Research Note

Protective effect of gallic acid on the thermal oxidation of corn and soybean oils during high temperature heating

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Abstract The comparative protective effects of gallic acid with well-known synthetic antioxidants (tert-butylhydroquinone, butylated hydroxyanisole, propylgallate) on the thermal oxidations of corn and soybean oils during heating for 8 h at 180°C were studied. The quantitative effects of gallic acid at three different concentrations on the time-course thermal oxidations in the two different vegetable oils were also studied for a prolonged heating of 6 days at 180°C. Gallic acid at 200 ppm exhibited higher protective activity than the synthetic antioxidants at the same concentration. Gallic acid also exhibited persistently strong protective activity, in a concentration dependent manner, on the changes in oxidation indices in corn and soybean oils throughout the prolonged heating period (6 days) at 180°C. The present results clearly suggested that gallic acid would be a potential natural substitute of synthetic antioxidants for the protection of vegetable oils during high temperature heating.

Keywords: gallic acid, thermal oxidation, vegetable oil, synthetic antioxidants, frying temperature

Introduction

Vegetable oils are frequently used as cooking media for high temperature heating of foods such as deep-fat frying. High temperature heating induces fast thermal oxidative changes, resulting in the loss of unsaturated fatty acids, and degradation of color, flavor, and nutritional quality of oil, and formation of toxic components (1-4). The lipid oxidation of vegetable oil at high temperatures is very complex. The major reactions during high temperature heating at deep-fat frying temperature include hydroperoxide formation and decomposition, conjugation of double bonds, carbonyl compound formation, and polymerization via complex free radical processes (1). The consumption of heat-treated oils has been reported to be toxic in animal models and human study (4-7).

Synthetic antioxidants such as *tert*-butylhydroquinone (TBHQ), butylated hydroxyanisole (BHA), and propylgallate (PG) are widely used for the inhibition of the oxidation of fats and oils. The protective activities of the synthetic antioxidants on the thermal oxidation of oils during frying or heating at frying temperature have been reported (8-11). However, consumers are increasingly conscious of the possible toxicity of synthetic antioxidants; thus, the popularity of natural antioxidants has increased. Natural compounds (tocopherols, tocotrienols, sesamol, sesaminol, oryzanol, squalene, and certain phytosterols) and extracts of plants, vegetables, and herbs (tea leaves, rosemary, sage, thyme, oregano, marjoram, and oat) have been reported to demonstrate protective activity toward the

thermal oxidation of oils during high temperature heating (12-16). However, only a few natural compounds or extracts from natural sources such as citric acid, tocopherols, rosemary extracts, and green tea extract are practically used for the protection of oils during the high temperature cooking process in the food industry.

Gallic acid (3,4,5-trihydroxybenzoic acid) is a natural compound, which is a type of phenolic acid, ubiquitously present in various plant sources. Gallic acid is widely accepted as a safe food additive in many countries without legislative restriction for its use in foods. It has been previously reported that gallic acid possesses strong antioxidative activity at ambient temperatures (2,17-19). However, the information on the effect of gallic acid on the high heat-treated thermal changes in vegetable oil is surprisingly scarce. Gallic acid has been reported to significantly decrease the *p*-anisidine value (*p*-AV) and iodine value (IV) changes in the corn oil during the frying process (20). The result was based on a single concentration treatment (200 ppm, w/v) during very short time frying process (30, 60, and 90 min only) with only one type of vegetable oil (corn oil). The effect of gallic acid at 500 ppm on the oxidative changes (polar compounds, volatile compounds, and hydroxynonenal) of purified canola oil triacylglycerol during short period (120 min) heating at 185°C has also been reported (21). The result was also based on the single concentration (500 ppm) of gallic acid on the thermal oxidation of purified canola triacylglycerols. The information on the protection activities of gallic acid and synthetic antioxidants against the thermal oxidation at frying temperature is essential for the evaluation of its potential as a

substitute for synthetic antioxidants. To the best of our knowledge, however, the comparative protective activity of gallic acid with the well-known synthetic antioxidants such as TBHQ, BHA, and PG against the thermal oxidations of vegetable oils treated at frying temperature has not been studied previously. Furthermore, the quantitative effects of gallic acid at various concentrations on the thermal oxidation of vegetable oils during the prolonged periods at frying temperature has not been previously reported.

Thus, the present study aimed to study (1) the comparative protective activity of gallic acid with well-known synthetic antioxidants (TBHQ, BHA, and PG) on the thermal oxidation of vegetable oils (corn and soybean oils) during 8 h heating at 180°C, and (2) the quantitative effects of gallic acid at three different concentrations (200, 500, and 1,000 ppm) on the time course thermal oxidations of corn and soybean oils during the prolonged period (6 days) of heating at 180°C. The oxidative changes in the vegetable oils were monitored by gas chromatographic analysis of fatty acid composition, spectrophotometric analysis of conjugated dienoic acid (CDA) content, and high-performance size-exclusion chromatographic analysis of polymers (trimer and higher molecular weight polymers).

Materials and Methods

Materials Corn and soybean oils were obtained from Samyang Well-Food Co (Incheon, Korea). TBHQ, BHA, and PG were purchased from Sigma-Aldrich (St. Louis, MO, USA). Methyl esters of myristic ($C_{14:0}$), palmitic ($C_{16:0}$), stearic ($C_{18:0}$), oleic ($C_{18:1}$), linoleic ($C_{18:2}$), and linolenic acids ($C_{18:3}$) were also purchased from Sigma-Aldrich. Polystyrene standards of specified molecular weight of 800, 2,000, and 4,000 g/mol were purchased from Supelco Inc. (Bellefonte, PA, USA). Methylene chloride (HPLC grade) and ethanol (HPLC grade) were purchased from Fisher Scientific (Fair Lawn, NJ, USA).

Short-term one spot study on thermal oxidation of vegetable oils

Gallic acid, BHA, PG, and TBHQ were first dissolved in ethanol to prepare the antioxidant solutions. For the short-term one spot thermal oxidation study, 5 g of vegetable oil (corn and soybean oils) was transferred into a serum bottle. Then, the appropriate volumes of the antioxidant ethanol solutions were added to sample bottles. All the samples were prepared in duplicate. The samples were placed in an air-forced draft oven at 180°C for 8 h. Then, the oxidation of the vegetable oils was determined by gas chromatographic analysis of fatty acid composition, spectrophotometric analysis of CDA contents, and high-performance size-exclusion liquid chromatographic analysis of polymer (trimer and higher molecular polymers).

Long-term continuous time course study on thermal oxidation of vegetable oils

For the long-term time course thermal oxidation study, 100 g of vegetable oil (corn and soybean oils) was transferred into a 250-mL capacity glass beaker. Then, the appropriate volumes

of the ethanol solution containing gallic acid were added to the sample beakers to make the oils containing 0, 200, 500, and 1,000 ppm gallic acid. All the samples were prepared in duplicate. The samples were placed in an air-forced draft oven for 6 days at 180°C. The oil samples (2 g) were collected after every 24 h heating for the analysis of oxidative indices of the oils.

Gas chromatographic analysis of fatty acid composition

The methyl esterification of the oil was conducted according to previous reports (22–24). Twenty mg of oil was weighed into a glass tube, and then 1 mL of 0.25 M sodium methoxide was added into the tube. The sample tubes were then placed in a heating block at 70°C for 20 min for methylation of fatty acids. The fatty acid methyl esters (FAME) were extracted with petroleum ether. The extracted FAME samples (1 mL) were injected into a gas chromatograph equipped with a flame ionization detector (GC-2010; Shimadzu, Tokyo, Japan). The column used was AT-SILA capillary column (30 m×0.25 mm, 0.25 µm film thickness, Altech Associate, Deerfield, IL, USA). The flow rate of the carrier gas (helium) was 1.0 mL/min. The injector and detector temperatures were 240 and 250°C, respectively. The column oven temperature was programmed with an initial temperature of 180°C for 1 min and then increased to 220°C at a rate of 2.0°C/min. It was then maintained for 3 min at 220°C. The identities of FAMEs were confirmed by conducting gas chromatography under conditions identical to those for authentic FAME. The integrated peak area of each resolved FAME peak was used to calculate the fatty acid compositions of the oils.

Conjugated dienoic acid contents

The CDA contents in oils were determined by measuring the spectrophotometric absorbance at 233 nm according to AOCS Official Method Ti la-64. The CDA content in the oil was expressed as a percent extinction coefficient ($^{1\%}E_{233nm}$) with a 1-cm light path length.

High-performance size exclusion chromatography (HPSEC)

High-performance size exclusion chromatography (HPSEC) was conducted to measure the polymer contents in vegetable oils according to the previous reported method (3). Two columns (Shodex GPC K-803 and Shodex GPC K-8025; Shoko Co., Ltd., Tokyo, Japan) connected in series were used for the separation of the polymers in oils. The oil (0.25 g) was dissolved in methylene chloride (10 mL) and filtered through syringe filter (PTFE, 0.45 µm, Agilent Technologies, Santa Clara, CA, USA). The sample was injected into an HPLC system (LC10AD; Shimadzu) equipped with UV detector (UV-160A; Shimadzu). Methylene chloride was used as a mobile phase at the flow rate of 0.8 mL/min. Polystyrene standards of specified molecular weight of 800, 2,000, and 4,000 g/mol were used as external standards to estimate the molecular weight of the chromatographic peaks obtained by the HPSEC. The polymer contents were expressed as the HPSEC peak areas (arbitrary unit) of the polymer (trimer and higher molecular polymers).

Statistical analysis Analysis of variance (ANOVA) and Duncan's multiple range test were used to ascertain the statistical differences of the data at $\alpha=0.05$ by using a SPSS statistical analysis program (SPSS ver. 19.0; SPSS Inc., Chicago, IL, USA).

Results and Discussion

Comparative protection effect of gallic acid with those of synthetic antioxidants on thermal oxidation of vegetable oils To study the comparative protective activity of gallic acid with the synthetic antioxidants (BHA, PG, and TBHQ) on the thermal oxidation of vegetable oils, the vegetable oils (corn and soybean oils) containing gallic acid at 200 and 500 ppm or synthetic antioxidants at a concentration of 200 ppm were placed in an oven for 8 h at 180°C. The changes in oxidation indices of corn and soybean oils with added gallic acid and synthetic antioxidants are shown in Table 1. The 8 h heating greatly induced the thermal oxidation of the vegetable oils. The heating resulted in significant changes in fatty acid composition of the vegetable oils. The heating induced a considerable decrease in the polyunsaturated fatty acids ($C_{18:2}$ and $C_{18:3}$) but an increase in the saturated fatty acids ($C_{14:0}$, $C_{16:0}$, and $C_{18:0}$) and monounsaturated fatty acid ($C_{18:1}$) (Table 1). The $C_{18:2}$ contents decreased from 59.80 to 54.31% and from 56.09 to 49.33% in corn and soybean oils after 8 h heating, respectively. The $C_{18:2}/C_{16:0}$ ratio, an oxidation index,

considerably decreased in the vegetable oils after heating at 180°C. Gallic acid and synthetic antioxidants prevented the compositional changes in the fatty acids in the vegetable oils. Among the synthetic antioxidants, TBHQ exhibited the highest inhibitory effect on the changes in the fatty acid composition in all the vegetable oils. The results agreed well with the previous reports (10,11), which exhibited the protective activity of synthetic antioxidants on the oxidative changes in vegetable oils during high temperature heating. TBHQ was considered to be more effective than BHA for the inhibition of oxidation reactions in oils during frying (11). Gallic acid at 200 ppm exhibited higher protective activity on the changes in fatty acid profiles to TBHQ in both corn and soybean oils at the same concentration ($p<0.05$). As the content of gallic acid increased from 200 to 500 ppm, the higher inhibitory effects on the changes in $C_{18:2}/C_{16:0}$ ratio were observed in the vegetable oils. The CDA contents of the vegetable oils increased significantly after the heating. Among the synthetic antioxidants, TBHQ exhibited the highest inhibitory effects on the CDA production in all the vegetable oils (Table 1). The 200 ppm gallic acid treatment greatly higher inhibitory activity on the CDA formation in corn and soybean oils than 200 ppm TBHQ. Heating at 180°C also significantly induced polymerization in the vegetable oils. The polymer production in the vegetable oils was effectively prohibited by the addition of the antioxidants. The 200 ppm gallic acid provided higher inhibitory effect on the polymerization than the 200 ppm TBHQ in corn and soybean oils ($p<0.05$). The

Table 1. Comparative protective activity of gallic acid with synthetic antioxidants (TBHQ, PG and BHA) on the changes in fatty acid composition and productions of CDA and polymers in corn and soybean oils during heating for 6 days at 180°C

OI ¹⁻⁴⁾	Control 0 h	Control 8 h	GA 200 ppm	GA 500 ppm	TBHQ 200 ppm	PG 200 ppm	BHA 200 ppm
Corn oil							
$C_{16:0}$	11.04±0.03	13.22±0.15	12.71±0.07	12.38±0.41	12.81±0.11	13.13±0.28	13.01±0.12
$C_{18:0}$	1.89±0.03	2.29±0.02	2.24±0.02	2.14±0.03	2.22±0.03	2.26±0.00	2.29±0.00
$C_{18:1}$	26.30±0.06	29.53±0.06	28.99±0.08	28.43±0.21	29.02±0.12	29.29±0.04	29.46±0.01
$C_{18:2}$	59.80±0.21	54.31±0.06	55.39±0.07	56.23±0.64	55.28±0.03	54.61±0.11	54.58±0.12
$C_{18:3}$	0.98±0.10	0.66±0.01	0.68±0.05	0.83±0.00	0.68±0.00	0.73±0.13	0.67±0.02
$C_{18:2}/C_{16:0}$	5.42±0.03 ^a	4.11±0.05 ^d	4.36±0.03 ^{bc}	4.54±0.20 ^b	4.32±0.03 ^{cd}	4.16±0.10 ^{cd}	4.19±0.04 ^{cd}
CDA	3.75±0.10 ^e	16.04±0.11 ^a	13.90±0.44 ^c	12.05±1.22 ^d	14.38±0.03 ^{bc}	15.32±0.09 ^{ab}	15.60±0.05 ^a
Polymers	0.00±0.00 ^c	2.82±0.34 ^a	2.26±0.08 ^{ab}	1.93±0.51 ^b	2.42±0.17 ^{ab}	2.66±0.01 ^a	2.77±0.01 ^a
Soybean oil							
$C_{16:0}$	11.29±0.10	15.12±0.08	13.47±0.46	12.77±0.07	14.07±0.08	15.00±0.16	14.83±0.01
$C_{18:0}$	3.94±0.02	5.19±0.06	4.62±0.07	4.47±0.08	4.88±0.02	5.11±0.23	5.15±0.02
$C_{18:1}$	21.68±0.08	26.06±0.18	24.35±0.59	23.43±0.11	24.84±0.15	25.49±0.76	25.71±0.06
$C_{18:2}$	56.09±0.16	49.33±0.23	52.15±0.82	53.56±0.18	51.27±0.09	49.50±0.84	49.57±0.20
$C_{18:3}$	7.01±0.01	4.32±0.09	5.42±0.30	5.78±0.07	4.95±0.00	4.91±0.30	4.73±0.29
$C_{18:2}/C_{16:0}$	4.97±0.06 ^a	3.26±0.03 ^e	3.88±0.19 ^c	4.19±0.04 ^b	3.64±0.01 ^d	3.30±0.09 ^e	3.34±0.01 ^e
CDA	6.02±0.16 ^d	20.51±0.44 ^a	16.60±1.41 ^b	13.55±0.52 ^c	19.01±1.11 ^{ab}	19.72±1.36 ^a	19.18±1.32 ^a
Polymers	0.00±0.00 ^d	5.46±0.10 ^a	2.86±0.10 ^c	2.14±0.28 ^c	4.32±0.16 ^b	5.26±0.08 ^a	4.32±0.74 ^b

Data with different superscript letters denote the significant difference within the same row at $\alpha=0.05$.

¹⁾OI, oxidation indices (mean values of duplicate analysis with standard deviations).

²⁾ $C_{16:0}$, $C_{18:0}$, $C_{18:1}$, $C_{18:2}$, and $C_{18:3}$ represent the % composition of palmitic, stearic, oleic, linoleic and linolenic acids in the oils, respectively.

³⁾CDA, conjugated dienoic acid content expressed as a percent solution extinction coefficient at 233 nm.

⁴⁾Polymers, trimer and higher molecular weight polymers expressed as the peak areas (arbitrary unit) obtained by high performance size exclusion chromatography.

polymer contents in soybean oil increased from 0 to 5.458 (peak area, arbitrary unit) after 8 h heating. The polymer contents in soybean oils treated with 200 ppm gallic acid and 200 ppm TBHQ were 2.861 and 4.317 (peak area), respectively, showing clear evidence of the strong anti-polymerization activity of gallic acid in soybean oil ($p<0.05$). The results also showed that gallic acid had significantly higher anti-polymerization activity than TBHQ at the same concentration. The information on the protective activity of gallic acid on the thermal oxidation of vegetable oils at frying temperature was surprisingly scarce. There was only a few reports on the protective activity of gallic acid on the thermal oxidation of vegetable oils (20,21). However, the comparative protective activity of gallic acid with the synthetic antioxidants on the thermal oxidation of vegetable oils has not been reported previously.

Long-term time course study on the effects of gallic acid on the thermal oxidation during prolonged period heating

Long-term

time-course protective effects of gallic acid addition at three different concentrations (200, 500, and 1,000 ppm) on the fatty acid compositional changes, CDA and polymer productions of the vegetable oils (corn and soybean oils) during heating for 6 days at 180°C are shown in Table 2. As the heating time increased from 0 to 6 days, the polyunsaturated fatty acids ($C_{18:2}$ and $C_{18:3}$) decreased, but the saturated fatty acids ($C_{14:0}$, $C_{16:0}$, and $C_{18:0}$) and monounsaturated fatty acid ($C_{18:1}$) increased significantly (Table 2). The relative contents of $C_{18:2}$ in corn and soybean oils decreased from 59.43 to 50.88% and 56.09 to 47.94% after 6 day continuous heating at 180°C, respectively (Table 2). The relative contents of $C_{16:0}$ in corn and soybean oils increased from 11.01 to 14.60% and 11.29 to 15.54% after 6 day continuous heating at 180°C, respectively. The addition of gallic acid significantly inhibited the compositional changes in these fatty acids in the vegetable oils. For example, the relative contents of $C_{18:2}$ in the corn oil containing 0 and 1,000 ppm gallic acid decreased from 59.43 to 50.88% and from 59.43 to 55.35% after 6 day heating at 180°C,

Table 2. Protective effects of gallic acid at different concentrations (200, 500, and 1,000 ppm) on the changes in fatty acid composition and productions of CDA and polymers in corn and soybean oils during heating for 6 days at 180°C

		0 day	1 day	2 day	3 day	4 day	5 day	6 day
Corn oil								
Control	$C_{16:0}$ ¹⁾	11.01±0.01	11.37±0.05	11.94±0.04	12.71±0.03	13.25±0.12	13.91±0.11	14.60±0.14
	$C_{18:0}$	1.97±0.02	2.02±0.00	2.10±0.00	2.27±0.06	2.32±0.00	2.52±0.10	2.55±0.02
	$C_{18:1}$	26.64±0.11	27.13±0.06	27.86±0.08	28.84±0.11	29.83±0.01	30.63±0.14	31.45±0.21
	$C_{18:2}$	59.43±0.21	58.68±0.12	57.33±0.04	55.52±0.06	53.95±0.09	52.36±0.14	50.88±0.34
	$C_{18:3}$	0.97±0.07	0.85±0.01	0.79±0.00	0.68±0.00	0.66±0.04	0.59±0.01	0.53±0.03
	$C_{18:2}/C_{16:0}$	5.40±0.02 ^a	5.16±0.03 ^a	4.80±0.01 ^a	4.37±0.01 ^c	4.07±0.04 ^c	3.76±0.04 ^d	3.49±0.06 ^d
	CDA ²⁾	3.75±0.10 ^a	8.41±0.06 ^a	16.52±0.34 ^a	24.36±0.52 ^a	30.54±0.86 ^a	34.65±0.62 ^a	37.45±0.52 ^a
	Polymers ³⁾	0.00±0.00 ^a	-	1.19±0.21 ^a	-	2.47±0.66 ^a	-	5.05±0.10 ^a
GA 200 ppm	$C_{16:0}$	11.01±0.01	11.36±0.03	11.94±0.42	12.13±0.07	12.70±0.02	13.35±0.25	13.84±0.31
	$C_{18:0}$	1.97±0.02	2.01±0.00	2.08±0.04	2.13±0.01	2.23±0.02	2.34±0.02	2.44±0.04
	$C_{18:1}$	26.64±0.11	27.01±0.01	27.35±0.00	28.13±0.23	29.03±0.21	29.83±0.21	30.70±0.25
	$C_{18:2}$	59.43±0.21	58.76±0.03	57.81±0.45	56.88±0.31	55.36±0.25	53.89±0.42	52.36±0.44
	$C_{18:3}$	0.97±0.07	0.87±0.01	0.86±0.05	0.73±0.00	0.69±0.05	0.61±0.05	0.66±0.16
	$C_{18:2}/C_{16:0}$	5.40±0.02 ^a	5.17±0.02 ^a	4.85±0.21 ^a	4.69±0.05 ^b	4.36±0.01 ^b	4.04±0.11 ^c	3.78±0.12 ^c
	CDA	3.75±0.10 ^a	6.62±0.14 ^b	11.41±0.70 ^b	17.92±1.28 ^b	25.52±1.35 ^b	30.70±1.51 ^b	34.82±0.47 ^b
	Polymers	0.00±0.00 ^a	-	0.26±0.06 ^b	-	1.88±0.21 ^{ab}	-	4.28±0.46 ^b
GA 500 ppm	$C_{16:0}$	11.01±0.01	11.35±0.00	11.58±0.06	11.76±0.06	12.03±0.08	12.60±0.11	13.23±0.11
	$C_{18:0}$	1.97±0.02	2.00±0.00	2.04±0.01	2.10±0.01	2.14±0.02	2.22±0.01	2.32±0.01
	$C_{18:1}$	26.64±0.11	26.96±0.00	27.27±0.03	27.78±0.11	28.17±0.11	28.93±0.08	29.73±0.08
	$C_{18:2}$	59.43±0.21	58.82±0.01	58.29±0.09	57.61±0.18	56.78±0.25	55.50±0.28	54.04±0.08
	$C_{18:3}$	0.97±0.07	0.87±0.01	0.83±0.00	0.77±0.01	0.90±0.04	0.77±0.08	0.70±0.12
	$C_{18:2}/C_{16:0}$	5.40±0.02 ^a	5.18±0.00 ^a	5.04±0.04 ^a	4.90±0.04 ^a	4.72±0.05 ^a	4.41±0.06 ^b	4.09±0.04 ^b
	CDA	3.75±0.10 ^a	6.46±0.07 ^b	10.45±0.46 ^b	13.78±0.35 ^c	18.8±0.123 ^c	25.71±0.61 ^c	30.67±0.19 ^c
	Polymers	0.00±0.00 ^a	-	0.21±0.07 ^b	-	1.21±0.13 ^b	-	2.99±1.01 ^{bc}
GA 1,000 ppm	$C_{16:0}$	11.01±0.01	11.39±0.08	11.51±0.06	11.73±0.01	11.91±0.01	12.24±0.00	12.69±0.08
	$C_{18:0}$	1.97±0.02	2.02±0.1	2.04±0.01	2.09±0.01	2.12±0.01	2.16±0.01	2.24±0.04
	$C_{18:1}$	26.64±0.11	26.98±0.04	27.30±0.05	27.67±0.02	27.98±0.00	28.38±0.11	29.01±0.24
	$C_{18:2}$	59.43±0.21	58.77±0.03	58.34±0.02	57.76±0.02	57.14±0.11	56.27±0.14	55.35±0.39
	$C_{18:3}$	0.97±0.07	0.86±0.00	0.83±0.00	0.77±0.01	0.87±0.10	0.96±0.01	0.72±0.04
	$C_{18:2}/C_{16:0}$	5.40±0.02 ^a	5.16±0.04 ^a	5.07±0.03 ^a	4.92±0.01 ^a	4.80±0.01 ^a	4.60±0.01 ^a	4.369±0.06 ^a
	CDA	3.75±0.10 ^a	6.51±0.10 ^b	10.74±0.03 ^b	13.97±0.33 ^c	16.83±0.41 ^c	21.38±0.97 ^d	25.49±1.42 ^d
	Polymers	0.00±0.00 ^a	-	0.20±0.01 ^b	-	1.04±0.04 ^b	-	2.19±0.29 ^c

Table 2. Continued

		0 day	1 day	2 day	3 day	4 day	5 day	6 day
		Soybean oil						
Control	C _{16:0}	11.29±0.10	11.77±0.27	12.47±0.32	13.15±0.13	14.08±0.13	14.83±0.22	15.54±0.00
	C _{18:0}	3.94±0.02	4.10±0.00	4.33±0.01	4.59±0.03	4.88±0.05	5.17±0.01	5.49±0.01
	C _{18:1}	21.68±0.08	22.24±0.06	23.10±0.04	24.05±0.06	24.96±0.12	26.02±0.01	26.97±0.00
	C _{18:2}	56.09±0.16	55.36±0.19	54.05±0.30	52.76±0.23	51.21±0.02	49.63±0.14	47.94±0.10
	C _{18:3}	7.01±0.01	6.54±0.03	6.07±0.01	5.46±0.01	4.89±0.06	4.36±0.06	4.07±0.11
	C _{18:2} /C _{16:0}	4.97±0.06 ^a	4.70±0.12 ^b	4.34±0.13 ^a	4.01±0.06 ^c	3.64±0.03 ^b	3.39±0.06 ^c	3.08±0.01 ^c
	CDA	6.02±0.16 ^a	14.83±0.28 ^a	24.53±0.26 ^a	33.63±0.79 ^a	38.06±0.21 ^a	40.30±0.63 ^a	42.98±0.07 ^a
	Polymers	0.00±0.00 ^a	-	1.40±0.28 ^a	-	4.03±0.68 ^a	-	6.43±0.32 ^a
GA 200 ppm	C _{16:0}	11.29±0.10	11.47±0.06	12.02±0.29	12.74±0.09	13.74±0.33	14.31±0.10	15.37±0.28
	C _{18:0}	3.94±0.02	4.04±0.01	4.21±0.04	4.46±0.06	4.72±0.04	5.01±0.05	5.25±0.14
	C _{18:1}	21.68±0.08	22.02±0.04	22.64±0.14	23.56±0.20	24.42±0.13	25.38±0.21	26.29±0.16
	C _{18:2}	56.09±0.16	55.77±0.08	54.83±0.26	53.55±0.17	51.98±0.42	50.41±0.23	48.63±0.72
	C _{18:3}	7.01±0.01	6.74±0.03	6.31±0.21	5.69±0.18	5.16±0.08	4.90±0.13	4.47±0.13
	C _{18:2} /C _{16:0}	4.97±0.06 ^a	4.86±0.03 ^{ab}	4.56±0.13 ^{ab}	4.21±0.04 ^{bc}	3.79±0.12 ^b	3.34±0.09 ^{bc}	3.09±0.10 ^c
	CDA	6.02±0.16 ^a	10.41±0.89 ^b	18.90±1.87 ^b	29.00±1.06 ^b	34.67±1.06 ^a	38.89±0.94 ^a	41.85±0.79 ^a
	Polymers	0.00±0.00 ^a	-	0.93±0.09 ^a	-	3.70±0.12 ^a	-	6.21±0.36 ^{ab}
GA 500 ppm	C _{16:0}	11.29±0.10	11.52±0.16	11.64±0.00	12.20±0.35	12.89±0.34	13.65±0.57	14.29±0.32
	C _{18:0}	3.94±0.02	4.02±0.01	4.12±0.04	4.27±0.05	4.47±0.04	4.72±0.12	5.00±0.18
	C _{18:1}	21.68±0.08	21.89±0.05	22.28±0.09	22.87±0.13	23.58±0.20	24.40±0.36	25.35±0.59
	C _{18:2}	56.09±0.16	55.77±0.04	55.42±0.07	54.57±0.41	53.42±0.48	51.98±0.59	50.52±0.62
	C _{18:3}	7.01±0.01	6.81±0.07	6.56±0.05	6.10±0.13	5.64±0.010	5.27±0.45	4.86±0.46
	C _{18:2} /C _{16:0}	4.97±0.06 ^a	4.84±0.07 ^{ab}	4.76±0.01 ^a	4.48±0.16 ^{ab}	4.15±0.15 ^a	3.81±0.20 ^b	3.62±0.12 ^b
	CDA	6.02±0.16 ^a	9.26±0.51 ^b	14.09±1.06 ^c	21.74±2.09 ^c	28.41±2.43 ^b	33.76±2.22 ^b	37.85±2.19 ^b
	Polymers	0.00±0.00 ^a	-	0.43±0.16 ^b	-	2.18±0.36 ^b	-	4.69±1.10 ^{bc}
GA 1,000 ppm	C _{16:0}	11.29±0.10	11.31±0.05	11.56±0.06	12.02±0.22	12.49±0.13	12.81±0.18	13.60±0.25
	C _{18:0}	3.94±0.02	4.02±0.00	4.09±0.00	4.17±0.05	4.29±0.06	4.51±0.06	4.75±0.11
	C _{18:1}	21.68±0.08	21.93±0.00	22.22±0.02	22.52±0.16	22.98±0.19	23.74±0.33	24.52±0.33
	C _{18:2}	56.09±0.16	55.92±0.04	55.52±0.07	54.98±0.04	54.19±0.29	53.39±0.46	51.88±0.35
	C _{18:3}	7.01±0.01	6.83±0.01	6.62±0.01	6.33±0.03	6.07±0.10	5.56±0.11	5.26±0.35
	C _{18:2} /C _{16:0}	4.97±0.06 ^a	4.94±0.03 ^a	4.80±0.03 ^a	4.58±0.09 ^a	4.34±0.07 ^a	4.17±0.10 ^a	3.75±0.10 ^a
	CDA	6.02±0.16 ^a	9.07±0.07 ^b	13.21±0.39 ^b	17.90±0.91 ^c	22.27±1.19 ^c	28.12±1.62 ^c	33.23±1.62 ^c
	Polymers	0.00±0.00 ^a	-	0.31±0.11 ^c	-	1.42±0.24 ^b	-	3.76±0.14 ^c

Data with different superscript letters denote the significant difference within the same oxidation indices (OI) at the same heating day at $\alpha=0.05$.

¹C_{16:0}, C_{18:0}, C_{18:1}, C_{18:2}, and C_{18:3} represent the % composition of palmitic, stearic, oleic, linoleic and linolenic acids in the oils, respectively.

²CDA, conjugated dienoic acid content expressed as a percent solution extinction coefficient at 233 nm.

³Polymers, trimer and higher molecular weight polymers expressed as the peak areas (arbitrary unit) obtained by high performance size exclusion chromatography.

respectively (Table 2). The C_{18:2}/C_{16:0} ratios in corn and soybean oils after continuous heating for 6 days at 180°C decreased from 5.40 to 3.49 and from 4.97 to 3.08, respectively (Table 2). The gallic acid addition significantly decreased the changes in C_{18:2}/C_{16:0} ratios in the oils during heating. As the contents of gallic acid increased from 200 to 1,000 ppm, the changes in C_{18:2}/C_{16:0} ratio in the oils significantly decreased ($p<0.05$). The gallic acid additions at 200, 500, and 1,000 ppm exerted the inhibition of 15.0, 31.1, and 45.6% of change of the ratio of C_{18:2}/C_{16:0} in the corn oil during 6 day heating at 180°C, respectively. The gallic acid additions at 200, 500, and 1,000 ppm exerted 0.5, 28.6, and 35.4% inhibition of the change of C_{18:2}/C_{16:0} ratio in the soybean oil during 6 day heating at 180°C, respectively. The CDA in the corn and soybean oils increased from 3.75 to 37.45 (¹%E_{233nm}) and 6.02 to 42.98 (¹%E_{233nm}) after 6 day heating at 180°C,

respectively. The gallic acid addition significantly decreased CDA content in the oils. The higher the contents of gallic acid, the lower the CDA formation during heating at 180°C. For example, the gallic acid additions at 200, 500, and 1,000 ppm exerted the inhibition of 7.8, 20.1, and 35.5% of change in the ratio of C_{18:2}/C_{16:0} in the corn oil during 6 day heating at 180°C, respectively. The effect of 1,000 ppm gallic acid addition exerted 35.5 and 26.4% inhibition of CDA formation in corn and soybean oils, respectively. As the heating time increased, the polymer contents in the vegetable oils also increased significantly. The polymer contents in corn and soybean oils increased from 0 to 5.05 and 6.43 (peak area, arbitrary unit) after 6 day heating, respectively. Gallic acid additions greatly decreased the formation polymers in the vegetable oils in a concentration dependent manner. The 1,000 ppm gallic acid treatment exerted 56.6 and 41.5%

inhibitions of polymer formation in corn and soybean oils after 6 day heating at 180°C, respectively. Note that the protective effects of gallic acid was consistently more effective in corn oil than in soybean oil on the changes in all the oxidation indices (fatty acid composition, CDA, and polymers) during the prolonged heating for 6 days. The oil type-dependent antioxidative activity of gallic acid may be because of the difference in the oxidative stability between these two vegetable oils. The higher protective activity of gallic acid in corn oil may be attributed to the higher oxidative stability of corn oil. There are many reports regarding the antioxidative properties of gallic acid at ambient temperature (2,17-19). However, there were only a few reports on the protective activity of gallic acid on the thermal oxidation of vegetable oils. Also, the comparative protective activity of gallic acid with the well-known synthetic antioxidants such as TBHQ, BHA, and PG against the thermal oxidations of vegetable oils treated at frying temperature has not been reported previously. Furthermore, the quantitative protective effects of gallic acid at various concentrations on the thermal oxidation of the various vegetable oils during the prolonged periods at frying temperature have not been previously studied. The present study shows the comparative protective effectiveness of gallic acid with well-known synthetic antioxidants (TBHQ, BHA, and PG) on the thermal oxidation of vegetable oils. The results show that gallic acid had the higher protective activity on the thermal oxidation of corn and soybean oils than the synthetic antioxidants (TBHQ, BHA, and PG) during the heating at 180°C. Furthermore, the present study showed the quantitative protective activity of gallic acids at three different concentration on the thermal oxidation of corn and soybean oils during the extended period (6 days) of heating at 180°C. Gallic acid provided persistently strong protective activity, in a concentration dependent manner, on the thermal oxidation of vegetable oils during the prolonged period (6 days) of heating. Gallic acid at 1,000 ppm exerted 45.6, 35.5, and 56.6% inhibitions on the changes in $C_{18:2}/C_{16:0}$ ratio, formation of conjugated dienoic acid and polymers in corn oil after continuous 6 day heating at 180°C, respectively. Gallic acid is widely accepted as a safe natural food additive in many countries without legislative restriction for its use in foods. The present results suggest that gallic acid would be a potential natural substitute of the synthetic antioxidants for the protection of vegetable oils during high temperature heating such as deep-fat frying. To confirm this idea, however, subsequent systematic study on the protective effect of gallic acid on the thermal oxidation of vegetable oils during frying under the practical conditions should be followed.

Disclosure The authors declare no conflict of interest.

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