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Utilization of *Diaphragma juglandis* extract as a natural antioxidant for improving the oxidative stability of soybean oil during deep frying

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ABSTRACT

Lipid oxidation significantly shortens the life of frying oils, and this challenge can be addressed by using antioxidants. This work aimed to investigate the effect of *Diaphragma juglandis* extract (DJE) on the oxidative stability of soybean oil during deep frying. *Tert*-butylhydroquinone (TBHQ) and tea polyphenol (TP) were applied as positive controls. A total of 31 polyphenols were determined in DJE, and catechin, quercitrin, taxifolin, quercetin 3-β-d-glucoside, epicatechin, gallic acid, and 3,4-dihydroxybenzoic acid were the main components. The antioxidants effectively delayed the degradation of triglycerides and inhibited the increase in the contents of *p*-anisidine, oxidized triglyceride monomers, triglyceride dimers, and triglyceride oligomers, with DJE exhibiting better performance. Moreover, DJE showed better inhibitory effect on the formation of (*E*)-2-alkenals, (*E,E*)-2,4-alkadienals, 4-oxo-alkanals, primary alcohols, and secondary alcohols detected by ^{1}H nuclear magnetic resonance than TBHQ and TP. Therefore, DJE has great potential as an excellent antioxidant in large-scale industrial applications.

1. Introduction

Frying is a popular method of cooking food around the globe; it is a fast, energy-efficient method to produce palatable food with excellent sensorial characteristics. These characteristics are associated with golden brownish appearance, crispy texture, and pleasant flavor typical for frying food (Wu et al., 2021a). However, the limitation of this technique is the rapid degradation of the quality and stability of oil during frying. Frying oils used continuously at elevated temperatures (approximately 180 °C or over) in the presence of oxygen and moisture from the food being fried are subject to oxidation, polymerization, and hydrolysis; the oil also accumulates lipid degradation products. These phenomena may be responsible for the formation of potentially toxic components, such as oxidized triglyceride (TAG) monomers (OxTGs), oxidized TAG polymers (TGPs), and toxic aldehyde compounds (Chen et al., 2021; Khor et al., 2020). Given the extensive mass exchange between the oil and food, fried food ultimately acquires the degradation products of the frying oil, thereby influencing the quality of the food.

The stability of frying oil can be improved using two common methods (Kmiecik, Gramza–Michalowska, & Korczak, 2018). The first method involves the optimization of frying conditions and using an oil of low degree of unsaturation. The second method involves the use of antioxidants. It is possible to divide antioxidants used for protecting oil during frying into natural and synthetic types (Wu et al., 2019). Several antioxidants, often of synthetic origin [butylated hydroxytoluene, butylated hydroxyanisole, *tert*-butylhydroquinone (TBHQ), propyl gallate], have been added to commercial frying oils to retard oxidation and enhance the performance of frying (Chen et al., 2021). However, synthetic antioxidants are less effective than natural antioxidants under frying conditions because they are erratic and can easily evaporate at elevated temperatures as a result of their structures (Guo et al., 2016). Aside from poor protection, synthetic antioxidants may also contribute to increasing health risks such as cancer and carcinogenesis (Olajide, Liu, Liu, & Weng, 2020). Hence, it remains a continuing endeavor to find effective exogenous antioxidants from natural sources to stabilize frying oils. The study of phenolic extracts from various parts of plants is on the rise in recent years, especially common spices and herbs (Kmiecik, Gramza-Michalowska, & Korczak, 2018; Wu et al., 2019). Polyphenols

Abbreviations: DJE, *Diaphragma juglandis* extract; TBHQ, *tert*-butylhydroquinone; TP, tea polyphenol; TAG, triglyceride; OxTGs, oxidized triglyceride monomers; TGPs, oxidized triglyceride polymers; HPSEC, high-performance size exclusion chromatography; PV, peroxide value; AV, acid value; *p*-AnV, *p*-anisidine value; TPC, total polar compounds; K232, conjugated dienes; K268, conjugated trienes; TGOs, triglyceride oligomers; TGDs, triglyceride dimers.

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are naturally occurring antioxidant compounds ubiquitous in plants and have biological activities (Wu et al., 2021b). During the frying process, the phenolic extracts of rosemary, sage, thyme, oregano, garlic, and nutmeg could effectively protect against oxidative deterioration without decreasing the sensory properties of fried products (Guo et al., 2016; Kmiecik, Gramza–Michalowska, & Korczak, 2018; Mutlu-Ingok, Catalkaya, Capanoglu, & Karbancioglu-Guler, 2021).

Diaphragma juglandis (*D. juglandis*) is obtained from the wooden diaphragm in the core of walnut (*Juglans regia L.*) and is thus known as walnut diaphragm. Since ancient times, it has been widely used as a traditional Chinese medicine for the treatment of kidney deficiency, reproductive diseases, diarrhea, and insomnia (Hu, Gao, & Mou, 2021; Zhang et al., 2022). Recent studies have confirmed that *D. juglandis* contains large amounts of bioactive components, including phenolic acids, flavonoids, saponins, quinones, alkaloids, polysaccharides, etc. (Liu, Zhao, Dai, Che, & Liu, 2019; Meng, Li, Xiao, Zhang, & Xu, 2017). However, it is usually discarded as waste during walnut processing in food factories because their major components are indigestible, such as fiber and lignin (Hu et al., 2020). Research efforts to make the most of agro-food wastes with potential nutritional value have gained worldwide popularity and importance. *D. juglandis* deserves a special attention as a potential source of natural antioxidants and other bioactive substances.

This study aimed to examine the influence of *D. juglandis* extract (DJE) on the prevention of thermal decomposition in soybean oil under deep frying conditions. Changes in TAGs, chemical parameters, and polar compounds during heating were evaluated. In addition, the generation and evolution of other oxidation products, including aldehydes and alcohols, were determined by ^{1}H nuclear magnetic resonance (NMR).

2. Materials and methods

2.1. Materials

The first-class soybean oil without antioxidant was provided by Yi Hai Kerry Co., Ltd. (Shanghai, China). Frozen fries were purchased from Simplot Food Co., Ltd. (Yinchuan, China). *D. juglandis* was supplied by Haozhou Mingjie Biotech Co. Ltd. (Anhui, China). To facilitate subsequent extraction of polyphenols, *D. juglandis* was pulverized using a grinding machine (model FW100, Taisite, Tianjin, China) and sifted through a 40-mesh sieve.

2.2. Preparation of phenolic extract

Polyphenols were extracted following the methods of Wu et al. (2021a) and L. Chen, Fan, Lin, Qian, Zengin, Delmas, Paoli, Teng, and Xiao (2020b) with slight modifications. *D. juglandis* powder (100 g) was extracted ultrasonically with 1000 mL of 80% (v/v) ethanol for 1 h at 25 °C (ultrasound power of 200 W). The extracted solution was obtained by centrifugation (H1750R, Xiangyi Centrifuge Instrument Co., Ltd., Changsha, China) at 3000 × g for 15 min at 4 °C. The remaining residue was re-extracted twice by 80% ethanol. Crude phenolic extract was acquired by evaporation of the organic solvent under reduced pressure at 40 °C.

AB-8 macroporous resin (Macklin Inc., Shanghai, China) was applied for further purification of polyphenol. Approximately 10 g of the crude extract of *D. juglandis* was dissolved in 300 mL of distilled water. The extract solution was subjected on a glass column (22 mm × 450 mm) wet-packed with 25 g of AB-8 macroporous resin. When the adsorption equilibrium was reached, the extract was first eluted with 100 mL of distilled water followed by 140 mL of 70% ethanol solution. After desorption, the extracts were combined and the solvents were removed using a rotary evaporator (R-SENCO, Shanghai, China). Finally, the aqueous layer was freeze dried using a lyophilizer to obtain the purified extract (Fig. S1).

2.3. Determination of total phenolic content

Total phenolic content in the extract was determined according to the modified Folin-Ciocalteu assay as described by Aladedunye and Matthaus (2014). Accordingly, 20 μL of the diluted samples were mixed with 100 μL of Folin–Ciocalteu reagent and 300 μL of Na_2CO_3 (10%). The mixture was incubated at room temperature for 1 h in the dark. Absorbance was recorded at 765 nm by UV-Vis spectrophotometer (UV1200, Shimadzu, Tokyo, Japan). The result was expressed as milligrams gallic acid equivalents (GAE) per gram extract.

2.4. Quantification of bioactive compounds in phenolic extract

In accordance with the methods of Zhuang et al. (2020) and Liu et al. (2019), the bioactive compounds in DJE were determined using a Q Exactive Orbitrap mass spectrometer coupled to a Vanquish ultra-performance liquid chromatography system (Thermo Fisher Scientific, Waltham, MA, USA). The chromatographic separation used an Acquity HSS T3 column (1.8 μm, 100 mm × 2.1 mm), with 0.1% formic acid in water (A) and 100% acetonitrile (B) as mobile phases. The system used the following gradient program: initial, 90% A; 2.0 min, 90% A; 6.0 min, 40% A; 9.0 min, 40% A; 9.1 min, 90% A; 12.0 min, 90% A. The flow rate, column oven temperature, and injection volume were set at 0.3 mL/min, 40 °C, and 2 μL, respectively.

The Q Exactive Orbitrap mass spectrometer was equipped with a heated electrospray ionization source operating in negative mode. During the analysis, the typical ion source conditions were as follows: spray voltage, 3.0 kV; capillary temperature, 320 ℃; probe heater temperature, 350 ℃; sheath gas, 40 arb; aux gas, 10 arb. Trans-ferulic acid, 4-hydroxybenzoic acid, vanillic acid, vanillin, gallic acid, *p*-hydroxycinnamic acid, benzoic acid, salicylic acid, protocatechualdehyde, 3,4-dihydroxybenzoic acid, caffeic acid, syringic acid, syringaldehyde, 4-hydroxy-3,5-dimethoxycinnamic acid, catechin, epicatechin, rutin, vitexin, luteolin, quercetin, apigenin, kaempferol, naringenin, naringenin chalcone, dihydrokaempferol, taxifolin, isorhamnetin, dihydromyricetin, quercitrin, and quercetin 3-β-d-glucoside were used as individual polyphenolic standards.

2.5. Frying procedure

Frying was carried out in a 6 L domestic electric fryer (EF-6, Vesta Corporation, Guangzhou, China). Tea polyphenol (TP) and TBHQ were separately added to soybean oil at a concentration of 200 mg/kg, while the same oil without any antioxidants was used as the control. Soybean oil was fortified with DJE at the final concentration of 200 mg GAE/kg. Each oil (5 L) was placed in the fryer, and the temperature was set as 180 °C. After heating the oil to the selected temperature (15 min), frozen fries (100 g) were fried for 3 min at 17 min intervals with a total of 8 h per day for four consecutive days. For each day, the fryer was turned off until the termination of the experiment, and the crumbs were removed with a mesh skimmer. The oil was covered, stored at ambient temperature (20 °C) and left overnight. At intervals of 0, 4, 8, 12, 16, 20, 24, 28, and 32 h, approximately 100 mL of sample was obtained and kept in the refrigerator of −20 °C for subsequent determination. During the frying process, no fresh oil was replenished.

2.6. Determination of the absolute content of TAGs

The relative content of TAGs of frying oils was analyzed by high-performance liquid chromatography (HPLC) as described by the American Oil Chemists' Society (AOCS) official method Ce 5c-93. The oil samples were determined by an Agilent 1200 Series HPLC system equipped with a refractive index detector (RID-10A; Shimadzu Corporation, Japan). Two LiChroCART 18e columns (5 μm, 4.6 mm × 250 mm, Merck Germany) were used for chromatographic separations. The mobile phase was composed of acetonitrile and acetone (25:75, v/v) at a

flow rate of 1 mL/min. The column temperature was set at 45 °C and the injection volume was 20 μL. POP (P, palmitic acid; O, oleic acid) of 99% purity was obtained from Larodan Fine Chemicals AB (Malmö, Sweden). Identification was achieved by comparing the retention time with the standard, and data were reported in terms of proportion. The relative contents of TAGs in oil samples during frying are listed in Table S1.

The determination of the relative content of TAGs could only give a comprehensive understanding of the relative oxidation rate of TAGs in frying oil. The absolute content of TAGs was determined using the method described by Chen, Chen, Wan, and Deng (2021) to effectively analyze and compare the obtained data,. The following example of control group was to illustrate this method. The initial content of total TAGs was assumed to be 100 g, and the initial relative content of LLLn (L, linoleic acid; Ln, linolenic acid) was 7.94%. Thus, the initial absolute content of LLLn was 7.94 g. After 32 h of frying, a fraction of TAGs was degraded, and the relative content of LLLn was 3.07%. Polar compounds comprise most of the degradation products formed during deep frying (Chen et al., 2021). Moreover, nonpolar compounds, such as unchanged TAGs and nonpolar dimers, are also present in the frying oil (Zhang, Qin, Li, Shen, & Saleh, 2015). The high-performance size exclusion chromatography (HPSEC) was used for the determination of unchanged TAGs in nonpolar compounds (Fig. S2). By subtracting polar compounds (29.34%, w/w) from the oil, the content of nonpolar compounds was 70.66 g, and the absolute content of total unchanged TAGs was 62.46 g [70.66 g × relative content of unchanged TAGs (88.39%)]. Therefore, the final absolute content of LLLn was 1.92 g [62.46 g × relative content of LLLn (3.07%)] during the frying process.

2.7. Determination of chemical parameters

Peroxide value (PV), acid value (AV), *p*-anisidine value (*p*-AnV), and total polar compounds (TPC) were analyzed following AOCS official methods Cd 8b-90, Cd 3d-63, Cd 18–90, and Cd 20–91, respectively. The levels of conjugated dienes (K232) and conjugated trienes (K268) were measured in frying media according to the GB/T 22500–2008. An oil sample (0.05–0.25 g) was dissolved in isooctane, and the absorbance was recorded at 232 nm and 268 nm. K232 and K268 can be obtained by Eq. (1):

$$E^{1\%}_{1\ cm\ (\lambda)} = \frac{A_{(\lambda)}}{\omega}$$

where $A_{(\lambda)}$ is the absorbance of sample at 232 and 268 nm, and ω is the concentration of the sample (g/100 mL).

2.8. Determination of oxidized and polymeric TAGs

The oxidized and polymeric TAGs in frying media were determined by HPSEC based on a previously described method (J. Chen et al., 2020a). Three oxidized polar compounds including TAG oligomers (TGOs), TAG dimers (TGDs), and OxTGs were determined. The limit of detection for individual fraction of TPC in oils was 0.01%, and it was previously validated (Cao et al., 2013).

2.9. Quantification of oxidation products by ^1H NMR

Aldehydes and alcohols in frying oils were determined by ^1H NMR according to Martin-Rubio, Sopelana, and Guillen (2018). Each sample (about 50 μL) was dissolved in 400 μL of deuterated chloroform ($CDCl_3$, 99.8 atom% D). The mixture was shaken well for 1 min at room temperature. NMR spectra were recorded using a Bruker Avance 400 spectrometer (Brucker, Switzerland) operating at 400 MHz. MestReNova 14 software (Mestrelab Research) was used to process and analyze the ^1H NMR spectra. Chemical shifts were calibrated against the known chloroform peak (7.26 ppm).

The representative ^1H NMR spectra of the oil samples are displayed in Fig. S3. Table S2 lists the assignment of the main signals of the oxidation products in samples. The concentrations of the oxidation products were computed using Eq. (2):

$$[OP(mmol/mol\,TAG)] = 1000*[(A_{OP}/n)/(A_I/4)]$$

where A_{OP} is the selected signal of an oxidation products, n is the number of protons generating the signal, and A_I is the area of the protons at *sn*-1 and *sn*-3 positions in the glycerol backbone of TAGs.

2.10. Statistical analysis

All measurements were repeated three times, and all experiments were carried out independently twice. Statistical analysis was carried out using one-way analysis of variance followed by Duncan's test with SPSS version 11.5 (SPSS, USA). Differences were considered significant when $p < 0.05$.

3. Results and discussion

3.1. Phenolic composition of DJE

The phenolic components and contents in DJE are shown in Table 1. A total of 31 components of DJE were successfully detected. The most abundant compounds in DJE were catechin, quercitrin, taxifolin, quercetin 3-β-d-glucoside, epicatechin, gallic acid, and 3,4-dihydroxybenzoic acid, and their contents are 9989.16, 6816.18, 569.39, 399.00, 362.10, 272.52, and 259.06 μg/g dry weight, respectively. Fig. 1 illustrates the chemical structure of the components of DJE. The contents of other fractions were low, ranging from 0.27 to 85.46 μg/g dry weight. As common bioactive polyphenols, these compounds are widely found in fruits and vegetables (Liu et al., 2019; Zhong, Farag, Chen, He, & Xiao, 2022). Previous studies demonstrated that polyphenols could offer good protection of oils against oxidative degradation during frying and

Table 1
Contents of bioactive compounds in DJE (μg/g of dry sample).

Compounds	Content	Compounds	Content
Catechin	9989.16 ± 0.73	Dihydrokaempferol	14.57 ± 0.17
Quercitrin	6816.18 ± 1.61	*p*-Hydroxycinnamic acid	10.17 ± 0.58
Taxifolin	569.39 ± 0.88	Caffeic acid	9.81 ± 0.07
Quercetin 3-β-D-glucoside	399.00 ± 1.07	Luteolin	7.60 ± 0.45
Epicatechin	362.10 ± 0.50	Salicylic acid	6.50 ± 0.28
Gallic acid	272.52 ± 0.52	Dihydromyricetin	5.75 ± 0.12
3,4-Dihydroxybenzoic acid	259.06 ± 0.09	Syringaldehyde	4.90 ± 0.03
Protocatechualdehyde	85.46 ± 0.63	Trans-ferulic acid	4.56 ± 0.19
Vanillic acid	66.06 ± 1.30	Naringenin chalcone	3.34 ± 0.10
Quercetin	54.10 ± 0.06	Vitexin	1.90 ± 0.19
Syringic acid	37.94 ± 0.22	Isorhamnetin	0.99 ± 0.14
Naringenin	31.84 ± 0.27	Kaempferol	0.96 ± 0.03
Benzoic acid	18.55 ± 0.07	Trans-cinnamic acid	0.74 ± 0.11
Rutin	17.32 ± 0.44	Apigenin	0.36 ± 0.05
4-Hydroxybenzoic acid	17.14 ± 0.10	4-Hydroxy-3,5-dimethoxycinnamic acid	0.27 ± 0.06
Vanillin	15.53 ± 0.45		

Results are presented as means ± SD.

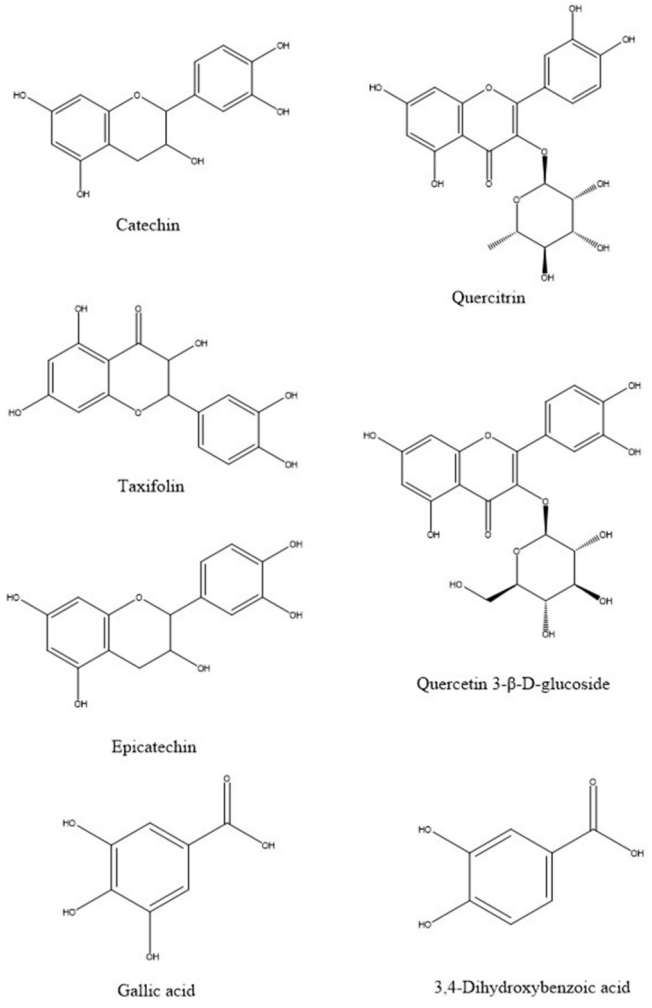

Fig. 1. Chemical structure of the main phenolic components in DJE.

storage (Li et al., 2021; Wu et al., 2019). Thus, given that it is rich in dietary polyphenols, *D. juglandis* has a huge potential to be developed as an excellent source of effective natural antioxidants instead of being relegated to agro-food wastes.

3.2. Effect of DJE on the absolute content of TAGs of frying oils

Edible oil is made up primarily of TAGs of fatty acids. The TAG structure is strongly associated with the oxidative stability, generation of oxidation products, and general physicochemical characteristics of oil (Zeb, 2012). Table 2 illustrates the evolution of the absolute content of TAGs in soybean oils added with different antioxidants during deep frying. A total of 13 TAGs were detected in oil samples. LLLn (7.94%), LLL (13.60%), OLL (12.56%), LLP (11.08%), LOP (8.39%), and OOL (8.63%) were the main components of fresh oil. During frying, most of the TAGs decreased with increasing frying time. LLLn, LLL, OLL, LLP, and OOL were the least stable in the control group, and more than 35% of them were degraded after frying. Their absolute degradation contents were 6.02, 6.04, 4.96, 4.63, and 3.78 g/100 g, respectively. A higher level of unsaturation of TAGs could increase the oxidation rate during thermal oxidation (Chen et al., 2021). The thermal oxidation of unsaturated TAGs mainly proceeds by free radical chain reactions (Wu et al., 2019). In comparison with control group, adding antioxidants could effectively delay the degradation of TAGs. The antioxidant activity of these additives is due to their capacity to be donors of hydrogen atoms or electrons and to capture the free radicals; more stable phenoxy radical intermediates could be produced. The effects of antioxidants on delaying the degradation of OLL and LLP were in the following order: DJE = TP > TBHQ. The degradation rate of OLL and LLP did not exceed 32% for DJE and TP groups. Compared with TBHQ, natural polyphenols are not susceptible to evaporate at high temperatures and some degradation products could display antioxidant activity. For instance, protocatechuic acid can be generated by the thermal degradation of quercetin (Wu et al., 2021a). These results indicated that DJE exhibited superior properties for improving the oxidative stability of frying oil.

3.3. Effect of DJE on the chemical parameters of frying oils

AV represents the level of free fatty acids (FFAs) liberated from the hydrolysis of TAGs. FFAs could be rapidly oxidized, thereby promoting further oxidation of polyunsaturated fats by solubilizing and activating the metal catalysts, which have an influence impact on the performance of the frying oils (Urbančič, Kolar, Dimitrijević, Demšar, & Vidrih, 2014). Fig. 2a shows the AV and their variations during deep frying. The AV of all of the frying oils increased as the frying duration was extended, while the increase rate was slowed down when antioxidants were added. The antioxidant effect followed the order of TP = DJE > TBHQ. Similarly, Li et al. (2021) also found that TBHQ and rosemary extracts can inhibit the increase in FFA in refined soybean oils.

PV is one of the oldest parameters for measuring the degree of primary oxidation in oils and fats. The changes in PV of oil samples during deep frying are shown in Fig. 2b. The PV of oils fluctuated with the extension of frying time, with the same trend reported in other study (Wu et al., 2021b). The reason for this result was that primary oxidation products (hydroperoxides) were unstable and easily breakable into small molecules (Su et al., 2022).

p-AnV was used to determine the content of aldehydes degraded by oils and fats. It was found to be relatively stable at high temperatures (Zhao, Zhang, Wang, & Devahastin, 2021). Compared with PV, *p*-AnV is more suitable for monitoring the oxidative state of frying oil. As shown in Fig. 2c, frying oil had higher *p*-AnV than fresh oil (2.80 units). With increasing usage time, the *p*-AnV of all the samples presented an overall trend of increasing first and then decreasing, which agreed well with a previous research (Xu et al., 2020). The reduced *p*-AnV in frying oil could be due to the evaporation or further oxidative degradation of unstable aldehydes. All antioxidants significantly inhibited the increase in *p*-AnV during dee frying. The final *p*-AnVs in the oil samples after frying were 114.96, 61.87, 82.71, and 36.95 units for control, TBHQ, TP, and DJE, respectively. The addition of DJE to the oil significantly reduced the *p*-AnV by up to 68%. The possible explanation for this difference was that the formed carbonyl compounds can be effectively trapped by natural polyphenols with high nucleophilicity (Zamora, Aguilar, Granvogl, & Hidalgo, 2016).

TPC is one of the most reliable and widely used indices to evaluate the deterioration of frying oil. The effects of different antioxidants on the TPC of frying oils are presented in Fig. 2d. TPC was initially present in the fresh oil (3.95%) in small amounts, and the increases in TPC were seen for all the samples at prolonged frying time. According to previous reports, the limited value of TPC was set at 25% in many European countries, including Belgium, France, Portugal, Italy, and Spain (Chen et al., 2021). After the experiment, the TPC content in the oil treated with DJE was the lowest, only 22.38%, which was significantly lower ($p < 0.05$) than that of the control sample (29.34%). This finding is consistent with the result on *p*-AnV, indicating that DJE could effectively prolong the life of frying oils.

K232 is associated with the production of primary lipid oxidation products, while K268 is used to characterize changes in carbonyl compounds (such as aldehydes and ketones; Zhao et al., 2021). The values of K232 and K268 in fresh oil were 3.22 and 1.43, respectively. The changes in K232 and K268 are displayed in Fig. 2e-f; both parameters increased with prolonged frying duration, as previously described by other investigators (Li et al., 2021; Zhao et al., 2021). After 32 h of frying, the K232 and K268 levels of oils added with DJE were the lowest.

Table 2
Evolution of the absolute content (%) of TAGs in soybean oils with addition of different antioxidants during deep frying.

Group	Time/h	TAG composition												
		LLnLn	LLLn	LLL	LnLP	OLLn	OLL	LLP	PLP	LOP	OOL	OOP	POP	OOO
Control	0	1.01 ± 0.06^{a}	7.94 ± 0.95^{a}	13.60 ± 1.06^{a}	3.66 ± 0.49^{a}	6.51 ± 0.26^{ab}	12.56 ± 0.55^{a}	11.08 ± 0.36^{a}	2.80 ± 0.11^{a}	8.39 ± 0.30^{a}	8.63 ± 0.23^{a}	3.78 ± 0.16^{a}	0.99 ± 0.03^{h}	4.07 ± 0.08^{a}
	4	0.87 ± 0.02^{b}	6.30 ± 0.10^{b}	9.62 ± 0.27^{b}	2.87 ± 0.07^{b}	4.23 ± 0.12^{d}	11.72 ± 0.41^{ab}	10.22 ± 0.45^{ab}	2.50 ± 0.04^{ab}	7.80 ± 0.13^{ab}	7.32 ± 0.55^{b}	3.16 ± 0.09^{ab}	1.18 ± 0.01^{gh}	3.18 ± 0.07^{b}
	8	0.80 ± 0.03^{b}	6.14 ± 0.22^{b}	7.98 ± 0.46^{bc}	2.61 ± 0.24^{b}	6.37 ± 0.57^{ab}	11.03 ± 0.37^{bc}	9.75 ± 0.16^{abc}	2.25 ± 0.10^{bc}	7.66 ± 0.27^{abc}	6.82 ± 0.15^{bc}	3.02 ± 0.11^{b}	1.41 ± 0.02^{fg}	2.86 ± 0.04^{bc}
	12	0.57 ± 0.05^{c}	4.42 ± 0.16^{c}	7.73 ± 0.36^{cd}	2.23 ± 0.09^{bc}	5.83 ± 0.35^{bc}	10.38 ± 0.20^{bc}	9.31 ± 0.70^{bc}	2.21 ± 0.03^{bc}	7.03 ± 0.28^{bcd}	6.57 ± 0.26^{bcd}	3.27 ± 0.13^{ab}	1.66 ± 0.02^{ef}	2.74 ± 0.19^{c}
	16	0.39 ± 0.01^{d}	3.67 ± 0.14^{cd}	5.80 ± 0.25^{e}	1.75 ± 0.08^{cd}	7.01 ± 0.41^{a}	9.72 ± 0.60^{cd}	9.09 ± 0.41^{bc}	2.15 ± 0.02^{cd}	6.66 ± 0.31^{cde}	5.98 ± 0.43^{cde}	3.30 ± 0.17^{ab}	1.98 ± 0.10^{de}	2.68 ± 0.05^{c}
	20	0.36 ± 0.09^{d}	3.31 ± 0.12^{cde}	7.64 ± 0.50^{cde}	1.50 ± 0.08^{d}	4.45 ± 0.25^{d}	6.78 ± 0.21^{f}	8.23 ± 0.60^{c}	2.25 ± 0.05^{bc}	6.82 ± 0.46^{bcde}	5.49 ± 0.19^{cde}	3.56 ± 0.11^{ab}	2.20 ± 0.06^{cd}	2.71 ± 0.15^{c}
	24	0.27 ± 0.00^{de}	2.81 ± 0.16^{def}	6.07 ± 0.49^{de}	1.46 ± 0.04^{d}	4.91 ± 0.22^{cd}	8.54 ± 0.44^{de}	8.38 ± 0.57^{c}	2.00 ± 0.11^{cd}	6.25 ± 0.40^{de}	5.54 ± 0.30^{cde}	3.47 ± 0.24^{ab}	2.53 ± 0.21^{bc}	2.80 ± 0.21^{bc}
	28	0.19 ± 0.01^{e}	2.16 ± 0.08^{ef}	7.48 ± 0.49^{cde}	1.20 ± 0.12^{d}	2.56 ± 0.18^{e}	8.10 ± 0.63^{ef}	6.76 ± 0.23^{d}	1.97 ± 0.14^{cd}	5.84 ± 0.32^{e}	4.93 ± 0.35^{de}	3.41 ± 0.24^{ab}	2.73 ± 0.07^{ab}	2.45 ± 0.13^{c}
	32	0.17 ± 0.01^{e}	1.92 ± 0.12^{f}	7.56 ± 0.55^{cde}	1.08 ± 0.12^{d}	2.68 ± 0.16^{e}	7.60 ± 0.40^{ef}	6.45 ± 0.29^{d}	1.88 ± 0.14^{d}	5.87 ± 0.32^{e}	4.85 ± 0.22^{e}	3.58 ± 0.31^{ab}	2.93 ± 0.24^{a}	2.61 ± 0.07^{c}
TBHQ	0	1.01 ± 0.06ab	7.94 ± 0.95^{a}	13.60 ± 1.06^{a}	3.66 ± 0.49^{a}	6.51 ± 0.26^{a}	12.56 ± 0.55^{a}	11.08 ± 0.36^{a}	2.80 ± 0.11^{a}	8.39 ± 0.30^{a}	8.63 ± 0.23^{a}	3.78 ± 0.16^{a}	0.99 ± 0.03^{e}	4.07 ± 0.08^{a}
	4	1.17 ± 0.13^{a}	7.15 ± 0.34^{ab}	12.80 ± 0.75^{ab}	2.94 ± 0.20^{ab}	3.51 ± 0.14^{b}	12.69 ± 0.49^{a}	10.66 ± 0.42^{ab}	2.12 ± 0.10^{b}	7.43 ± 0.53^{ab}	6.86 ± 0.39^{b}	2.65 ± 0.22^{b}	0.95 ± 0.07^{e}	3.08 ± 0.12^{b}
	8	1.13 ± 0.05^{a}	6.88 ± 0.54^{ab}	11.96 ± 1.03^{abc}	2.80 ± 0.24^{bc}	3.04 ± 0.15^{bc}	12.70 ± 0.83^{a}	10.53 ± 0.37^{ab}	2.09 ± 0.09^{b}	7.11 ± 0.29^{bc}	6.66 ± 0.45^{bc}	2.66 ± 0.19^{b}	1.07 ± 0.01^{de}	2.95 ± 0.03^{b}
	12	0.88 ± 0.02^{bc}	5.19 ± 0.12^{cd}	9.78 ± 0.49^{cd}	2.26 ± 0.19^{bcd}	2.55 ± 0.13^{c}	9.55 ± 0.73^{bcd}	8.02 ± 0.76^{cde}	2.06 ± 0.24^{b}	5.63 ± 0.14^{d}	5.22 ± 0.28^{d}	2.34 ± 0.07^{b}	1.04 ± 0.01^{e}	2.27 ± 0.06^{d}
	16	0.93 ± 0.01^{b}	5.93 ± 0.33^{bc}	11.65 ± 0.62^{abc}	2.50 ± 0.26^{bcd}	3.18 ± 0.09^{bc}	10.94 ± 0.60^{ab}	9.68 ± 0.65^{abc}	2.09 ± 0.11^{b}	6.76 ± 0.21^{bcd}	5.77 ± 0.42^{bcd}	2.79 ± 0.15^{b}	1.41 ± 0.14^{cd}	3.05 ± 0.06^{b}
	20	0.83 ± 0.03^{bc}	5.44 ± 0.18^{cd}	11.16 ± 0.86^{abcd}	2.29 ± 0.09^{bcd}	2.83 ± 0.07^{c}	10.35 ± 0.52^{bc}	9.14 ± 0.37^{bcd}	1.89 ± 0.17^{b}	6.56 ± 0.52^{bcd}	6.05 ± 0.38^{bcd}	2.93 ± 0.28^{b}	1.60 ± 0.18^{bc}	2.74 ± 0.13^{bc}
	24	0.72 ± 0.01^{cd}	4.87 ± 0.14^{cd}	10.60 ± 0.37^{abcd}	2.18 ± 0.20^{bcd}	2.55 ± 0.12^{c}	9.50 ± 0.56^{bcd}	8.33 ± 0.33^{cde}	1.91 ± 0.14^{b}	6.22 ± 0.18^{bcd}	5.50 ± 0.29^{cd}	2.75 ± 0.25^{b}	1.68 ± 0.06^{abc}	2.78 ± 0.22^{bc}
	28	0.64 ± 0.00^{d}	4.58 ± 0.17^{cd}	9.72 ± 0.38^{cd}	2.00 ± 0.11^{cd}	2.63 ± 0.33^{c}	8.79 ± 0.63^{cd}	7.77 ± 0.60^{de}	1.90 ± 0.29^{b}	6.00 ± 0.26^{cd}	5.19 ± 0.14^{d}	3.01 ± 0.27^{b}	1.89 ± 0.10^{ab}	2.78 ± 0.17^{bc}
	32	0.57 ± 0.01^{d}	4.02 ± 0.22^{d}	9.01 ± 0.62^{d}	1.75 ± 0.08^{d}	1.85 ± 0.17^{d}	8.20 ± 0.42^{d}	6.99 ± 0.37^{e}	2.06 ± 0.23^{b}	5.87 ± 0.51^{cd}	4.98 ± 0.43^{d}	2.92 ± 0.28^{b}	1.98 ± 0.16^{a}	2.38 ± 0.20^{cd}
TP	0	1.01 ± 0.06^{b}	7.94 ± 0.95^{a}	13.60 ± 1.06^{a}	3.66 ± 0.49^{a}	6.51 ± 0.26^{a}	12.56 ± 0.55^{ab}	11.08 ± 0.36^{a}	2.80 ± 0.11^{a}	8.39 ± 0.30a	8.63 ± 0.23^{a}	3.78 ± 0.16^{a}	0.99 ± 0.03^{d}	4.07 ± 0.08^{a}
	4	1.25 ± 0.09^{a}	7.17 ± 0.33^{ab}	13.73 ± 0.84^{a}	2.80 ± 0.14^{b}	2.25 ± 0.22^{bc}	13.64 ± 0.40^{a}	10.92 ± 0.74^{a}	2.13 ± 0.14^{b}	7.71 ± 0.55^{ab}	7.22 ± 0.39^{b}	2.61 ± 0.17^{b}	0.95 ± 0.04^{d}	2.88 ± 0.11^{b}
	8	1.20 ± 0.05^{a}	7.10 ± 0.34^{abc}	13.44 ± 0.77^{a}	2.65 ± 0.22^{bc}	2.07 ± 0.15^{bcd}	12.10 ± 0.63^{ab}	9.97 ± 1.10^{ab}	2.29 ± 0.12^{b}	7.55 ± 0.29^{ab}	6.82 ± 0.38^{b}	2.60 ± 0.21^{b}	1.12 ± 0.02^{cd}	3.01 ± 0.11^{b}
	12	0.97 ± 0.09^{b}	6.34 ± 0.48^{bcd}	13.63 ± 0.63^{a}	2.53 ± 0.24^{bc}	2.16 ± 0.16^{bcd}	11.97 ± 0.58^{ab}	9.93 ± 0.38^{ab}	2.23 ± 0.23^{b}	7.45 ± 0.28^{abc}	6.94 ± 0.34^{b}	2.83 ± 0.29^{b}	1.28 ± 0.05^{cd}	2.56 ± 0.03^{b}
	16	0.94 ± 0.02^{bc}	6.03 ± 0.48^{bcd}	12.86 ± 0.84^{ab}	2.44 ± 0.13^{bc}	2.56 ± 0.27^{b}	11.54 ± 0.53^{bc}	9.57 ± 0.42^{abc}	2.21 ± 0.19^{b}	7.14 ± 0.41^{bcd}	6.59 ± 0.63^{bc}	2.90 ± 0.20^{b}	1.49 ± 0.04^{bc}	2.67 ± 0.14^{b}
	20	0.87 ± 0.04^{bcd}	5.54 ± 0.28^{cde}	11.81 ± 0.73^{abc}	2.23 ± 0.25^{bc}	2.05 ± 0.09^{bcd}	10.97 ± 0.65^{bcd}	9.70 ± 0.51^{ab}	2.06 ± 0.20^{b}	6.77 ± 0.14^{bcd}	6.51 ± 0.43^{bc}	3.11 ± 0.13^{ab}	1.66 ± 0.25^{ab}	2.88 ± 0.18^{b}
	24	0.79 ± 0.01^{cd}	5.09 ± 0.33^{de}	11.67 ± 0.58^{abc}	2.17 ± 0.19^{bc}	1.74 ± 0.12^{cd}	10.91 ± 0.51^{bcd}	9.14 ± 0.67^{abc}	2.24 ± 0.06^{b}	6.54 ± 0.35^{bcd}	6.28 ± 0.22^{bc}	3.08 ± 0.19^{b}	1.77 ± 0.09^{ab}	2.74 ± 0.05^{b}
	28	0.76 ± 0.01^{d}	4.44 ± 0.21^{e}	10.56 ± 0.48^{bc}	2.15 ± 0.21^{bc}	1.57 ± 0.11^{d}	9.72 ± 0.69^{cd}	8.31 ± 0.55^{bc}	1.96 ± 0.09^{b}	6.32 ± 0.31^{cd}	5.50 ± 0.26^{c}	3.15 ± 0.17^{ab}	1.86 ± 0.13^{ab}	2.75 ± 0.31^{b}
	32	0.56 ± 0.00^{e}	4.23 ± 0.30^{e}	9.48 ± 0.59^{c}	1.84 ± 0.07^{c}	1.82 ± 0.18^{cd}	9.08 ± 0.71^{d}	7.53 ± 0.33^{c}	2.08 ± 0.18^{b}	6.24 ± 0.29^{d}	5.33 ± 0.32^{c}	2.98 ± 0.26^{b}	2.01 ± 0.11^{a}	2.54 ± 0.19^{b}
DJE	0	1.01 ± 0.06^{bc}	7.94 ± 0.95^{a}	13.60 ± 1.06^{a}	3.66 ± 0.49^{a}	6.51 ± 0.26^{a}	12.56 ± 0.55^{ab}	11.08 ± 0.36^{a}	2.80 ± 0.11^{a}	8.39 ± 0.30^{a}	8.63 ± 0.23^{a}	3.78 ± 0.16^{a}	0.99 ± 0.03^{cd}	4.07 ± 0.08^{a}
	4	1.28 ± 0.07^{a}	7.22 ± 0.23^{ab}	14.01 ± 0.64^{a}	2.70 ± 0.30^{bc}	2.30 ± 0.09^{cd}	12.72 ± 0.72^{a}	10.84 ± 0.57^{ab}	2.16 ± 0.11^{b}	7.38 ± 0.69^{ab}	6.80 ± 0.41^{b}	2.39 ± 0.20^{c}	0.90 ± 0.05^{d}	2.56 ± 0.12^{c}
	8	1.17 ± 0.02^{a}	6.63 ± 0.16^{abc}	13.80 ± 0.60^{a}	2.68 ± 0.20^{bcd}	2.04 ± 0.12^{de}	12.28 ± 0.71^{ab}	10.64 ± 0.87^{ab}	2.05 ± 0.11^{b}	7.34 ± 0.40^{ab}	6.46 ± 0.38^{bc}	2.62 ± 0.15^{bc}	1.00 ± 0.03^{cd}	2.61 ± 0.07^{c}
	12	1.03 ± 0.02^{b}	6.52 ± 0.40^{abcd}	12.68 ± 0.70^{ab}	2.72 ± 0.10^{b}	1.63 ± 0.05^{e}	11.91 ± 0.61^{abc}	10.16 ± 0.54^{ab}	2.11 ± 0.08^{b}	7.05 ± 0.36^{ab}	6.46 ± 0.43^{bc}	2.71 ± 0.11^{bc}	1.25 ± 0.06^{bcd}	3.01 ± 0.17^{bc}
	16	0.88 ± 0.02^{cd}	6.08 ± 0.45^{bcd}	12.35 ± 0.79^{ab}	2.49 ± 0.26^{bcd}	2.49 ± 0.12^{c}	11.73 ± 0.60^{abc}	9.83 ± 0.38^{abc}	2.05 ± 0.11^{b}	7.05 ± 0.39^{ab}	6.47 ± 0.23^{bc}	2.92 ± 0.06^{bc}	1.37 ± 0.09^{abc}	2.94 ± 0.22^{bc}
	20	0.84 ± 0.01^{d}	5.51 ± 0.41^{cde}	12.19 ± 0.32^{ab}	2.39 ± 0.10^{bcd}	2.00 ± 0.06^{de}	10.44 ± 0.76^{bc}	9.21 ± 0.44^{abc}	1.95 ± 0.08^{b}	6.76 ± 0.28^{b}	6.07 ± 0.23^{bc}	2.70 ± 0.17^{bc}	1.47 ± 0.03^{ab}	3.11 ± 0.13^{b}
	24	0.82 ± 0.02^{d}	5.29 ± 0.18^{cde}	10.93 ± 0.51^{bc}	2.22 ± 0.07^{bcd}	1.93 ± 0.10^{de}	9.83 ± 0.80^{cd}	9.06 ± 0.59^{bc}	1.84 ± 0.05^{b}	6.68 ± 0.30^{b}	5.88 ± 0.49^{bc}	3.08 ± 0.15^{b}	1.59 ± 0.02^{ab}	3.29 ± 0.11^{b}
	28	0.80 ± 0.08^{d}	5.01 ± 0.33^{de}	9.21 ± 0.60^{c}	1.89 ± 0.04^{cd}	3.11 ± 0.09^{b}	9.31 ± 0.49^{d}	8.27 ± 0.55^{c}	2.09 ± 0.17^{b}	6.49 ± 0.71^{b}	5.73 ± 0.48^{bc}	2.78 ± 0.20^{bc}	1.68 ± 0.31^{b}	3.23 ± 0.20^{b}

(*continued on next page*)

Table 2 (*continued*)

Group	Time/h	TAG composition												
		LLnLn	LLLn	LLL	LnLP	OLLn	OLL	LLP	PLP	LOP	OOL	OOP	POP	OOO
	32	0.64 ± 0.01^{e}	4.34 ± 0.40^{e}	8.93 ± 0.25^{c}	1.89 ± 0.08 ^{cd}	1.95 ± 0.04^{de}	9.05 ± 0.48^{d}	7.99 ± 0.37^{c}	1.95 ± 0.10^{b}	5.96 ± 0.25^{b}	5.29 ± 0.33^{c}	2.93 ± 0.15^{bc}	1.75 ± 0.12^{a}	3.15 ± 0.14^{b}

Results are means ± SD of triplicate determinations. Column values in the same treatment with the different superscript lowercased letters are significantly different ($p < 0.05$). *Abbreviations:* TAGs, triglycerides; Ln, linolenic acid; L, linoleic acid; O, oleic acid; P, palmitic acid; TBHQ, *tert*-butylhydroquinone; TP, tea polyphenol; DJE, *Diaphragma juglandis* extract.

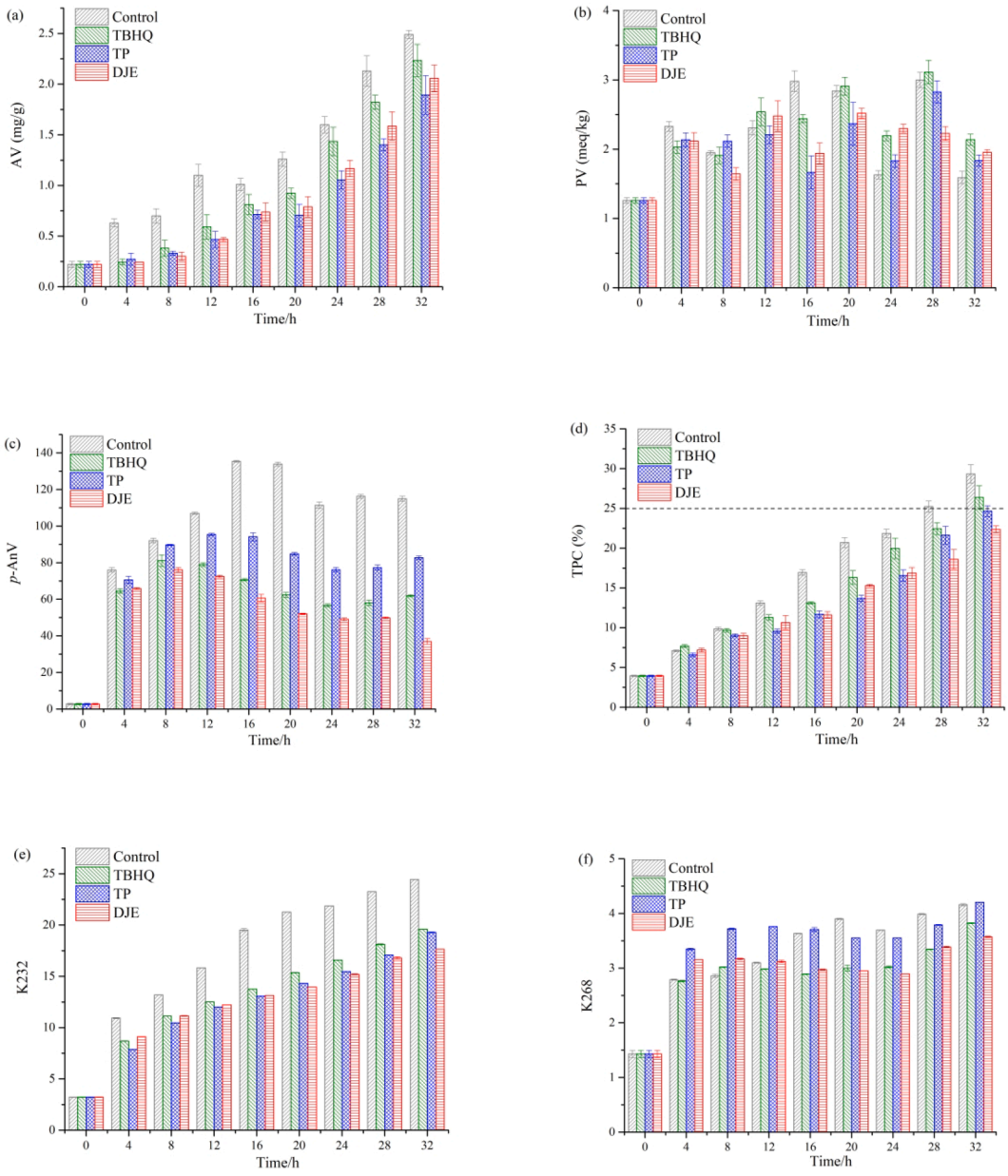

Fig. 2. Evolution of (a) AV, (b) PV, (c) *p*-AnV, (d) TPC, (e) K232, and (f) K268 in soybean oils with added different antioxidants during deep frying.

These results further elucidate that DJE could achieve better antioxidant effect than TBHQ and TP.

3.4. Effect of DJE on the oxidized and polymeric TAGs of frying oils

During frying, unsaturated lipids undergo oxidation to produce a wide variety of compounds. The new compounds differ from the major compounds originally present in oil or fats with respect to molecular weight and polarity. Oxidized and polymeric TAGs derived from oil deterioration comprise the majority of the non-volatile degradation products in TPC, which has been widely investigated in terms of its involvement in quality evaluation and health implications of frying oils (Dobarganes & Marquez-Ruiz, 2015). Table 3 displays the evolution of OxTGs, TGDs, and TGOs in soybean oils added with different antioxidants during deep frying.

OxTGs evolve mainly through secondary lipid oxidation during

Table 3
Evolution of OxTGs, TGDs, and TGOs (w/w, %) in soybean oils with added different antioxidants during deep frying.

Polar compound composition (%)	Time/h	Antioxidant			
		Control	TBHQ	TP	DJE
OxTGs	0	1.42 ± 0.01^{a}	1.42 ± 0.01^{a}	1.42 ± 0.01^{a}	1.42 ± 0.01^{a}
	4	2.56 ± 0.02^{b}	3.08 ± 0.03^{a}	2.65 ± 0.04^{b}	2.98 ± 0.07^{a}
	8	3.36 ± 0.09^{a}	3.45 ± 0.10^{a}	3.54 ± 0.10^{a}	3.49 ± 0.12^{a}
	12	4.25 ± 0.11^{a}	3.68 ± 0.06^{bc}	3.38 ± 0.09^{c}	3.80 ± 0.08^{b}
	16	4.90 ± 0.16^{a}	3.67 ± 0.08^{b}	3.91 ± 0.15^{b}	3.65 ± 0.13^{b}
	20	5.42 ± 0.02^{a}	3.84 ± 0.19^{b}	3.85 ± 0.22^{b}	3.88 ± 0.07^{b}
	24	5.10 ± 0.14^{a}	3.98 ± 0.08^{b}	4.03 ± 0.11^{b}	3.69 ± 0.10^{b}
	28	5.33 ± 0.30^{a}	3.76 ± 0.23^{bc}	4.47 ± 0.16^{b}	3.62 ± 0.06^{c}
	32	5.48 ± 0.08^{a}	3.66 ± 0.16^{bc}	4.30 ± 0.29^{b}	3.12 ± 0.12^{c}
TGDs	0	0.25 ± 0.00^{a}	0.25 ± 0.00^{a}	0.25 ± 0.00^{a}	0.25 ± 0.00^{a}
	4	2.08 ± 0.02^{a}	1.81 ± 0.12^{b}	1.32 ± 0.03^{c}	1.66 ± 0.03^{b}
	8	3.22 ± 0.07^{a}	2.72 ± 0.07^{b}	2.26 ± 0.02^{c}	2.46 ± 0.08^{c}
	12	4.49 ± 0.03^{a}	3.38 ± 0.15^{b}	2.62 ± 0.10^{c}	3.08 ± 0.07^{b}
	16	5.81 ± 0.10^{a}	3.94 ± 0.10^{b}	3.34 ± 0.06^{c}	3.45 ± 0.13^{c}
	20	7.02 ± 0.06^{a}	4.96 ± 0.24^{b}	3.98 ± 0.14^{c}	4.90 ± 0.10^{b}
	24	7.36 ± 0.05^{a}	6.27 ± 0.08^{b}	4.82 ± 0.09^{d}	5.17 ± 0.05^{c}
	28	8.47 ± 0.21^{a}	6.54 ± 0.41^{b}	6.11 ± 0.16^{bc}	5.42 ± 0.22^{c}
	32	9.42 ± 0.16^{a}	7.49 ± 0.17^{b}	7.01 ± 0.32^{bc}	6.24 ± 0.39^{c}
TGOs	0	0.16 ± 0.01^{a}	0.16 ± 0.01^{a}	0.16 ± 0.01^{a}	0.16 ± 0.01^{a}
	4	0.69 ± 0.07^{a}	0.47 ± 0.05^{ab}	0.43 ± 0.05^{b}	0.42 ± 0.08^{b}
	8	1.23 ± 0.10^{a}	0.95 ± 0.10^{ab}	0.81 ± 0.10^{b}	0.77 ± 0.05^{b}
	12	1.99 ± 0.00^{a}	1.29 ± 0.07^{b}	1.11 ± 0.07^{b}	1.07 ± 0.10^{b}
	16	3.52 ± 0.03^{a}	1.80 ± 0.06^{b}	1.49 ± 0.12^{bc}	1.32 ± 0.17^{c}
	20	5.09 ± 0.16^{a}	2.53 ± 0.18^{b}	2.09 ± 0.08^{bc}	1.89 ± 0.06^{c}
	24	5.77 ± 0.07^{a}	3.14 ± 0.11^{b}	2.81 ± 0.13^{b}	2.20 ± 0.08^{c}
	28	7.24 ± 0.11^{a}	3.92 ± 0.20^{b}	4.02 ± 0.09^{b}	2.55 ± 0.05^{c}
	32	9.20 ± 0.18^{a}	4.94 ± 0.19^{b}	4.84 ± 0.21^{b}	3.26 ± 0.14^{c}

Results are presented as means ± SD. Values with different superscript letters superscript in the same row are significantly different between groups ($p < 0.05$). *Abbreviations:* TGOs, triglyceride oligomers; TGDs, triglyceride dimers; OxTGs, oxidized triglyceride monomers; TBHQ, *tert*-butylhydroquinone; TP, tea polyphenol; DJE, *Diaphragma juglandis* extract.

frying and are TAGs with at least one of their fatty acyl groups oxidized, such as hydroxyl, keto, and epoxy TAGs (Xu et al., 2019). Their molecular weights are similar to non-altered TAGs. OxTGs have attracted considerable attention due to their high absorbability in vivo and negative health effects on some organisms (Khor et al., 2020; Li et al., 2022). As illustrated in Table 3, the OxTG levels in all oil samples increased at first and then decreased slightly during the frying process. Xu et al. (2019) found that OxTGs could be involved in the polymerization reaction during heating, leading to a decrease in OxTGs. Moreover, the greatest increase in OxTGs occurred in the control group after 32 h of frying, from 1.42% before frying to 5.48%, which confirmed that the unprotected oil is more susceptible to oxidation than oils added with the antioxidants during frying. The delaying effects of DJE was the strongest; OxTGs only increased by 1.72, which was significantly lower ($p < 0.05$) than the values observed when TBHQ (2.24) and TP (2.88) were used.

TGPs, including TGOs and TGDs, are the most specific substances in used frying oils and are generated by the polymerization of oxidized TAGs with the linkages of C—C, C—O, and O—O covalent bonds (Chen et al., 2021). Their molecular weights are greater than those of the original TAGs. For nutritional effect, David, González-Muñoz, Benedí, Bastida, and Sánchez-Muniz (2010) reported that the presence of TGPs in oxidized oils could lead to intestinal oxidative stress in animals. As shown in Table 3, the initial TGO (0.16%) and TGD (0.25%) contents in fresh oil were low and did not exceed 0.3% (Xu et al., 2020). The TGO and TGD contents in the oils of the four sample groups increased as frying time lengthened. The increase was greater in the control group than in the other groups, indicating that adding antioxidants could effectively delay the formation of TGPs. After the experiment, the TGP contents in control, TBHQ, TP, and DJE oils were 18.62%, 12.43%, 11.85%, and 9.50%, respectively. The upper limit of TGPs between 10% and 16% has been suggested by the European regulatory authorities (Chen et al., 2021). Given that 10% was set as the frying oil rejection for TGPs, the oil added with DJE was the only candidate that did not exceed the upper limit, which clearly showed that DJE oil remained stable even after 32 h of frying.

Overall, DJE could effectively reduce the oxidized and polymeric TAG formation during deep frying. This finding could be due to the powerful antioxidant capacities and synergistic interactions of the polyphenols (Wu et al., 2021b). DJE was also less volatile and more stable than synthetic antioxidants (Kmiecik, Gramza–Michalowska, & Korczak, 2018). In addition, natural polyphenols could act as polymerization inhibitor that underwent acid-catalyzed decomposition reactions with activation energy lower than that of the formation of polymeric TAGs under the frying conditions (Gertz, 2004).

3.5. *Effect of DJE on the oxidation products of frying oils by ^{1}H NMR*

^{1}H NMR is a powerful tool used to monitor the oxidative status of frying oil (Li, Li, Wang, & Liu, 2020; Martínez-Yusta, Goicoechea, & Guillén, 2014). Hydroperoxides are unstable and can easily break into secondary oxidation compounds at frying temperature because of their diverse structures. Some of these compounds, including aldehydes and alcohols, could be observed by ^{1}H NMR. These groups could be either in small molecules or in truncated acyl groups of TAG structures (Guillén & Uriarte, 2012). The effects of different antioxidants on the oxidation products of frying oils are shown in Fig. 3. The production of these compounds is closely related to the original lipid composition.

Fig. 3a-d shows that the principal aldehydes of frying oil are *n*-alkanals, (E)-2-alkenals, and (*E,E*)-2,4-alkadienals, with 4-oxo-alkanals in smaller concentrations than the other aldehydes. As the frying duration increased, the concentrations of the aldehydes first increased and then leveled off, consistent with the finding in prior studies (Martínez-Yusta & Guillén, 2014). After adding antioxidants, the formation of aldehydes was significantly delayed, and the performance of DJE was better for (*E*)-2-alkenals, (*E,E*)-2,4-alkadienals, and 4-oxo-alkanals. Similar phenomena were obtained by Wu et al. (2021a); they stated that adding *Camellia oleifera* seed cake polyphenols extract could effectively delay the increase in these aldehydes in refined soybean oil during frying. Natural polyphenols are primarily known to be strong free radical scavengers and also regarded as good carbonyl scavengers that trap toxicologically relevant aldehydes produced during frying (Wu et al., 2019; Zamora et al., 2016). The latter is influenced by the

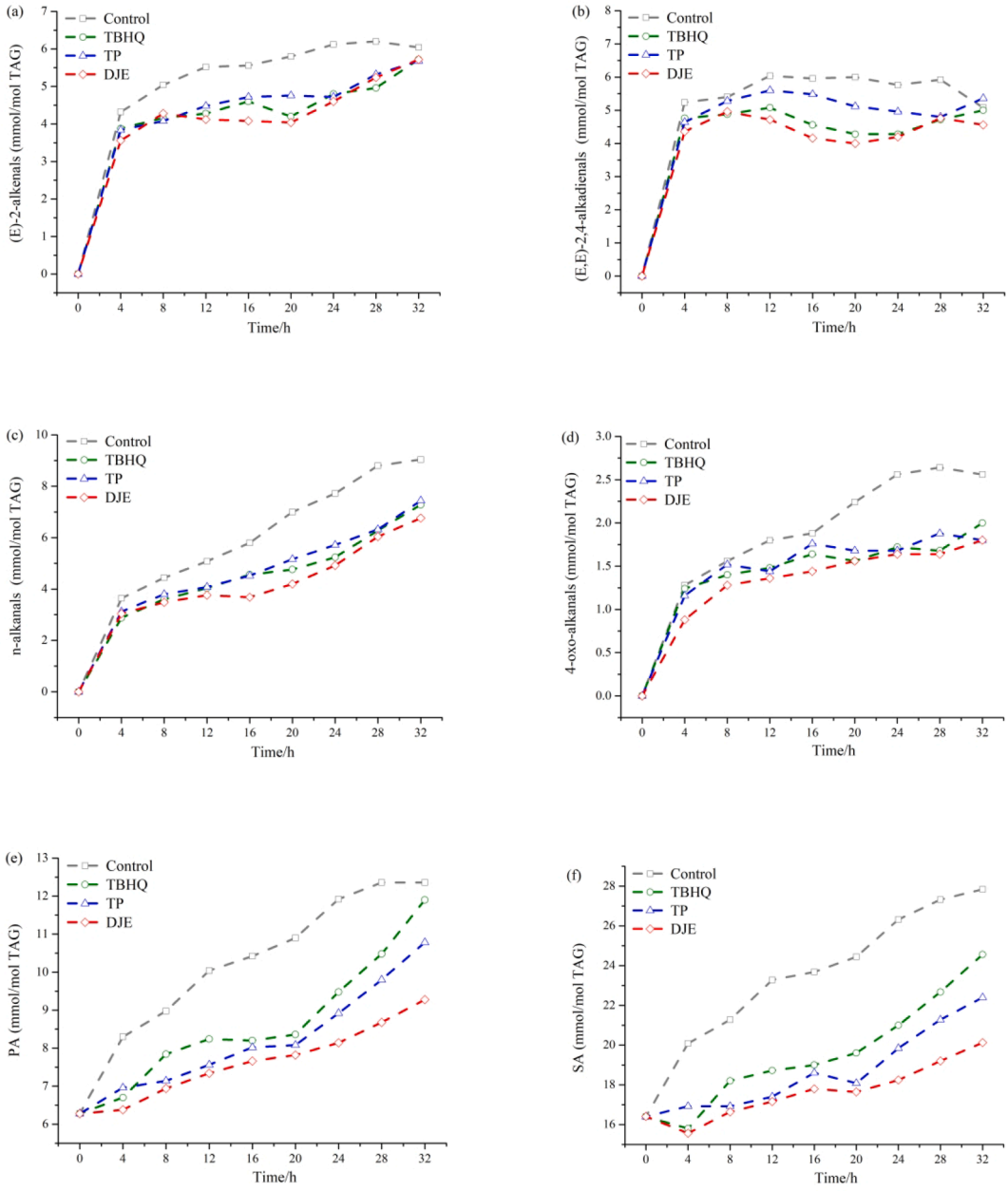

Fig. 3. Evolution of the concentration of oxidation products in soybean oils with added different antioxidants during deep frying by ^{1}H NMR: (a) (*E*)-2-alkenals; (b) (*E,E*)-2,4-alkadienals; (c) *n*-alkanals; (d) 4-oxo-alkanals; (e) PA; (f) SA.

chemical structure of polyphenols, and the reaction mainly occurs in m-diphenols or in the parts with m-diphenol groups in complex polyphenols (Zamora & Hidalgo, 2018). Fig. 3e-f shows the changes of the concentration of alcohols in frying medium. The concentration of alcohols also increased with increasing heating time, and the levels of secondary alcohols (SA) were higher than those of primary alcohols (PA). After 32 h of frying, the levels of PA and SA in oils treated with DJE increased the least, which were lower than that of control sample. These findings further proved that DJE had excellent inhibitory effect against lipid oxidation during deep frying.

4. Conclusions

This study successfully applied DJE as antioxidant to delay the oxidation of refined soybean oil during deep frying. The thermal oxidation of unsaturated TAGs was effectively delayed after adding DJE, especially OLL and LLP. In terms of *p*-AnV, OxTGs, TGOs, TGDs, (*E*)-2-alkenals, (*E,E*)-2,4-alkadienals, 4-oxo-alkanals, primary alcohols, and secondary alcohols, the oils treated with DJE had lower values than the control oil and the oils added with the other antioxidants. Given that 10% is taken as the frying oil rejection for TGPs, the oil added with DJE was the only candidate that did not exceed the upper limit. Hence, DJE exhibited superior properties for enhancing the oxidative stability of frying oil. As many types of polyphenols were identified in DJE, future work will be required to elucidate the detailed and specific scientific information on the antioxidant mechanism of these polyphenols under actual frying conditions.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence

the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fochx.2022.100359.

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