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ORIGINAL PAPER

Comparative Fingerprint Changes of Toxic Volatiles in Low PUFA Vegetable Oils Under Deep-Frying

L. Molina-Garcia[1,2] · C. S. P. Santos[1] · S. C. Cunha[1] · S. Casal[1,3] · J. O. Fernandes[1]

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Abstract The volatile fraction of three vegetable oils recommended for deep-frying due to their high MUFA:PUFA ratios, namely extra-virgin olive oil, peanut oil and canola oil, was compared before and after frying potatoes, with a particular focus on toxic volatiles. For the purpose, a headspace solid-phase-micro extraction technique coupled with gas chromatography and mass spectrometry was optimized, with semi-quantification achieved using two internal standards. Significant qualitative and quantitative differences were observed, both before and after frying. From a total of 51 compounds, aldehydes were the main group formed after deep-frying, their nature and abundance being highly associated with the initial fatty acid composition, particularly linoleic acid ($r^2 = -0.999$, $p \leq 0.001$). Globally, extra-virgin olive oil revealed fewer formations of unsaturated aldehydes, including toxic ones, and correlated with lower amounts of degradation indicators, as polar compounds ($r^2 = 0.998$, $p \leq 0.001$) and *p*-anisidine value ($r^2 = 0.991$, $p \leq 0.001$). Despite the similarities in total unsaturation degree between canola and peanut oils, the former presented lower amount of volatiles, including *E,E*-2,4-decadienal and acrolein, the more toxic ones. These results highlight for the pertinence of volatile analyses to evaluate and compare oil degradation under thermal and oxidative stress, while complementing other degradation indicators. Additionally, the optimized methodology allows a direct comparison of different oil matrices, supporting further developments into more general methods for volatiles quantification, enabling more efficient comparison of results between research teams.

Keywords Deep-frying · Volatile fraction · Oxidative stability · *E,E*-2,4-decadienal · Acrolein · Aldehydes · HS–SPME–GC–MS

Introduction

Frying is one of the most widely used practices in food preparation, particularly deep-frying. Despite various calls for reduced fat intake, its fast and easy preparation, relatively low price and desirable properties of color, texture, and flavor, contributes to its global use [1]. These positive attributes results from the chemical and physical changes that take place during frying, including oxidation, hydrolysis and polymerization [1]. However, these reactions also lead to the formation of undesirable compounds, which change the functional, sensory and nutritional properties of oils [2–4], calling their safety regarding human consumption into question. Therefore, it is important to find the most suitable oils, presenting good technological properties for the purpose, together with advantages for human health.

From a nutritional point of view, the consumption of unsaturated oils should be favored. However, this same unsaturation reduces the oils oxidative stability at high temperatures [2]. Thus, frying oils with a

L. Molina-Garcia and C.S.P. Santos contributed equally to this work.

✉ S. Casal
sucasal@ff.up.pt

[1] LAQV-REQUIMTE, Laboratory of Bromatology and Hydrology, Faculty of Pharmacy, University of Porto, Rua Jorge de Viterbo Ferreira, 228, 4050-313 Porto, Portugal

[2] Department of Physical and Analytical Chemistry, Faculty of Experimental Sciences, University of Jaén, Campus las Lagunillas, E-23071 Jaén, Spain

[3] EPIUnit-ISPUP, University of Porto, Rua das Taipas, 135, 4050-600 Porto, Portugal

balanced polyunsaturated: monounsaturated fatty acids (PUFA:MUFA) ratio should be considered [5], depending on availability, economic aspects and tradition of each country.

Many types of vegetable oils are available for deep-frying purposes, among the most common worldwide are sunflower, soybean and corn, and some others [6]. Despite their high smoke points and worldwide availability, they are rapidly degraded under thermal stress due to their high PUFA content. Hence, oils with lower PUFA content could be the more appropriate choice [7]. Among these, olive oil has the disadvantage of its high price [8] while peanut oil, despite being recognized for its resistance to thermal oxidation and recommended for deep-frying, in particular by Portuguese official entities [9, 10], is also expensive and only seasonally available in only some countries. Canola oil, with a growing availability in various countries, presents also a relatively high level of MUFA, but it shrouded in a significant amount of PUFA and some controversy to its deep-frying suitability [11]. It is also generally consensual that the frying medium degradation depends on the food being processed, and therefore frying tests should only be carried out with real food frying [4, 12].

General oil degradation is usually assessed by the total polar compounds (TPC), including polymerized, hydrolyzed and oxidized compounds, formed during frying, but an effective and detailed comparison of different vegetable oils demands a comprehensive study of the compounds that are altered during the frying process, their nature and concentration, particularly those with recognized implications for consumer's health, such as volatile aldehydes. In fact, some volatile compounds, particularly *E,E*-2,4-decadienal, *E,E*-2,4-heptadienal, *E*-2-decenal and *E*-2-undecenal are correlated with common lipid degradation parameters, therefore regarded as deterioration "markers" [2, 13].

Headspace solid-phase micro extraction combined with gas chromatography and mass spectrometry (HS–SPME/GC–MS) has been widely used to extract, separate and identify volatile compounds from edible oils [14]. HS–SPME is a solvent-free extraction technique, with rapid sampling and low cost and it can be easily automated [15]. However, its selectivity depends on the fiber coating type, while its effectiveness is influenced by several factors, including sample amount, agitation and extraction times, as well as temperature, internal standard type and amount, etc. This requires a careful selection and optimization [16], but the diversity of methodological variations reduces the possibility of comparison between published work on different oils and frying conditions.

Aware that few studies were published on real frying conditions [2, 3, 17], and none of them focused their attention on the comparison of oils with high MUFA:PUFA ratios, the aim of this study was to compare the volatile profiles of common high MUFA:PUFA oils, particularly extra virgin olive oil (EVOO), peanut (PO), and canola oils (CO), before and after real deep-frying of potatoes. Our purpose was to evaluate several volatile families of oils and discuss their origins and correlations with classical primary and secondary degradation indicators, with a particular focus on the most toxic volatiles. To support this study, an HS–SPME/GC–MS method that could be adapted to the three vegetable oils was previously optimized, taking into account their volatile diversities before and after potatoes deep-frying. It was also our purpose to provide a methodology that could be extended to other processing conditions and research groups, ensuring a broader comparison of results.

Materials and Methods

Chemicals and Materials

All reagents and standards were of analytical or chromatographic grade and were supplied by Merck (Darmstadt, Germany) or Sigma–Aldrich (St. Louis, USA). The manual SPME device and SPME fibers used, 50/30 μm divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS), were supplied by Supelco (Bellefonte, PA, USA). Prior to use, fibers were conditioned accordingly with the manufacturer's recommendations. Two internal standards (IS) 4-methyl-2-pentanol and 1,2,3-trichloropropane (Sigma) solutions were prepared in ethanol (800 μg mL^{-1} and 200 μg mL^{-1}, respectively). Three vegetable oils were assayed: an EVOO from the northeast of Portugal (Valpaços); a PO purchased in a local market in Porto (Portugal) and CO purchased in a foreign market in Paris (France). White potatoes of the *Fontane* variety were also purchased in a local market.

Frying Conditions

Domestic deep-fat electric fryers (1.75 L capacity, TRISTAR, FR-6929 model, The Netherlands) were used for the deep-frying assays, using 1.5 L of oil at 175 °C. Fresh potatoes, sliced in toothpicks (1 × 1 × 4 cm), were washed, drained, and 50 g were fried per batch, during 6 min, with an intermittent frying frequency of 30 min, in a total of 8 h of continuous heating. Frying temperature was periodically verified with a calibrated digital thermometer. For analysis, oil samples were collected at time zero and after 8 h of frying, being preserved under refrigeration (4 °C) in totally filled vials closed under a nitrogen stream to avoid further oxidative degradation.

Chemical Analyses

Volatile Compounds

The HS–SPME technique coupled with GC–MS was optimized for the separation and identification of volatile

compounds. The subsequent application of the method in the oils used for potatoes deep-frying with semi-quantitative determination, using two IS, was performed, as detailed below and justified under the discussion section.

HS–SPME Extraction

An accurate amount of oil (1.5 g) was placed into a 20 mL glass vial (La-Pha-Pack GmBH, Germany) with a magnetic glass stir bar (VWR, Germany), spiked with 4 µg of 4-methyl-2-pentanol and 6 µg of 1,2,3-trichloropropane from the IS working solutions and immediately closed with an aluminum cover with Teflon septum (La-Pha-Pack GmBH, Germany). The vial was then inserted into a metal block stabilized at 50 °C and heated during 5 min in order to allow equilibration of the volatiles released into the headspace, while stirring (200 rpm) (Cimarec, ThermoScientific, USA). After equilibration, a manual SPME holder (Supelco) containing the fiber (DVB/CAR/PDMS 50/30 µm film thickness; Supelco) was inserted into the vial and exposed to the headspace for 30 min, maintaining constant temperature and stirring conditions. Once completed, volatiles were thermally desorbed for 5 min in the injector port (270 °C) of the GC–MS system.

Gas Chromatographic Analysis

A gas chromatograph 6890 (Agilent, Little Falls, DE, USA) equipped with an electronically controlled split/splitless injection port was interfaced to a single Quadrupole Mass Selective Detector (5973B, Agilent) with an electron ionization chamber. GC separation was performed on a fused-silica SPB-5 Capillary GC column (60 m × 0.32 mm I.D. × 1 µm film thickness, Supelco). Helium was the carrier gas used with a constant flow of 1 mL/min and internal pressure of 70 kPa. The injection was made in splitless mode at 270 °C for 5 min. The operating conditions were as follows: the oven temperature was set initially at 40 °C (5 min hold), increased to 150 °C at 4 °C/min and finally increased again to 240 °C at 10 °C/min (3.5 min hold). Total run time was 45 min. The MS transfer line was held at 250 °C. Mass spectrometric parameters were set as follows: electron ionization with 70 eV energy; ion source temperature, 250 °C and MS quadrupole temperature, 200 °C. The MS system was routinely set in full scan mode being the scanning from *m/z* 20 to 450 at 2 scans per second. Agilent ChemStation (version D.0200SP1) was used for data collection/processing and GC–MS control.

Compounds were identified by comparing the respective mass spectra with a mass spectral database (WILEY7n.L). In addition, identification was complemented by matching relative retention times with data found in the literature. The compounds 4-methyl-2-pentanol and 1,2,3-trichloropropane were chosen as IS, since they are not usually present in the volatile fraction of the oils analyzed [18, 19] and give rise to well-separated peaks under the selected chromatographic conditions. With a retention time of 17.2 min, 4-methyl-2-pentanol was used for semi-quantification of compounds with a retention time lower than 24 min, while 1,2,3-trichloropropane, being retained for 25.5 min, was used for the less volatile compounds. The relative levels of the investigated compounds were calculated from the peak area ratios of the compounds of interest to the peak area of the IS, therefore reported on internal standard equivalents.

Fatty Acids

The fatty acid composition of the studied oils was evaluated by GC after cold transmethylation, according to Commission Regulation EEC N.º 2568/91 [20], using a FAME CP-Select CB column (50 m × 0.25 mm × 0.2 mm) on a Chrompack (CP 9001) gas chromatograph with flame ionization detection. The temperature of the injection port and detector were 230 °C and 250 °C, respectively. The carrier gas was helium, and the oven had a temperature gradient from 120 to 200 °C. Fatty acids identification and FID calibration were accomplished with a certified standard mixture of fatty acid methyl esters (TraceCert-Supelco 37 component FAME mix, USA). Results were expressed on a relative fatty acid basis.

Total Polar Compounds

Total Polar Compounds were initially estimated on the basis of the dielectric constant changes, as frequent in several restaurants and industrial frying facilities, using a *Food Oil Sensor* (C-CIT Sensors AG, Switzerland), after calibration with a "zero" and "4.0" control, acquired from Sigma-Aldrich (USA), according to the manufacturer operation guide. Later, detail on the polar compounds (PC) individual fractions was achieved by high-performance size-exclusion chromatography (HPSEC), using monostearin (Sigma-Aldrich, USA) as IS according to [21]. The PC fractions were analyzed in a Jasco chromatograph (Japan) using a Phenogel column (100 Å, 600 × 7.8 mm ID, 5 µm film, Phenomenex, USA), THF as mobile phase at a flow rate 1 mL/min, and an evaporative light scattering detector (Sedere, Sedex 75, France), operating at 20 °C with an air pressure of 2 bar. The polar fractions contents, including dimeric and polymeric triglycerides (DPTG) and oxidized triglycerides (OTG) were calculated on a mass basis [22].

Anisidine Value

The total contents of secondary oxidation products, namely unsaturated aldehydes, were estimated by the *p*-anisidine value (*p*-AV) according to ISO 6885:2006 [23].

Statistical Analysis

All determination and experiments were performed in triplicate and results reported in terms of the mean and standard deviation. Significance of the differences between means in oil samples was determined using ANOVA and Tukey as the *post hoc* test, the differences between means before and after deep-frying were studied applying the *t* Test, both with a significance level of $\alpha = 0.05$. Data were also subjected to principal component analysis (PCA), and Pearson's correlations. SPSS software, version 20.0 (IBM Corporation, New York, U.S.A.) was applied to these statistical studies.

Results and Discussion

Optimization of HS–SPME Conditions

The HS–SPME technique was evaluated taking into account the extraction temperature, equilibrium time, extraction time, and desorption time. Figure 1 gives the details for some selected volatile compounds, by optimized parameters. Olive oil heated at 175 °C for 8 h was used for the initial optimization purposes, since it presents the highest chemical complexity in terms of volatiles diversity (unrefined). Mixed DVB/CAR/PDMS fibers were selected for our study due to the ability for isolation of compounds with different physical–chemical properties and proven suitability for vegetable oils [24].

Extraction of volatiles is known to be enhanced by sample agitation, with magnetic stirring widely used by other authors [14], usually around 200 rpm [18, 24, 25]. A special reference should be made to the stir bars used, because the usual Teflon coated ones might retain some components from the oil matrix, introducing an external source of error and contamination (data not shown). The problem was solved by using glass covered stir bars.

Extraction temperatures of 40, 50, 65, 80, and 100 °C were tested, maintaining the other variables constant in all cases (Fig. 1a). In general, an increase in extraction temperature led to an increase in the peak area in most of the selected compounds, particularly aldehydes, the prevailing ones (e.g., 2,4-decadienal). However, for some compounds, a decrease in the peak area is observed at higher temperatures (e.g., hexanal), or even their complete disappearance, as for decane despite its high boiling point (173.8–174.4 °C). Additionally, the onset of new compounds (not shown) is also noticed at the highest temperatures which could be related with unwanted "*in situ*" formation from precursors present in the sample. Considering all these factors together with the fact that an excessive increase in temperature can cause premature desorption of volatile compounds, 50 °C was finally selected as the optimum sample temperature for both the extraction and the equilibrium steps.

Stabilization of the headspace in the vial was reached by studying different equilibration times (2, 5, 10 and 15 min) before contact with the fiber, maintaining the remaining parameters constant (Fig. 1b). Although reduced changes in the peak areas of hexanal, and 2,4-decadienal were observed, for all the times tested the RSD was lower than 25%, and lower chromatographic peak resolution was obtained for some volatiles when using only 2 min. Therefore, 5 min of equilibrium time was chosen as a compromise between peak resolution and sample throughput.

To optimize extraction time, 15, 30, 45 and 60 min were assayed, while maintaining the already optimized conditions. Overall, an increase of the global detector signal with extraction time was observed, but prolonged times (higher than 30 min) cause a decrease in the peak area for some compounds, such as hexanal (Fig. 1c). In addition, lower peak resolution of some compounds was observed when an exposure time of 45 min or higher was used. Therefore, 30 min of extraction time was selected for further experiments which, besides providing generally good results in terms of compound amounts and chromatographic resolution (reduced overload), allowed a relatively good sample throughput, compatible with the total chromatographic time of each run.

Regarding the range of desorption time tested (1–5 min), only formic acid had statistical significant area increases, but resolution increased with time (Fig. 1d), probably as a consequence of a deeper desorption and cleaning of the fiber between extractions. Therefore, desorption time of 5 min was chosen, maintaining again a compromise between peak resolution and sample throughput. It was verified that no need for further cleaning of the fiber was necessary, being ready to be used in the next sample.

On the basis of the optimized conditions, reproducibility was tested. Figure 2 shows chromatograms of the volatiles extracted from two different olive oils sub-samples treated in the same way. Identical volatiles profile can be observed, with variabilities inferior to 10% (RSD) (data not shown), attesting the method's accuracy.

Vegetable Oils Alterations with Potato Deep-Frying

Most of the volatiles formed by thermal degradation have their origin in the fatty acids profile. Therefore, to support the discussion of the volatile patterns formed under thermal and oxidative stress, we also analyzed the fatty acids composition of oils, presented in Table 1, Significant statistically chemical differences are observed, with MUFA varying from 56% in PO to 74% in EVOO, with

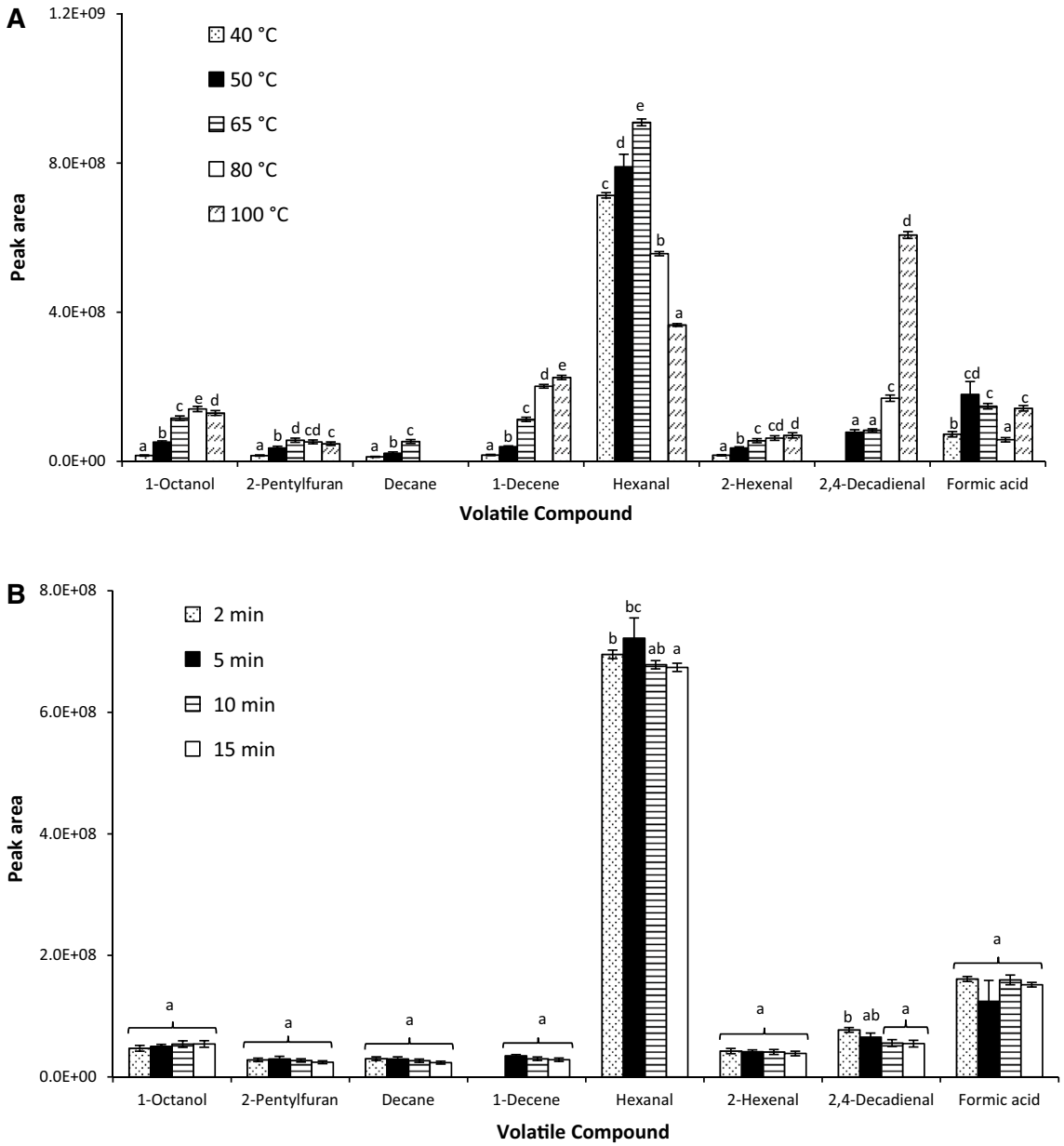

Fig. 1 Optimization of HS–SPME conditions for olive oil sample after frying: **a** sample extraction temperature; **b** equilibrium time; **c** extraction time; and **d** desorption time. ([a–e]for significant differences ($p \leq 0.05$) between optimization parameters)

oleic acid (C18:1n-*9*) as the main compound. In the case of total PUFA content, CO is the richest (28.4%), while EVOO contain the lowest amount (9.3%), with linoleic acid (C18:2n-*6*) as the most abundant, particularly in PO, followed by linolenic acid (C18:3n-*3*), particularly relevant in CO, with 9.3% against less than 1% on the other oils. After frying, the PUFA proportion is slightly reduced on all oils, indicating their degradation during the process, being, among others, the precursor of some volatiles. Despite the recognized toxicity of *p*-anisidine, this test is still being used for research purposes as a tool to evaluate the extension of aldehydes formation due to thermal decomposition of hydroperoxides (principally 2-alkenals and 2,4-alkadienals) [26], indicative of secondary oxidation reactions. Statistical significant differences indicate a higher thermal fatty acids oxidation degree in the case of PO and CO, without distinguishing both (Table 1).

Total polar compounds are widely regarded as one of the most reliable measures of total oxidative degradation extension [27], and were also evaluated in this study (Table 1). The results revealed a similar degradation after 8 h of frying on both PO and CO, with 21%, against only

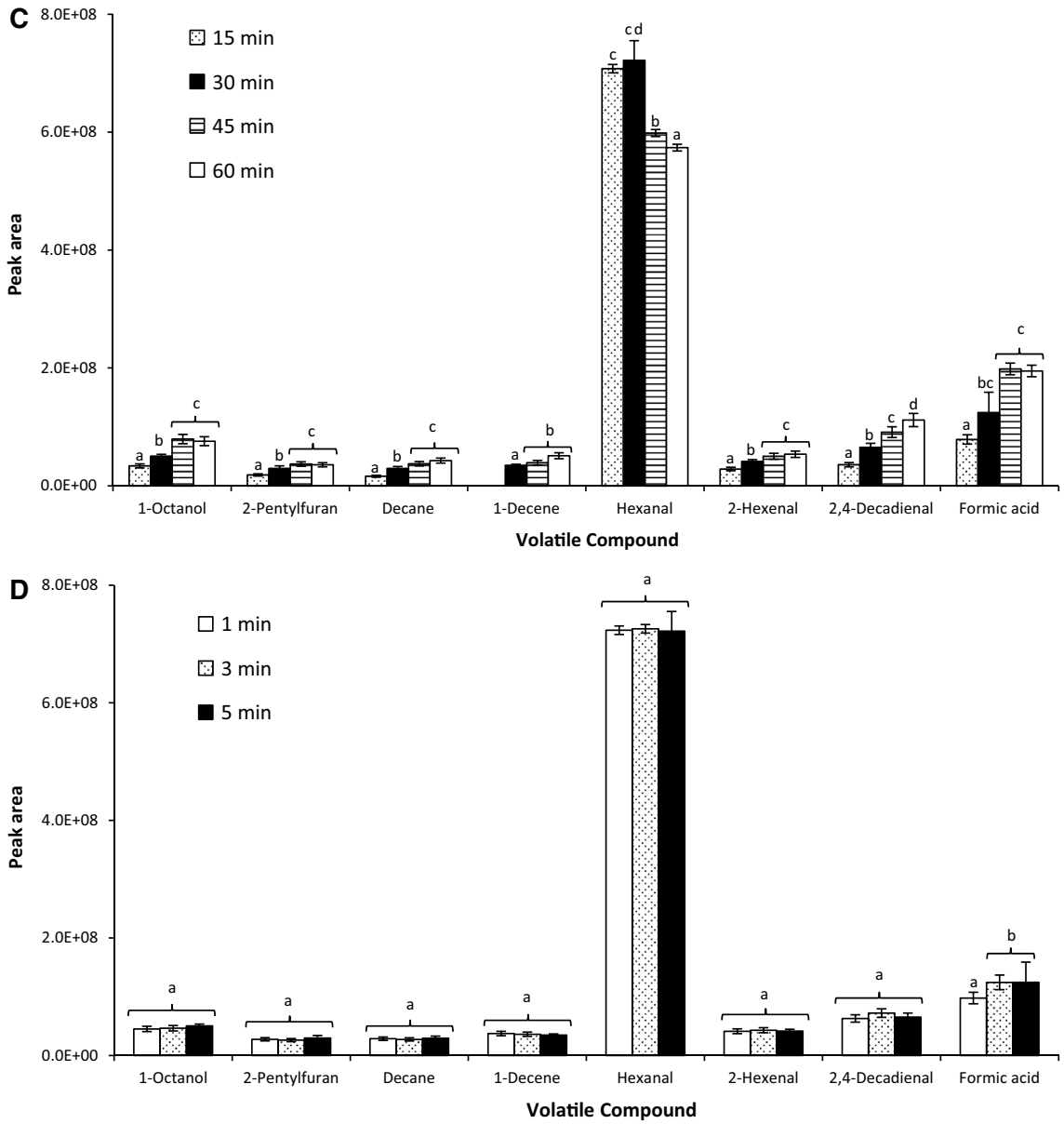

Fig. 1 continued

16% in EVOO, indicative of its high stability under these processing conditions. Similar trends were verified after detailed analysis by HPSEC, with lower content of all polar fractions in EVOO, and similar results between PO and CO, although the former had a comparatively higher DPTG contents while CO showed higher oxidation products (OTG).

The volatile fractions were analyzed by the optimized HS–SPME/GC–MS method. As detailed in Table 2, a total of fifty-one volatile compounds were identified and quantified in internal standard equivalents. Non-heated unrefined olive oil showed a higher complexity (16 volatile compounds) than the other two non-heated oils (10 for PO and 5 for CO), both refined. As expected, after being used in the deep-frying process, all the samples showed a pronounced complexity, with an increment of number (32, 30, and 25, for EVOO, PO, and CO, respectively) and amount of volatiles (Fig. 3). The families of compounds of most concern from health point of view, such as aldehydes, will be described in more detail below, together with a brief discussion about the compounds quantified, and its possible association with the fatty acid profile, supported by the statistical data detailed in Table 3.

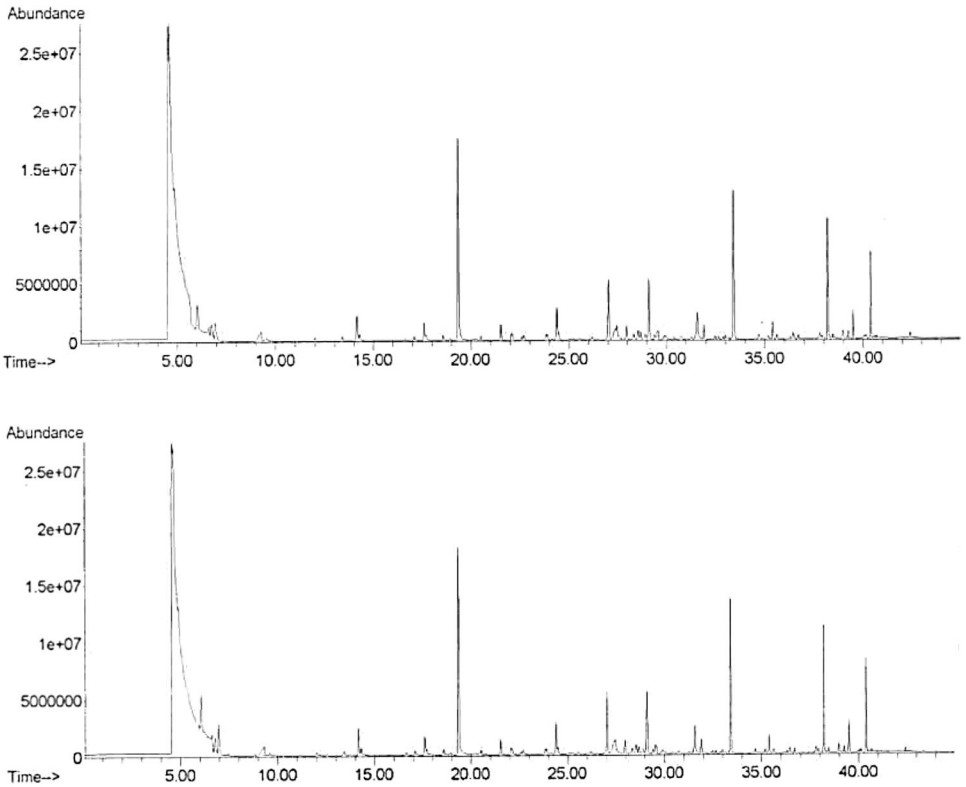

Fig. 2 Chromatograms of replicate heated EVOO under the optimized HS–SPME conditions

Hydrocarbons, Ketones, Alcohols, Carboxylic Acids, and Furan Derivatives

Saturated hydrocarbons (alkanes) were presented in the volatile fraction of the three unheated oils tested, whereas unsaturated hydrocarbons (alkenes) were only detected in unheated EVOO. Generally, after the frying process, a decrease of alkanes was observed, with significant statistical differences before and after frying (Table 3). This disappearance could be explained by their boiling points close to temperatures used under frying [28]. Naturally terpenic hydrocarbons such as alpha-farnesene and copaene, were observed only in original EVOO [29]. Alkylbenzenes compounds, particularly toluene, were the most abundant hydrocarbons in the volatile fraction of the three fresh oils. During deep-frying, an important enhancement of toluene amounts in EVOO was observed while, conversely, a slight but statistically significant decrease was perceived in both PO and CO (Table 3).

Ketones were formed in small quantities during deep-frying, being totally absent in CO (Table 3). EVOO formed a higher number of different alcohols after frying, specifically 1-heptanol and 1-octanol, two cleavage products from methyl oleate hydroperoxides [30]. Nevertheless, PO presented the total highest alcohol amounts due to a high formation ratio of 1-octen-3-ol (Table 2), subsequent to linoleic acid degradation [30]. Significant statistical differences for alcoholic compounds were obtained after deep-frying for the three oils (Table 3).

In terms of carboxylic acids, hexanoic acid presented a higher formation ratio in the case of PO, being absent in CO. It has been reported that hexanoic acid may result from the secondary decomposition of hexanal and 2,4-decadienal [30], which is well correlated with the higher amounts of these two aldehydes found in our study for PO, as detailed below.

Although absent in the three oils before heating, two furan derivatives were detected after deep-frying process, 2-pentylfuran in the three oil samples, and 5-butylhydro-2(3*H*)-furanone in EVOO only. Furan formation in foods has been attributed, among other mechanism pathways, to PUFA oxidation induced by thermal treatment [31]. Particularly, formation of 2-pentylfuran could be associated with methyl linoleate hydroperoxide degradation [32], correlating to linoleic acid amount in PO.

Aldehydes

Alkanals, alkenals and alkadienals are the family of volatiles presenting a greater and more marked rise when oils are subjected to frying, as can be appreciated in Fig. 3. In general, regardless of oil type, these results were consistent with other studies which applied frying temperatures, even after a short time [2, 13, 17, 33–39]. An ability to induce toxicological effects has been attributed to these

Table 1 Fatty acids composition (relative %) and degradation indicators of EVOO, PO and CO, before and after deep-frying

	EVOO		*t* Test		PO		*t* Test		CO		*t* Test	
	Before frying	After frying	Score	*p*	Before frying	After frying	Score	*p*	Before frying	After frying	Score	*p*
FAME (%)												
C18:1n-9	70.71 ± 0.51^{c}	70.92 ± 0.04^{C}	−0.70	>0.05	52.94 ± 0.02^{a}	53.92 ± 0.04^{A}	−37.76	≤0.001	57.85 ± 0.07^{b}	59.39 ± 0.14^{B}	−16.82	≤0.001
C18:2n-6	8.55 ± 0.03^{a}	7.16 ± 0.03^{A}	59.22	≤0.001	25.51 ± 0.04^{c}	22.73 ± 0.03^{C}	99.06	≤0.001	19.05 ± 0.01^{b}	17.80 ± 0.08^{B}	26.85	≤0.001
C18:3n-3	0.80 ± 0.01^{b}	0.57 ± 0.01^{B}	23.25	≤0.001	0.18 ± 0.00^{a}	0.13 ± 0.00^{A}	14.55	≤0.001	9.28 ± 0.00^{c}	7.85 ± 0.00^{C}	2251.49	≤0.001
Degradation indicators												
TPM (%)	7 ± 0^{a}	16 ± 0^{A}	−13.63	≤0.001	10 ± 0^{b}	21 ± 0^{B}	−87.75	≤0.001	10 ± 0^{c}	21 ± 0^{B}	−13.21	≤0.001
PC (%)	1.43 ± 0.21^{a}	8.63 ± 0.35^{A}	−30.51	≤0.001	2.98 ± 0.33^{c}	11.71 ± 0.21^{B}	−38.63	≤0.001	2.07 ± 0.18^{a}	11.33 ± 0.29^{B}	−47.09	≤0.001
DPTG (%)	0.22 ± 0.01^{a}	2.84 ± 0.00^{A}	−1500.29	≤0.001	0.53 ± 0.01^{b}	4.56 ± 0.01^{C}	−281.85	≤0.001	0.68 ± 0.00^{c}	4.49 ± 0.00^{B}	−1617.80	≤0.001
OTG (%)	n.d.	4.23 ± 0.02^{A}	–	–	n.d.	4.75 ± 0.00^{B}	–	–	n.d.	5.35 ± 0.01^{C}	–	–
p-AV	17 ± 2^{a}	88 ± 9^{A}	−131.15	≤0.001	28 ± 1^{c}	149 ± 2^{B}	−22.82	≤0.001	24 ± 0^{b}	178 ± 20^{B}	−296.18	≤0.001

[a–c] Different letters indicate significant differences ($p \leq 0.05$) between the different original oils

[A–C] Different letters indicate significant differences ($p \leq 0.05$) between the different oils after potatoes deep-frying

EVOO extra virgin olive oil, *PO* peanut oil, *CO* canola oil, *C18:1n-9* oleic acid, *C18:2n-6* linoleic acid, *C18:3n-3* linolenic acid, *TPM* total polar material, *PC* polar compounds, *DPTG* dimeric and polymeric triglycerides, *OTG* oxidized triglycerides, *p-AV* anisidine value

compounds [36] being therefore the ones that require more attention from the safety point of view.

The global aldehyde increase is in accordance with the *p*-AV, before and after frying, as presented in Table 1. In addition, strong Pearson's correlations were found between *p*-AV and unsaturated aldehydes for the three oils tested (EVOO: $r^2 = 0.991$, $p \leq 0.001$; PO and CO: $r^2 = 0.998$, $p \leq 0.001$).

As detailed in Table 2, alkanals from 5 to 10 carbon atoms were found in very low quantities in unheated EVOO and PO, being absent in CO. An increase diversity was observed after deep-frying, being this increment most prominent in the case of EVOO due to a high formation of nonanal and octanal, probably associated with the highest content in oleic acid, since they are known to be released by hemolytic fission of its R–O bond [40]. Pentanal and hexanal are formed in a greater amount in PO, which could be explained by the higher abundance of linoleic acid in this oil (Table 1) [40]. Significant statistical differences were observed for alkanals when the three oils were compared after deep-frying (EVOO > PO > CO), or when the same oil was compared before and after deep-frying (Table 3).

Concerning unsaturated aldehydes, it is worth highlighting that they are considered to be more harmful than alkanals, alkadienals presenting the most toxic effects [36]. These compounds are almost absent in unheated oils, but a significant increase occurs during the deep-frying process. Alkenals formed have from 3 to 11 carbon atoms and the total amount is statistically higher for PO (Table 3), correlated with the highest abundance of linoleic acid, the main source of 2-heptenal and 2-octenal, the two major alkenals formed in this oil. The formation of acrolein (2-propenal), with recognized carcinogenic effects, was only observed in heated PO. Acrolein production from PO subjected to mild temperature frying (175 °C) was observed in this work (3.46 μg g^{-1}), despite being reported to be usually formed at higher temperatures. This finding is in accordance with the results reported by Fullana *et al.* and Katragadda *et al.*, who also described acrolein formation in cooking oils treated at medium temperatures [33, 36]. Guillen and Uriarte, and Katragadda *et al.* associated the higher emission of acrolein from virgin linseed oil and safflower oil, in comparison with other type of oils analyzed, with its greater content of PUFA [34, 36]. This could also be an explanation for our results. Despite its lower abundance in linoleic acid, EVOO also forms a large quantity of alkenals after deep-frying which is associated with the important formation of *E*-2-decenal and 2-undecenal, alkenals derived from oleic acid [41]. It should also be highlighted that 2-butenal, *E*-2-pentenal and benzaldehyde are only formed in CO, certainly derived from linolenic acid decomposition. In addition, 2-butenal and benzaldehyde have also been described as toxic [42].

Table 2 Semi-quantification of volatiles compounds (μg g^{-1} of internal standard equivalents) of EVOO, PO and CO, before and after deep-frying

Compound (μg g^{-1})	EVOO				PO				CO			
	Before frying	RSD (%)	After frying	RSD (%)	Before frying	RSD (%)	After frying	RSD (%)	Before frying	RSD (%)	After frying	RSD (%)
Alkanes												
Hexane[a]	1.74 ± 0.29	16	n.d.	–	2.24 ± 0.17	7	1.51 ± 0.03	2	1.53 ± 0.29	19	n.d.	–
2,2,4-Trimethylpentane[a]	n.d.	–	n.d.	–	1.39 ± 0.18	13	n.d.	–	n.d.	–	n.d.	–
Heptane[a]	4.31 ± 0.38	9	6.38 ± 0.12	2	7.03 ± 0.77	11	4.11 ± 0.08	2	4.45 ± 0.92	21	3.64 ± 0.13	3
1-Methoxyhexane[a]	0.16 ± 0.01	6	n.d.	–	n.d.	–	n.d.	–	n.d.	–	n.d.	–
Alkenes												
R-1-methyl-4-(1-methylethyl)-cyclohexene[b]	n.d.	–	1.13 ± 0.01	1	n.d.	–	n.d.	–	n.d.	–	n.d.	–
3,7-Dimethyl-1,3,7-Octatriene[b]	0.61 ± 0.05	7	n.d.	–	n.d.	–	n.d.	–	n.d.	–	n.d.	–
4,8-Dimethyl-1,3,7-Nonatriene[b]	2.07 ± 0.38	18	n.d.	–	n.d.	–	n.d.	–	n.d.	–	n.d.	–
Sesquiterpenes												
Copaene[b]	0.58 ± 0.09	16	n.d.	–	n.d.	–	n.d.	–	n.d.	–	n.d.	–
Alpha-farnesene[b]	0.46 ± 0.14	29	n.d.	–	n.d.	–	n.d.	–	n.d.	–	n.d.	–
Alkylbenzenes												
Toluene[a]	15.15 ± 2.52	17	36.43 ± 6.23	17	19.58 ± 3.93	20	14.76 ± 0.67	5	11.90 ± 2.89	24	10.44 ± 0.04	0
Ethylbenzene[a]	n.d.	–	0.85 ± 0.15	18	0.43 ± 0.05	12	n.d.	–	0.21 ± 0.03	14	n.d.	–
Dimethylbenzene (p/m/o)[a]	2.74 ± 0.59	21	4.03 ± 0.97	24	2.96 ± 0.66	22	1.70 ± 0.19	11	1.65 ± 0.30	18	1.05 ± 0.02	1
Ketones												
2-Heptanone[a]	n.d.	–	n.d.	–	n.d.	–	0.39 ± 0.10	24	n.d.	–	n.d.	–
3-Butyl-cyclopentanone[b]	n.d.	–	1.84 ± 0.06	3	n.d.	–	1.17 ± 0.10	9	n.d.	–	n.d.	–
Caprolactam[b]	n.d.	–	n.d.	–	3.10 ± 0.68	22	n.d.	–	n.d.	–	n.d.	–
Alcohols												
1-Penten-3-ol[a]	n.d.	–	n.d.	–	n.d.	–	n.d.	–	n.d.	–	0.48 ± 0.06	13
1-Pentanol[a]	n.d.	–	1.04 ± 0.03	2	n.d.	–	2.32 ± 0.05	2	n.d.	–	0.51 ± 0.01	1
Z-3-Hexen-1-ol[a]	3.97 ± 0.21	5	n.d.	–	n.d.	–	n.d.	–	n.d.	–	n.d.	–
1-Hexanol[a]	1.12 ± 0.07	6	n.d.	–	n.d.	–	n.d.	–	n.d.	–	n.d.	–
1-Heptanol[b]	n.d.	–	2.84 ± 1.00	35	n.d.	–	n.d.	–	n.d.	–	n.d.	–
1-Octen-3-ol[b]	n.d.	–	2.56 ± 0.07	3	n.d.	–	8.66 ± 0.60	7	n.d.	–	n.d.	–
1-Octanol[b]	n.d.	–	4.81 ± 0.17	4	n.d.	–	3.51 ± 0.29	8	n.d.	–	n.d.	–
Carboxylic acids												
Acetic acid[a]	n.d.	–	1.12 ± 0.01	1	n.d.	–	0.74 ± 0.02	3	n.d.	–	0.68 ± 0.17	24
Hexanoic acid[b]	n.d.	–	1.73 ± 0.16	9	0.80 ± 0.24	30	10.24 ± 2.99	29	n.d.	–	n.d.	–
Nonanoic acid[b]	n.d.	–	0.87 ± 0.16	18	n.d.	–	1.06 ± 0.13	13	n.d.	–	n.d.	–

Table 2 continued

Compound (μg g^{-1})	EVOO				PO				CO			
	Before frying	RSD (%)	After frying	RSD (%)	Before frying	RSD (%)	After frying	RSD (%)	Before frying	RSD (%)	After frying	RSD (%)
Furan derivatives												
2-Pentylfuran[b]	n.d.	–	1.41 ± 0.05	3	n.d.	–	3.46 ± 0.23	7	n.d.	–	1.77 ± 0.19	10
5-Butyldihydro-2(3H)furanone[b]	n.d.	–	1.01 ± 0.06	6	n.d.	–	n.d.	–	n.d.	–	n.d.	–
Alkanals												
2-Methylbutanal[a]	n.d.	–	1.87 ± 0.24	13	n.d.	–	n.d.	–	n.d.	–	1.37 ± 0.04	3
Pentanal[a]	n.d.	–	0.97 ± 0.02	2	n.d.	–	2.74 ± 0.11	4	n.d.	–	0.50 ± 0.04	8
Hexanal[a]	0.58 ± 0.01	2	4.74 ± 0.79	17	0.36 ± 0.05	12	12.43 ± 0.32	3	n.d.	–	4.47 ± 0.35	8
Heptanal[a]	n.d.	–	3.48 ± 0.22	6	n.d.	–	2.03 ± 0.03	1	n.d.	–	n.d.	–
Benzaldehyde[b]	n.d.	–	n.d.	–	n.d.	–	n.d.	–	n.d.	–	5.86 ± 0.13	2
Octanal[b]	n.d.	–	14.99 ± 0.18	1	n.d.	–	9.15 ± 0.71	8	n.d.	–	5.99 ± 0.42	7
Nonanal[b]	0.92 ± 0.14	15	58.42 ± 0.10	0	0.49 ± 0.02	3	29.14 ± 3.40	12	n.d.	–	22.07 ± 2.27	10
Decanal[b]	n.d.	–	1.26 ± 0.03	2	n.d.	–	0.60 ± 0.02	3	n.d.	–	n.d.	–
Alkenals												
2-Propenal[a]	n.d.	–	n.d.	–	n.d.	–	3.63 ± 0.46	13	n.d.	–	n.d.	–
2-Butenal[a]	n.d.	–	n.d.	–	n.d.	–	n.d.	–	n.d.	–	2.30 ± 0.22	9
E-2-Pentenal[a]	n.d.	–	n.d.	–	n.d.	–	n.d.	–	n.d.	–	1.11 ± 0.11	9
2-Methyl-4-pentenal[a]	1.16 ± 0.06	5	n.d.	–	n.d.	–	n.d.	–	n.d.	–	n.d.	–
2-Hexenal[a]	7.26 ± 0.25	3	0.93 ± 0.07	7	n.d.	–	2.03 ± 0.01	0	n.d.	–	0.80 ± 0.05	6
2-Heptenal[b]	n.d.	–	15.06 ± 0.75	5	n.d.	–	45.77 ± 2.51	5	n.d.	–	22.20 ± 1.08	5
E-2-octenal[b]	n.d.	–	7.30 ± 0.21	3	n.d.	–	14.67 ± 1.37	9	n.d.	–	6.80 ± 0.49	7
2-Nonenal[b]	n.d.	–	5.78 ± 0.04	1	n.d.	–	3.24 ± 0.28	9	n.d.	–	2.94 ± 0.27	9
E-2-decenal[b]	n.d.	–	45.56 ± 1.08	2	n.d.	–	30.77 ± 3.22	10	n.d.	–	15.30 ± 1.66	11
2-Undecenal[b]	n.d.	–	33.09 ± 0.98	3	n.d.	–	17.91 ± 1.38	8	n.d.	–	11.66 ± 1.28	11
Alkadienals												
E,E-2,4-hexadienal[a]	0.48 ± 0.05	10	n.d.	–	n.d.	–	n.d.	–	n.d.	–	n.d.	–
Z,E 2,4-heptadienal[b]	n.d.	–	1.52 ± 0.04	2	n.d.	–	1.92 ± 0.14	7	n.d.	–	9.44 ± 0.54	6
E,E-2,4-heptadienal[b]	n.d.	–	3.89 ± 0.17	4	n.d.	–	n.d.	–	n.d.	–	32.10 ± 1.69	5
2,4-Nonadienal[b]	n.d.	–	n.d.	–	n.d.	–	n.d.	–	n.d.	–	n.d.	–
Z,E 2,4-decadienal[b]	n.d.	–	6.27 ± 0.08	1	n.d.	–	10.62 ± 0.85	8	n.d.	–	6.05 ± 0.70	12
E,E-2,4-decadienal[b]	n.d.	–	14.09 ± 0.11	1	n.d.	–	33.87 ± 2.74	8	n.d.	–	19.02 ± 1.89	10

[a] -4-Methyl-2-pentanol

[b] -1,2,3-Trichloropropane

EVOO extra virgin olive oil, *PO* peanut oil, *CO* canola oil, *RSD* relative standard deviation, *n.d.* not detected

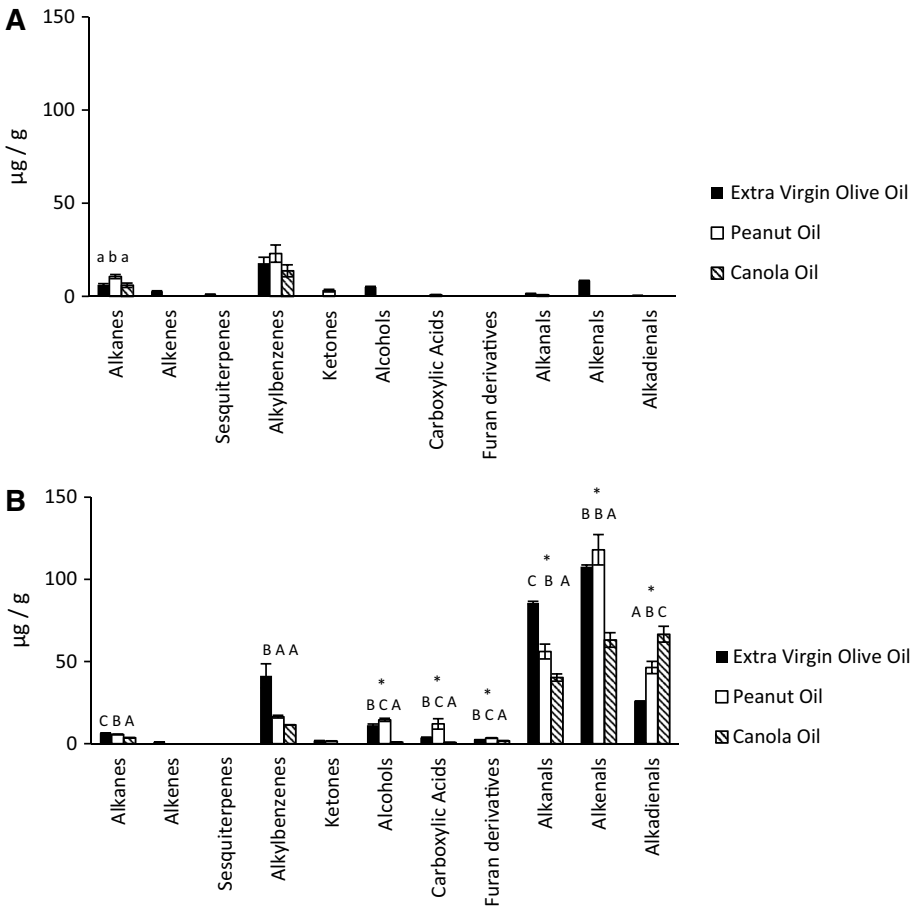

Fig. 3 Volatile compounds grouped by chemical classes, before (**a**) and after (**b**) potato deep-frying, for EVOO, PO and CO. [$^{a-c}$ for significant differences ($p \leq 0.05$) between original oils; $^{A-C}$ for significant differences ($p \leq 0.05$) between oils after deep-frying; *consistent increase on all oils after deep-frying]

Alkadienals (2,4-) with 6 to 10 carbon atoms were also found, with both (*Z,E*) and (*E,E*) isomers distinguished. Significant statistical differences were found for the abundance of alkadienals in the three oils after processing, with the highest content in CO and the lowest in EVOO (Table 3). In CO, the presence of *E,E*-2,4-heptadienal was verified, probably originated from oxidation of methyl linolenate hydroperoxide [30]. However, special attention should be attributed to *E,E*-2,4-decadienal, formed by peroxidation of linoleic acid [43], which has important genotoxic and cytotoxic effects. Higher abundance of this toxic aldehyde was observed for PO which is in agreement with its greater content in the precursor fatty acid, linoleic acid. Romano *et al*. also reported good correlation between *E,E*,-2,4-decadienal and TPC in frying oils, so it could be possible to consider this compound as a suitable marker for detecting oxidative degradation, as also indicated by Boskou *et al*. while quantifying this compound by HPLC [13, 43].

Global Analysis of Volatiles and Chemical Characterization

The previous results showed that neither traditional degradation indicators nor total volatile provide accurate information about oils oxidation when oils with similar fatty acid ratios are being compared. Only a detailed analysis of volatile compounds, mainly *E,E*-2,4-decadienal, allowed a clear distinction of the degradation degree of the three oils. Indeed, regardless of the oil type, strong Pearson's correlations were found between degradation indicators and *E,E*-2,4-decadienal (TPC: $r^2 = 0.922$, $p \leq 0.001$; PC: $r^2 = 0.934$, $p \leq 0.001$; DPTG: $r^2 = 0.937$, $p \leq 0.001$; OTG: $r^2 = 0.882$, $p \leq 0.001$; and *p*-AV: $r^2 = 0.882$, $p \leq 0.001$). Interestingly, despite the lower content of total volatiles shown by CO in comparison with EVOO and PO, and the same trend observed for aldehydes, the sum of toxic aldehydes clearly differentiates the three oils, EVOO < CO < PO, with a similar trend to those observed for *E,E*-2,4-decadienal values.

These observations are supported by the PCA analysis performed on the global data (Fig. 4). Dimension 1 was characterized positively by furan derivatives, alkanals, alkadienals, total volatile, toxic volatiles, alkenals, alcohols, and carboxylic acids correlated with degradation indicators, and negatively by alkanes and sesquiterpenes. Dimension 2 was characterized positively by C18:1n-9, alkenes and akylbenzenes, and negatively by PUFA, C18:2n-6 and C18:3n-3. Thus, unheated oils were

Table 3 Semi-quantification of total volatile family (μg g^{-1} of internal standard equivalents) of EVOO, PO and CO, before and after deep-frying

Compound (μg g^{-1})	EVOO		*t* Test		PO		*t* Test		CO		*t* Test	
	Before frying	After frying	Score	*p*	Before frying	After frying	Score	*p*	Before frying	After frying	Score	*p*
Alkanes	6.20 ± 0.67^{a}	6.38 ± 0.12^{C}	−0.45	>0.05	10.66 ± 1.11^{b}	5.62 ± 0.06^{B}	7.85	≤0.001	5.98 ± 1.20^{a}	3.64 ± 0.13^{A}	3.36	≤0.05
Alkenes	2.68 ± 0.34	1.13 ± 0.01	8.01	≤0.001	n.d.	n.d.	–	–	n.d.	n.d.	–	–
Sesquiterpenes	1.04 ± 0.23	n.d.	–	–	n.d.	n.d.	–	–	n.d.	n.d.	–	–
Alkylbenzenes	17.89 ± 3.11	41.31 ± 7.36^{B}	−5.08	≤0.05	22.97 ± 4.64	16.46 ± 0.85^{A}	2.39	>0.05	13.76 ± 3.22	11.49 ± 0.03^{A}	1.22	>0.05
Ketones	n.d.	1.84 ± 0.06	–	–	3.10 ± 0.68	1.56 ± 0.20	3.80	≤0.05	n.d.	n.d.	–	–
Alcohols	5.09 ± 0.28	11.25 ± 0.74^{B}	−13.60	≤0.001	n.d.	14.49 ± 0.94^{C}	–	–	n.d.	0.99 ± 0.07^{A}	–	–
Carboxylic acids	n.d.	3.72 ± 0.31^{B}	–	–	0.80 ± 0.24	12.04 ± 3.14^{C}	−6.19	≤0.05	n.d.	0.68 ± 0.17^{A}	–	–
Furan derivatives	n.d.	2.42 ± 0.02^{B}	–	–	n.d.	3.46 ± 0.23^{C}	–	–	n.d.	1.77 ± 0.19^{A}	–	–
Alkanals	1.50 ± 0.13	85.73 ± 0.88^{C}	−164.14	≤0.001	0.85 ± 0.06	56.08 ± 4.52^{B}	−21.16	≤0.001	n.d.	40.26 ± 2.21^{A}	–	–
Alkenals	8.43 ± 0.19	107.72 ± 1.07^{B}	−158.25	≤0.001	n.d.	118.02 ± 9.23^{B}	–	–	n.d.	63.12 ± 4.40^{A}	–	–
Alkadienals	0.48 ± 0.05	25.77 ± 0.02^{A}	−813.41	≤0.001	n.d.	46.41 ± 3.73^{B}	–	–	n.d.	66.61 ± 4.82^{C}	–	–
Total	43.30 ± 3.61^{b}	287.27 ± 8.76^{B}	−44.63	≤0.001	38.38 ± 4.89^{b}	274.14 ± 21.06^{B}	−18.89	≤0.001	19.74 ± 4.42^{a}	188.56 ± 11.61^{A}	−23.54	≤0.001

[a–c] Difference letters indicate significant differences ($p \leq 0.05$) between the different original oils

[A–C] Different letters indicate significant differences ($p \leq 0.05$) between the different oils after to be subjected to potatoes deep-frying

EVOO extra virgin olive oil, *PO* peanut oil, *CO* canola oil, *n.d.* not detected

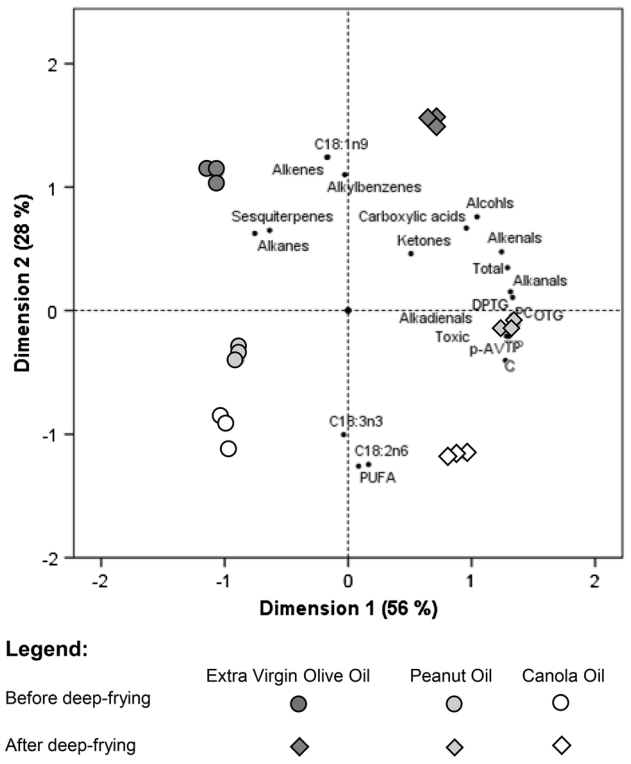

Fig. 4 Principal component analysis obtained from the volatile families, chemical characterization before and after potatoes deep-frying

clearly distinguished from the processed ones, as well as the EVOO from the other oils, with a strong involvement of fatty acids in this distinction, while the other oils presented also differ between them. Before frying, EVOO was associated with alkanes, sesquiterpenes and alkenes, whereas PO and CO were closely related with PUFA and their main fatty acids (C18:2n-6 and C18:3n-3). After frying, EVOO was related with alkylbenzenes, PO was associated with alkadienals, toxic volatiles and degradation indicators, and CO was not linked to any specific family. As mentioned above, alkadienals were strongly linked to the classical degradation indicators, TPC, PC and their fractions, and *p*-AV.

Conclusions

The volatile profile of three vegetable oils, EVOO, PO and CO was evaluated by an optimized HS–SPME/GC–MS method, before and after deep-frying potatoes. To the best of our knowledge, this is the first comparative study focused on high MUFA:PUFA ratio vegetables oils. The optimized methodology allowed us to compare the three oils under the same analytical basis, by the use of appropriate internal standards, a situation that can extend its comparison with future works with different oils and processing conditions.

Despite all three oils being recommended for frying, due to their low content of polyunsaturated fatty acids, significant statistical differences between the volatiles of the three oils, both before and after potato deep-frying were found. In addition, strong Pearson's correlations were found between *p*-AV and unsaturated aldehydes for the three oils tested. Globally, EVOO showed a greater stability against oxidative thermal degradation, particularly regarding the formation of volatile aldehydes. Moreover, the abundance and formation of some harmful volatile compounds, such as *E,E*-2,4-decadienal, and acrolein, was higher in PO, which is apparently related to its greater content of linoleic acid. Regardless of the oil type, strong Pearson's correlations were also found between degradation indicators and *E,E*-2,4-decadienal, corroborating the possibility of considering this compound to be a suitable marker for detecting thermal oxidative degradation in vegetable oils with lower PUFA contents. Indeed, only the detailed analysis of the volatile fraction, particularly *E,E*-2,4-decadienal allowed us to distinguish the degradation degree and pattern of the three oils, and therefore their potential toxicity under thermal and oxidative stress: EVOO < CO < PO. The formation of acrolein at temperatures as low as 175 °C has also been demonstrated in this study.

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