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Original article

Quality assessment of refined oil blends during repeated deep frying monitored by SPME–GC–EIMS, GC and chemometrics

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Summary The aim of this study was to investigate the effect of the refined palm oil addition (20%) on the fatty acid and sterol compositions of refined olive oil or refined soya bean oil and also to investigate the formation of total polar compounds and volatile compounds in these oil blends during fifty successive deep-frying sessions of potato fries at 180 °C. The blend of refined olive oil and refined palm oil exhibited a higher chemical stability during the frying process than that of refined soya bean oil and refined palm oil. Indeed, the total polar compounds and volatile compounds formed, especially 2,4-decadienal, were found to be relatively increased in the refined soya bean oil/refined palm oil blend reaching 36.50% and 46.70%, respectively, after fifty deep-frying sessions. Moreover, the degradation of linoleic acid and β-sitosterol was significantly ($P < 0.05$) observed for the refined soya bean oil/refined palm oil blend. The results have proven that the proper blending of monounsaturated refined olive oil with refined palm oil increases its stability and hence improves the quality of such olive oil during frying process.

Keywords Deep-frying, gas chromatography, principal component analysis, refined oils, solid-phase microextraction, total polar compounds, vegetable oil blend, volatile compounds.

Introduction

Frying is one of the oldest cooking methods and is considered as the most widespread technique that exists in the world. This process is a quick method for cooking, which provides consumers with food of desirably appealing taste characteristics (Chiou *et al.*, 2013). During frying, the oil repeatedly used at elevated temperatures can be exposed to the moisture from the foodstuff and atmospheric oxygen particularly when cooling (Zribi *et al.*, 2013, 2014). Accordingly, the main reactions that may occur are oxidation, polymerisation, isomerisation, cyclisation and hydrolysis (Wang *et al.*, 2013; Kalogianni & Karastogiannidou, 2015), resulting in the production of a large number of volatile and nonvolatile compounds. These compounds will in turn also adversely affect the stability of the frying oil; the food fried in the deteriorated oil acquires a significant amount of decomposition products that may have adverse effects on the safety, flavour, nutritional value and the stability of the fried food. Moreover, several studies have shown that a number of volatile compounds formed during frying exhibit carcinogenic, mutagenic and genotoxic properties that may also cause a hazard to the exposed professionals (Zhang *et al.*, 2015). Therefore, the thermal stability of frying oils is a vital criterion in the selection of a frying medium. The search for an oil with the improved frying stability has led to several modifications of the fatty acid composition of many commodity oils. In this respect, there are several methods used to improve the stability of the used oils during frying. One of these methods is to use the oils rich in saturated fatty acids (SFA) or monounsaturated fatty acids (MUFA), because the refined seed oils characterised by the presence of high percentages of polyunsaturated fatty acids (PUFA) oxidise much faster than those rich in SFA or MUFA. Indeed, several research studies have shown that the reduction in linolenic acid and linoleic percentages in the frying oils increases significantly their oxidative stabilities. According to Romano *et al.* (2012), the reduction of the linoleic acid to <3% of the total percentage of fatty acids is required to obtain a good stability of the oil and to limit the development of

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undesirable flavours. Besides, the partial hydrogenation of fats decreases their percentages in polyunsaturated fatty acids and provides a higher resistance to thermo-oxidative degradation, prolonging their frying-lives, and until recently, they were the principal frying medium for industrial frying operations (Przybylski *et al.*, 2013; Zribi *et al.*, 2016). However, in response to current *trans*-fats labelling regulations, a new generation of frying oils with modified fatty acids and other compounds have been developed. Thus, the basic objective of the present study was to investigate and compare the thermo-oxidative stability of two oil blends during fifty successive deep-frying sessions of potato fries at 180 °C. Hence, refined olive oil (ROO) or refined soya bean oil (RSO), as reasonable sources of MUFA or PUFA, respectively, was each mixed with another vegetable oil rich in SFA, such as refined palm oil (RPO).

Materials and methods

Oil samples

The studied oils during the deep-frying process, which were obtained from the National Oil Office of Sfax, Tunisia, were RPO, ROO and RSO. Each oil blend (RSO/RPO or ROO/RPO) was prepared in the volume ratio of 80:20.

Frying process

The potato variety used for this study was Spunta from Tunisia. The samples were peeled, cut approximately in even pieces (5 cm in length and 0.5 cm in thickness), washed and wiped before the deep-frying experiments.

Deep frying was carried out in a common domestic-type electric fryer equipped with a thermostat. In every frying session, 100 g of potato fries was deep-fried for 9 min at 180 °C in 1.4 L of refined oil blend. After 30 min of cooling, the deep frying was repeated fifty times using new potatoes in the same oil blend (Zribi *et al.*, 2016). Indeed, ten deep-frying sessions were performed each day. Besides, each oil blend was kept overnight in a tightly sealed dark glass bottle at room temperature to be reused the next day. Together with the oils sampled after twenty-five deep fryings and after fifty deep fryings, the samples of the fresh oil blends (at t = 0) were stored in sealed dark glass bottles at −20 °C until examination.

Determination of total polar compounds

Total polar compounds (TPC) were analysed using a Testo 270 Deep-frying Oil (Tester, Testo Inc., Lenzkirch, Germany) in the oil blends during the deep-frying process (Zribi *et al.*, 2016).

Determination of volatile compounds

The extraction and the identification of the volatile compounds of the studied oils were performed as described previously by Ammar *et al.* (2014).

Determination of fatty acids composition

FAMEs were determined according to the method adopted by the International Olive Oil Council (IOOC, 2001a,b). These compounds were analysed as described by our previous research work (Zribi *et al.*, 2014).

Iodine values (IV) were determined from the percentages of the fatty acids using the following formula (Ben Brahim *et al.*, 2015):

IV = (% palmitoleic acid (C16:1) × 1.001) + (% oleic acid (C18:1) × 0.899) + (% linoleic acid (C18:2) × 1.814) + (% linolenic acid (C18:3) × 2.737).

Determination of sterols composition

The sterols, extracted from the studied vegetable oils, were determined according to the method adopted by the International Olive Oil Council (IOOC, 2013). The method for analysing these compounds was described previously by Jabeur *et al.* (2014).

Statistical analysis

The results were expressed as mean ± standard deviation (SD) of three measurements for the analytical determination. The significant differences between the values of all parameters were determined at $P < 0.05$ according to the one-way ANOVA: *post hoc* comparisons (Student–Newman–Keuls test). This statistical analysis was performed using SPSS Statistics 17.0 for Windows.

The principal component analysis (PCA) was applied to the data set of all analyses performed for fresh oil blends and those obtained after the deep-frying sessions. PCA plots were performed using XLSTAT software for Windows (v.2014.1.08, Addinsoft, New York, NY).

Results and discussion

Changes in the total polar compounds during frying

The TPC determination is recognised as the most reliable method to measure the oil degradation (Marmesat *et al.*, 2007; Zribi *et al.*, 2014).

Indeed, a high and significant ($P < 0.05$) increase in TPC is observed in the case of the RSO/RPO blend, which ranged from 10.00 to 36.50%. However, a low but significant ($P < 0.05$) increase in these compounds is recorded for the ROO/RPO blend, which varied from 9.00 to 31.50% (data not shown). These results are in

agreement with the findings of previous research studies (Zribi *et al*., 2014) and can be explained by considering that the refined olive oil, although rich in MUFA, is actually very stable with respect to the thermal degradation. Omar *et al*. (2014) suggested that the oil blends rich in SFA have the lowest TPC throughout frying and thus are able to resist more to thermoxidation.

Changes in volatile compounds during frying

Although the volatile compounds in frying oils change continually, their evaluation in the frying oil can be considered as a marker of oil deterioration. However, care should be taken when interpreting the data on volatile compounds in used frying oils because of the fluctuations in the formation and degradation of these substances at frying temperatures. In our experiments, SPME–GC–EIMS was used to identify the volatile compounds in refined oil blends, such as aldehydes, alcohols, alkanes and terpene hydrocarbons (Table 1).

Among these decomposition products, aldehydes, which are generated mainly from frying oil via β-scission of alkoxy radicals formed by the homolytic cleavage of fatty acid hydroperoxides (Fujisaki *et al*., 2002),

Table 1 Most important volatile compounds of refined oil blends detected during fifty successive deep-frying sessions

Volatile compounds (%)	LRI	ROO/RPO at t = 0	ROO/RPO after 25 D-Fs	ROO/RPO after 50 D-Fs	RSO/RPO at t = 0	RSO/RPO after 25 D-Fs	RSO/RPO after 50 D-Fs
Aldehydes							
(E)-2-Hexenal	856	–	0.6	–	–	0.4	–
(Z)-2-Heptenal	963	3.3	6.8	5.1	1.4	7.3	6.1
(E,Z)-2,4-Heptadienal	1001	–	–	–	–	2.0	1.2
(E,E)-2,4-Heptadienal	1012	–	0.8	0.5	–	3.8	2.2
(E)-2-Octenal	1062	–	3.8	3.9	–	4.9	3.3
Decanal	1206	–	–	0.6	–	–	1.0
(E,E)-2,4-Nonadienal	1216	–	–	0.5	–	0.5	0.5
4-Oxononanal	1248	–	–	–	–	–	1.8
(E,Z)-2,4-Decadienal	1293	–	6.3	6.0	–	11.1	10.6
(E,E)-2,4-Decadienal	1316	–	20.7	18.4	–	37.6	36.1
Total aldehydes		3.3	39.0	35.0	1.4	67.6	62.8
Alcohols							
1-Hexanol	869	–	–	–	–	–	–
1-Octen-3-ol	980	–	1.9	1.4	–	2.5	2.5
Dimethyl cyclohexanol	1040	–	1.0	0.8	–	1.5	0.9
Menthol	1174	1.6	–	–	1.2	–	–
Total alcohols		1.6	2.9	2.2	1.2	4.0	3.4
Esters							
(Z)-3-Hexenyl acetate	1008	–	–	–	–	–	–
1-Hexyl acetate	1010	–	–	–	–	–	–
Methyl 2-methyldodecanoate	1552	–	–	–	–	–	–
Alkanes							
n-Undecane	1100	0.9	–	–	1.2	–	–
2-Methyldodecane	1262	2.5	–	–	2.2	–	–
n-Tridecane	1300	3.2	–	–	3.1	–	–
n-Tetradecane	1400	24.8	3.6	1.7	31.6	1.2	2.5
n-Hexadecane	1600	1.7	–	–	2.4	–	–
Total alkanes		33.1	3.6	1.7	40.5	1.2	2.5
Terpene hydrocarbons							
Monoterpene hydrocarbons							
Limonene	1032	–	–	–	–	–	–
(E)-β-Ocimene	1052	–	–	–	–	–	–
Oxygenated monoterpenes							
Camphor	1145	4.9	–	–	8.3	–	–
Menthone	1155	–	–	–	1.0	–	–
Menthol	1174	1.6	–	–	1.2	–	–
Total oxygenated monoterpenes		6.5	–	–	10.5	–	–
Sesquiterpene hydrocarbons							
(E,E)-α-Farnesene	1508	–	–	–	–	–	–

LRI, linear retention index; ROO, refined olive oil; RPO, refined palm oil; RSO, refined soya bean oil; D-Fs, deep fryings.

are the most important and have the most abundant derivatives. Furthermore, the flavour of fried foods and oils is strongly characterised by these chemicals because of their low thresholds. For instance, 2-hexenal derived from linolenic acid has an unpleasant grassy aroma. In contrast, 2,4-decadienal and 2-heptenal derived from linoleic acid give a desirable flavour to fried foods (Romano *et al*., 2013). Thus, linoleic acid is mainly responsible for the desirable deep-fat fried flavour (Choe & Min, 2007; Ramadan & Wahdan, 2012). Different oils produce different flavours during deep frying due to the differences in the quality and quantity of fatty acids in their compositions. The acceptability of these aldehydes is also known to depend on their concentrations. Volatile aldehydes are also known to strongly contribute to the odour in a room where frying is taking place. It is well established that these aldehydes are highly reactive and toxic at high concentrations. In general, unsaturated aldehydes such as alkenals and alkadienals show much more severe toxicity than alkanals (Fujisaki *et al*., 2002).

As shown in Table 1, aldehydes increased sharply for the RSO/RPO blend from 1.4% to 67.6% after twenty-five successive deep-frying sessions, whereas they slightly increased for the ROO/RPO blend from 3.3% to 39.0% after the same frying sessions and then a slight decrease was observed at the end of frying for both oil blends (62.8% and 35.0% for RSO/RPO and ROO/RPO blends, respectively).

Indeed, aldehydes such as (*Z*)-2-heptenal, (*E*,*Z*)-2,4-heptadienal, (*E*,*E*)-2,4-heptadienal, (*E*)-2-octenal, (*E*,Z)-2,4-decadienal, (*E*,*E*)-2,4-decadienal and an alcohol derivative such as 1-octen-3-ol are the major volatile compounds detected by the SPME method in the oil blends during the successive deep-frying sessions, particularly in the case of the RSO/RPO blend. Choe & Min (2007) reported that 2-octenal, 1-octen-3-ol, 2-heptenal, 2,4-heptadienal and 2,4-decadienal are the major volatile compounds in soya bean oil at 200 °C. Among these compounds, 2,4-decadienal is considered as the major contributor to deep-fried flavour. The formation of this volatile compound from the oxidation of linoleic acid in the frying oil blends has been suggested by Choe & Min (2007) (data not shown). Lower percentages of (*E*,Z)-2,4-decadienal and (*E*,*E*)-2,4-decadienal were observed in the ROO/RPO blend (6.0 and 18.4%, respectively) than in RSO/RPO blend (10.6 and 36.1%) at the end of frying (Table 1). Thus, the high PUFA percentage of the frying oil is considered to promote the formation of (*E*,*E*)-2,4-decadienal. Besides, (*Z*)-2-heptenal derived from linoleic acid and (*E*,*Z*)-2,4-heptadienal and (*E*,*E*)-2,4-heptadienal derived from linolenic acid are detected especially in the RSO/RPO blend after fifty successive deep-frying sessions as compared to those in the ROO/RPO blend. Consequently, the presence of these compounds could be proposed as an alternative marker for monitoring the thermal degradation of frying oils.

Changes in *cis*- and *trans*-fatty acid compositions during frying

For the fresh oil blends, the main fatty acids detected during this study are palmitic acid (20.31% for the RSO/RPO blend and 21.23% for the ROO/RPO blend), stearic acid (2.96% for the ROO/RPO blend and 3.68% for the RSO/RPO blend), oleic acid (27.04% for the RSO/RPO blend and 53.33% for the ROO/RPO blend), linoleic acid (18.97% for the ROO/RPO blend and 42.54% for the RSO/RPO blend) and linolenic acid (0.66% for the ROO/RPO blend and 5.42% for the RSO/RPO blend) (Table 2).

During the deep-frying process, a slight decrease (not significant; $P > 0.05$) in UFA percentages of the studied oil blends and a consequent slight increase (not significant; $P > 0.05$) in SFA percentages are observed (Table 2). Indeed, while a very small increase (not significant; $P > 0.05$) in C16:0 percentages is detected for oil blends, a significant decrease ($P < 0.05$) in PUFA percentages is detected, especially in the case of RSO/RPO blend.

With regard to *trans*-PUFA percentage, a relatively high and significant increase ($P < 0.05$) is shown for the RSO/RPO blend from 0.36 to 0.48% after the deep-frying process, whereas a very small but statistically significant ($P < 0.05$) increase in these compounds is detected for the ROO/RPO blend from 0.22 to 0.27% (Table 2).

Furthermore, C18:2/C16:0 ratio is used as an indicator for the assessment of the oxidative deterioration degree of frying oils (Zribi *et al*., 2013). Indeed, the lowest decrease in C18:2/C16:0 is shown for the ROO/RPO blend ranging between 0.89 and 0.81 after the deep-frying process, while the highest one is observed for the RSO/RPO blend varying between 2.09 and 1.99 (Table 2).

The highest decrease in IV is shown from 116.51 to 112.42 in the case of the RSO/RPO blend and the lowest reduction is observed from 85.97 to 83.78 for the ROO/RPO blend after fifty successive deep-frying sessions (Table 2). This could be explained by the great resistance of the major fatty acids (MUFA) present in the ROO/RPO blend to the oxidative deterioration compared to the lower resistance of PUFA present in the RSO/RPO blend during the frying process.

Similar results published by Sunil *et al*. (2015) have demonstrated that blending a polyunsaturated oil like sunflower oil with a saturated one like coconut oil leads to the relatively high increase in SFA, thus raising the stability of oil blends towards oxidation during frying.

Table 2 *cis*- and *trans*-Fatty acid compositions of refined oil blends during fifty successive deep-frying sessions

Fatty acids (%)	FRPO	FROO	FRSO	ROO/RPO at t = 0	ROO/RPO after 25 D-Fs	ROO/RPO after 50 D-Fs	RSO/RPO at t = 0	RSO/RPO after 25 D-Fs	RSO/RPO after 50 D-Fs
C12:0	0.31 ± 0.00	–	–	0.05 ± 0.00Aa	0.05 ± 0.00Aa	0.05 ± 0.00Aa	0.05 ± 0.00Aa	0.05 ± 0.00Aa	0.06 ± 0.00Aa
C14:0	1.04 ± 0.01*	0.01 ± 0.00**	0.07 ± 0.00***	0.21 ± 0.00Aa	0.21 ± 0.00Aa	0.21 ± 0.00Aa	0.30 ± 0.00Ab	0.31 ± 0.00ABb	0.32 ± 0.00Bb
C16:0	43.96 ± 0.26*	17.56 ± 0.12**	10.99 ± 0.09***	21.23 ± 0.17Aa	21.36 ± 0.14Aa	21.50 ± 0.20Aa	20.31 ± 0.13Ab	20.41 ± 0.10Ab	20.53 ± 0.16Ab
C16:(1n-9) + (1n-7)	0.23 ± 0.00*	2.27 ± 0.02**	0.14 ± 0.00***	1.81 ± 0.01Aa	1.85 ± 0.01Ba	1.90 ± 0.01Ca	0.20 ± 0.00Ab	0.20 ± 0.00Ab	0.22 ± 0.00Bb
C17:0	0.08 ± 0.00*	0.05 ± 0.00**	0.09 ± 0.00*	0.06 ± 0.00Aa	0.06 ± 0.00Aa	0.06 ± 0.00Aa	0.10 ± 0.00Ab	0.10 ± 0.00Ab	0.10 ± 0.00Ab
C17:1	0.03 ± 0.00*	0.08 ± 0.00**	0.05 ± 0.00***	0.05 ± 0.00Aa	0.06 ± 0.00Aa	0.06 ± 0.00Aa	0.05 ± 0.00Aa	0.05 ± 0.00Aa	0.06 ± 0.00Aa
C18:0	4.02 ± 0.03*	2.56 ± 0.02**	4.00 ± 0.03*	2.96 ± 0.03Aa	2.98 ± 0.02Aa	2.99 ± 0.03Aa	3.68 ± 0.03Ab	3.70 ± 0.02Ab	3.73 ± 0.03Ab
C18:(1n-9) + (1n-7)	37.66 ± 0.23*	56.05 ± 0.39**	24.23 ± 0.20***	53.33 ± 0.43Aa	54.05 ± 0.35Ba	54.70 ± 0.52Ba	27.04 ± 0.17Ab	28.32 ± 0.14Bb	29.54 ± 0.21Cb
C18:2	11.87 ± 0.07*	19.97 ± 0.14**	52.71 ± 0.45***	18.97 ± 0.15Aa	18.18 ± 0.12Ba	17.50 ± 0.16Ca	42.54 ± 0.28Ab	41.66 ± 0.21Bb	40.91 ± 0.29Cb
C18:3	0.29 ± 0.00*	0.76 ± 0.00**	7.14 ± 0.06***	0.66 ± 0.00Aa	0.53 ± 0.00Ba	0.35 ± 0.00Ca	5.42 ± 0.03Ab	4.87 ± 0.02Bb	4.18 ± 0.03Cb
C20:0	0.35 ± 0.00*	0.47 ± 0.00**	0.36 ± 0.00*	0.45 ± 0.00Aa	0.45 ± 0.00Aa	0.45 ± 0.00Aa	0.19 ± 0.00Ab	0.19 ± 0.00Ab	0.19 ± 0.00Ab
C20:(1n-9)	0.16 ± 0.00*	0.22 ± 0.00**	0.22 ± 0.00**	0.22 ± 0.00Aa	0.22 ± 0.00Aa	0.23 ± 0.00Aa	0.12 ± 0.00Ab	0.14 ± 0.00Bb	0.16 ± 0.00Cb
TC18:1	0.04 ± 0.00*	0.06 ± 0.00**	0.04 ± 0.00*	0.05 ± 0.00Aa	0.12 ± 0.00Ba	0.14 ± 0.00Ca	0.03 ± 0.00Ab	0.06 ± 0.00Bb	0.12 ± 0.00Cb
∑(TC18:2 + TC18:3)	0.28 ± 0.00*	0.23 ± 0.00**	0.37 ± 0.00***	0.22 ± 0.00Aa	0.24 ± 0.00Ba	0.27 ± 0.00Ca	0.36 ± 0.00Ab	0.39 ± 0.00Bb	0.48 ± 0.00Cb
∑SFA (%)	49.76 ± 0.30 *	20.65 ± 0.14**	15.51 ± 0.12***	24.96 ± 0.20Aa	25.11 ± 0.16Aa	25.26 ± 0.23Aa	24.63 ± 0.16Ab	24.76 ± 0.12Ab	24.93 ± 0.19Aa
∑MUFA (%)	38.08 ± 0.23*	58.62 ± 0.41**	24.64 ± 0.20***	55.41 ± 0.44Aa	56.18 ± 0.36Ba	56.89 ± 0.53Ba	27.41 ± 0.17Ab	28.71 ± 0.14Bb	29.98 ± 0.21Cb
∑PUFA (%)	12.16 ± 0.07*	20.73 ± 0.14**	59.85 ± 0.51***	19.63 ± 0.15Aa	18.71 ± 0.12Ba	17.85 ± 0.16Ca	47.96 ± 0.31Ab	46.53 ± 0.22Bb	45.09 ± 0.32Cb
∑UFA (%)	50.24 ± 0.30*	79.35 ± 0.55**	84.49 ± 0.71***	75.04 ± 0.59Aa	74.89 ± 0.48Aa	74.74 ± 0.69Aa	75.37 ± 0.48Aa	75.24 ± 0.36Aa	75.07 ± 0.53Aa
C18:2/C16:0	0.27	1.13	4.79	0.89	0.85	0.81	2.09	2.04	1.99
IV	56.41	90.96	137.08	85.97	84.87	83.78	116.51	114.56	112.42

FRPO, fresh refined palm oil; FROO, fresh refined olive oil; FRSO, fresh refined soya bean oil; RPO, refined palm oil; ROO, refined olive oil; RSO, refined soya bean oil; D-Fs, deep fryings; SFA, saturated fatty acids; MUFA, monounsaturated fatty acids; PUFA, polyunsaturated fatty acids; UFA, unsaturated fatty acids; IV, iodine value.

Each value represents the mean of three determinations ($n = 3$) and three independent experiments ± standard deviation.

Different symbols (*, ** and ***) within the same row indicate significant differences ($P < 0.05$) between the fresh and refined oil sample groups.

Different uppercase letters (A, B and C) within the same row indicate significant differences ($P < 0.05$) for the same refined oil blend.

Different lowercase letters (a and b) within the same row indicate significant differences ($P < 0.05$) between the refined oil blends for the same frying session.

Table 3 Sterols composition of refined oil blends during fifty successive deep-frying sessions

Sterols (%)	FRPO	FROO	FRSO	ROO/RPO at t = 0	ROO/RPO after 25 D-Fs	ROO/RPO after 50 D-Fs	RSO/RPO at t = 0	RSO/RPO after 25 D-Fs	RSO/RPO after 50 D-Fs
Cholesterol	2.37 ± 0.01*	0.17 ± 0.00**	0.25 ± 0.00***	0.23 ± 0.00Aa	0.22 ± 0.00Aa	0.20 ± 0.00Ba	0.33 ± 0.00Ab	0.31 ± 0.00Bb	0.29 ± 0.00Cb
Brassicasterol	–	–	–	–	–	–	–	–	–
24-Methylene-cholesterol	0.15 ± 0.00*	0.11 ± 0.00**	0.07 ± 0.00***	0.14 ± 0.00Aa	0.14 ± 0.00Aa	0.15 ± 0.00Aa	0.09 ± 0.00Ab	0.11 ± 0.00Bb	0.12 ± 0.00Bb
Campesterol	16.01 ± 0.09*	3.48 ± 0.02**	23.87 ± 0.12***	8.35 ± 0.03Aa	8.11 ± 0.05Ba	7.89 ± 0.04Ca	20.65 ± 0.06Ab	20.49 ± 0.09Bb	20.37 ± 0.08Bb
Campestanol	0.05 ± 0.00*	0.05 ± 0.00*	0.17 ± 0.00**	0.05 ± 0.00Aa	0.08 ± 0.00Ba	0.11 ± 0.00Ca	0.16 ± 0.00Ab	0.18 ± 0.00Bb	0.23 ± 0.00Cb
Stigmasterol	8.41 ± 0.05*	0.78 ± 0.00**	20.11 ± 0.10***	2.85 ± 0.01Aa	2.71 ± 0.02Ba	2.62 ± 0.01Ca	18.86 ± 0.05Ab	18.74 ± 0.08Bb	18.59 ± 0.07Cb
Δ-7-Campesterol	0.12 ± 0.00*	0.09 ± 0.00**	0.56 ± 0.00***	0.10 ± 0.00Aa	0.13 ± 0.00Ba	0.18 ± 0.00Ca	0.45 ± 0.00Ab	0.47 ± 0.00Bb	0.51 ± 0.00Cb
Δ-5-23-Stigmastadienol	0.07 ± 0.00*	0.05 ± 0.00**	0.09 ± 0.00***	0.06 ± 0.00Aa	0.07 ± 0.00Aa	0.10 ± 0.00Ba	0.08 ± 0.00Ab	0.10 ± 0.00Bb	0.12 ± 0.00Cb
Clerosterol	1.13 ± 0.00*	1.27 ± 0.01**	0.27 ± 0.00***	1.20 ± 0.00Aa	1.33 ± 0.01Ba	1.40 ± 0.01Ca	0.32 ± 0.00Ab	0.38 ± 0.00Bb	0.45 ± 0.00Cb
β-Sitosterol	62.78 ± 0.37*	81.39 ± 0.60**	45.68 ± 0.23***	76.80 ± 0.31Aa	76.61 ± 0.46Aa	76.49 ± 0.38Aa	50.98 ± 0.15Ab	50.62 ± 0.23Bb	50.24 ± 0.20Cb
Sitostanol	1.08 ± 0.00*	1.23 ± 0.00**	1.62 ± 0.00***	1.20 ± 0.00Aa	1.39 ± 0.01Ba	1.54 ± 0.01Ca	1.52 ± 0.00Ab	1.76 ± 0.00Bb	1.97 ± 0.00Cb
Δ-5-Avenasterol	4.72 ± 0.03*	9.48 ± 0.06**	1.88 ± 0.01***	7.09 ± 0.03Aa	7.04 ± 0.04ABa	6.99 ± 0.03Ba	2.02 ± 0.01Ab	1.90 ± 0.01Bb	1.81 ± 0.01Cb
Δ-5-24-Stigmastadienol	0.72 ± 0.00*	0.81 ± 0.00**	0.90 ± 0.00***	0.80 ± 0.00Aa	0.86 ± 0.00Ba	0.91 ± 0.00Ca	0.85 ± 0.00Ab	0.91 ± 0.00Bb	0.98 ± 0.00Cb
Δ-7-Stigmastanol	1.78 ± 0.01*	0.42 ± 0.00**	2.87 ± 0.01***	0.47 ± 0.00Aa	0.66 ± 0.00Ba	0.79 ± 0.00Ca	2.48 ± 0.01Ab	2.85 ± 0.01Bb	3.19 ± 0.01Cb
Δ-7-Avenasterol	0.61 ± 0.00*	0.67 ± 0.00**	1.66 ± 0.00***	0.66 ± 0.00Aa	0.65 ± 0.00Aa	0.63 ± 0.00Ba	1.21 ± 0.00Ab	1.18 ± 0.00Bb	1.13 ± 0.00Cb

FRPO, fresh refined palm oil; FROO, fresh refined olive oil; FRSO, fresh refined soya bean oil; RPO, refined palm oil; ROO, refined olive oil; RSO, refined soya bean oil; D-Fs, deep fryings.

Each value represents the mean of three determinations ($n = 3$) and three independent experiments ± standard deviation.

Different symbols (*, ** and ***) within the same row indicate significant differences ($P < 0.05$) between the fresh and refined oil sample groups.

Different uppercase letters (A, B and C) within the same row indicate significant differences ($P < 0.05$) for the same refined oil blend.

Different lowercase letters (a and b) within the same row indicate significant differences ($P < 0.05$) between the refined oil blends for the same frying session.

Changes in sterol compositions during frying

Sterols present in oils/fats undergo oxidation process as a result of many factors such as high temperature, oxygen and the presence of free radicals and peroxides (Ramadan, 2013, 2015).

The most common oxidation mechanism of sterols is autoxidation. Hence, the oxidation of the main sterols such as β-sitosterol, campesterol and stigmasterol leads to the formation of 7α-hydroxy, 7β-hydroxy, 7-keto, 5α,6α-epoxides, 5β,6β-epoxides and triols during the frying process. The common pathways of sterol oxidation are adapted from Kamal-Eldin & Lampi (2008) (data not shown).

The most abundant sterols found in the frying oil blends include β-sitosterol, campesterol, stigmasterol and Δ-5-avenasterol (Table 3; Fig. 1). Other sterols such as Δ-7-stigmastanol and Δ-7-avenasterol are found in lower concentrations. In fact, the highest decrease in β-sitosterol is significantly recorded ($P < 0.05$) for the RSO/RPO blend ranging from 50.98% to 50.24%. However, its lowest decrease (not significant; $P > 0.05$) is observed for the ROO/RPO blend varying from 76.80% to 76.49% after fifty successive deep-frying sessions (Table 3). The small decrease in the major sterols recorded for the ROO/RPO blend at the end of frying can be explained by the presence of Δ-5-avenasterol and Δ-7-avenasterol,

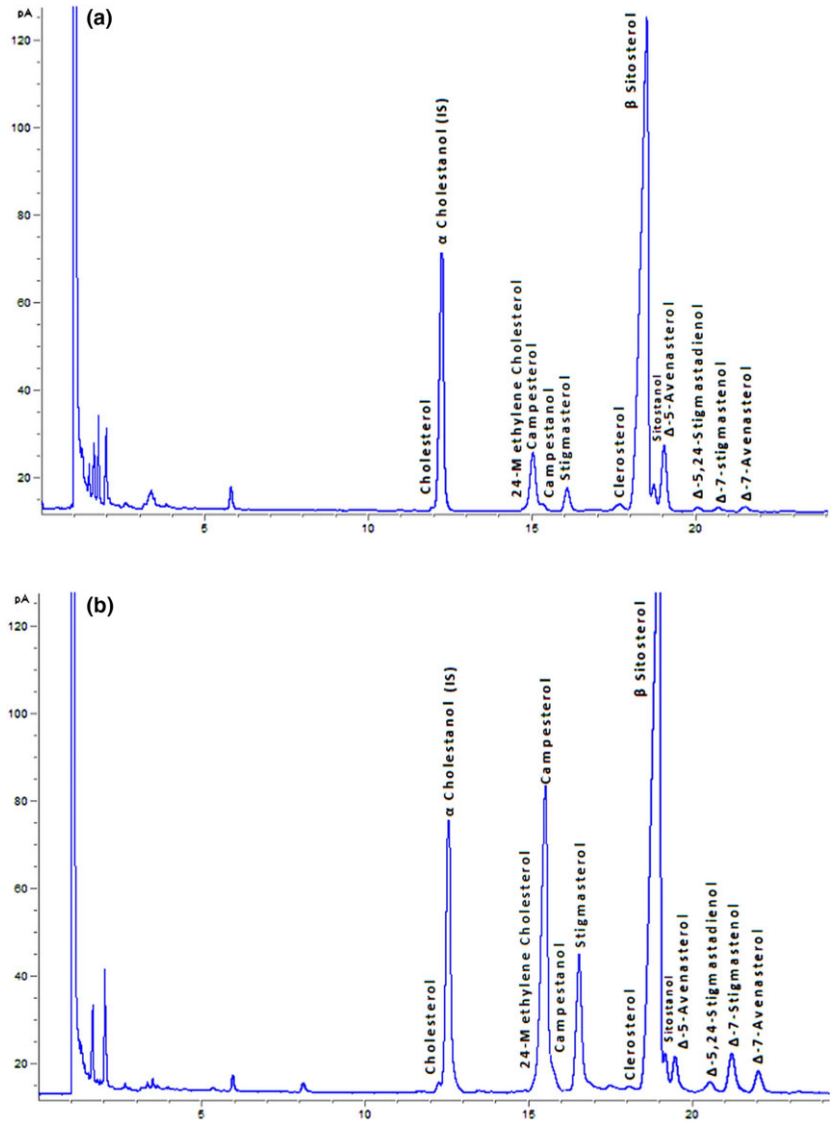

Figure 1 Typical gas chromatograms showing sterols obtained in the analysis of fresh ROO/fresh RPO blend (a) and fresh RSO/fresh RPO blend (b).

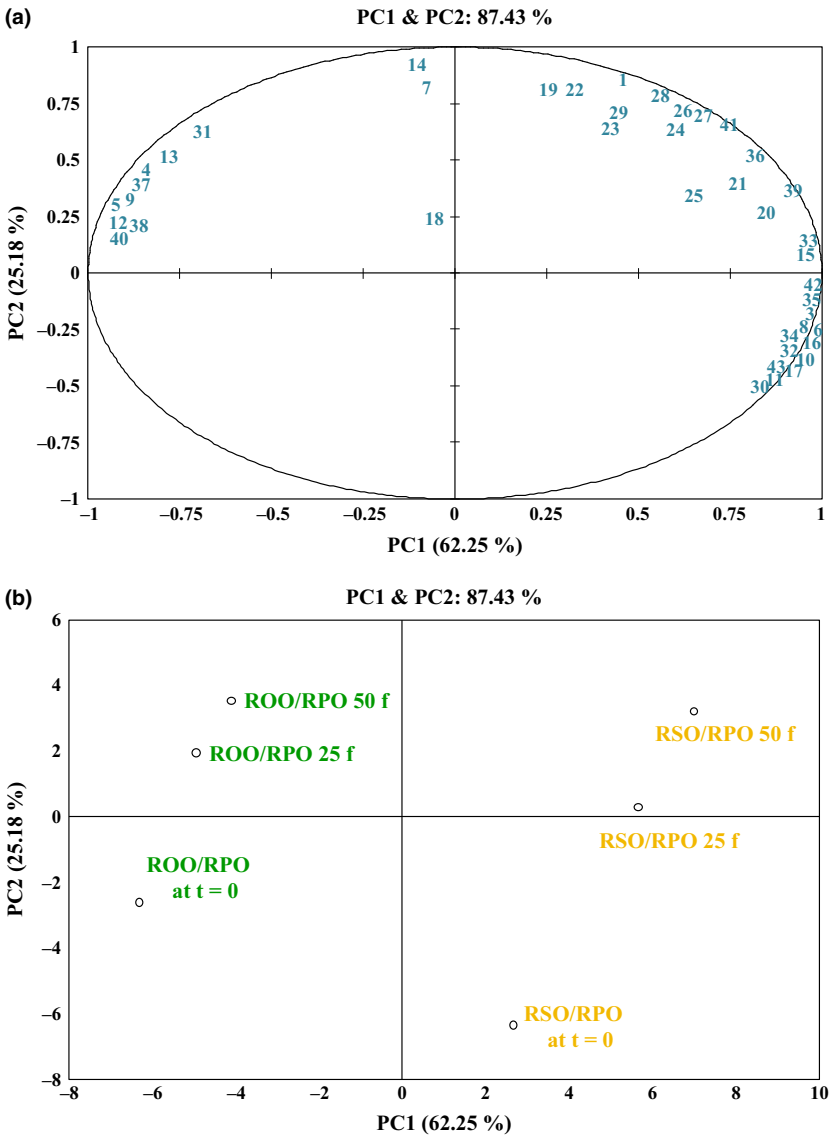

Figure 2 Principal component analysis applied to all analyses performed during successive deep-frying sessions (a: loading plot; b: score plot).

which contain ethylidene groups (CH_3–CH=). According to Singh (2013), these ethylidene-containing side-chain sterols can protect oils subjected to frying temperatures from oxidative degradation.

It should also be noted that the level of Δ-7-stigmastanol increases significantly ($P < 0.05$) from 0.47 and 2.48% to 0.79 and 3.19% for the ROO/RPO and RSO/RPO blends, respectively, after fifty successive deep-frying sessions as shown in Table 3.

Chemometric analysis

PCA was applied to the data set of all analyses performed for fresh oil blends and those obtained after each twenty-five successive deep-frying sessions at 180 °C considering forty-three variables (1: TPC; 2: C12:0; 3: C14:0; 4: C16:0; 5: C16:1; 6: C17:0; 7: C17:1; 8: C18:0; 9: C18:1; 10: C18:2; 11: C18:3; 12: C20:0; 13: C20:1; 14: TC18:1; 15: ∑(TC18:2 + TC18:3); 16: C18:2/C16:0; 17: IV; 18: (*E*)-2-hexenal; 19: (*Z*)-2-heptenal; 20: (*E*,*Z*)-2,4-heptadienal; 21: (*E*,*E*)-2,4-heptadienal; 22: (*E*)-2-octenal; 23: decanal; 24: (*E*,*E*)-2,4-nonadienal; 25: 4-oxononanal; 26: (*E*,*Z*)-2,4-decadienal; 27: (*E*,*E*)-2,4-decadienal; 28: 1-octen-3-ol; 29: dimethyl cyclohexanol; 30: cholesterol; 31: 24-methylene-cholesterol; 32: campesterol; 33: campestanol; 34: stigmasterol; 35: Δ-7-campesterol; 36: Δ-5-23- stigmastadienol; 37: clerosterol; 38: β-sitosterol; 39: sitostanol; 40: Δ-5-avenasterol; 41: Δ-5-24-stigmastadienol; 42: Δ-7-stigmastanol; and 43: Δ-7-avenasterol) presented in the loading plot (Fig. 2a) and six observations shown in the score plot (Fig. 2b). By observing the eigenvalues, it can be noted

that two principal components were sufficient to account for 87.43% of the total variance (PC1, 62.25% and PC2, 25.18%) (Fig. 2a and b).

Indeed, it is evident that while PC1 separates ROO/RPO blend from RSO/RPO blend, PC2 can distinguish each frying session. Moreover, these principal components have confirmed that the quality of the ROO/RPO and RSO/RPO blends diminishes during the deep-frying process, specifically for the RSO/RPO blend as revealed by Fig. 2b. Indeed, the fresh oil blend RSO/RPO at t = 0 is highly and negatively related to PC2. Nevertheless, the oil blends RSO/RPO twenty-five f and RSO/RPO fifty f are highly and positively related to PC1, which are mainly correlated with the significant increase in the *trans*-PUFA percentages (15), (*E*,*Z*)-2,4-heptadienal (20), (*E*,*E*)-2,4-heptadienal (21) and Δ-7-stigmastanol (42). They are also correlated with the significant decrease in PUFA such as linoleic acid (10) and linolenic acid (11) and in the major sterols such as campesterol (32) and stigmasterol (34). Moreover, the oil blends ROO/RPO at t = 0, ROO/RPO twenty-five f and ROO/RPO fifty f are highly and negatively related to PC1. As shown in Fig. 2, they are characterised by the highest percentages of MUFA especially in oleic acid (9), also of β-sitosterol (38), by the moderate percentages of SFA especially in palmitic acid (4) and by the presence of Δ-5-avenasterol (40), considered as a natural antioxidant (Singh, 2013), when compared to the blends of RSO/RPO after each twenty-five deep-frying session.

Conclusion

The changes in the compositions of the studied oil blends were observed in the study, and the ROO/RPO blend is found to have better frying performance than the RSO/RPO blend during fifty successive deep-frying sessions at 180 °C. Thus, blending ROO with 20% of RPO has proven to be of great importance to maintain a low deterioration during the repeated deep-frying session. This finding can be seen as a source of useful information to food processors and consumers who are looking for stable oil in industrial frying.

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Conflicts of interest

The authors declare no conflict of interests.

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