Impact of potatoes deep-frying on common monounsaturated-rich vegetable oils: a comparative study

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Abstract Aiming to distinguish the nutritional and safety impacts on consumer's health of prolonged frying with vegetable oils rich in monounsaturated fatty acids (MUFA), namely peanut oil (PO), canola oil (CO) and extra virgin olive oil (EVOO), a domestic deep-frying assay using fresh potatoes was implemented (175 °C, 8 h per day, up to 28 h). Based on a total polar compounds (TPC) degradation limit of 25%, PO and CO enabled 18–20 h of frying, while EVOO allowed significantly higher frying hours (> 28 h). Despite the non-significant variations in oxidized triglycerides contents observed through time, and loss of all major antioxidants during the first 8 to 12 h of frying, PO showed statistically higher amounts of conjugated dienes (27 at 20 h; against 19 in CO and 17 in EVOO) and CO of anisidine value (252 at 20 h; against 209 in PO and 100 in EVOO), indicative of different oxidation patterns. This was corroborated with the analysis of major volatiles, with PO and CO being statistically richer in alkenals and alkadienals, respectively.

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Therefore, despite the MUFA predominance, differences in their unsaturation profile impact on the type and amount of degradation products formed under prolonged frying and consequently on consumer's health. As to EVOO use for prolonged frying, despite its increased resistance to oxidation and lower risk of formation of unhealthy volatiles, it loses its pool of natural bioactive compounds in the first hours of frying.

Keywords Domestic frying · Extra virgin olive oil · Peanut oil · Canola oil · Bioactivity · Oxidation

Introduction

Frying is one of the oldest cooking methods, used both in domestic and industrial food preparation. Its popularity is largely sustained by the unique sensorial attributes of fried foods (crust, taste, colour, and flavour) together with the advantages of being a fast and simple preparation method. However, the adequacy of different fats and oils for the high temperatures of deep-frying is still a highly debated issue, while the shadow on fried food nutritional impact persists despite the absence of clear evidences of deleterious effects of vegetable oils on cardiovascular health (Sayon-Orea et al. 2015).

Oil selection for deep-frying purposes should be based on several factors, including its nutritional properties, palatability and ability to withstand high temperatures for long periods of time. Therefore, thermo-oxidative stability is an important criterion, being largely dependent on the fatty acid composition, together with the presence of minor compounds in the unsaponifiable fraction that might delay or induce oxidation. In this sense, vegetable oils with higher saturation degree are usually more stable to thermo-

oxidation, though they may increase the risk for cardiovascular diseases (Sayon-Orea et al. 2015). In opposition, oils richer in polyunsaturated fatty acids (PUFA) are advantageous from the nutritional point of view but are generally more unstable at frying temperatures (Petersen et al. 2013), with a premature loss of frying performance, together with the formation of degradation compounds, whose safety is still under debate. Therefore, recommendations on oils with a balanced proportion of saturated fatty acids (SFA) and PUFA as well as a high content of monounsaturated fatty acids (MUFA), particularly oleic acid, have increased (Bastida and Sánchez-Muniz 2015). Nowadays, industry provides several options in this field, particularly high-oleic modified oils, as high-oleic sunflower, high-oleic soybean or more recently even high-oleic safflower oils. However, these products are not yet available for domestic frying. On the shelf, consumers and small restaurants usually have access to oil blends based on sunflower and soybean oils, rich in PUFA. Nevertheless, the oils naturally richer in MUFA are restricted to peanut oil, olive oil and rapeseed (canola), which are highly dependent on geographical availability and tradition and are usually more expensive than blends. In addition, doubts on olive oil adequacy for frying persist, particularly virgin olive oil, due to the absence of refining.

Most works on the oxidative stability of oleic-rich oils under potatoes deep-frying use PUFA rich oils as reference, as soybean or sunflower oil (Abenoza et al. 2016; Aladedunye and Przybylski 2009; Casal et al. 2010; Olivero-David et al. 2014; Petersen et al. 2013; Serjouie et al. 2010; Taha et al. 2014; Xu et al. 2015). However, only few direct comparisons of naturally high-MUFA were performed and none on these three naturally MUFA-rich oils available for domestic/restaurant frying: peanut, canola and olive oil. Although being expectable that all these three oils are stable under frying, minor differences that may influence their nutritional and health properties can only be perceived with a direct comparison under similar processing conditions to those performed under real frying.

Therefore, the aim of the present work was to compare the nutritional and safety alterations induced by real intermittent deep-frying at 175 °C of fresh potatoes on three monounsaturated-rich oils commonly available to consumers—EVOO, PO and CO.

Materials and methods

Samples

Tested frying oils included commercial EVOO and PO acquired in Portugal and CO in France. Potatoes (*Solanum tuberosum* L., Fontane variety, Portugal) were peeled,

sliced ($1 \times 1 \times 4$ cm), emerged for 5 min in water, drained and partially dried over paper towels before frying.

Deep-frying process

Deep-frying was performed in domestic electric fryers (TRISTAR, FR-6929 model, The Netherlands; 1.75 L capacity), using 1.5 L of oil, without reposition (0% turn-over). Potatoes (50 g) were fried during 6 min for every 30 min, during 8 h per day, in a total of 28 h. Oil samples were collected every 4 h (excepting the first day), closed in a nitrogen atmosphere, and stored at 4 °C for further analyses.

Analytical parameters

Colour

Colour was measured with a Minolta CR-400 colorimeter (Konica Minolta Optics Inc., Japan) with illuminant D65. The colour space system used a CIE $L^*a^*b^*$ system to represent colour coordinate values. Colour change (ΔE) was calculated as: $\Delta E = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}}$.

Polar compounds by high-performance size-exclusion chromatography (HPSEC)

Polar compounds were quantified according to Márquez-Ruiz (2017). Briefly, a solution containing an accurate amount of internal standard (1 mg, monostearin, Sigma-Aldrich, USA) and sample (50 mg) was prepared in petroleum ether and loaded in a solid-phase extraction cartridge of silica (1 g, Finisterre, Teknokroma, Spain), previously conditioned with hexane:diethyl ether (87:13, v/v, 10 mL). The polar compounds were eluted with diethyl ether (10 mL), and finally with the hexane:diethyl ether solution (10 mL) for elution of neutral lipids. After evaporation using a nitrogen stream, the polar compounds were dissolved in THF and analysed in a Jasco chromatograph (Japan), with a Phenomenex (USA) column (Phenogel, 100 Å, 600 × 7.8 mm ID, 5 µm film), using THF as mobile phase at a flow rate 1 mL/min, and evaporative light scattering detection (Sedere, Sedex 75, France). Total polar compounds (TPC), dimeric and polymeric triglycerides (DPTG), and oxidized triglycerides (OTG) were expressed in g/100 g of vegetable oil based on the internal standard response.

Anisidine value

Secondary oxidation products, particularly unsaturated aldehydes, were measured by the anisidine value (p -AV)

according to ISO 6885:2006 (2006). Briefly, anisidine solution (0.25 g/100 mL) was prepared in acetic acid and added to a sample solution, prepared in isooctane. The anisidine value is equivalent to one hundred times the increase in absorbance, measured at a wavelength of 350 nm (Shimadzu, UV-1800 model, Japan), of a test solution when reacted with *p*-anisidine.

Extinction coefficients

Extinction coefficients at 232 nm and 270 nm (K_{232} and K_{270} , respectively) were determined in isooctane (Shimadzu, UV-1800 model, Japan), following the analytical method described in Commission Regulation (EEC) No. 2568/1991 (1991).

Fatty acids composition

Fatty acids composition was evaluated by gas chromatography (GC) after cold transmethylation, according to Commission Regulation (EEC) No. 2568/1991 (1991). Briefly, after sample dissolution in heptane (15 mg/mL), glycerides reacted with 200 μ L of KOH 2 M in methanol. The supernatant was injected (1 μ L; 250 °C) at a slit ratio of 1:50 in a Chrompack CP 9001 gas chromatograph (Middelburg, The Netherlands) with flame ionization detection (FID) at 270 °C. Separation was achieved on a FAME CP-Select CB column (Agilent, 0.25 μ m, 50 m $\times$ 0.25 mm, USA) heated from 140 (5 min hold) to 220 °C (15 min hold) at a 5 °C/min rate. FID response factors for each individual fatty acid were calculated using a certified standard mixture of fatty acids methyl esters (TraceCert - Supelco 37 component FAME mix, USA). Fatty acids were expressed in relative percentage of total calibrated responses and as palmitic acid (C16:0) ratios for adjusted variations during frying.

Minor antioxidant compounds

Tocopherols were determined by normal phase HPLC (Jasco, Japan), with tocol as internal standard (Matreya, USA) (Casal et al. 2010). To an accurate amount of oil (40 mg), tocol was added as internal standard and then hexane for dissolution purposes. After homogenization and centrifugation, 20 μ L were injected in the HPLC system (Jasco FP-2020 Plus, Japan), equipped with a fluorescence detector (λ_{exc} . 290 nm/ λ_{em} . 330 nm). Separation was achieved with a silica gel column (Supelco, Supelcosil LC-SI, 75 $\times$ 3.0 mm, 3 μ m; Bellefonte, PA), using a mixture of hexane/dioxane (97.5:2.5, v/v) at 0.7 mL/min (room temperature). Individual calibration curves were prepared for each tocopherol standard (Sigma-Aldrich, Germany), with mean linear dynamic ranges from 1 to 39 μ g

($R^2 > 0.998$) for α -tocopherol, 1 to 35 μ g ($R^2 > 0.999$) for β -tocopherol, 1 to 43 μ g ($R^2 > 0.999$) for γ -tocopherol, and 1 to 46 μ g ($R^2 > 0.999$) for δ -tocopherol, being the results expressed as mg/kg of vegetable oil, with a quantification limit of 2 μ g/kg.

β -carotene was estimated by UV/Vis absorbance (BMG Labtech, Germany), based on Nagata and Yamashita (1992). After oils dissolution (1:10 oil:solvent ratio) in acetone-hexane (4:6 v/v), the optical density of the supernatant was measured at 663 nm, 645 nm, 505 nm and 453 nm (Shimadzu, UV-1800 model, Japan). The carotenoids content was estimated by following formula: β -carotene (mg/100 ml) = $0.216 \times A_{663} - 1.220 \times A_{645} - 0.304 \times A_{505} + 0.452 \times A_{453}$, being the results expressed in mg/kg of vegetable oils.

Antioxidant activity

The antioxidant activity was evaluated in the fresh vegetable oils, after dilution with ethyl acetate (1:3, m/v) (Pérez-Jiménez et al. 2008). Total reducing capacity was determined by the colorimetric Folin–Ciocalteu method. Briefly, 25 μ L of sample or standard solutions of gallic acid were mixed with 125 μ L of 10% Folin–Ciocalteu reagent, incubated for 8 min at room temperature in the dark, followed by addition of 125 μ L of 7.5% Na_2CO_3 aqueous solution. After homogenization, incubation in the dark for further 30 min at room temperature, and centrifugation (18,000 g, 5 min; Eppendorf, 5810R model, Germany), the solutions were transferred to 96-well microplates for readings at 765 nm using a UV–visible microplate reader (BMG Labtech, Spectrostar nano model, Germany).

The capacity to scavenge radicals was evaluated by the 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical assay. Concisely, 40 μ L of sample or standard solutions were mixed with methanolic solution of DPPH (0.065 mM; 200 μ L), homogenized and incubated in the dark for 30 min at room temperature, centrifuged (18,000 g, 5 min) and transferred to 96-well microplate for absorbance recordings at 517 nm.

The β -carotene/linoleic acid bleaching assay was determined at 470 nm. Briefly, 20 mg of linoleic acid, 200 mg of Tween 80 and 1 mL of β -carotene solution (0.4 mg/mL in chloroform stabilized with ethanol) were vortexed for 2 min and chloroform was removed using a stream of nitrogen for 30 min. A total of 50 mL of demineralized water air-sparged during 30 min was then added to the mixture, which was vortexed to form a clear solution. In a 96-well microplate, 20 μ L of each solvent (control), sample or standard solution plus 200 μ L of the prepared β -carotene solution were added. The assay was monitored at 470 nm using the abovementioned microplate kinetic reader, at 45 °C, for every 10 min up to 60 min, with 5 min agitation prior to each reading.

For all three assays, gallic acid (Sigma-Aldrich, USA) was used as a standard, using calibration curves ranging from 0.005 to 0.25 mg/mL in the total reducing capacity assay and from 0.00025 to 0.025 mg/mL for the others ($R^2 > 0.998$), being the results expressed in mg of gallic acid equivalents (GAE)/kg of vegetable oil.

Volatile compounds

The volatile compounds of the oils were analysed by head-space solid-phase micro extraction (HS-SPME) technique coupled with GC-EI-MS (Agilent, Little Falls, DE, USA), according to Molina-Garcia et al. (2017) using two internal standards (4-methyl-2-pentanol and 1,2,3-trichloropropane, Sigma, USA) and DVB/CAR/PDMS fibres (50/30 μ m film thickness; Supelco). Volatiles from 1.0 g of oil were adsorbed during 30 min at 50 °C (200 rpm; Cimatec, ThermoScientific, USA) and thermally desorbed for 5 min in the injector port (splitless mode; 270 °C) of the GC–MS system. Chromatographic separation was performed on a fused-silica SPB-5 Capillary GC column (60 m $\times$ 0.32 mm I.D. $\times$ 1 μ m film thickness, Supelco) with a temperature gradient ranging from 40 to 240 °C (45 min). The MS transfer line was held at 250 °C, the ion source temperature at 250 °C, and MS quadrupole temperature at 200 °C, with electron ionization of 70 eV; set in full scan mode (m/z 20–450 at 2 scan/s). Compounds were identified by comparing the respective mass spectra with a mass spectral database (WILEY7n.L) and semi-quantification achieved as internal standard equivalents from their peak area ratios, with a quantification limit of 0.1 mg/kg.

Statistical analysis

All analytical determinations were performed in triplicate and results were expressed as mean and standard deviation (SD). Significant differences were determined using ANOVA or independent-samples *t* test. Normal distribution of the residuals and homogeneity of variance were evaluated by ShapiroWilk's ($n < 50$), and Levene's tests, respectively. Afterwards, dependent variables were analysed using a one-way ANOVA with or without Welch's correction, depending if the requirement of the homogeneity of variances was verified or not. Furthermore, if a statistical significant effect was found, post hoc tests, Tukey's and Dunnett T3, were also applied for means comparison, depending if equal variances were assumed or not.

Linear adjustments between frying time and TPC, DPTG, and OTG were assessed. The comparisons between linear adjustments for the different compounds in the three vegetable oils were checked by analysis of covariance. Pearson's correlations were established between the different parameters. Principal component analysis (PCA)

was applied for summarizing the impact of intermittent deep-frying of fresh potatoes in vegetable oils quality.

All statistical tests were performed using SPSS software, version 20 (IBM Corporation, Chicago, IL, USA), and statistical significance was set at $p < 0.05$.

Results and discussion

Colour

Before frying, significant differences ($p < 0.05$) between oils were observed (Table 1), including the typical greenish shades in EVOO due to chlorophyll presence, and light yellow in refined PO and CO, lighter in the latter. During deep-frying, significant differences between oils and for different frying times were observed ($p < 0.05$). Generally, a^* increased in all vegetable oils, while L^* and b^* were reduced in PO and CO but increased in EVOO. ΔE increased in all vegetable oils, but PO colour was more stable, followed by EVOO (higher b^* changes), while greater variations were perceived in CO (on all colour coordinates). These colour alterations are the combined result of polymerization and oxidation, degradation of natural pigments in unrefined EVOO, and formation of browning compounds from Maillard reaction (Aladedunye and Przybylski 2009; Lalas 2009).

Polar compounds

Before deep-frying, all oils presented a similar TPC content, below 3% (Fig. 1a). A gradual increase was observed with deep-frying, with PO and CO presenting similar TPC increases and rejection points (25%) at 18 h and 20 h, respectively. On the other hand, EVOO presented a slower formation of TPC with time, achieving only 22% at 28 h. All frying sessions ended due to oil volume reduction. These observations are supported by the linear adjustments presented in Online Resource 1 and their statistical differences. These rejection points were in agreement with the literature (Abenoza et al. 2016; Casal et al. 2010; Serjouie et al. 2010), except when replenishment is used, delaying the TPC limits by repetitive dilution (Aladedunye and Przybylski 2009).

Within the TPC, DPTG are large non-volatile molecules that provide stable information on the oil degradation under deep-frying conditions, taking some countries to impose a limit of 12 g per 100 g. In this study, DPTG formation trends were similar to those obtained for the TPC, with PO and CO exceeding 12% at 16–18 h, while EVOO remained below this limit up to the final assayed oil sampled at 28 h (Fig. 1b). In accordance with the linear adjustments for DPTG during intermittent deep-frying, EVOO was differentiated from the other vegetable oils (Online Resource 1).

Table 1 Degradation indicators changes in vegetable oils during intermittent deep-frying of fresh potatoes

Oil types	Frying time (h)	L*	a*	b*	ΔE	p-AV	K ₂₃₂	K ₂₇₀	TFA (relative %)
EVOO	0	17.8 ± 0.0 ^{a,A}	0.5 ± 0.0 ^{a,A}	0.9 ± 0.0 ^{a,A}	–	17 ± 2 ^{a,A}	2.2 ± 0.0 ^{a,A}	0.2 ± 0.0 ^{a,A}	0.03 ± 0.00 ^{a,A}
	8	17.7 ± 0.1 ^{a,A}	1.5 ± 0.0 ^{a,B}	2.3 ± 0.0 ^{a,B}	1.7 ± 0.0 ^{b,A}	88 ± 9 ^{a,BC}	10.0 ± 0.7 ^{a,B}	2.2 ± 0.2 ^{a,B}	0.16 ± 0.01 ^{a,B}
	12	18.0 ± 0.2 ^{a,ABC}	2.0 ± 0.1 ^{a,C}	3.1 ± 0.0 ^{a,C}	2.7 ± 0.0 ^{b,B}	87 ± 5 ^{a,B}	11.5 ± 1.8 ^{a,B}	2.4 ± 0.4 ^{a,BC}	0.24 ± 0.05 ^{a,BC}
	16	18.0 ± 0.2 ^{a,ABC}	2.3 ± 0.0 ^{a,D}	4.3 ± 0.0 ^{a,D}	3.8 ± 0.0 ^{b,C}	114 ± 2 ^{a,D}	12.1 ± 0.2 ^{a,B}	2.5 ± 0.2 ^{a,BC}	0.26 ± 0.00 ^{a,C}
	20	18.9 ± 0.1 ^{a,B}	2.2 ± 0.1 ^{a,CD}	3.8 ± 0.0 ^{a,E}	3.9 ± 0.0 ^{b,D}	100 ± 4 ^{a,BCD}	17.0 ± 1.2 ^{a,C}	2.9 ± 0.1 ^{a,C}	0.30 ± 0.04 ^{a,C}
	24	19.6 ± 0.0 ^{a,C}	2.8 ± 0.0 ^{a,E}	4.5 ± 0.0 ^{a,F}	4.6 ± 0.0 ^{b,E}	109 ± 13 ^{a,CD}	17.0 ± 0.2 ^{a,C}	3.0 ± 0.1 ^{a,C}	0.42 ± 0.03 ^{a,D}
	28	19.2 ± 0.1 ^{a,BC}	3.0 ± 0.1 ^{a,E}	4.8 ± 0.0 ^{a,G}	4.9 ± 0.0 ^{a,G}	135 ± 10 ^{a,E}	16.4 ± 2.0 ^{a,C}	2.9 ± 0.5 ^{a,C}	0.51 ± 0.02 ^{a,E}
PO	0	23.6 ± 0.1 ^{b,D}	2.5 ± 0.0 ^{a,AB}	9.1 ± 0.0 ^{a,B}	–	28 ± 1 ^{c,A}	4.7 ± 0.1 ^{c,A}	3.0 ± 0.0 ^{c,A}	0.18 ± 0.00 ^{b,A}
	8	22.8 ± 0.0 ^{c,C}	2.2 ± 0.0 ^{b,A}	9.4 ± 0.0 ^{c,C}	0.9 ± 0.1 ^{a,A}	149 ± 2 ^{b,B}	21.7 ± 1.5 ^{c,B}	4.5 ± 0.1 ^{b,C}	0.33 ± 0.00 ^{b,B}
	12	22.6 ± 0.0 ^{c,C}	2.3 ± 0.0 ^{b,A}	9.3 ± 0.0 ^{c,C}	1.1 ± 0.1 ^{a,A}	153 ± 3 ^{b,B}	21.5 ± 0.7 ^{c,B}	3.8 ± 0.1 ^{b,B}	0.40 ± 0.02 ^{b,C}
	16	21.7 ± 0.0 ^{c,AB}	2.6 ± 0.0 ^{b,B}	9.3 ± 0.0 ^{c,C}	1.9 ± 0.1 ^{a,B}	206 ± 1 ^{b,C}	26.5 ± 3.2 ^{c,C}	4.2 ± 0.4 ^{b,BC}	0.43 ± 0.01 ^{b,D}
	20	22.0 ± 0.0 ^{c,B}	3.2 ± 0.0 ^{b,C}	9.3 ± 0.0 ^{c,C}	2.0 ± 0.1 ^{a,B}	209 ± 7 ^{b,C}	27.4 ± 0.5 ^{c,C}	4.4 ± 0.2 ^{b,BC}	0.45 ± 0.01 ^{b,D}
	24	21.5 ± 0.0 ^{c,A}	3.7 ± 0.0 ^{b,D}	8.2 ± 0.0 ^{c,A}	2.5 ± 0.1 ^{a,C}	206 ± 10 ^{b,C}	29.8 ± 0.9 ^{c,CD}	5.3 ± 0.1 ^{c,D}	0.53 ± 0.00 ^{b,E}
	28	21.6 ± 0.2 ^{b,ABC}	4.3 ± 0.1 ^{b,D}	8.1 ± 0.1 ^{c,A}	2.8 ± 0.3 ^{a,C}	207 ± 11 ^{b,C}	32.4 ± 1.4 ^{c,D}	5.4 ± 0.4 ^{b,D}	0.55 ± 0.02 ^{a,b,E}
CO	0	24.5 ± 0.1 ^{c,D}	1.7 ± 0.0 ^{b,A}	8.7 ± 0.0 ^{b,E}	–	24 ± 0 ^{b,A}	3.6 ± 0.3 ^{b,A}	0.7 ± 0.1 ^{b,A}	0.26 ± 0.01 ^{c,A}
	8	22.2 ± 0.1 ^{b,C}	3.6 ± 0.1 ^{c,B}	9.2 ± 0.1 ^{b,E}	3.0 ± 0.2 ^{c,A}	178 ± 20 ^{b,B}	12.6 ± 1.4 ^{b,B}	4.2 ± 1.0 ^{b,B}	0.38 ± 0.01 ^{c,B}
	12	21.9 ± 0.0 ^{b,C}	4.0 ± 0.0 ^{c,C}	8.7 ± 0.0 ^{b,E}	3.4 ± 0.1 ^{c,B}	237 ± 19 ^{c,C}	14.9 ± 0.6 ^{b,B}	4.3 ± 0.2 ^{c,B}	0.39 ± 0.05 ^{b,BC}
	16	20.5 ± 0.0 ^{b,B}	4.2 ± 0.0 ^{c,D}	7.7 ± 0.0 ^{b,D}	4.8 ± 0.1 ^{c,C}	256 ± 11 ^{c,C}	18.7 ± 1.0 ^{b,C}	4.6 ± 0.4 ^{b,B}	0.45 ± 0.01 ^{c,BCD}
	20	20.6 ± 0.0 ^{b,B}	4.8 ± 0.0 ^{c,E}	7.2 ± 0.0 ^{b,C}	5.5 ± 0.1 ^{c,C}	252 ± 7 ^{c,C}	18.9 ± 0.0 ^{b,C}	4.8 ± 0.1 ^{c,B}	0.47 ± 0.04 ^{b,CD}
	24	20.2 ± 0.0 ^{b,A}	5.2 ± 0.0 ^{c,F}	6.0 ± 0.0 ^{b,B}	6.2 ± 0.1 ^{c,D}	275 ± 20 ^{c,C}	20.5 ± 1.9 ^{b,C}	5.0 ± 0.2 ^{b,B}	0.51 ± 0.03 ^{b,DE}
	28	19.6 ± 0.1 ^{a,A}	5.3 ± 0.0 ^{c,F}	5.7 ± 0.0 ^{b,A}	6.8 ± 0.1 ^{c,E}	257 ± 11 ^{c,C}	20.3 ± 1.8 ^{b,C}	5.0 ± 0.10 ^{b,B}	0.57 ± 0.01 ^{b,E}

Superscript different letters indicate statistically significant differences ($p < 0.05$); small letters between different vegetable oils for the same frying time and large letters within each vegetable oil during frying time

Fig. 1 Changes in the vegetable oils during intermittent deep-frying of fresh potatoes: **a** Total Polar Compounds (TPC); **b** Dimeric Polymeric Triglycerides (DPTG); **c** Oxidized Triglycerides (OTG)

Oxidized triglycerides are probably the molecules that raise more concern from a health point of view, being readily absorbed and having potential effects on lipid metabolism (Li et al. 2016). According to Fig. 1c, equivalent amounts of OTG were observed on the three oils through the entire assay ($p > 0.05$). This observation was reconfirmed by linear adjustments for OTG during intermittent deep-frying, without differentiation between the tested oils (Online Resource 1).

Other oxidation indicators

Regardless of the oil, a significant increase of p -AV ($p < 0.05$) was verified with time (Table 1). A higher

formation rate was verified in the first 8–12 h of deep-frying, more significant in CO, followed by a general stabilization, consistent with most frying assays without replenishment (Casal et al. 2010; Petersen et al. 2013; Taha et al. 2014; Xu et al. 2015), resulting from a probable equilibrium between formation of carbonyls from hydroperoxides and loss of carbonyls by volatilization of smaller molecules or other chemical reactions (Farhoosh et al. 2012). However, EVOO presented a significantly lower p -AV value for all time intervals tested ($p < 0.05$).

Oxidation can also be deduced from structural alterations in the unsaturated fatty acids double bonds position and conformation, with formation of conjugated dienes (K_{232}) and trienes (K_{270}) (Farhoosh et al. 2012), or isomerization to *trans*-fatty acids (TFA) (Tsuzuki et al. 2010). During deep-frying, K_{232} increased significantly ($p < 0.05$) in all oils, particularly in the first 8 h of frying (Table 1), consistent with the p -AV results. Again, for each sampling time, EVOO presented lower K_{232} values ($p < 0.05$), followed by CO, with significantly higher amounts in PO ($p < 0.05$). The K_{270} trend did not allow the previous distinction, with similar amounts between CO and PO, both with higher amounts than EVOO, indicative of lower formation of secondary oxidation compounds in the latter. TFA increased consistently ($p < 0.05$) in the three oils, with equivalent amounts at 28 h ($p > 0.05$), but all below 0.6% (Table 1), of no concern from a health point of view, and in agreement with other frying studies using these vegetable oils (Aladedunye and Przybylski 2009; Casal et al. 2010).

Aware that fatty acid oxidation affects the nutrition value of foods and conditions the formation of oxidation products, a detailed study of the individual fatty composition was performed (Online Resource 2). As expected, oleic acid (C18:1n-9) was the major fatty acid in all oils. However, different ($p < 0.05$) initial MUFA amounts were shown: EVOO (71%), CO (58%) and PO (53%) (Online Resource 2). Focusing on the PUFA contents, linoleic acid (C18:2n-6) was lower in EVOO and similar in both PO and CO, while linolenic acid (C18:3n-3) was significantly higher in CO ($p < 0.05$). Therefore, despite the similar total PUFA contents in PO and CO, the C18:3n-3/C18:2n-6 ratio was higher in CO while the MUFA/PUFA ratio was higher in EVOO and similar in PO and CO (Online Resource 2).

During deep-frying, the relative proportion of MUFA to PUFA increased appreciably ($p < 0.05$) in all oils (Online Resource 2) due to PUFA loss. Using palmitic acid as reference due to its increased stability to oxidation (Aladedunye and Przybylski 2009), standardized losses were calculated based on Online Resource 2 data. Losses were proportional to the amounts of each fatty acid, therefore with higher reduction of oleic acid in EVOO (8.5%) in

comparison with PO (4.1%) and CO (4.9%), higher losses of linolenic acid in PO (7.9%) and linolenic acid (18:3n3) in CO (3.2%). Interestingly, the total fatty acids degradation extent (sum of MUFA and PUFA losses) was similar in the three oils, with 12.2% in PO, 12.9% in EVOO and 13.3% in CO. Therefore, the effect of frying on the unsaturated fatty acid degradation is similar in its global extension, but might derive from different fatty acids types, whose degradation products are responsible for the different oxidation markers discussed previously. Additionally, fatty acid oxidation may also be affected by other components in the lipid matrix, namely antioxidant compounds, justifying their study, as detailed below.

Minor antioxidants compounds and antioxidant activity

Tocopherols are among the most important natural lipophilic antioxidants. Before frying, CO contained the highest total tocopherol amounts (810 mg/kg) followed by PO (535 mg/kg), and EVOO (366 mg/kg) ($p < 0.05$), all within the ranges presented in the literature (Codex Alimentarius Commission 2015). A fast degradation was observed in the first hours of frying, with total loss at 8 h to 12 h, probably derived from its scavenging activity of the peroxy radicals formed during oxidation (Aladedunye and Przybylski 2013), and consistent with several frying studies (Casal et al. 2010; Olivero-David et al. 2014; Taha et al. 2014; Xu et al. 2015).

EVOO presented statically higher ($p < 0.05$) total content of phenolic compounds before heating (564 mg GAE/kg vs 29 in PO and 33 in CO), imposed by its physical extractive process and absence of refining (Boskou 2011). However, their potential effect as antioxidants was also transient, with a 83% loss after 8 h of frying for EVOO ($p < 0.05$) and complete degradation for PO and CO, resulting probably from a combination of steam distillation, thermal degradation, or its use as effective antioxidants (Abenoza et al. 2016).

Concerning β -carotene, it can also react with radicals from decomposition of lipid hydroperoxides to form stable β -carotene radicals (Aladedunye and Przybylski 2013). Before deep-frying, EVOO presented the highest contents ($p < 0.05$) (14.8 mg/kg vs. 0.7 in PO and 0.6 in CO) but no significant differences between oils were observed from the 8th hour onward, indicative that most of EVOO β -carotene was also lost in the first hours of frying. The slight, but statistically significant ($p < 0.05$), β -carotene increase observed between the 8th and 28th hours of frying on the three oils, was probably derived from leaching of potatoes β -carotene.

The antioxidant activity assays tested were based in hydrogen atom transfer (β -carotene/linoleic acid bleaching)

and both electron and hydrogen atom transfer (DPPH). Before frying, CO presented the highest activity in the DPPH assay ($p < 0.05$) (72 mg GAE/kg, followed by 62 in PO and 56 in EVOO), but a significant decrease was observed on all oils ($p < 0.05$) after 8 h of deep-frying, of 90%, 74% and 69% for EVOO, PO and CO, respectively. In opposition, in the β -carotene/linoleic acid bleaching assay, fresh EVOO presented the highest activity ($p < 0.05$) (88 mg GAE/kg, against 69 in CO and 63 in PO), but again with a significant reduction at 12 h ($p < 0.05$) in all oils, of 73%, 82% and 77% for EVOO, PO and CO, respectively, and total absence of activity from this point forward. Therefore, independently of oil type, the antioxidant activity decreased very fast under real deep-frying, as did the most important compounds with recognized antioxidant activity. Interestingly, the degradation of minor antioxidant compounds occurred in the first hours of frying, but no increased oxidation rate was observed thereafter, as supported by the p -AV or OTG results previously discussed.

Volatile compounds

We have further explored the volatile fraction, as its constituents include those derived from fatty acid degradation, as well as from other minor constituents, both from oils and potatoes. HS-SPME is shown to be among the most popular techniques for the analysis of volatile compounds of edible oils (Sghaier et al. 2016), but few studies were developed under deep-frying real conditions (Warner 2009; Zhang et al. 2015; Petersen et al. 2013).

The volatile compounds analysed herein, grouped by chemical families, are presented in Table 2, while selected compounds being detailed in the Table 3. Before deep-frying, EVOO presented a more complex volatile profile, with the presence of “fresh” volatiles, such as alkanes, sesquiterpenes, alkanals, alkenals, alkadienals and alcohols, produced through biogenic pathways (Campestre et al. 2017), whereas both PO and CO shown a lighter profile due to losses along the refining process. Alkanals, alkenals and alkadienals contents increased during frying, in accordance to other studies (Warner 2009; Petersen et al. 2013), but with a distinct pattern on each oil (Table 2). After 28 h of deep-frying, EVOO exhibit more alkanals ($p < 0.05$), PO more alkenals ($p < 0.05$) and CO more alkadienals ($p < 0.05$), which is in line with their PUFA patterns and losses. These compounds are very distinct from a health of view, with alkanals being less deleterious than alkenals or alkadienals, in this order (Katragadda et al. 2010).

Low amounts of 2,4-decadienal are determinant for the typical deep-fried flavour, while 2-heptenal and *E*-2-octenal are implicated in the typical deep-fried odour (Warner 2009). Interestingly, 2,4-decadienal, together with alkylbenzenes,

Table 2 Changes of volatile families (mg/kg of internal standard equivalents) in vegetable oils during intermittent deep-frying of fresh potatoes

Oil types	Frying time (h)	Alkanes	Alkenes	Sesquiterpenes	Alkylbenzenes	Alkanals	Alkenals
EVOO	0	6.2 ± 0.7 ^{a,B}	2.7 ± 0.3 ^D	1.0 ± 0.2	17.9 ± 3.1 ^C	1.5 ± 0.1 ^{b,A}	8.4 ± 0.2 ^A
	8	6.4 ± 0.1 ^{c,B}	1.1 ± 0.0 ^{BC}	n.d.	41.3 ± 7.4 ^{b,C}	85.7 ± 0.9 ^{c,D}	107.7 ± 1.1 ^{b,D}
	12	0.5 ± 0.2 ^{a,A}	1.3 ± 0.3 ^C	n.d.	0.3 ± 0.0 ^{a,A}	83.8 ± 9.8 ^{b,CD}	103.8 ± 4.7 ^{b,D}
	16	0.6 ± 0.1 ^A	0.7 ± 0.1 ^{AB}	n.d.	0.4 ± 0.0 ^{AB}	66.4 ± 8.0 ^{b,BC}	78.4 ± 9.5 ^{a,BC}
	20	0.6 ± 0.0 ^{b,A}	0.7 ± 0.1 ^{AB}	n.d.	0.5 ± 0.0 ^B	77.9 ± 2.2 ^{c,BCD}	83.3 ± 3.0 ^{b,C}
	24	0.8 ± 0.1 ^{b,A}	0.5 ± 0.1 ^A	n.d.	0.9 ± 0.5 ^{AB}	61.5 ± 10.7 ^{b,B}	62.0 ± 12.6 ^{a,B}
	28	0.7 ± 0.1 ^{b,A}	0.6 ± 0.0 ^A	n.d.	n.d.	66.8 ± 2.5 ^{c,BC}	61.5 ± 1.8 ^{b,B}
PO	0	10.7 ± 1.1 ^{a,C}	n.d.	n.d.	23.0 ± 4.6 ^B	0.8 ± 0.1 ^{a,A}	n.d.
	8	5.6 ± 0.1 ^{b,B}	n.d.	n.d.	16.5 ± 0.8 ^{a,B}	56.1 ± 4.5 ^{b,C}	118.0 ± 9.2 ^{b,C}
	12	0.6 ± 0.1 ^{a,A}	n.d.	n.d.	0.4 ± 0.0 ^{a,A}	43.6 ± 3.0 ^{a,B}	125.2 ± 4.9 ^{c,C}
	16	n.d.	n.d.	n.d.	n.d.	69.9 ± 2.0 ^{b,D}	131.5 ± 0.6 ^{b,C}
	20	n.d.	n.d.	n.d.	n.d.	51.7 ± 0.2 ^{b,C}	76.2 ± 3.8 ^{b,A}
	24	n.d.	n.d.	n.d.	n.d.	72.0 ± 4.1 ^{b,D}	95.5 ± 11.0 ^{b,B}
	28	0.5 ± 0.1 ^{a,A}	n.d.	n.d.	n.d.	50.9 ± 1.5 ^{b,BC}	71.6 ± 2.1 ^{c,A}
CO	0	6.0 ± 1.2 ^{a,ABCD}	n.d.	n.d.	13.8 ± 3.2 ^A	n.d.	n.d.
	8	3.6 ± 0.1 ^{a,D}	n.d.	n.d.	11.5 ± 0.0 ^{a,A}	40.3 ± 2.2 ^{a,BC}	63.1 ± 4.4 ^{a,BC}
	12	8.3 ± 0.9 ^{b,D}	n.d.	n.d.	24.7 ± 4.5 ^{b,B}	28.3 ± 2.7 ^{a,A}	59.6 ± 7.3 ^{a,BC}
	16	0.5 ± 0.04 ^C	n.d.	n.d.	n.d.	38.0 ± 0.3 ^{a,BC}	64.7 ± 1.2 ^{a,C}
	20	0.5 ± 0.1 ^{a,ABC}	n.d.	n.d.	n.d.	33.9 ± 4.8 ^{a,AB}	43.9 ± 6.2 ^{a,A}
	24	0.3 ± 0.1 ^{a,AB}	n.d.	n.d.	n.d.	43.8 ± 3.3 ^{a,C}	66.9 ± 4.1 ^{a,C}
	28	0.3 ± 0.04 ^{a,A}	n.d.	n.d.	n.d.	39.3 ± 3.0 ^{a,BC}	51.3 ± 3.7 ^{a,AB}
Oil types	Frying time (h)	Alkadienals	Ketones	Alcohols	Carboxylic acids	Furan derivatives	Total
EVOO	0	0.5 ± 0.1 ^A	n.d.	5.1 ± 0.3 ^A	n.d.	n.d.	43 ± 4 ^{b,A}
	8	25.8 ± 0.02 ^{a,D}	1.8 ± 0.1 ^C	11.2 ± 0.7 ^{b,C}	3.7 ± 0.3 ^{a,A}	2.4 ± 0.02 ^{b,AB}	287 ± 9 ^{b,D}
	12	24.3 ± 1.1 ^{a,D}	1.5 ± 0.1 ^{b,B}	7.7 ± 0.4 ^{b,B}	4.0 ± 0.6 ^{b,AB}	3.7 ± 0.5 ^{b,C}	231 ± 17 ^{b,C}
	16	15.3 ± 1.9 ^{a,C}	1.3 ± 0.1 ^{b,AB}	7.9 ± 1.2 ^{b,B}	5.6 ± 0.8 ^{a,ABC}	2.3 ± 0.3 ^{a,AB}	179 ± 22 ^{a,B}
	20	15.7 ± 0.7 ^{a,C}	1.4 ± 0.04 ^{c,B}	7.8 ± 0.3 ^{b,B}	6.3 ± 0.2 ^{a,C}	2.5 ± 0.2 ^{b,B}	197 ± 6 ^{b,BC}
	24	11.4 ± 2.3 ^{a,B}	1.0 ± 0.2 ^{ab,A}	6.5 ± 1.3 ^{b,AB}	6.0 ± 1.7 ^{a,BC}	1.9 ± 0.5 ^{a,AB}	152 ± 30 ^{a,B}
	28	11.8 ± 0.3 ^{a,B}	1.0 ± 0.04 ^{b,A}	6.5 ± 0.2 ^{c,AB}	4.1 ± 0.2 ^{a,ABC}	1.6 ± 0.1 ^{a,A}	155 ± 5 ^{ab,B}
PO	0	n.d.	3.1 ± 0.7 ^{ABC}	n.d.	0.8 ± 0.2 ^A	n.d.	38 ± 5 ^{b,A}
	8	46.4 ± 3.7 ^{b,B}	1.6 ± 0.2 ^C	14.5 ± 0.9 ^{c,D}	12.0 ± 3.1 ^{b,B}	3.5 ± 0.2 ^{c,A}	274 ± 21 ^{b,CD}
	12	48.0 ± 2.9 ^{b,B}	0.4 ± 0.02 ^{a,A}	12.9 ± 0.1 ^{c,D}	9.6 ± 0.2 ^{c,B}	4.6 ± 0.2 ^{c,B}	245 ± 11 ^{b,C}
	16	44.1 ± 2.1 ^{b,B}	0.4 ± 0.1 ^{a,AB}	14.5 ± 0.8 ^{c,D}	25.8 ± 1.6 ^{b,C}	3.7 ± 0.3 ^{b,A}	290 ± 3 ^{b,D}
	20	26.7 ± 0.4 ^{b,A}	0.5 ± 0.0 ^{a,A}	7.8 ± 0.8 ^{b,B}	14.3 ± 3.1 ^{b,B}	3.0 ± 0.3 ^{b,A}	180 ± 8 ^{b,B}
	24	31.6 ± 2.4 ^{b,A}	0.7 ± 0.0 ^{a,BC}	10.3 ± 1.1 ^{c,C}	27.8 ± 4.2 ^{b,C}	3.7 ± 0.6 ^{b,A}	242 ± 24 ^{b,C}
	28	27.8 ± 1.5 ^{b,A}	0.4 ± 0.0 ^{a,A}	5.2 ± 0.2 ^{b,A}	9.7 ± 2.8 ^{b,B}	3.8 ± 0.1 ^{c,BC}	170 ± 9 ^{b,B}
CO	0	n.d.	n.d.	n.d.	n.d.	n.d.	20 ± 4 ^{a,A}
	8	66.6 ± 4.8 ^{c,B}	n.d.	1.0 ± 0.1 ^{a,AB}	0.7 ± 0.2 ^{a,A}	1.8 ± 0.2 ^{a,AB}	189 ± 12 ^{a,C}
	12	41.1 ± 5.4 ^{b,A}	n.d.	3.4 ± 0.5 ^{a,C}	2.7 ± 0.2 ^{a,B}	1.6 ± 0.2 ^{a,A}	170 ± 22 ^{a,CD}
	16	42.0 ± 1.7 ^{b,A}	1.3 ± 0.3 ^b	0.9 ± 0.1 ^{a,AB}	7.6 ± 0.3 ^{a,D}	2.1 ± 0.1 ^{a,BC}	157 ± 2 ^{a,BCD}
	20	35.5 ± 5.7 ^{c,A}	0.8 ± 0.0 ^b	0.6 ± 0.0 ^{a,A}	4.6 ± 0.4 ^{a,C}	1.9 ± 0.2 ^{a,AB}	122 ± 17 ^{a,B}
	24	44.9 ± 4.0 ^{c,A}	1.3 ± 0.3 ^b	1.5 ± 0.0 ^{a,B}	9.5 ± 1.4 ^{a,E}	2.8 ± 0.2 ^{ab,D}	171 ± 13 ^{a,CD}
	28	40.2 ± 2.6 ^{c,A}	n.d.	1.1 ± 0.1 ^{a,AB}	5.0 ± 0.2 ^{a,C}	2.4 ± 0.1 ^{b,CD}	140 ± 10 ^{a,BC}

Superscript different letters indicate statistically significant differences ($p < 0.05$): small letters between different vegetable oils for the same frying time and large letters within each vegetable oil during frying time. n.d., not detected

Table 3 Changes in selected volatile compounds (mg/kg of internal standard equivalents) in vegetable oils during intermittent deep-frying of fresh potatoes

Oil type	Frying time (h)	Hexanal	Octanal	Nonanal	2-Propenal	2-Butenal	2-Heptenal	2-Octenal
EVOO	0	0.6 ± 0.0 ^{b,A}	n.d.	0.9 ± 0.1 ^{b,A}	n.d.	n.d.	n.d.	n.d.
	8	4.7 ± 0.8 ^{a,B}	15.0 ± 0.2 ^{c,AB}	58.4 ± 0.1 ^{c,D}	n.d.	n.d.	15.1 ± 0.8 ^{a,CD}	7.3 ± 0.2 ^{a,BC}
	12	7.1 ± 1.6 ^{b,BC}	15.8 ± 1.4 ^{c,B}	56.9 ± 6.4 ^{c,D}	n.d.	n.d.	17.7 ± 2.4 ^{a,D}	8.4 ± 1.2 ^{b,C}
	16	7.0 ± 1.4 ^{a,BC}	13.5 ± 1.2 ^{c,AB}	41.8 ± 4.6 ^{c,BC}	2.5 ± 0.6 ^a	0.4 ± 0.1 ^a	12.8 ± 1.5 ^{a,BC}	6.1 ± 0.8 ^{a,AB}
	20	8.4 ± 0.2 ^C	14.9 ± 0.9 ^{c,AB}	49.3 ± 1.4 ^{b,C}	4.0 ± 0.7	n.d.	12.3 ± 0.7 ^{a,ABC}	6.6 ± 0.3 ^{a,ABC}
	24	8.8 ± 0.7 ^{a,C}	11.8 ± 2.5 ^{b,A}	35.6 ± 7.0 ^{b,B}	3.0 ± 0.8	n.d.	8.6 ± 1.8 ^{a,A}	4.9 ± 1.0 ^{a,A}
	28	8.4 ± 0.4 ^{a,C}	13.2 ± 0.7 ^{c,AB}	39.9 ± 1.2 ^{c,BC}	n.d.	n.d.	9.2 ± 0.6 ^{a,AB}	5.2 ± 0.1 ^{a,A}
PO	0	0.4 ± 0.1 ^{a,A}	n.d.	0.5 ± 0.0 ^{a,A}	n.d.	n.d.	n.d.	n.d.
	8	12.4 ± 0.3 ^{b,B}	9.2 ± 0.7 ^{b,BC}	29.1 ± 3.4 ^{b,D}	3.6 ± 0.5 ^B	n.d.	45.8 ± 2.5 ^{c,C}	14.7 ± 1.4 ^{b,BC}
	12	n.d.	8.9 ± 0.6 ^{b,BC}	29.5 ± 2.5 ^{b,D}	2.6 ± 0.2 ^A	n.d.	55.8 ± 1.5 ^{b,D}	18.3 ± 0.3 ^{c,C}
	16	27.7 ± 1.2 ^{c,D}	10.2 ± 0.1 ^{b,C}	24.5 ± 0.3 ^{b,CD}	4.5 ± 0.4 ^{b,B}	n.d.	55.3 ± 0.6 ^{c,D}	22.1 ± 1.0 ^{b,D}
	20	20.6 ± 1.7 ^{b,C}	7.3 ± 0.3 ^{b,A}	18.4 ± 1.8 ^{a,B}	n.d.	n.d.	33.4 ± 2.3 ^{b,B}	12.5 ± 0.7 ^{b,AB}
	24	33.6 ± 0.1 ^{b,E}	9.7 ± 0.7 ^{ab,C}	20.4 ± 2.9 ^{a,BC}	n.d.	n.d.	39.0 ± 3.5 ^{c,B}	17.6 ± 2.9 ^{b,C}
	28	12.9 ± 1.5 ^{b,B}	8.2 ± 0.1 ^{b,B}	25.7 ± 0.5 ^{b,CD}	2.4 ± 0.4 ^A	n.d.	27.3 ± 0.5 ^{c,A}	9.6 ± 0.1 ^{c,A}
CO	0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	8	4.5 ± 0.4 ^{a,A}	6.0 ± 0.4 ^{a,AB}	22.1 ± 2.3 ^{a,D}	n.d.	2.3 ± 0.2 ^B	22.2 ± 1.1 ^{b,B}	6.8 ± 0.5 ^{a,AB}
	12	4.1 ± 0.4 ^{a,A}	5.2 ± 0.4 ^{a,A}	15.5 ± 2.3 ^{a,ABC}	n.d.	0.7 ± 0.01 ^A	17.0 ± 0.7 ^{a,A}	5.8 ± 0.7 ^{a,A}
	16	10.1 ± 0.8 ^{b,D}	5.4 ± 0.1 ^{a,A}	13.3 ± 0.8 ^{c,A}	4.5 ± 0.2 ^{b,B}	3.2 ± 0.1 ^{b,C}	22.0 ± 0.2 ^{b,B}	7.9 ± 0.1 ^{a,BC}
	20	7.2 ± 0.9 ^{a,BC}	4.9 ± 0.6 ^{a,A}	14.6 ± 2.0 ^{a,AB}	3.8 ± 0.6 ^{AB}	1.9 ± 0.4 ^B	15.6 ± 1.8 ^{a,A}	5.6 ± 0.8 ^{a,A}
	24	8.6 ± 0.6 ^{a,CD}	7.2 ± 0.9 ^{a,B}	19.3 ± 2.7 ^{a,BCD}	2.7 ± 0.3 ^A	2.2 ± 0.3 ^B	22.6 ± 1.5 ^{b,B}	8.6 ± 1.1 ^{a,C}
	28	6.0 ± 0.8 ^{a,B}	6.3 ± 0.2 ^{a,AB}	20.7 ± 1.3 ^{a,CD}	2.5 ± 0.8 ^A	1.2 ± 0.2 ^A	16.8 ± 0.8 ^{b,A}	6.3 ± 0.4 ^{b,AB}
Oil type	Frying time (h)	2-Decenal	2-Undecenal	<i>E,E</i> -2,4-Decadienal	<i>Z,E</i> -2,4-Decadienal	<i>E,E</i> -2,4-Heptadienal	2-Pentylfuran	Benzaldehyde
EVOO	0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	8	45.6 ± 1.1 ^{c,C}	33.1 ± 1.0 ^{c,C}	14.1 ± 0.1 ^{a,C}	6.3 ± 0.1 ^{a,D}	3.9 ± 0.2 ^{a,B}	1.4 ± 0.1 ^{a,A}	n.d.
	12	41.0 ± 0.5 ^{c,C}	29.5 ± 0.3 ^{c,C}	12.8 ± 0.3 ^{a,C}	5.3 ± 0.2 ^{a,C}	4.4 ± 0.8 ^{a,B}	2.0 ± 0.3 ^{a,B}	n.d.
	16	29.8 ± 3.3 ^{c,AB}	21.0 ± 2.3 ^{b,AB}	8.2 ± 0.9 ^{a,B}	3.7 ± 0.5 ^{a,AB}	2.4 ± 0.3 ^{a,A}	1.7 ± 0.2 ^{a,AB}	n.d.
	20	31.6 ± 0.7 ^{c,B}	22.3 ± 0.6 ^{c,B}	8.6 ± 0.2 ^{a,B}	4.1 ± 0.2 ^{a,B}	2.5 ± 0.2 ^{a,A}	1.8 ± 0.1 ^{a,AB}	n.d.
	24	23.8 ± 4.8 ^{b,A}	16.6 ± 3.3 ^A	5.8 ± 1.2 ^{a,A}	2.9 ± 0.5 ^{a,A}	1.6 ± 0.3 ^{a,A}	1.4 ± 0.3 ^{a,A}	n.d.
	28	24.6 ± 0.5 ^{c,A}	17.6 ± 0.7 ^{c,AB}	6.1 ± 0.1 ^{a,A}	3.0 ± 0.1 ^{a,A}	1.6 ± 0.0 ^{a,A}	1.6 ± 0.1 ^{a,AB}	n.d.
PO	0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	8	30.8 ± 3.2 ^{b,C}	17.9 ± 1.4 ^{b,CD}	33.9 ± 2.7 ^{c,B}	10.6 ± 0.8 ^{b,B}	n.d.	3.5 ± 0.2 ^{b,A}	n.d.
	12	24.9 ± 1.5 ^{b,B}	18.2 ± 1.3 ^{b,D}	33.2 ± 2.1 ^{b,B}	10.7 ± 0.6 ^{b,B}	n.d.	4.6 ± 0.2 ^{b,B}	n.d.
	16	24.8 ± 0.6 ^{b,B}	18.6 ± 0.8 ^{b,D}	30.5 ± 1.4 ^{c,B}	10.1 ± 0.7 ^{b,B}	n.d.	3.7 ± 0.3 ^{b,A}	n.d.
	20	15.1 ± 0.6 ^{b,A}	11.4 ± 0.1 ^{b,A}	18.6 ± 0.4 ^{b,A}	6.0 ± 0.02 ^{b,A}	n.d.	3.0 ± 0.3 ^{b,A}	n.d.
	24	19.1 ± 2.4 ^{ab,A}	14.9 ± 1.7 ^{BC}	22.1 ± 2.5 ^{c,A}	7.1 ± 0.7 ^{c,A}	n.d.	3.7 ± 0.6 ^{c,A}	n.d.
	28	16.5 ± 0.4 ^{b,A}	12.1 ± 0.8 ^{b,AB}	20.0 ± 1.2 ^{c,A}	6.8 ± 0.3 ^{c,A}	n.d.	3.8 ± 0.1 ^{c,AB}	n.d.
CO	0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	8	15.3 ± 1.7 ^{a,C}	11.7 ± 1.3 ^{a,D}	19.0 ± 1.9 ^{b,B}	6.0 ± 0.7 ^{a,C}	32.1 ± 1.7 ^{b,B}	1.8 ± 0.2 ^{a,AB}	5.9 ± 0.1 ^C
	12	11.0 ± 2.2 ^{a,AB}	8.5 ± 1.4 ^{a,B}	12.3 ± 2.4 ^{a,A}	4.0 ± 0.8 ^{a,AB}	18.7 ± 1.6 ^{b,A}	1.6 ± 0.2 ^{a,A}	3.1 ± 0.4 ^A
	16	12.6 ± 0.5 ^{a,ABC}	9.2 ± 0.4 ^{a,BC}	12.3 ± 0.7 ^{b,A}	4.3 ± 0.2 ^{a,AB}	18.0 ± 0.6 ^{b,A}	1.7 ± 0.0 ^{a,A}	3.9 ± 0.1 ^{AB}
	20	10.0 ± 1.5 ^{a,A}	3.3 ± 0.5 ^{a,A}	10.2 ± 1.5 ^{a,A}	3.3 ± 0.5 ^{a,A}	16.4 ± 2.8 ^{b,A}	1.6 ± 0.1 ^{a,A}	3.4 ± 0.7 ^{AB}
	24	14.8 ± 1.3 ^{a,BC}	11.1 ± 0.7 ^{CD}	14.2 ± 1.4 ^{b,A}	5.0 ± 0.5 ^{b,BC}	18.3 ± 1.4 ^{b,A}	2.4 ± 0.3 ^{b,C}	4.3 ± 0.6 ^B
	28	12.1 ± 0.7 ^{a,ABC}	8.7 ± 0.4 ^{c,BC}	12.4 ± 0.8 ^{b,A}	4.1 ± 0.2 ^{b,AB}	17.6 ± 1.3 ^{b,A}	2.1 ± 0.0 ^{b,BC}	3.6 ± 0.1 ^{AB}

Superscript different letters indicate statistically significant differences ($p < 0.05$); small letters between different vegetable oils for the same frying time and large letters within each vegetable oil during frying time. n.d., not detected

Fig. 2 Principal component analysis of vegetable oils during intermittent deep-frying of fresh potatoes: **a** loadings of variables; **b** Extra Virgin Olive Oil (EVOO), Peanut Oil (PO) and Canola Oil (CO) at different frying times

benzaldehyde, 2-propenal (acrolein), 2-butenal (crotonal), are also recognised toxic compounds (Warner 2009; Hecht et al. 2015; LoPachin and Gavin 2014). In general, EVOO presented lower levels of all these volatile degradation compounds (Table 3), except total alkylbenzenes at 8 h (Table 2). Benzaldehyde and crotonal were significantly present in CO, whereas *E,E*-2,4-decadienal and furans were detected in higher amounts in PO. The emitted off-flavours (Table 3) were mainly oleic acid degradation products (octanal, nonanal, *E*-2-decenal, and 2-undecenal—a fruity, plastic or waxy odours), expected from its higher prevalence, but also from linoleic (hexanal, and 2-pentylfuran—a grassy, plastic or fruity odours) and linolenic (acrolein, and *E,E*-2,4-heptadienal—a fishy, acrid or oily odours) (Warner 2009). Significant Pearson's correlations were verified between several volatile families, such as alkenals and *p*-AV for PO ($r^2 = 0.651$, $p < 0.05$), and CO ($r^2 = 0.864$, $p \leq 0.001$), as well as alkadienals and *p*-AV for PO ($r^2 = 0.594$, $p < 0.05$), and CO ($r^2 = 0.664$, $p < 0.05$). Also, significant Pearson's correlations between volatile compounds, namely *E*-2-decenal and TPC ($r^2 = 0.634$, $p < 0.05$) or DPTG ($r^2 = 0.601$, $p < 0.05$), was only verified for CO. These correlations between volatile compounds and common lipid degradation parameters are in agreement with literature (Petersen et al. 2013).

Principal component analysis

To ascertain which parameters better summarize the impact of intermittent deep-frying of fresh potatoes in the three oils, a PCA was performed. It allowed explaining 64% of total data variance by using two principal dimensions, as represented in Fig. 2. Dimension 1, which comprises 42%

of the total variance, was characterized in the positive region by the major degradation indicators, namely TPC and its fractions, *p*-AV, K_{232} , K_{270} , ΔE and a^* , alkadienals, alkenals, furan derivatives and carboxylic acids, while the negative region was influenced by more protective components, as total tocopherols, antioxidant activity and phenolics, together with alkanes, alkylbenzenes, sesquiterpenes, and alkenes. Dimension 2, which justifies 22% of the total variance observed, was characterized in the positive region by L^* , b^* , C18:2n-6, and C18:3n-3, while alkenes, alkanals, C18:1n-9, C16:0, and β -carotene were increased in the negative region. Thus, six distinct groups are represented, with a clear distinction of EVOO from the other two oils. The later showed higher eigenvalues in dimension 2 through the entire frying time, and a similar evolution trend through dimension 1 with frying, towards increased oxidation markers. Generally, at 28 h, EVOO had lower eigenvalues of dimension 1 than the other two oils, which supports a lower oxidation of EVOO against PO and CO.

These PCA results corroborate the increased formation of primary and secondary oxidation compounds, and polar compounds for PO and CO in comparison to EVOO, while a distinction of the two (CO and PO) is not clearly perceptible.

Conclusion

EVOO showed increased resistance under tested frying conditions. This cannot be attributed to its richness in antioxidants, as these were loss in the first hours of frying, but likely to its low PUFA amounts, particularly linolenic

acid. This early loss of antioxidants should impact on consumer's choices, questioning the relevance of using EVOO for prolonged frying. On the other hand, all the three oils are adequate for prolonged frying, but the degradation compounds formed in this process are different, as confirmed herein. Therefore, stating that monounsaturated oils are preferable for prolonged frying may be insufficient since the polyunsaturated pool is responsible for the formation of different oxidation products, some of which with potentially greater impact on consumer's health. Further studies focused on these minor differences should be explored.

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