDA contents during heating, followed by sesamin and sesamol, and CDA decreasing activity of sesamolin was significantly higher than that of α-tocopherol. Higher CDA contents in sesamol-added TSSO than sesamin- or sesamolin-added TSSO might be partly resulted from the fast degradation of sesamol to conjugated compounds via a ring opening at high temperature (28). Sesamol lowered PAV of TSSO very effectively and its effect was significantly higher than that of α-tocopherol. However, sesamolin and sesamin did not show significant decrease in PAV of TSSO, when comparing to the values of the control oil. Sesamol was reported to be more effective in decreasing PAV than α-tocopherol during microwave heating (22). Phenolic hydroxy group and higher solubility in the oil of sesamol than other phenolic compounds at high temperature (24, 29) were suggested to result in better antioxidant activity in the thermooxidation of oil.

Changes of fatty acid composition of TSSO added with sesamol, sesamin, sesamolin, or α-tocopherol during heating at 180°C for 10 hr are shown in Table 4. During heating, the control oil showed a decrease in linoleic acid and increase in palmitic acid, resulting in P/L ratio (content ratio of palmitic acid to linoleic acid) increase. Increase in P/L ratio is a common phenomenon found in

Table 5. Regression analyses between content ratio of palmitic acid to linoleic acid (P/L ratio) and oxidation time in tocopherol-stripped sunflower oil added with lignan compounds (1,000 ppm) during heating at 180°C for 10 hr

Additive	Regression parameters[1)]		
	a	b	R^2
None	0.0104[a 2)]	0.1062	0.9908
Sesamol	0.0063[b]	0.1119	0.9429
Sesamin	0.0083[b]	0.1152	0.9741
Sesamolin	0.0100[ab]	0.1067	0.9813
α-Tocopherol	0.0089[ab]	0.1090	0.9255

[1)]P/L ratio = a × heating time (hr) + b, R^2; correlation coefficient.
[2)]Different letters mean significant differences in the degradation rate at α = 0.05.

Table 6. Contents of lignan compounds added to tocopherol-stripped sunflower oil during heating of the oil at 180°C for 10 hr

Additive	Oxidation time (hr)	Contents (ppm)	Relative retention (%)	Regression parameters[1)]		
				a	b	R^2
Sesamol	0	1,000.0±14.6	100.0	-76.8[a 2)]	976.4	0.9828
	2	836.5±14.6	83.6			
	4	606.2±8.9	60.6			
	6	500.4±37.0	50.0			
	8	409.3±20.8	40.9			
	10	202.4±18.6	20.2			
Sesamin	0	1,000.0±6.5	100.0	-55.3[b]	997.3	0.9789
	2	913.8±6.5	91.4			
	4	773.0±6.0	77.3			
	6	614.8±29.5	61.5			
	8	546.1±20.0	54.6			
	10	478.7±22.4	47.9			
Sesamolin	0	1,000.0±89.8	100.0	-54.8[b]	988.5	0.9885
	2	891.4±89.8	89.1			
	4	746.7±19.8	74.7			
	6	653.0±18.1	65.3			
	8	525.2±13.3	52.5			
	10	471.8±20.1	47.2			
α-Tocopherol	0	1,000.0±10.4	100.0	-64.7[ab]	953.3	0.9682
	2	830.4±10.4	83.0			
	4	621.9±21.6	62.2			
	6	536.5±20.6	53.7			
	8	451.5±19.5	45.2			
	10	338.6±15.8	33.9			

[1)]Lignan compound retention (ppm) = a × heating time (hr) + b, R^2; correlation coefficient.
[2)]Different letters mean significant differences in the degradation rate at α = 0.05.

heated oil (18, 30, 31). P/L ratio in control samples increased from 0.11 to 0.22, whereas addition of sesamol, sesamin, and sesamolin decreased the P/L ratio increase in TSSO with heating time as shown in Table 5. P/L ratio increasing rate ('a' value of the regression equation) was the lowest in sesamol-added oil and thus sesamol was the most effective in decreasing thermooxidation of TSSO.

The antioxidant activity of sesamol, sesamin, and sesamolin shown in the oxidation of sunflower oil at high temperature provides a possibility of another natural antioxidant in deep-fat frying. Roasted sesame oil itself has been limited in the use at high temperature due to its low smoking point (10). Purified sesamol, sesamin, and sesamolin instead of roasted sesame oil can add to the frying oil to decrease the frying oil oxidation.

Changes of lignan compounds contents of tocopherol-stripped sunflower oil during heating Changes in contents of sesamol, sesamin, sesamolin, and α-tocopherol and their regression with the time during heating of TSSO at 180°C for 10 hr are shown in Table 6. Contents of sesamol, sesamin, and sesamolin decreased during heating of TSSO due to their degradation. The degradation rates of sesamol, sesamin, and sesamolin were 76.8, 55.3, and 54.8 ppm/hr, respectively, and sesamol was degraded faster than sesamin, sesamolin, or α-tocopherol. This indicates that sesamol is less stable than sesamin, sesamolin, or α-tocopherol, which might be related with its higher antioxidative activity in the thermooxidation of TSSO. Sesamol exerted higher antioxidant activity and thus its degradation was faster than other lignan compounds. Shukla *et al.* (32) reported a complete destruction of sesamol by heating at 180°C for 4 hr. Higher antioxidant activity of sesamol and higher retention of sesamin and sesamolin with lower degradation rates than those of α-tocopherol suggest that lignan compounds extracted from roasted sesame oil could replace α-tocopherol for a natural-grade antioxidant.

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