# **Research Article**

# Frying stability of canola oil in presence of pumpkin seed and olive oils

#### Ashraf Gohari Ardabili, Reza Farhoosh and Mohammad Hossein Haddad Khodaparast

Faculty of Agriculture, Department of Food Science and Technology, Ferdowsi University of Mashhad, Mashhad, Iran

Frying performance of canola oil (CO) was investigated in the presence of 5, 10, and 15% levels of virgin olive oil (VOO) and pumpkin seed oil (PSO) during frying of potatoes at 180°C. Acid value, carbonyl value, total polar compounds content, and total tocopherols content of the oil samples were determined during the frying process. VOO and PSO addition improved the frying stability of the CO. Frying performance of the CO increased more in the presence of PSO than in the presence of the VOO. The PSO levels higher than 5% exerted pro-oxidant effects, indicating the necessity of investigation at lower levels. The better antioxidative effect of PSO was attributed to its probably different phenolic composition.

Keywords: Canola oil / Frying stability / Natural antioxidant / Pumpkin seed oil / Virgin olive oil

Received: November 26, 2009/ Revised: April 26, 2010/ Accepted: May 9, 2010

DOI: 10.1002/ejlt.200900257

# 1 Introduction

Frying is one of the most popular methods of processing of foods in which a foodstuff is submerged in heated oil exposed to atmospheric oxygen, moisture from the foodstuff, and high temperature with simultaneous heat and mass transfer [1]. The nutritive value of fried food increases due to the oil absorption, since frying oils are rich in vitamin E and unsaturated fatty acids [2]. The oil also causes desired sensory characteristics, golden brown color, and crispiness of the food product which is fried; therefore, the frying oil quality is of great importance with regard to the quality of fried food [1].

Under frying conditions, oxidation, hydrolysis, and thermal degradations are relatively rapid without detectable induction period [3]. Degradation of the oil during frying

Fax: +98-511-8787430

nutritional properties of the oil and fried food beside introducing toxic substances to them [4]. To overcome the stability problems of frying oils, synthetic antioxidants, such as butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), and *tert*-butyl hydroquinone (TBHQ) have been used as food additives. But recent studies have provided evidence for their role as carcinogens [5]. Due to the safety concerns and also the increased level of consumer awareness toward their nutritional values and health effects, there has been an increasing trend in adding suitable harmless natural antioxidants as alternatives to the synthetic ones. Non-glyceride fraction of vegetable oils contains variable

results in the formation of volatile and nonvolatile compounds, which naturally influence the sensory and

compositions of tocols and unique components that not only contribute to their oxidative stability but also provide dietary antioxidants [6]. Virgin olive oil (VOO) and pumpkin seed oil (PSO) are the products consumed as unrefined, and thus are rich in naturally occurring antioxidants which are removed during the refining process of most other vegetable oils. The VOO has good resistance to the deterioration at elevated temperatures due to the presence of natural antioxidants such as tocopherols, sterols, and polyphenolic compounds [7]. This oil is unique both because of the richness in monounsaturated fatty acids and containing significant amounts of health-promoting micronutrients [8]. The PSO is used widespread as salad oil giving a very agreeable taste. Palmitic,

**Correspondence:** Reza Farhoosh, Faculty of Agriculture, Department of Food Science and Technology, Ferdowsi University of Mashhad, P.O. Box 91775-1163, Mashhad, Iran **E-mail:** rfarhoosh@um.ac.ir

Abbreviations: AV, acid value; CO, canola oil; CV, carbonyl value; FAME, fatty acid methyl ester; IV, iodine value; PSO, pumpkin seed oils; PUFA, polyunsaturated fatty acids; PV, peroxide value; SFA, saturated fatty acids; TP, total phenolics; TPC, total polar compounds; TT, total tocopherols; VOO, virgin olive oils

stearic, oleic, and linoleic acids make up about 98% of total amount of its fatty acids [9]. Very low levels of linolenic acid and other highly unsaturated fatty acids provide the PSO with a high oxidative stability for storage or industrial purposes and low free radical production in human diets. The content of vitamin E, especially  $\gamma$ -tocopherol, in the PSO is very high [10]. There are some health benefits reported for the PSO, especially in preventing the growth and reducing the size of prostate gland. Also, there is an evidence for the PSO in retarding the progression of hypertension, mitigating hypercholesterolemia and arthritis, reducing the bladder and urethral pressure, and alleviating diabetes by promoting hypoglycemic activity [11].

The aim of this study was to evaluate the effect of the PSO on the frying stability of canola oil (CO) compared with that of the VOO.

# 2 Materials and methods

#### 2.1 Materials

Dried pumpkin seeds (*C. pepo* subsp. *pepo* var. Styriaca) were obtained from the crops grown in Tabriz, Iran. They were stored in sealed polyethylene plastic vessels at 4°C until analysis and oil extraction. The VOO with no added anti-oxidants in glass bottles was purchased from a local shop. Refined, bleached, and deodorized CO with no added anti-oxidants was supplied by Ghoncheh (Sari, Iran) and mixed with different percentages (5, 10, and 15) of the VOO and PSO. Fatty acid methyl ester (FAME) standards and all chemicals and solvents of analytical reagent grade were purchased from Merck (Darmstadt, Germany) and Sigma–Aldrich (St. Louis, MO).

## 2.2 Oil extraction

After initial cleaning to remove impurities, dried pumpkin seeds were ground to a fine powder using a grinder (Toos Shekan, Iran). The powder was extracted with *n*-hexane (1:4 w/v) by agitation in the shaker at ambient temperature in the dark for 36 h. The solvent was evaporated *in vacuo* at 40°C to dryness. Oil was stored in the sealed bottle under a nitrogen atmosphere and light protected until analysis and using in frying experiment.

#### 2.3 Frying process

Potatoes were peeled and sliced into 6 cm  $\times$  1 cm  $\times$  1 cm pieces. They were rinsed with cold water and dried with a towel prior to being submerged into the oil. Experiments were carried out using a 2.5 L capacity domestic deep-fat fryer equipped with a removable stainless steel wire basket and a thermostat. The ratio of potato to oil was constant during total frying operation. Potatoes were fried at 180  $\pm$  5°C for 5 min; break time between two successive frying was 15 min.

To avoid temperature losses in the oil during frying, small amounts of potatoes (40 g) were fried each time. Frying sessions lasted continuously for 8 h/day. Thirty milliliter of oil sample from each fryer was withdrawn at 4 h intervals and after cooling to room temperature, flushed with nitrogen and stored at  $-18^{\circ}$ C until analysis. No fresh oil was added for replacement of the oil removed during sampling. After each frying session, the fryer was switched off and the oil left at room temperature until the next session. Fryers were switched on 20 min before beginning of frying each day to heat oil up to the desired frying temperature. Each frying experiment was carried out in duplicate.

#### 2.4 Fatty acid composition

The fatty acid composition of the oil samples was determined by injecting the FAMEs into a gas–liquid chromatograph (Hewlett-Packard, Santa Clarita, USA) equipped with a flame ionization detector and a BPX 70 capillary column (60 m × 0.22 mm i.d., 0.2  $\mu$ m film thickness), using helium as the carrier gas at a flow rate of 0.7 mL/min. The FAMEs were prepared by shaking of a solution of oil in hexane (0.3 g in 7 mL) with 7 mL of 2 N methanolic potassium hydroxide. The solution was kept at 50–55°C for 15 min. After shaking, the solution was allowed to settle for 5 min. The upper layer was collected for GC analysis after mixing with anhydrous natrium sulfate and filtering. The oven temperature was maintained at 198°C and those of the injector and detector at 280 and 250°C, respectively. Analysis was done in duplicate and data was reported as relative area percentages.

#### 2.5 Acid value (AV)

Acid value were measured by a titration method defined in American Oil Chemists' Society's Official Methods Cd 3d– 63 [12].

# 2.6 Peroxide value (PV)

Peroxide value was determined with the spectrophotometric method of the International Dairy Federation as described by Shantha and Decker [13] (thiocyanate method).

#### 2.7 Iodine value (IV)

Iodine value was determined according to the AOAC Official Methods 920.158 (Hanus method) [14].

#### 2.8 Total phenolics (TP) content

The determination of TP content was done spectrophotometrically using Folin–Ciocalteau's reagent as described by Capannesi *et al.* [15]. A calibration curve of gallic acid in methanol was performed in a concentration range of 0.04– 0.40 mg/mL.

pn
s stu
this
.⊑
eq
nin
xar
ê
nds
ble
٦e
급
an
SO
PSO
nd
), an
00V
e CO, VO
A)
of th€
ŝ
acteristics
eri
act
าสเ
l C
mical
chei
ne
sor
p
ເສ
tior
ositi
du
cor
id
, ac
atty
efé
Τhe
÷
<u>e</u>
able
F

					CO/VOO			CO/PSO	
Parameter	CO	VOO	PSO	95:5	90:10	85:15	95:5	90:10	85:15
Fatty acids (%)									
C14:0	I	$0.33\pm0.08$	I	0.02	0.03	0.05	I	I	Ι
C16:0	$5.02\pm0.45\mathrm{b}$	$10.63\pm0.15\mathrm{a}$	$10.68\pm0.42$ a	5.30	5.58	5.86	5.30	5.59	5.87
C16:1	$0.66\pm0.32$ a	$0.51\pm0.01\mathrm{a}$	$0.58\pm0.14\mathrm{a}$	0.65	0.65	0.64	0.66	0.65	0.65
C18:0	$2.60\pm0.05~{ m c}$	$3.74\pm0.07~\mathrm{b}$	$8.67\pm0.27$ a	2.66	2.71	2.77	2.90	3.21	3.51
C18:1	$62.51 \pm 0.92$ a	$62.17\pm0.25$ a	$38.42\pm0.37~\mathrm{b}$	62.49	62.48	62.46	61.31	60.10	58.90
C18:2	$19.46\pm0.41~\mathrm{b}$	$20.05 \pm 0.33  { m b}$	$39.84\pm0.08~\mathrm{a}$	19.49	19.52	19.55	20.48	21.50	22.52
C18:3	$7.29\pm0.58$ a	$1.04\pm0.11~\mathrm{b}$	$0.68\pm0.14~{\rm c}$	6.98	6.67	6.35	6.96	6.63	6.30
C20:0	I	$0.92\pm0.11$	I	0.05	0.09	0.14	I	I	I
C20:1	I	$0.11\pm0.05\mathrm{b}$	$1.14\pm0.00~\mathrm{a}$	0.01	0.01	0.02	0.06	0.11	0.17
SFA	$7.62\pm0.45~{ m c}$	$15.62\pm0.11\mathrm{b}$	$19.35\pm0.16\mathrm{a}$	8.02	8.42	8.82	8.21	8.79	9.38
MUFA	$63.17\pm0.50$ a	$62.79 \pm 0.29 a$	$40.13\pm0.23\mathrm{b}$	65.15	65.13	65.11	62.02	60.87	59.71
PUFA	$26.75 \pm 0.36 \ b$	$21.08\pm0.45~{ m c}$	$40.52\pm0.06~\mathrm{a}$	26.47	26.18	25.90	27.44	28.13	28.82
PUFA/SFA	$3.51\pm0.18~\mathrm{a}$	$1.35\pm0.04\mathrm{c}$	$2.09\pm0.01~\mathrm{b}$	3.40	3.29	3.19	3.44	3.37	3.30
AV (mg KOH/g oil)	$0.20\pm0.00\ c$	$0.36\pm0.00\mathrm{b}$	0.78 ±0.02 a	0.21	0.22	0.22	0.23	0.26	0.29
PV (meq O2/kg oil)	$0.51\pm0.07~{ m c}$	$6.89\pm0.12\mathrm{b}$	$10.85\pm0.62~\mathrm{a}$	0.83	1.15	1.47	1.03	1.54	2.06
IV (g of I2/100 g oil)	$108.98 \pm 0.91$ a	$89.38 \pm 0.87 \ c$	$104.36 \pm 0.04  {\rm b}$	108.00	107.02	106.04	108.75	108.52	108.29
TP content (mg gallic acid/kg oil)	$44.29 \pm 3.42 \ { m b}$	$25.67\pm0.90~{ m c}$	$66.27 \pm 3.69  \mathrm{a}$	43.36	42.43	41.50	45.39	46.49	47.59
TT content (mg α-tocopherol/kg oil)	$714.18 \pm 10.79 \ { m b}$	$584.50 \pm 16.69  ext{ c}$	$882.65 \pm 18.32$ a	707.70	701.21	694.73	722.60	731.03	739.45

© 2010 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

4 2 2 2 Ξĺ0 calculated from the data of the corresponding oils.

# Eur. J. Lipid Sci. Technol. 2010, 112, 871-877

#### 2.9 Total tocopherols (TT) content

The TT content was determined according to the colorimetric method described by Wong *et al.* [16].

## 2.10 Carbonyl value (CV)

The CV of the oils was measured according to the method developed by Endo *et al.* [17]. using 2-propanol and 2,4-decadienal as solvent and standard, respectively [18].

# 2.11 Total polar compounds (TPC) content

The TPC content was determined according to the economical micro method described by Schulte [19] with a slight modification on removing the solvent from the eluate: The solvent was evaporated in a vacuum oven at  $40^{\circ}$ C for 25 min rather than by compressed air or nitrogen. This made it possible to determine the TPC content of more samples in shorter times.

#### 2.12 Statistical analysis

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

## 3 Results and discussion

The fatty acid composition and some chemical characteristics of the oils and blends examined in this study are summarized in Table 1. The CO and VOO were characterized with the high levels of oleic acid ( $\sim$ 62%) and the PSO stood out for its high levels of oleic (38.4%) and linoleic (39.8%) acids. A high amount of linolenic acid (7.3%) was detected in the CO which this makes it more susceptible to the oxidative deterioration. The PSO had the highest level of saturated fatty acids (SFA, 19.4%), followed by the VOO (15.6%) and CO (7.6%). Because of the higher level of oleic acid, the CO and VOO showed significantly higher amounts of monounsaturated fatty acids (MUFA) compared to the PSO (~63 vs.  $\sim$ 40%). On the contrary, the PSO (40.5%) contained polyunsaturated fatty acids (PUFA) significantly higher than those of the CO (26.8%) and VOO (21.1%). These differences in the fatty acid composition of the oils studied were reflected in their significantly different amounts of the IVs (109, 89.4, and 104.4 g/100 g for the CO, VOO, and PSO, respectively) and PUFA/SFA ratios (3.51, 1.35, and 2.09 for the CO, VOO, and PSO, respectively). The PUFA/SFA ratio (also known as polyene index) is usually taken as a measure of the extent of polyunsaturation of an oil and, obviously, of its tendency to undergo autoxidation [20]. As can be seen in Table 1, the blending of the CO with the VOO and PSO led to slight decreases in its PUFA/SFA ratio, especially in the CO/VOO blends.

The AV (mg KOH/g oil) and PV (meq  $O_2/kg$  oil) of the oils ranged from 0.20 to 0.78 and from 0.51 to 10.85, respectively. The CO had the highest initial quality (AV = 0.2 and PV = 0.51), followed by the VOO (AV = 0.36 and PV = 6.89) and PSO (AV = 0.78 and PV = 10.85). Despite the significantly lower initial qualities of the VOO and PSO, the AV and PV of the CO blends indicated no considerable changes and were around the acceptable limits. The TT and TP contents (mg/kg) of the CO, VOO, and PSO were 714.2 and 44.3, 584.5 and 25.7,

Table 2. The acid value (AV, mg KOH/g oil) of the CO as affected by the VOO and PSO during frying at 180°C

			CO/VOO			CO/PSO	
Time (h)	СО	95:5	90:10	85:15	95:5	90:10	85:15
0	$0.20\pm0.00\ m\ E$	$0.20\pm0.001DE$	$0.21\pm0.00lCD$	$0.22\pm0.01lC$	$0.22\pm0.01~k~C$	$0.25\pm0.00~kB$	$0.28\pm0.01lA$
4	$0.37\pm0.00lB$	$0.33\pm0.01~k~C$	$0.34\pm0.01~k~C$	$0.30\pm0.00~kD$	$0.29\pm0.01~j~D$	$0.26\pm0.01~kE$	$0.39\pm0.01~kA$
8	$0.52\pm0.02kA$	$0.35\pm0.01~kD$	$0.35\pm0.03~kD$	$0.31\pm0.01~kE$	$0.34\pm0.03~j~DE$	$0.41\pm0.03jC$	$0.47\pm0.01~j~B$
12	$0.66\pm0.01jA$	$0.47\pm0.01jBC$	$0.45\pm0.01jCD$	$0.42\pm0.01jD$	$0.48\pm0.03~i~BC$	$0.46\pm0.04jCD$	$0.50\pm0.01$ ij B
16	$0.80\pm0.01iA$	$0.62\pm0.03iB$	$0.63\pm0.06iB$	$0.52\pm0.03iC$	$0.51\pm0.03iC$	$0.54\pm0.01~i~C$	$0.53\pm0.02~i~C$
20	$1.02\pm0.02hA$	$0.77\pm0.02~h~B$	$0.79\pm0.01~h~B$	$0.74\pm0.03hB$	$0.70\pm0.02\ h\ B$	$0.77\pm0.13hB$	$0.78\pm0.04~h~B$
24	$1.34\pm0.00~gA$	$1.01\pm0.03~g~C$	$1.01\pm0.04~g~C$	$1.10\pm0.01~gB$	$0.90\pm0.03~g~D$	$0.94\pm0.01~gD$	$1.04\pm0.01~\text{g C}$
28	$1.78\pm0.02fA$	$1.28\pm0.04fB$	$1.29\pm0.01fB$	$1.23\pm0.01fC$	$1.13\pm0.02fE$	$1.19 \pm 0.04  f  D$	$1.31\pm0.02fB$
32	$2.20\pm0.04~e~A$	$1.62\pm0.04~e~C$	$1.66\pm0.01~e~C$	$1.76\pm0.02~e~B$	$1.37\pm0.02~e~E$	$1.40\pm0.04~e~DE$	$1.44\pm0.03~e~D$
36	$2.56\pm0.03~d~A$	$2.03\pm0.06~d~C$	$2.08\pm0.01~d~BC$	$2.14\pm0.02~d~B$	$1.76\pm0.03~d~D$	$1.70\pm0.02$ d D	$1.91\pm0.06~d~C$
40	$2.73\pm0.10~\text{c}~\text{A}$	$2.59\pm0.05~c~B$	$2.66\pm0.02~c~AB$	$2.72\pm0.02~c~A$	$2.26\pm0.05~c~D$	$2.22\pm0.01~c~D$	$2.46\pm0.04~c~C$
44	$3.79\pm0.03bA$	$2.96\pm0.04~b~B$	$3.01\pm0.05~b~B$	$3.04\pm0.03bB$	$2.61\pm0.03bD$	$2.68\pm0.02~b~D$	$2.82\pm0.00~b~C$
48	$4.63\pm0.03$ a A	$3.97\pm0.05~a~C$	$4.02\pm0.01$ a C	$4.22\pm0.01~a~B$	$3.52\pm0.07$ a $E$	$3.60\pm0.03~a~E$	$3.80\pm0.04~a~D$

Means  $\pm$  SD within a column with the same lowercase letters are not significantly different at p < 0.05.

Means  $\pm$  SD within a row with the same uppercase letters are not significantly different at p < 0.05.

			CO/VOO			CO/PSO	
Time (h) CO	CO	95:5	90:10	85:15	95:5	90:10	85:15
0	$5.32 \pm 2.31$ i A	$5.63 \pm 1.25\mathrm{jA}$	$5.63\pm0.51~\mathrm{gA}$	$5.63\pm2.52~\mathrm{gA}$	$5.91 \pm 1.18$ i A	$6.02\pm1.17\mathrm{hA}$	$5.60\pm1.73\mathrm{eA}$
4	$9.56\pm1.25~\mathrm{hB}$	$14.95 \pm 1.39\mathrm{iA}$	$14.54 \pm 1.21{ m fA}$	$11.84\pm1.17~\mathrm{fAB}$	$12.62\pm0.60\mathrm{hAB}$	$9.58\pm4.15~\mathrm{gh}\mathrm{B}$	$10.97\pm2.07~\mathrm{d}~\mathrm{B}$
8	$17.66\pm0.81~\mathrm{g~B}$	$19.35\pm2.40~\mathrm{h~B}$	$22.70\pm1.72$ eA	$13.94 \pm 0.88  { m fC}$	$14.21\pm1.06~{ m gh}~{ m C}$	$12.84 \pm 2.60~{ m fg}~{ m C}$	$12.86 \pm 1.03 ~ m d~C$
12	$21.90\pm0.98\mathrm{fB}$	$24.81 \pm 0.56\mathrm{gA}$	$26.43\pm1.01$ de A	$20.38\pm2.93~\mathrm{e~B}$	$15.79 \pm 1.75~{ m g~C}$	$15.45\pm2.08~\mathrm{ef~C}$	$19.55 \pm 1.70 \ c \ B$
16	$23.47\pm1.11\mathrm{fB}$	$29.29 \pm 1.28{ m fA}$	$30.35\pm2.63$ cd A	$21.08\pm2.08~\mathrm{e~BC}$	$16.76\pm1.91~\mathrm{fg}~\mathrm{D}$	$19.24\pm1.50~\mathrm{e~CD}$	$19.31 \pm 1.11 \text{ c CD}$
20	$29.83 \pm 2.16  ext{ e B}$	$36.94\pm2.02$ de A	$31.24 \pm 1.83 ~ m c~B$	$26.94 \pm 1.87 ~ m d~C$	$19.30 \pm 1.90  ext{ ef E}$	$23.26 \pm 2.34 \ { m d} \ { m D}$	$21.16\pm0.28~\mathrm{cDE}$
24	$28.37 \pm 5.37 \mathrm{eB}$	$35.25 \pm 2.33$ e A	$32.80 \pm 2.01  \mathrm{c  A}$	$27.49 \pm 2.20 \ dB$	$22.48\pm0.99$ cd C	$26.43\pm2.00$ cd BC	$25.97\pm1.79~\mathrm{b}\mathrm{BC}$
28	$33.90 \pm 1.04~{ m d~C}$	$42.53\pm1.76~{ m bc}~{ m A}$	$38.65 \pm 3.47 \mathrm{\ b} \mathrm{\ B}$	$32.65\pm3.78~{ m bc}~{ m CD}$	$21.48 \pm 1.15$ de E	$29.70 \pm 1.79 \text{ c D}$	$29.29\pm3.66~\mathrm{ab}~\mathrm{D}$
32	$44.71 \pm 3.85 \text{ b B}$	$48.68\pm2.51~\mathrm{a~A}$	$38.20 \pm 1.12  \mathrm{b}  \mathrm{C}$	$30.21\pm1.32~{ m cd}~{ m D}$	$23.73\pm1.58~ m bcd~F$	$30.61\pm3.15~{ m cd}~{ m D}$	$29.03 \pm 2.28$ ab DE
36	$40.98\pm0.97~\mathrm{bc}~\mathrm{AB}$	$44.55 \pm 4.90 \mathrm{b}\mathrm{A}$	$38.19\pm 6.27~\mathrm{b}~\mathrm{ABC}$	$30.40\pm5.15~{ m cd}~{ m DE}$	$25.43 \pm 1.88~\mathrm{abc}~\mathrm{E}$	$36.34\pm5.69~\mathrm{bc}~\mathrm{BCD}$	$32.39\pm2.16~\mathrm{a~CD}$
40	$49.45\pm3.06~\mathrm{a}~\mathrm{A}$	$41.88\pm3.33~\mathrm{bc}~\mathrm{B}$	$40.69\pm1.90~\mathrm{b~B}$	$29.51\pm3.16~{ m cd}~{ m D}$	$25.10\pm0.65~\mathrm{abc}~\mathrm{E}$	$34.49\pm1.62~{ m bc}~{ m C}$	$31.58\pm1.99~\mathrm{a~CD}$
44	$38.10 \pm 0.41  \mathrm{cA}$	$39.36\pm1.04~ m cd~A$	$41.45 \pm 4.73 \mathrm{b}\mathrm{A}$	$39.07 \pm 3.76  \mathrm{a  A}$	$26.49 \pm 2.23$ ab C	$38.41 \pm 1.21 ~\mathrm{bA}$	$31.78\pm3.68~\mathrm{a}~\mathrm{B}$
48	$41.29\pm5.01~{ m bc}~{ m B}$	$36.85\pm0.81$ de BC	$47.13\pm2.55$ a A	$35.42\pm4.48~\mathrm{ab}~\mathrm{C}$	$27.81 \pm 3.81 \text{ a D}$	$42.48\pm3.22$ a AB	$32.43\pm4.18~\mathrm{a~CD}$

row with the same uppercase letters are not significantly different at p<0.05.

SD within a

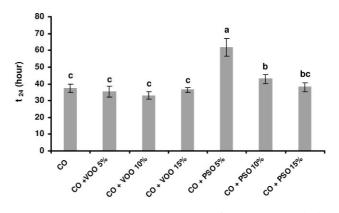
 $+\!\!+\!\!$ 

Means

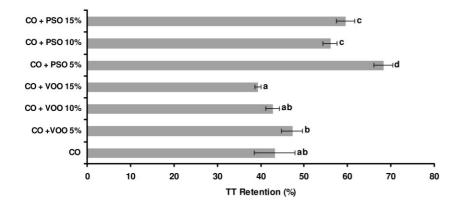
Table 3. The carbonyl value (CV,  $\mu$ mol/g) of the CO as affected by the VOO and PSO during frying at 180°C

Table 2 shows the AV of the CO as affected by the VOO and PSO over a 48 h frying at 180°C. AV increases due to the progressive hydrolytic reactions between oil and moisture from foods during frying process [21]. High AV is not accepted in any commercial product because of the strong off-flavor caused by the degradation products of the free fatty acids during deep-fat frying. Thus, AV as a measure of total free fatty acids present in frying oils has been used to study the hydrolytic degradations of the fried oils [22]. Our results in the present study indicated that the AV increased in the all oil samples during the frying process. The highest increase amount (4.43 U from initial) was observed for the CO with no added oils. Blending of the CO resulted in the lower increases of the AV at the end of the frying process. The COs containing the 5, 10, and 15% of the PSO underwent the AV increases (3.30, 3.35, and 3.52 U, respectively) lower than those of the VOO (3.77, 3.81, and 4.00 U, respectively). As can be seen, the CO/PSO (95:5) blend had the highest resistance to the production of hydrolytic compounds. Also, the hydrolytic stability of the CO decreased as the contribution of the VOO and PSO increased.

As can be seen in Table 3, the CV of the CO increased from 5.32 to 49.45  $\mu$ mol/g after 40 h frying and then decreased significantly. This has been attributed to the decomposition of carbonyl compounds during the prolonged heating period and the formation of new compounds that were not detectable by the CV assay [23]. Such a trend was observed for the blends containing the VOO as well, whereas the CV of all the CO/PSO blends increased almost linearly and more mildly till the end of the frying process. This indicates the higher stability of the PSO blends against the unsuitable sensory variations during the frying process. As can be seen in Table 3, the least rate of the CV



**Figure 1.** The time required to reach a TPC content of 24% ( $t_{24}$ ) for the CO as affected by the VOO and PSO during frying at 180°C. Means ± standard errors (SE) with the same lowercase letters are not significantly different at p<0.05.



**Figure 2.** The TT retention (%) in the CO as affected by the VOO and PSO after 48 h frying at 180°C. Means  $\pm$  standard errors (SE) with the same lowercase letters are not significantly different at *p*<0.05.

variations in the PSO blends was found in the CO/PSO (95:5) blend.

The TPC content is considered to be one of the most useful analytical criteria for comparing the quality of frying fats and oils, and specific TPC-based cutoff points have been established for discarding them [24]. In many European countries, frying fats and oils containing 24-27% of the TPC content have been recommended to be discarded [25]. The TPC contents of all the oil samples studied increased linearly although the rate of increases was significantly different among them. Assuming that the limit of acceptance for the TPC content is 24%, the time required to reach this limit was calculated as a measure of frying stability  $(t_{24})$ . A higher  $t_{24}$  value means more stability over the frying process. As can be seen in Fig. 1, there were no significant differences among the  $t_{24}$  values of the CO and COs containing the VOO. Furthermore, the CO/PSO blends and especially the CO containing 5% of the PSO showed much more considerable frying stability.

The percentage of TT retention after 48 h frying at 180°C is shown in Fig. 2. Tocopherols are important biological antioxidants which has been associated with the reduction of heart disease, delay of Alzheimer's disease, and prevention of cancer. They have widely been used as antioxidants for frying fats and oils, margarines, fried snacks and so on [26]. The frying process decreased the TT content of all the tested oils in a time-dependent manner. The lowest percentages of TT retention were found in the CO and its blends with the VOO, while the PSO significantly caused slower rates of reduction in the TT content of the corresponding blends.

# 4 Conclusions

Monitoring of the different parameters during frying of CO at 180°C revealed that the stability of the CO increased more in the presence of the PSO than in the presence of the VOO. This shows that the blending of less stable oils with the PSO can improve their antioxidative potential. Meanwhile, the PSO demonstrated *in vitro* and *in vivo* to be able to increase the antioxidant strength and health-promoting effect

of diets. The PSO levels higher than 5% mostly exerted the pro-oxidant effects, indicating the necessity of the stability investigations on its lower levels.

It was interesting to find that the better frying performance of the PSO blends was in spite of the fact that there were no considerable differences among the PUFA/SFA ratios and TP and TT contents of all the blends (Table 1). This can be attributed to the differences in their tocopherols and especially phenolic compositions. Therefore, there is still a lot to know about the antioxidative effects of the PSO. In addition, further studies are required to fully understand the role of PSO in the oil stability and its oxidation behavior because many other pro-oxidative (*e.g.*, protochlorophyll and protophaeophytin) and antioxidative substances (*e.g.*, polyphenols and certain sterols) are possibly present. In addition, it would be of interest to extract the unsaponifiable matter of the PSO and to examine the most powerful antioxidative component(s) in it.

The authors have declared no conflict of interest.

#### References

- Warner, K., Chemistry of frying oils, in: Akoh, C. C. Min, D. B. (Eds.), *Food Lipids: Chemistry, Nutrition, and Biotechnology* CRC Press, USA 2008, pp. 189–202.
- [2] Fillion, L., Henry, C. J. K., Nutrient losses and gains during frying: A review. Int. J. Food Sci. Nutr. 1998, 49, 157–168.
- [3] Hawrysh, Z. J., McMullen, L. M., Lin, C., Tokarska, B., Hardin, R. T., Effect of butylhydroquinone on canola oil thermal stability. *Can. Inst. Food Sci. Technol. J.* 1990, 23, 94–100.
- [4] Choe, E., Min, D. B., Mechanisms and factors for edible oil oxidation. Comp. Rev. Food Sci. Food Saf. 2006, 5, 169–186.
- [5] Hou, D. X., Potential mechanism of cancer chemoprevention by anthocyanin. *Curr. Adv. Mol. Med.* 2003, *3*, 149–159.
- [6] Shahidi, F., Shukla, V. K. S., Nontriacylglycerol constituents of fats, oils. *Inform* 1996, 7, 1227–1232.
- [7] Valavanidis, A., Nisiotou, C., Papageorgiou, Y., Kremli, I., et al., Comparison of the radical scavenging potential of polar and lipidic fractions of olive oil and other vegetable oils under

normal conditions and after thermal treatment. J. Agric. Food Chem. 2004, 52, 2358–2365.

- [8] Owen, R. W., Mier, W., Giacosa, A., Hull, W. E., et al., Phenolic compounds and squalene in olive oils: The concentration and antioxidant potential of total phenols, simple phenols, secoiridoids, lignans, and squalene. *Food Chem. Toxicol.* 2000, 38, 647–659.
- [9] Tsaknis, J., Lalas, S., Lazos, E. S., Characterization of crude and purified pumpkin seed oil. *Gras. Aceit.* 1997, 48, 267– 272.
- [10] Murkovic, M., Hillebrand, A., Draxl, S., Winkler, J., Pfannhauser, W., Distribution of fatty acids and vitamin E content in pumpkin seeds (*Cucurbita pepo L.*) in breeding lines. *Acta Hortic.* 1999, 492, 47–55.
- [11] Caili, F., Huan, S., Quanhong, L., A review on pharmacological activities and utilization technologies of pumpkin. *Plant Foods Hum. Nutr.* 2006, 61, 73–80.
- [12] AOCS, Official Methods and Recommended Practices of the American Oil Chemists' Society, AOCS Press, Champaign, IL, USA 1993.
- [13] Shantha, N. C., Decker, E. A., Rapid, sensitive, iron-based spectrophotometric methods for determination of peroxide values of food lipids. *J. AOAC Int.* 1994, 77, 421–424.
- [14] AOAC, Official Methods of Analysis, Association of Official Analytical Chemists, Washington, DC, USA 2005.
- [15] Capannesi, C., Palchetti, I., Mascini, M., Parenti, A., Electrochemical sensor and biosensor for polyphenols detection in olive oils. *Food Chem.* 2000, *71*, 553–562.
- [16] Wong, M. L., Timms, R. E., Goh, E. M., Colorimetric determination of total tocopherols in palm oil, olein and stearin. J. Am. Oil Chem. Soc. 1988, 65, 258–261.
- [17] Endo, Y., Li, C. M., Tagiri-Endo, M., Fugimoto, K., A modifiedmethod for the estimation of total carbonyl

compounds in heated and frying oils using 2-propanol as a solvent. J. Am. Oil Chem. Soc. 2001, 10, 1021–1024.

- [18] Farhoosh, R., Moosavi, S. M. R., Determination of carbonyl value in rancid oils: A critical reconsideration. *J. Food Lipids* 2006, 13, 298–305.
- [19] Schulte, E., Economical micromethod for determination of polar components in frying fats. *Eur. J. Lipid Sci. Technol.* 2004, 106, 772–776.
- [20] Mendez, E., Sanhueza, J., Speisky, H., Valenzuela, A., Validation of the Rancimat test for the assessment of the relative stability of fish oils. *J. Am. Oil Chem. Soc.* 1996, 73, 1033–1037.
- [21] Frega, N., Mozzon, M., Lercker, G., Effect of free fatty acids on the oxidative stability of vegetable oils. J. Am. Oil Chem. Soc. 1999, 76, 325–329.
- [22] Gertz, C., Chemical changes of oils and fats at elevated temperatures, in: Bell, B. M. (Ed.), *Fat in the Diet*, Barnes and Associates, Bridgwater, England 1996, pp. 15–21.
- [23] Farhoosh, R., Moosavi, S. M. R., Carbonyl value in monitoring of the quality of used frying oils quality. *Anal. Chim. Acta* 2008, 617, 18–21.
- [24] Firestone, D., Regulation of frying fats and oils, in: Perkins, E. G. Erickson, M. D. (Eds.), *Deep Frying: Chemistry, Nutrition and Practical Applications*, AOCS Press, Champaign, IL, USA 1996, pp. 323–334.
- [25] Paul, S., Mittal, G. S., Regulating the use of degraded oil/fat in deep-fat/oil food frying. *Crit. Rev. Food Sci. Nutr.* 1997, 37, 635–662.
- [26] Akoh, C. C., Handbook of functional lipids, in: Lee, J. H. Min, D. B. (Eds.), *Nutraceuticals, Aging, and Food Oxidation*, CRC Press, Taylor & Francis Group USA 2006, pp. 325– 350.