Research Article

Frying performance of the hull oil unsaponifiable matter of *Pistacia atlantica* subsp. *mutica*

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The anti-rancidity effect of the hull oil unsaponifiable matter (USM, 100 ppm) of *Pistacia atlantica* subsp. *mutica* (Bene) on sunflower oil (SFO) during frying at 180 °C was investigated and compared to that of *tert*-butylhydroquinone (TBHQ, 100 ppm). The unsaponifiable constituents of the Bene hull oil (BHO) were separated into hydrocarbons (3.7%), carotenes (3.6%), tocopherols and tocotrienols (24.7%), linear and triterpenic alcohols (0.9%), methylsterols (5.7%), sterols (3.2%), triterpenic dialcohols (4.7%), and triterpenic dialcohol methylesters (4.5%), by means of silica gel TLC. The results obtained from the measurements of total polar compounds, conjugated diene value, carbonyl value, and acid value during 32 h of frying showed that the frying stability of SFO improves more in the presence of the USM of BHO than in the presence of TBHQ. Moreover, compared to TBHQ, the USM had a better protective effect on the indigenous tocopherols of SFO during frying.

Keywords: Antioxidant / Bene hull oil / Frying process / *Pistacia atlantica* subsp. *mutica* / Rancidity / Unsaponifiable matter

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1 Introduction

Antioxidants are major ingredients that protect the quality of oils and fats by retarding oxidation. The low-cost synthetic antioxidants propyl gallate (PG), butylated hydroxytoluene (BHT), butylated hydroxyanisole (BHA) and *tert*-butylhydroquinone (TBHQ) are often used to retard lipid oxidation. They are very effective during storage and transport of oils and fats, but are less effective at frying temperatures due to their volatility and decomposition [1]. Moreover, there are some serious problems concerning the safety and toxicity of such synthetic antioxidants related to their metabolism and possible absorption and accumulation in the body organs and tissues [2, 3]. A consumer-friendly way of improving oxidative stability of frying oils and fats is the addition of natural antioxidants.

Pistacia atlantica subsp. *mutica* widely grows in the Zagrossian region of Iran at 600–3000 m above sea level [4]. Its fruits, which are called "Bene" in Iran, are round to oval, somewhat flat, and 0.5–0.7 cm in diameter. Bene have a wooden hard shell covered with a rather dry hull, which can be easily removed by pressing between fingers. This soft hull is dark green in color, comprises ~24% of the whole fruit (~25% kernel and ~51% hard shell) and yields up to ~30% oil [5]. Previous studies on *P. atlantica* dealt with the chemical composition and oxidative stability of the kernel oil from its current subspecies in Iran [6], the oxidative stability and antioxidant activity of the hull oil from *P. atlantica* subsp. *mutica* [7], and the anti-rancidity effect of Bene hull oil (BHO) compared with sesame and rice bran oils during the frying process of sunflower oil (SFO) [8]. Among the common vegetable oils, BHO contains exceptional amounts of unsaponifiable matter (USM, ~6.5%) [7]. The USM fraction of vegetable oils naturally contains hydrocarbons, terpene alcohols, sterols and tocopherols, and typically constitutes 0.5–2.5% of the vegetable oils, although some vegetable oils have exceptional amounts of 5–6% [9]. The effectiveness of the USM fraction of vegetable oils in retarding oil deterioration has been studied by many investigators [10–13].

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In this research, the anti-rancidity effect of USM from BHO on SFO during frying at 180 °C was investigated.

2 Materials and methods

2.1 Materials

The ripe fruits of Bene were collected from the fields of Islamabad in the Ilam province. Refined, bleached, and deodorized SFO with no added antioxidants was supplied by Segol (Nishaboor, Iran). The oil samples were stored at –18 °C until analysis. Fatty acid methyl ester (FAME) standards and all chemicals and solvents used in this study were of analytical reagent grade and supplied by Merck (Darmstadt, Germany) and Sigma-Aldrich (St. Louis, MO, USA).

2.2 Oil extraction

After drying in the shade, the dark green soft hulls of Bene fruits were separated from the dark brown hard shells. The hulls were ground in a grinder. The powders were extracted with *n*-hexane (1 : 4 wt/vol) by agitation in a dark place at ambient temperature for 48 h. The solvent was evaporated *in vacuo* at 40 °C to dryness.

2.3 USM extraction

In a volume flask, 5 g of the crude oil was saponified with 50 mL 1 N ethanolic KOH. Potassium hydroxide in a capped flask was heated in an oven for 1 h at 95 °C. After cooling, 100 mL of distilled water was added and mixed. The resulting solution was extracted two times with 100 mL diethyl ether. The upper organic layers were combined and washed twice with 75 mL distilled water, once with 100 mL 0.5 N ethanolic KOH, and then 100 mL distilled water until neutrality. The organic layer was then separated and dried over Na_2SO_4. After filtration of this solution, the solvent was evaporated to dryness under vacuum at 45 °C. To purify more effectively, the dry USM was dissolved with chloroform and, after filtration, was evaporated to dryness under vacuum at 45 °C [14]. The yield of USM extraction was about 6.5 wt-%.

2.4 Thin-layer chromatography fractionation of the USM

A chloroform solution (5%) of the USM (50 mg/plate) was streaked using a thin-layer chromatography (TLC) applicator (CAMAG, Muttenz, Switzerland) along a line at 1 cm from the edges of a 20 cm × 20 cm plate coated with a 0.5-mm layer of silica gel (G), which had been activated for 15 min at 110 °C. The plate was developed in ascending direction for 15 cm with the solvent system *n*-hexane/diethyl ether (7 : 3, vol/vol). The developed plate was then dried with a hairdryer, and visualization of the chromatogram was carried out by spraying a saturated solution of $K_2Cr_2O_7$ in H_2SO_4 (80%) and then carbonating at 130 °C for 25 min. Fractions with the same R_f were carefully scraped from the plate and thoroughly extracted with chloroform; then the extract was filtered through a 0.45-μm membrane filter (Millipore, HVLP) and evaporated to near dryness *in vacuo* below 40 °C. The residue was weighed to determine the yield of each fraction [15].

2.5 Frying process

Potatoes were peeled and cut into pieces (7.0 cm × 0.5 cm × 0.3 cm) and submerged in water until needed. Potato pieces were fried in the SFO. The oil (2.5 L) was placed in a 2.5-L capacity benchtop deep-fryer (Tefal model 1250; France) and heated to 180 °C. Potato pieces were fried in 20-g batches at constant frying temperature. The batches were fried at 7-min intervals for 8 h per day for four consecutive days. At the end of each 4-h period, about 20 g of the frying oil was filtered into a screw-cap vial and promptly stored in the dark at 4 °C until use. The volume of oil was not replenished during the frying process. Frying experiments were conducted in duplicate on each frying medium [16].

2.6 Analytical methods

The fatty acid composition of the SFO was determined by gas-liquid chromatography and was reported in relative area percentages. Fatty acids were transesterified into their corresponding FAME by vigorous shaking of a solution of oil in hexane (0.3 g in 7 mL) with 2 mL of 7 N methanolic potassium hydroxide at 50 °C for 10 min. The FAME were identified using an HP-5890 chromatograph (Hewlett-Packard, CA, USA) equipped with a CP-SIL 88 (Supelco, Bellefonte, PA, USA) capillary column of fused silica, 60 m in length × 0.22 mm I.D., 0.2 μm film thickness, and a flame ionization detector (FID). Nitrogen was used as carrier gas with a flow rate of 0.75 mL/min. The oven temperature was maintained at 198 °C and that of the injector and detector at 250 °C [17].

The spectrophotometric method of the International Dairy Federation as described by Shantha and Decker [18] was used to determine peroxide values (PV, thiocyanate method). Acid values (AV) were determined according to the AOCS Official Method Cd 3d-63 [19]. Total tocopherol (TT) contents were determined according to the colorimetric method described by Wong et al. [20]. Total polar compound (TPC) contents were determined according to the economical micro method developed by Schulte [21].

Carbonyl values (CV) of the oils were measured according to the method developed by Endo et al. [22] using 2-propanol and 2,4-decadienal as solvent and standard, respectively [23]. The conjugated diene value (CDV) was measured spectrophotometrically at 234 nm and read against HPLC-grade hexane as a blank. The oil samples were diluted to 1 : 600 with hexane. An extinction coefficient of 29,000 mol/L was utilized

to quantify the concentration of conjugated dienes formed during oxidation [24].

2.7 Statistical analysis

All experiments and measurements were carried out in triplicate, and the data were subjected to analysis of variance (ANOVA). ANOVA and regression analyses were performed according to the MStatC and Excel software. Significant differences between means were determined by Duncan's multiple range tests; p values less than 0.05 were considered statistically significant.

3 Results and discussion

The initial chemical characteristics of the SFO are shown in Table 1. The fatty acid composition of the SFO consisted mainly of oleic acid (18:1, 28.0%) and linoleic acid (18:2, 54.2%), in accordance with those reported in the literature for SFO. The PV and AV of the SFO were 0.3 meq/kg and 0.2 mg/g, respectively, indicating that the SFO was unoxidized and of high initial quality. The SFO examined in this study had a considerable content of tocopherols (740.3 mg/kg), so that its TT content was higher than those reported of common vegetable oils with an average of about 600 mg/kg [25].

The unsaponifiable constituents of the BHO were separated into hydrocarbons, carotenes, tocopherols and tocotrienols, linear and triterpenic alcohols (4,4'-dimethylsterols), methylsterols (4-methylsterols), sterols (desmethylsterols), triterpenic dialcohols, and triterpenic dialcohol methylesters by means of silica gel TLC (Fig. 1). Tocopherols and tocotrienols were the major constituents (24.7%) of the USM of BHO. These compounds are particularly important functional constituents of the USM of vegetable oils. They display antioxidant properties and they are active as vitamin E, which makes them particularly important for human health [26]. The second major constituents of the USM with a total yield of about 20% were the sterols, methylsterols, triterpenic alcohols and triterpenic dialcohols. These steroidal phytochemicals contained in vegetable oils are hypocholesterolemic and may also be potent antioxidants [27]. The USM contained about 3.7% hydrocarbons. These compounds are mainly linear saturated chains of 15–33 carbon atoms; in food matrices, most of the hydrocarbons have an odd number of carbon atoms and are mainly constituted by squalene [26]. It has been indicated that squalene has a potential to retard the degradation of unsaturated fatty acids in lipid systems heated at high temperatures [28]. Carotenes constituted about 3.6% of the USM. These compounds have been shown to protect lipids from free-radical autoxidation by reacting with peroxyl radicals, thereby inhibiting propagation and promoting termination of the oxidation chain reaction [29, 30], and also to be effective quenchers of singlet oxygen during inhibition of photooxidation [31].

Figure 2 shows the TPC content of the SFO as affected by 100 ppm of TBHQ or USM of BHO during frying at 180 °C. There was no statistically significant difference between the initial TPC content of the SFO and those of the SFO containing TBHQ or USM of BHO. The TPC contents increased linearly with the frying time, with high correlation coefficients

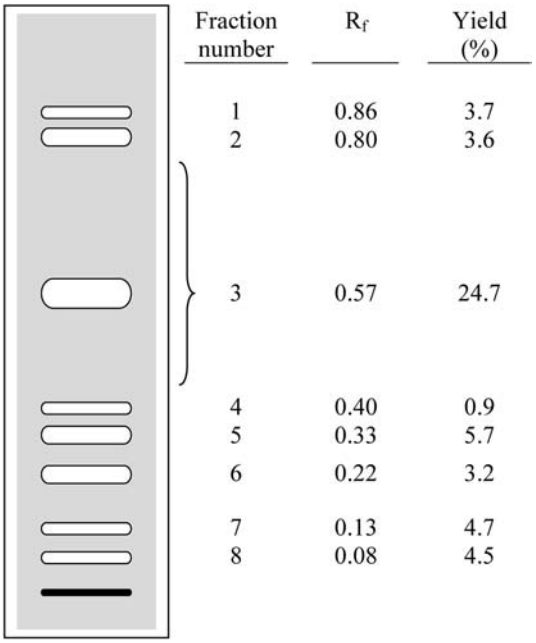

Figure 1. TLC fractionation of the USM of BHO: (1) hydrocarbons; (2) carotenes; FAME (unsaponifiable impurity); (3) tocopherols and tocotrienols; (4) linear and triterpenic alcohols (4,4'-dimethylsterols); (5) methylsterols (4-methylsterols); (6) sterols (desmethylsterols); (7) triterpenic dialcohols; (8) triterpenic dialcohol methyl esters (unsaponifiable impurity). The mobile phase was *n*-hexane/diethyl ether (7 : 3, vol/vol); the TLC layer was sprayed with a saturated solution of $K_2Cr_2O_7$ in H_2SO_4 (80%) and then carbonized at 130 °C for 25 min.

Table 1. The initial chemical characteristics of SFO.

Fatty acids	Amount [%]
14:0	0.1 ± 0.2
16:0	8.5 ± 0.2
16:1	0.2 ± 0.1
18:0	4.8 ± 0.1
18:1	28.0 ± 0.0
18:2	54.2 ± 0.2
18:3	2.8 ± 0.2
20:1	0.4 ± 0.1
22:0	0.9 ± 0.1
Peroxide value [meq O_2/kg oil]	0.3 ± 0.1
Acid value [mg KOH/g oil]	0.2 ± 0.0
Total tocopherol content [mg α-tocopherol/kg oil]	740.3 ± 14.1

(R^2 >0.99). Research has shown that the fraction of polar compounds isolated from oxidized oils is toxic to laboratory animals [32]. Therefore, it has been recommended that frying oils containing more than 24–27% of TPC content should be discarded [33]. Both the SFO and the SFO containing TBHQ reached the discarding range of TPC content during frying, but the SFO containing USM did not. Assuming that the limit of acceptance for the TPC content is 24%, the time required to reach this limit was considered as a measure of frying stability. As can be seen in Fig. 2, SFO showed a frying stability significantly lower (25.4 h) than that of SFO containing TBHQ or USM (32.1 and 36.7 h, respectively). It was interesting to find that the frying stability of SFO increased significantly more in the presence of USM than in the presence of TBHQ.

The CDV is a good classical index of primary oxidative changes in lipids under frying conditions [34]. This quantitative criterion of lipid oxidation linearly increased, in parallel to an increase in frying time, so that the CDV of SFO showed an increase of 481% (61.6 mmol/L) after 32 h of frying (Table 2). This amount for the SFO containing TBHQ and USM was 393% (47.8 mmol/L) and 378% (48.7 mmol/L), respectively, indicating their antioxidative potential and a relatively better capability of USM for resistance to the production of conjugated diene hydroperoxides under the frying process conditions.

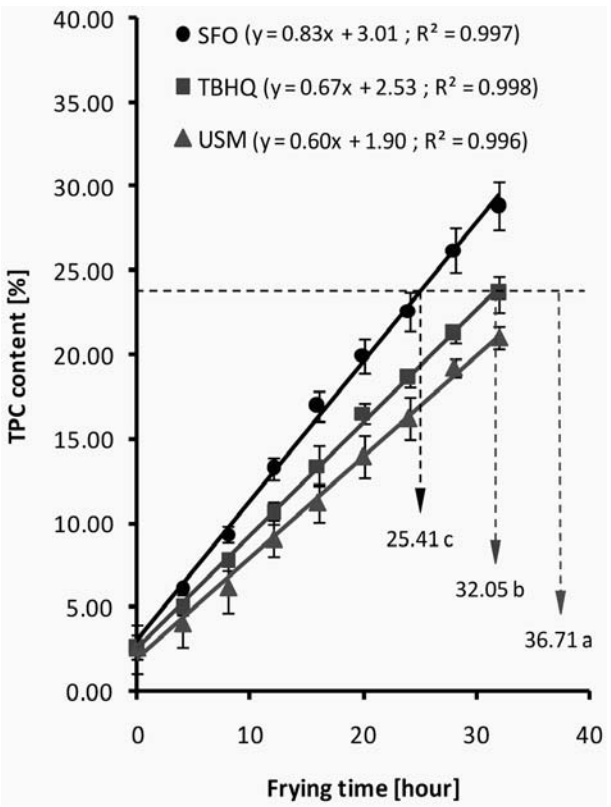

Figure 2. TPC content of SFO as affected by TBHQ (100 ppm) and the USM (100 ppm) of BHO during the frying process at 180 °C. The quantities with the same lowercase letters are not significantly different at p <0.05.

The CV does not measure primary products of oxidation (hydroperoxides) but secondary decomposition products such as aldehydes and ketones [35]. The determination of carbonyl compounds in heated and frying oils is very important for evaluating their quality because these compounds often contribute to rancid and unpleasant flavors and reduce the nutritional value of fried foods [22, 36]. During the frying process, the CV of SFO with an increase of 798% linearly changed from 7.9 to 70.9 μmol/g (Table 2). The rate of change in the CV of the SFO considerably decreased in the presence of TBHQ or USM, resulting in increased percentages of the CV of 318 and 304, respectively, after 32 h of frying.

Prior to performing the frying process, the SFO had a TT content of 730.0 mg/kg, and the addition of 100 ppm of TBHQ or USM caused no statistically significant changes in the initial TT content of the SFO (Table 2). The TT content of SFO decreased by 67% to 241.0 mg/kg at the end of the frying process. The decrease for SFO containing TBHQ or USM was about 45 and 40%, respectively, indicating the protective effect of USM and TBHQ on the tocopherols of SFO.

Changes in AV of SFO in the presence of TBHQ or USM during frying at 180 °C are shown in Fig. 3. AV, which is used to assess the degradation of the frying oil, increased exponentially for SFO from hour 0 to hour 32 of frying. The steady

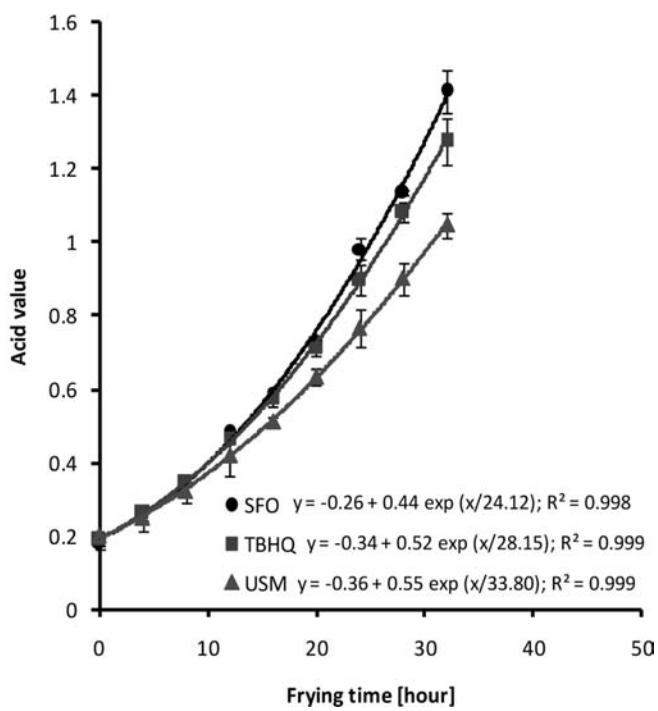

Figure 3. AV of SFO as affected by TBHQ (100 ppm) and the USM (100 ppm) of BHO during the frying process at 180 °C.

Table 2. CDV, CV, and TT content of SFO as affected by TBHQ (100 ppm) and the USM (100 ppm) of BHO during the frying process at 180 °C.[†]

Time [h]	CDV [mmol/L]			CV [μmol/g]			TT [mg/kg]		
	SFO	TBHQ	USM	SFO	TBHQ	USM	SFO	TBHQ	USM
0	$10.6 \pm 0.5^{i,A}$	$9.7 \pm 0.3^{i,A}$	$10.2 \pm 0.9^{h,A}$	$7.9 \pm 0.5^{g,A}$	$8.5 \pm 0.4^{h,A}$	$8.2 \pm 0.2^{g,A}$	$730.0 \pm 12.2^{a,A}$	$725.3 \pm 16.7^{a,A}$	$733.5 \pm 17.0^{a,A}$
4	$17.3 \pm 0.4^{h,A}$	$14.2 \pm 0.5^{h,B}$	$14.0 \pm 0.5^{g,B}$	$13.4 \pm 0.6^{f,B}$	$16.1 \pm 0.7^{g,A}$	$10.0 \pm 0.6^{f,C}$	$592.1 \pm 10.9^{b,B}$	$674.2 \pm 21.5^{b,A}$	$688.1 \pm 16.1^{ab,A}$
8	$23.7 \pm 0.1^{g,A}$	$18.5 \pm 0.7^{g,B}$	$19.8 \pm 0.4^{f,B}$	$22.2 \pm 1.1^{e,A}$	$18.1 \pm 0.5^{f,B}$	$15.3 \pm 0.6^{e,C}$	$523.5 \pm 4.7^{c,B}$	$653.6 \pm 23.3^{b,A}$	$660.8 \pm 12.1^{b,A}$
12	$32.6 \pm 0.4^{f,A}$	$24.2 \pm 1.4^{f,B}$	$26.3 \pm 0.9^{e,B}$	$24.5 \pm 1.2^{e,A}$	$23.6 \pm 1.2^{e,A}$	$17.0 \pm 1.6^{e,B}$	$420.4 \pm 2.6^{d,B}$	$612.7 \pm 22.9^{c,A}$	$616.5 \pm 4.4^{c,A}$
16	$34.8 \pm 0.9^{e,A}$	$27.4 \pm 0.6^{e,C}$	$30.4 \pm 1.3^{d,B}$	$35.7 \pm 1.4^{d,A}$	$24.5 \pm 1.7^{de,B}$	$21.9 \pm 1.1^{d,B}$	$395.8 \pm 14.1^{de,C}$	$539.2 \pm 26.2^{d,B}$	$606.3 \pm 11.5^{c,A}$
20	$45.5 \pm 0.0^{d,A}$	$34.1 \pm 1.1^{d,B}$	$37.0 \pm 0.8^{c,B}$	$39.4 \pm 2.4^{d,A}$	$27.6 \pm 1.0^{cd,B}$	$23.1 \pm 1.6^{cd,C}$	$364.6 \pm 10.1^{e,B}$	$513.4 \pm 22.1^{de,A}$	$538.8 \pm 13.0^{d,A}$
24	$48.7 \pm 0.9^{c,A}$	$38.8 \pm 1.0^{c,B}$	$39.3 \pm 1.0^{c,B}$	$47.6 \pm 2.4^{c,A}$	$30.3 \pm 0.8^{bc,B}$	$25.3 \pm 1.8^{bc,C}$	$319.0 \pm 16.5^{f,B}$	$489.3 \pm 32.9^{ef,A}$	$518.3 \pm 15.2^{d,A}$
28	$58.5 \pm 0.9^{b,A}$	$43.7 \pm 0.7^{b,B}$	$45.2 \pm 0.9^{b,B}$	$58.1 \pm 2.6^{b,A}$	$32.1 \pm 1.3^{ab,B}$	$30.2 \pm 1.7^{ab,B}$	$284.5 \pm 1.6^{g,B}$	$458.5 \pm 33.3^{ef,A}$	$454.9 \pm 5.9^{e,A}$
32	$61.6 \pm 1.2^{a,A}$	$47.8 \pm 1.1^{a,B}$	$48.7 \pm 1.3^{a,B}$	$70.9 \pm 1.5^{a,A}$	$35.5 \pm 1.7^{a,B}$	$33.1 \pm 1.8^{a,B}$	$241.0 \pm 7.2^{h,B}$	$397.6 \pm 31.6^{f,A}$	$437.8 \pm 5.9^{e,A}$

[†] Means ± SD (standard deviation) within a column with the same lowercase letters are not significantly different at $p < 0.05$. For each parameter experimented, means ± SD within a row with the same uppercase letters are not significantly different at $p < 0.05$.

rise in the AV can be attributed partly to hydrolysis of triacylglycerols and partly to the component carboxyl groups present in oxidative and/or polymeric products of frying [16, 37, 38]. As can be seen, USM and TBHQ showed exponential changes in the AV of the SFO as well. This indicates that the USM could reduce the oxidative and thermal degradation taking place in unsaturated fatty acids in a better manner than TBHQ.

4 Conclusions

Hydrolytic and oxidative rancidities are the most important occurrences in frying processes and lead to the development of various off-flavors and off-odors in fried foods and oils. Our results in this study indicated that hydrolytic reactions and also the creation of primary and secondary products of lipid oxidation during the frying process of SFO are retarded more in the presence of USM of BHO than in the presence of the powerful synthetic antioxidant TBHQ. Moreover, compared to TBHQ, USM had a better protective effect on the indigenous tocopherols of SFO during the frying process.

Conflict of interest statement

The authors have declared no conflict of interest.

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