# CHANGES IN THE PHYSICOCHEMICAL AND NUTRITIONAL PARAMETERS OF PICUAL AND ARBEQUINA OLIVE OILS DURING FRYING

MARÍA ABENOZA, PATRICIA DE LAS HERAS, MARTA BENITO, ROSA ORIA and ANA CRISTINA SÁNCHEZ-GIMENO<sup>1</sup>

Tecnología de los Alimentos, Facultad de Veterinaria, Universidad de Zaragoza, C/ Miguel Servet 177, CP 50013, Zaragoza, Spain

<sup>1</sup>Corresponding author. TEL: 0034-976761000 ext. 4149; FAX: 0034-976761590; EMAIL: anacris@unizar.es

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# ABSTRACT

Deep fat frying is an important cooking process in Mediterranean countries. Olive oil is a very convenient fat to use for this culinary purpose. The chemical composition of olive oils differs from edible oils in terms of fatty acid and antioxidant compounds that gives olive oil its greater stability. The aim of this work was to describe the stability of Picual and Arbequina olive oil during deep frying of frozen potatoes in comparison with high oleic sunflower oil. Changes in different physicochemical and nutritional parameters were studied during frying. Picual olive oil had a higher stability in comparison with high oleic sunflower oil and Arbequina olive oil. Picual olive oil is very suitable for frying because it is able to undergo the greatest number of frying cycles without exceeding the limits allowed by regulations. This behavior is due to its phenolic content, the lower loss in tocopherol and better stability.

## **PRACTICAL APPLICATIONS**

The information gained from this research could be very appropriate for consumers and for the industry to know which variety of olive oil is more suitable for frying longer frying cycles without exceeding the limits allowed by regulation and remain in good quality.

# INTRODUCTION

The deep fat frying method – i.e., the process by which food is cooked through immersion in hot oil – is considered to be the oldest and most common unit operation for food preparation, especially in the Mediterranean area. The aim of deep fat frying is to seal the food by immersing it in hot oil so that all the flavors and juices are retained in the crispy crust. The quality of the products cooked using this method depend not only on the frying conditions such as the temperature of the heated oil, the frying time, the food weight in proportion to the frying oil volume but also on the types of oil and food used (Varela 1994). The chemical composition of the frying oils also has an influence on the frying process. Usually, many oils can be used for frying – e.g., palm oil, corn oil, cotton oil, soya oil, sunflower oil (Valenzuela *et al.* 2003).

During the frying process, there are many physicochemical changes in food as well as in oil (Valdés and García 2006). The quality of frying oils worsens if used constantly. For this reason, frying oil has a limited shelf life established by regulations. For Spanish regulations (Boletín Oficial del Estado, 1989), which are similar to other European regulations, a maximum level of 25% polar compounds is accepted before the frying oil must be discarded. The oil damage is mainly due to three different factors: the moisture of food, which may cause hydrolysis and free fatty acid formation; the atmospheric oxygen, which enters the oil from the surface of the container (this factor increases the oxidative alteration); and the high temperature at which the operation takes place (a factor that results in thermal alteration). As a result of deterioration, the oil sustains some physical, chemical and nutritional changes. Deep frying of foods promotes a complex pattern of thermolytic reactions in the frying oils, resulting in increased free fatty acids, which accelerate the formation of primary and secondary oxidation products, modifying the nutritional and sensorial properties of oils. The oil sustains some physical changes: the color darkens, the viscosity increases and smoke appears.

Extra virgin olive oil is a very interesting vegetable oil because of its nutritional value, especially the high contents of oleic acid and of minor components with strong antioxidant activity (phenols and tocopherols) and also because of its appreciated flavor.

Because the most appropriate frying oil should be low in free fatty acids and polar compounds, extra virgin olive oil is a very interesting option when looking for a frying oil (Yaghmur et al. 2001). In previous studies, the stability of olive oil during frying was studied (Gómez-Alonso et al. 2003; Giungato et al. 2004; Casal et al. 2010; Santos et al. 2013; Summo et al. 2014, etc.). The stability and frying oil performance are affected by many factors such as cultivar, geographical origin, olive ripening, the processing and storage that influence minor compounds, and fatty acid profiles and concentrations. The production of olive oil is very important in Spain and there are many different quality labels associated with different olive varieties. Some authors studied the effect of olive variety (for Italians varieties) on stability during frying of oils (Summo et al. 2013). In other studies, a Picual monovarietal olive oil was used for frying (Olivero-David et al. 2014). Akil et al. (2015) in previous study described the stability of Arbequina olive oil during deep frying in comparison with Picual olive oil stability. In these studies, replenishment with unused oil was carried out after some frying cycles. Although in this study physical changes in olive oil and total phenol content changes were not included.

The aim of this work was to determine how the olive oil stability changes during frying using different monovarietal olive oils (Picual and Arbequina) without refilling the oil with unused oil to follow the oil damage. Physicochemical and nutritional characterization will be carried out during the frying process for the monovarietal olive oils in comparison with frying in high oleic sunflower oil.

## MATERIALS AND METHODS

#### **Materials**

The following material was purchased at a local store: extra virgin Arbequina olive oil, extra virgin Picual olive oil, high oleic sunflower oil and frozen potatoes. The initial composition of different oils is shown in Table 1.

### Methods

**Frying Process.** Frying was performed using a domestic fryer (DeLonghi Easy Clean) at 180C for 3 min. The ratio food/oil was 200 g/4 L. Frying temperature was controlled using a probe. No oil replacement was carried out during frying.

**Determination of the Percentage in Weight of Polar Compounds.** A Testo 265 oil sensor instrument was used as in previous works (Martínez-Yusta and Guillén 2014) as a rapid measurement of polar compounds. The measurements are based on the dielectric constant of the oil and are directly converted by the instrument into percentages in weight of polar compounds. This method has a good correlation with the official method (Dobarganes 2007; Osawa *et al.* 2012) based on gravimetric measurement using silica column chromatography. Successive frying cycles were carried out to get the maximum detection level of the instrument (23–24% polar compounds).

**Free Fatty Acid.** The free acidity (% oleic acid) was determined using the method described in annex II of the European regulations (CEE 1991).

**Peroxide Value.** Peroxide value (milliequivalent active oxygen/kg oil) was determined using the method described in annex III of the European regulations (CEE 1991).

**lodine Value.** Iodine value (g iodine/100 g oil) was determined using the method described in annex XVI of the European regulations (CEE 1991).

 $K_{232}$  and  $K_{270}$ .  $K_{232}$  and  $K_{270}$  were determined using the method described in annex IX of the European regulations (CEE 1991).

**Fatty Acid Profile.** Total fatty acids were transmethylated according to Frega and Bocci (2001). About two drops of olive oil were dissolved in six drops of a solution of 2 N KOH in methanol and then 2 mL of n-hexane was added. The mixture was vigorously shaken with a vortex for 2 min,

**TABLE 1.** PHYSICOCHEMICAL PARAMETERS OF DIFFERENT OILS USED FOR FRYING

Free fatty acid (% oleic acid)	Oleic acid (%)	Total phenols (mg gallic acid/kg oil)	Peroxide value (mEqO <sub>2</sub> active/kg oil)	lodine value (g iodine/100 g oil)	Viscosity (mPa.s)
0.17 ± 0.02	79.24 ± 0.12	522.75 ± 4.43	1.30 ± 0.33	85.5 ± 3.56	62.17 ± 0.00
$0.12 \pm 0.02$	70.51 ± 0.20	216.29 ± 10.35	1.20 ± 0.21	88.18 ± 0.82	$61.54 \pm 0.00$
$0.07\pm0.02$	$80.30\pm0.03$	-	$1.65 \pm 0.05$	$93.10 \pm 2.98$	$59.91 \pm 0.03$
	Free fatty acid (% oleic acid) 0.17 ± 0.02 0.12 ± 0.02 0.07 ± 0.02	Free fatty acid         Oleic acid (%)           0.17 ± 0.02         79.24 ± 0.12           0.12 ± 0.02         70.51 ± 0.20           0.07 ± 0.02         80.30 ± 0.03	Free fatty acid (% oleic acid)         Total phenols (mg gallic acid/kg oil)           0.17 ± 0.02         79.24 ± 0.12         522.75 ± 4.43           0.12 ± 0.02         70.51 ± 0.20         216.29 ± 10.35           0.07 ± 0.02         80.30 ± 0.03         -	Free fatty acid (% oleic acid)         Total phenols (mg gallic acid/kg oil)         Peroxide value (mEqO <sub>2</sub> active/kg oil)           0.17 ± 0.02         79.24 ± 0.12         522.75 ± 4.43         1.30 ± 0.33           0.12 ± 0.02         70.51 ± 0.20         216.29 ± 10.35         1.20 ± 0.21           0.07 ± 0.02         80.30 ± 0.03         -         1.65 ± 0.05	Free fatty acid (% oleic acid)         Total phenols (mg gallic acid/kg oil)         Peroxide value (mEqO <sub>2</sub> active/kg oil)         Iodine value (g iodine/100 g oil)           0.17 ± 0.02         79.24 ± 0.12         522.75 ± 4.43         1.30 ± 0.33         85.5 ± 3.56           0.12 ± 0.02         70.51 ± 0.20         216.29 ± 10.35         1.20 ± 0.21         88.18 ± 0.82           0.07 ± 0.02         80.30 ± 0.03         -         1.65 ± 0.05         93.10 ± 2.98

Values reported are mean values and standard deviations of three replicates.

a spatula tip of sodium sulfate anhydrous was added and the mixture was shaken again. The sample  $(0.4 \ \mu L)$  was injected into a gas chromatograph (Hewlett-Packard 5890 CG) equipped with a split-splitless injector and a flame ionization detector. A DB-225,  $30 \times 0.25$  mm ID and  $0.15 \,\mu$ m column (J&W Scientific, Agilent, Albany, CA) was used. The injector and detector temperatures were set at 250C. The oven temperature was kept at 190C for 1 min, then programmed from 190 to 210C at 4C/min, kept at 210C for 5 min, then heated from 210 to 215C at 3C/min and finally kept 18 min at the last temperature. Nitrogen was used as a carrier gas at a flow rate of 1.0 mL/min. The peak identification was carried out by comparing the peak retention time with those of the standard mixture. An internal standard was used for the quantification of fatty acids. The GC response factor of each fatty acid was calculated using the internal standard. The results were expressed as g fatty acid/ 100 g total fatty acids (%).

**α-Tocopherol Content.** A solution of oil in hexane was analyzed by high performance liquid chromatography (HPLC) with a Zorbax SB-C18 phase-reverse column and eluted with acetonitrile/water (99:1, v/v) at a flow rate of 1 mL/min. The injection volume was 20 μL. A photodiode matrix detector (G1315B, series 1100) was used. Chromatograms were registered at 295 nm. Results were expressed as mg α-tocopherol/kg oil.

**Total Phenol Content.** The extraction of the total phenols from the olive oil was carried out following the method described by Favati *et al.* (1994). The phenols were extracted by solid phase extraction using Isolute C18 cartridges (6 mL/1 g solid phase). The extract was dried at 30C in a rotary evaporator, and the residue was dissolved in 5 mL of methanol. For the colorimetric determination of total phenols, 2.5 mL of extract was mixed with 1.25 mL of Folin–Ciocalteu reagent, and after 3 min, 2.5 mL of sodium carbonate was added. The absorption of the solution was measured at 725 nm. Results were expressed as mg gallic acid/kg oil.

**Oxidative Stability.** Stability was expressed as the oxidation induction time (h) measured with a Rancimat 743 apparatus (Metrohm, Herisau, Switzerland) using an oil sample of 3 g warmed to 120C with 20 L/h air flow. The induction time is the time needed to reach the break point of this curve. The break point is designated as the intersection of the two extrapolated straight parts of the curve (Laübli and Brutell 1986).

**Color and Pigment Determination.** Determination of Chlorophyll and Carotenoid Compounds. Chlorophyll and carotenoid concentrations were calculated from the absorption spectra of the virgin olive oil spectra for each sample (7.5 g) dissolved in cyclohexane (25 mL) (Mínguez-Mosquera *et al.* 1991). The maximum absorption is related to the chlorophyll fraction at 670 nm and to the carotenoid fraction at 470 nm. The values of the coefficients of specific extinction applied were  $E_0 = 613$  for pheophytin as a major component in the chlorophyll fraction and  $E_0 = 2,000$  for lutein as a major component in the carotenoid fraction. The concentrations of chlorophyll and carotenoids were expressed as mg of pheophytin and lutein per kg oil, respectively.

Color Measurement. The CIELAB color space (CIE 1986) was examined with a spectrophotometer (Avantes Ava Spec 1024) after the spectra were obtained. Illuminant D65 was chosen, along with observer CIE64. The following color coordinates were determined: lightness ( $L^*$ ), redness ( $a^*$ , red-green) and yellowness ( $b^*$ , yellow-blue).

**Viscosity Measurement.** An Anton Paar MC301 rheometer was used for viscosity measurement. A concentric cylinder probe was used and a 100/1/s shear rate.

**Statistical Analysis.** Statistical analysis was performed using Statgraphics Plus 5.1 (Statpoint Technologies, Inc., Warrenton, VA). Results were expressed as mean  $\pm$  standard deviation of three samples and as least-square means  $\pm$  95% confidence interval. Significant differences among samples were determined by analysis of variance (one-way) and a multiple range test.

## **RESULTS AND DISCUSSION**

The evolution of the total polar compounds during frying of frozen potatoes is shown in Fig. 1. These compounds increased for the two olive oils and also for high oleic sunflower oil as they are formed during oil degradation. For high oleic sunflower oil, the limit established for Spanish



▲ High oleic sunflower oil  $\rightarrow$  y=0.0837x+18.169 R<sup>2</sup>=0.9618 ◆ Arbequina olive oil  $\rightarrow$  y=0.1371x+14.143 R<sup>2</sup>=0.9676 ■ Picual olive oil  $\rightarrow$  y=0.1005x+15.225 R<sup>2</sup>=0.9381

FIG. 1. EVOLUTION OF TOTAL POLAR COMPOUNDS ALONG FRYING CYCLES IN DIFFERENT OILS

TABLE 2. EVOLUTION OF FREE FATTY ACID AND THE PEROXIDE VALUE INDEX ALONG FRYING CYCLES IN DIFFERENT OILS
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	Free fatty acid (	% oleic acid)		Peroxide value (	mEq O <sub>2</sub> active/kg oil)	
Frying cycles	Picual olive oil	Arbequina olive oil	High oleic sunflower oil	Picual olive oil	Arbequina olive oil	High oleic sunflower oil
0	$0.18 \pm 0.02^{a}$	0.12 ± 0.02 <sup>b</sup>	0.07 ± 0.02°	$1.30 \pm 0.33^{a}$	$1.20 \pm 0.40^{a}$	$1.63 \pm 0.05^{a}$
10	$0.20 \pm 0.03^{a}$	$0.13 \pm 0.02^{b}$	$0.13 \pm 0.02^{b}$	$9.40 \pm 0.23^{b}$	8.45 ± 0.39°	$11.09 \pm 1.94^{a}$
20	$0.22 \pm 0.02^{a}$	$0.15 \pm 0.02^{b}$	$0.16 \pm 0.02^{b}$	$10.58 \pm 0.22^{b}$	$10.02 \pm 0.27^{b}$	$25.45 \pm 1.97^{\circ}$
30	$0.27 \pm 0.02^{a}$	$0.25 \pm 0.03^{a}$	$0.24 \pm 0.02^{a}$	11.09 ± 0.15 <sup>b</sup>	$10.69 \pm 0.34^{b}$	34.38 ± 2.19 <sup>a</sup>
40	$0.32 \pm 0.02^{a}$	$0.29 \pm 0.03^{b}$	$0.30 \pm 0.02^{b}$	11.86 ± 0.25 <sup>b</sup>	12.53 ± 0.79 <sup>b</sup>	$38.80 \pm 1.85^{\circ}$
50	$0.39 \pm 0.02^{b}$	$0.35 \pm 0.02^{a}$	$0.36 \pm 0.02^{a}$	$10.31 \pm 0.40^{b}$	11.31 ± 0.30 <sup>b</sup>	$24.50 \pm 1.88^{a}$
58/60	$0.48 \pm 0.03^{a}$	$0.47 \pm 0.02^{a}$	$0.42 \pm 0.03^{b}$	$9.65 \pm 0.30^{a}$	$10.40 \pm 0.48^{a}$	$11.10 \pm 2.01^{a}$
63/70	$0.59\pm0.05^{\text{a}}$	$0.55\pm0.04^{\text{a}}$	-	$8.11\pm0.53^{ m b}$	$9.89\pm0.14^{\rm a}$	-

Values reported are mean values and standard deviations of three replicates. For each parameter, different letters for the same frying cycles indicate statistically significant differences ( $P \le 0.05$ ) among oils.

regulations for polar compounds (25%) in heated fats (Boletín Oficial del Estado 1989) was reached after 58 frying cycles. For Arbequina olive oils, this limit was obtained after 63 frying cycles. Picual olive oils had a higher stability during frying and reached 70 frying cycles without exceeding the limit of 25% total polar compounds. In our previous studies (Sánchez-Gimeno et al. 2008a,b) using Empeltre olive oil and Empeltre-Arbequina olive oil, we managed to reach 60-66 frying cycles. Casal et al. (2010) showed that extra virgin olive oil had the highest stability during frying whereas sunflower oil reached the 25% polar compounds cut-off point at least 9 h before the other oils. The higher stability for olive oils is due to the phenol content and higher oleic acid content. Also, Picual olive oil had more stability in comparison with Arbequina olive oil as the phenol content was also higher (see below). As the experiment was carried out without any oil replenishment between different frying cycles, the oil degraded more quickly, but we tried to follow the real degradation during frying. In accordance with other authors (Cuesta et al. 2001), the polar compound increases fit linear adjustments when frying is performed with low or null oil turnover.

Acidity increased slightly and proportionally with frying time (Table 2), which is probably derived from the moisture content in the presence of food (Andrikopoulos *et al.* 2002; Casal *et al.* 2010; Santos *et al.* 2013). Similar values were observed for the three oils but in general significant differences were observed when comparing Picual olive oil and high oleic sunflower oil.

An increase in the peroxide value (Table 2) was verified for all the oils during frying as other authors have described (Andrikopoulos *et al.* 2002; Casal *et al.* 2010). A maximum peak was observed at around 40 frying cycles especially for high oleic sunflower oil. Other authors (Akil *et al.* 2015) showed a similar result for sunflower oil after frying of French fries. For the two olive oils, the evolution was almost the same. Significant differences were observed when comparing with high oleic sunflower oil.

 $K_{232}$  and  $K_{270}$  (Table 3) increased during frying with the lowest level for olive oils and the highest for high oleic sunflower oil as other authors have described (Quiles *et al.* 2002).  $K_{232}$  indicates the formation of conjugated dienes while  $K_{270}$  is associated with the formation of conjugated trienes and carbonyl compounds.

TABLE 3.	EVOLUTION C	0F K232 AND K	270 ALONG FRYING	i CYCLES IN DIFFERE	NT OILS

	K <sub>232</sub> (Abs 232 nm)			K <sub>270</sub> (Abs 270 nm)		
Frying cycles	Picual olive oil	Arbequina olive oil	High oleic sunflower oil	Picual olive oil	Arbequina olive oil	High oleic sunflower oil
0	1.53 ± 0.01 <sup>c</sup>	1.01 ± 0.1 <sup>b</sup>	$2.22 \pm 0.03^{a}$	0.13 ± 0.00°	0.07 ± 0.01 <sup>b</sup>	0.85 ± 0.02 <sup>a</sup>
10	$1.67 \pm 0.04^{b}$	1.56 ± 0.09 <sup>b</sup>	$2.22 \pm 0.07^{a}$	$0.47 \pm 0.01^{b}$	$0.44 \pm 0.05^{b}$	$1.12 \pm 0.04^{a}$
20	$2.02 \pm 0.01^{b}$	1.88 ± 0.15 <sup>b</sup>	$2.45 \pm 0.04^{a}$	$0.71 \pm 0.01^{b}$	$0.65 \pm 0.05^{b}$	$1.34 \pm 0.02^{a}$
30	$2.26 \pm 0.04^{b}$	$2.13 \pm 0.18^{b}$	$2.71 \pm 0.06^{a}$	0.88 ± 0.03°	$0.77 \pm 0.06^{b}$	$1.50 \pm 0.04^{a}$
40	$2.54 \pm 0.01^{b}$	$2.67 \pm 0.09^{a}$	$2.77 \pm 0.08^{a}$	$1.03 \pm 0.00^{\rm b}$	$1.10 \pm 0.07^{b}$	$1.54 \pm 0.04^{a}$
50	$2.70 \pm 0.02^{b}$	$2.72 \pm 0.03^{b}$	$2.89 \pm 0.03^{a}$	$1.11 \pm 0.01^{b}$	1.11 ± 0.01 <sup>b</sup>	$1.64 \pm 0.01^{a}$
58/60	$2.71 \pm 0.02^{b}$	$2.65 \pm 0.16^{b}$	$2.90 \pm 0.05^{\circ}$	$1.13 \pm 0.01^{b}$	$1.09 \pm 0.05^{b}$	$1.67 \pm 0.02^{a}$
63/70	$2.84 \pm 0.02^{a}$	$2.84 \pm 0.06^{a}$	_	$1.20 \pm 0.01^{a}$	$1.20 \pm 0.08^{a}$	_

Values reported are mean values and standard deviations of three replicates. For each parameter, different letters for the same frying cycles indicate statistically significant differences ( $P \le 0.05$ ) among oils.



Values reported are mean values and standard deviations of three replicates. (▲- High oleic sunflower oil, ◆ Arbequina olive oil, ■ Picual olive oil).



The iodine value (Fig. 2) decreased during frying due to the decrease of the unsaturated fatty acids. For Picual olive oil, this value was the lowest during frying. This is probably a consequence of the lower linoleic acid content (4%) in comparison with the Arbequina olive oil content (9%) and the high oleic sunflower oil content (10%).

The evolution of fatty acids is shown in Table 4. Two relevant fatty acids such as linoleic acid and oleic acid are shown during frying. For linoleic acid, significant changes were observed during frying between the three oils. This fatty acid content was higher for high oleic sunflower oil and lower for Picual olive oil. Along frying small changes were observed. Oleic acid content decreased in all the oils during frying. The content was very similar for both Picual olive oil and high oleic sunflower oil (around 80%), although significant differences were observed. Arbequina olive oil had a lower content (around 70%). Olivero-David et al. (2014) described a different behavior for frying in Picual olive oil (linoleic acid decreased, whereas little difference was observed in oleic acid), which may be due to the oil replenishment in this case. Akil et al. (2015) reported that oleic acid was relatively stable during the short-term



Values reported are mean values and standard deviations of three replicates. ( $\blacktriangle$  - High oleic sunflower oil,  $\blacklozenge$  Arbequina olive oil,  $\blacksquare$  Picual olive oil).

FIG. 3. EVOLUTION OF TOTAL PHENOLS ALONG FRYING CYCLES IN DIFFERENT OILS

deep-frying tests using Spanish, Portuguese and Brazilian olive oils. In other previous works, oleic acid was shown to decrease significantly when linoleic acid content remained constant in the oil (Romero *et al.* 1995, 2000; Chatzilazarou *et al.* 2006).

The total phenol content (Fig. 3) decreased with the number of frying cycles for both Picual and Arbequina olive oils. The higher content for Picual olive oils might explain the higher stability and higher number of frying cycles before reaching the limit established by regulations for total polar compounds. The frying procedure reduced the content of phenols, especially in the last frying cycles (90% for Picual olive oil and 75% for Arbequina olive oil), probably as a result of thermal destruction of these molecules or because they are used in the protection of the oils against oxidation (Quiles *et al.* 2002). The phenols are eliminated during vegetable oil refining, and for this reason, they are absent in high oleic sunflower oil.

Because Arbequina olive oil is rich in linoleic acid, it might be less indicated for frying as they will consume higher amounts of antioxidants (Brenes *et al.* 2002; Allouche *et al.* 2007).

TABLE 4. EVOLUTION OF OLEIC AND LINOLEIC ACIDS ALONG FRYING CYCLES IN DIFFERENT OILS

	Oleic acid (C18: (%)	1)		Linoleic acid (C (%)	18:2)	
Frying cycles	Picual olive oil	Arbequina olive oil	High oleic sunflower oil	Picual olive oil	Arbequina olive oil	High oleic sunflower oil
0	$79.24 \pm 0.12^{b}$	70.51 ± 0.20 <sup>c</sup>	80.30 ± 0.03 <sup>a</sup>	4.41 ± 0.01 <sup>c</sup>	9.77 ± 0.05 <sup>b</sup>	10.55 ± 0.01ª
10	$78.61 \pm 0.08^{b}$	70.35 ± 0.02°	$79.47 \pm 0.04^{a}$	4.45 ± 0.01°	$9.66 \pm 0.07^{b}$	$10.49 \pm 0.01^{a}$
20	$78.09 \pm 0.00^{\rm b}$	70.17 ± 0.05 <sup>c</sup>	79.71 ± 0.01 <sup>a</sup>	$4.54 \pm 0.07^{\circ}$	$9.60 \pm 0.01^{b}$	$10.50 \pm 0.00^{a}$
30	$77.40 \pm 0.01^{b}$	69.65 ± 0.26 <sup>c</sup>	$78.05 \pm 0.19^{\circ}$	$4.60 \pm 0.02^{\circ}$	$9.50 \pm 0.17^{ m b}$	$10.29 \pm 0.09^{a}$
40	$76.95 \pm 0.01^{b}$	69.42 ± 0.00°	78.02 ± 0.01 <sup>a</sup>	4.59 ± 0.01°	$9.61 \pm 0.03^{b}$	$10.34 \pm 0.01^{a}$
50	$76.23 \pm 0.14^{\text{b}}$	69.11 ± 0.05 <sup>c</sup>	$77.38 \pm 0.02^{\circ}$	4.68 ± 0.02°	$9.59 \pm 0.02^{b}$	$10.26 \pm 0.02^{a}$
58/60	$75.71 \pm 0.07^{b}$	68.57 ± 0.20 <sup>c</sup>	$76.36 \pm 0.60^{\circ}$	$4.79 \pm 0.00^{\circ}$	$9.55 \pm 0.03^{b}$	$10.16 \pm 0.01^{a}$
63/70	$74.98 \pm 0.01^{a}$	$68.44 \pm 0.02^{b}$	-	$4.21 \pm 0.01^{b}$	$9.58 \pm 0.01^{a}$	-

Values reported are mean values and standard deviations of three replicates. For each parameter, different letters for the same frying cycles indicate statistically significant differences ( $P \le 0.05$ ) among oils.

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Values reported are mean values and standard deviations of three replicates. (▲ - High oleic sunflower oil, ◆ Arbequina olive oil, ■ Picual olive oil).

FIG. 4. EVOLUTION OF  $\alpha\text{-}\mathsf{TOCOPHEROL}$  along frying cycles in different oils

The  $\alpha$ -tocopherol content for different oils during frying is shown in Fig. 4. This content decreased for all the oils during frying (72% for high oleic sunflower oil, 71.5% for Arbequina olive oil and 54% for Picual olive oil). These values were obtained at frying cycle numbers 58–60. For other authors (Akil *et al.* 2015), the degradation rate of tocopherols was higher in extra virgin olive oil compared with seed oils. High oleic sunflower oil was richer in this nutritional compound. At the end of the frying cycles, this content was similar to the olive oil  $\alpha$ -tocopherol content. Picual olive oil had a larger content in comparison with Arbequina olive oil. The chemical composition of olive oils, particularly the amount of natural antioxidants, is an important parameter of their predictive behavior for the frying process (Casal *et al.* 2010).

Allouche *et al.* (2007) showed that, when heating Picual and Arbequina olive oil to 180C, tocopherol loss was more significant in Arbequina olive oil whereas total phenol content loss was greater in Picual olive oil. We observed similar results in our study as we already discussed. The oxidative stability (Fig. 5) decreased for all the samples while frying. The higher phenol content,  $\alpha$ -tocopherol content and oleic acid content for Picual olive oils could explain their higher oxidative stability in comparison with Arbequina olive oil. This value was similar for high oleic sunflower oil and for Arbequina olive oil. Velasco and Dobarganes (2002) established that the compounds that particularly contribute to the oxidative stability of virgin olive oils are phenol compounds.

The changes in pigment content (chlorophylls and carotenoids) while frying were similar (Fig. 6). For both pigments, a decrease was observed in all the oils. Picual olive oil had a higher chlorophyll content in terms of the raw olive oil compared with Arbequina and, of course, the high oleic sunflower oil. However, at the end of the frying cycles, the M. ABENOZA ET AL.

content was similar for the two olive oils. For carotenoids, the content in the raw oil was higher for Arbequina olive oil even after frying. The color of the oils was strongly connected to the amount of pigments that in turn depended on the olive varieties (Del Carlo *et al.* 2010). This behavior is related to the color coordinates (Table 5).  $L^*$  value increased



Values reported are mean values and standard deviations of three replicates. (▲- High oleic sunflower oil, ◆ Arbequina olive oil, ■ Picual olive oil).

FIG. 5. EVOLUTION OF OXIDATIVE STABILITY ALONG FRYING CYCLES IN DIFFERENT OILS



Values reported are mean values and standard deviations of three replicates. (▲ - High oleic sunflower oil, ◆ Arbequina olive oil, ■ Picual olive oil).

FIG. 6. EVOLUTION OF CHLOROPHYLLS (A) AND CAROTENOIDS (B) ALONG FRYING CYCLES IN DIFFERENT OILS

	۲*			a*			$p^*$		
Frying cycles	Picual olive oil	Arbequina olive oil	High oleic sunflower oil	Picual olive oil	Arbequina olive oil	High oleic sunflower oil	Picual olive oil	Arbequina olive oil	High oleic sunflower oil
0	83.41 ± 0.95 <sup>c</sup>	88.54 ± 0.06 <sup>b</sup>	$104.59 \pm 0.06^{a}$	-13.47 ± 0.43 <sup>c</sup>	$-1.23 \pm 0.23^{a}$	$-1.73 \pm 0.06^{b}$	$13.38 \pm 0.13^{b}$	$22.78 \pm 0.56^{a}$	7.71 ± 0.08
10	87.76 ± 0.49℃	$95.56 \pm 0.02^{\rm b}$	$102.20 \pm 0.02^{a}$	-12.25 ± 0.21 <sup>c</sup>	$-2.90 \pm 0.32^{b}$	$-2.25 \pm 0.05^{a}$	$13.70 \pm 0.27^{b}$	$25.05 \pm 0.49^{a}$	$11.04 \pm 0.11$
20	91.81 ± 0.75 <sup>c</sup>	$93.31 \pm 0.26^{b}$	$101.67 \pm 0.03^{a}$	-9.72 ± 0.12 <sup>c</sup>	$-6.78 \pm 0.04^{b}$	$-2.53 \pm 0.16^{a}$	$16.01 \pm 0.23^{b}$	$26.46 \pm 0.39^{a}$	$11.82 \pm 0.26$
30	$92.79 \pm 0.29^{b}$	$93.39 \pm 0.16^{b}$	$98.49 \pm 0.04^{a}$	$-5.94 \pm 0.49^{b}$	-6.83 ± 0.08 <sup>€</sup>	$-2.85 \pm 0.01^{a}$	$17.70 \pm 0.54^{b}$	$27.74 \pm 0.37^{a}$	$12.43 \pm 0.19$
40	$93.15 \pm 0.84^{b}$	$94.28 \pm 0.31^{b}$	$99.85 \pm 0.05^{a}$	$-0.44 \pm 0.50^{a}$	-6.94 ± 0.16 <sup>c</sup>	$-3.42 \pm 0.04^{b}$	$21.08 \pm 0.83^{b}$	$28.67 \pm 0.49^{a}$	$20.74 \pm 0.07$
50	$94.86 \pm 0.18^{b}$	$95.92 \pm 0.28^{a}$	86.70 ± 0.48 <sup>c</sup>	$0.17 \pm 0.15^{a}$	-7.54 ± 0.09 <sup>c</sup>	$-4.50 \pm 0.03^{b}$	21.81 ± 0.42 <sup>c</sup>	$29.55 \pm 0.24^{a}$	$23.05 \pm 0.23$
58/60	$96.51 \pm 0.24^{b}$	$98.70 \pm 0.29^{a}$	82.42 ± 0.58 <sup>c</sup>	$1.60 \pm 0.13^{a}$	-7.73 ± 0.24 <sup>c</sup>	$-2.95 \pm 0.03^{b}$	$25.24 \pm 1.46^{b}$	$34.76 \pm 0.30^{a}$	$26.95 \pm 0.56$
63/70	$97.19 \pm 0.11^{b}$	$99.46 \pm 0.58^{a}$	I	$2.48 \pm 0.23^{a}$	$-7.10 \pm 0.28^{b}$	I	$23.18 \pm 0.45^{b}$	39.31 ± 0.23 <sup>a</sup>	I





CHANGES IN OLIVE OIL DURING FRYING

60

80



<sup>▲</sup> High oleic sunflower oil  $\rightarrow$  y=3.3447x - 7.3722 R<sup>2</sup>=0.8635 ♦ Arbequina olive oil → y=0.5853x + 53.465 R<sup>2</sup>= 0.9147 ■ Picual olive oil → y=0.6262x+53.122 R<sup>2</sup>=0.5173

FIG. 7. EVOLUTION OF VISCOSITY (A) ALONG FRYING CYCLES AND WITH POLAR COMPOUNDS (B) IN DIFFERENT OILS

while frying for the two olive oils as the pigment content decreased. For high oleic sunflower oil, a decrease was observed during frying. The  $b^*$  values increased for all the samples with significant differences between different oils. The  $a^*$  values for Picual olive oil were more negative at the beginning of frying (a greener color of the oils due to the higher chlorophyll content). At the end of frying cycles, these values were more positive (a redder color of the oils) as a consequence of the frying cycles.

The viscosity of different oils while frying is shown in Fig. 7. Viscosity increased with the number of the frying cycles due to degradation of compounds as other authors have described (Santos et al. 2005; Sánchez-Gimeno et al. 2008a,b). The viscosity of high oleic sunflower oil was lower in comparison with the two olive oils. However, during the last frying cycles, this value was higher for high oleic sunflower oil. Arbequina and Picual olive oils had similar viscosity values. As previously described (Sánchez-Gimeno et al. 2008b), viscosity is related to the total polar compounds (Fig. 7) and could be used as an index of oil degradation. Because high oleic sunflower oil degradation was faster than olive oil degradation, the slope of the fitting line was higher. Valdés and García (2006) also described greater changes in viscosity of high oleic sunflower oil after heating at frying temperatures in comparison with olive oil.

## CONCLUSIONS

Olive variety affects the olive oil chemical composition and stability. Although repeated frying cycles decreased the oxidative stability in all the oils studied, oil stability was higher and degradation was lower during frying with Picual olive oil in comparison with high oleic sunflower oil and Arbequina olive oil. For this reason, Picual olive oils could be recommended as obtaining higher quality fried potatoes and longer shelf life of the frying oils.

# **CONFLICT OF INTEREST**

The authors declare no conflicts of interest. The authors alone are responsible for the content and writing of this article.

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