Journal of Food Engineering 119 (2013) 40–45

Contents lists available at SciVerse ScienceDirect

Journal of Food Engineering

journal homepage: www.elsevier.com/locate/jfoodeng

Screw press extraction of almond (*Prunus dulcis* (Miller) D.A. Webb): Oil recovery and oxidative stability

Marcela L. Martínez [a,b,c,*], Ma. Cecilia Penci [b,d], Ma. Andrea Marin [c,b], Pablo D. Ribotta [b,d], Damián M. Maestri [a,b]

[a] Instituto Multidisciplinario de Biología Vegetal (IMBIV, CONICET – UNC), Av. Vélez Sarsfield 1611, X5016GCA Córdoba, Argentina
[b] Facultad de Ciencias Exactas, Físicas y Naturales (FCEFyN – UNC), Av. Vélez Sarsfield 1611, X5016GCA Córdoba, Argentina
[c] Instituto de Ciencia y Tecnología de los Alimentos (ICTA), Av. Vélez Sarsfield 1611, X5016GCA Córdoba, Argentina
[d] Instituto de Ciencia y Tecnología de Alimentos Córdoba (ICYTAC – CONICET), Universidad Nacional de Córdoba (UNC), Juan Filloy s/n, Ciudad Universitaria, 5016 Córdoba, Argentina

ARTICLE INFO

Article history:
Received 20 December 2012
Received in revised form 6 May 2013
Accepted 7 May 2013
Available online 15 May 2013

Keywords:
Almond oil
Screw press extraction
Stability
Natural antioxidants

ABSTRACT

The objectives of this work were to study the combined effects of seed moisture content and pressing temperature on oil recovery and quality parameters of almond oil (AO) and to evaluate the effectiveness of natural (rosemary extract and ascorbyl palmitate) and synthetic antioxidants (TBHQ) on the oxidative stability of AO analyzing chemical changes during an accelerated thermo-oxidation assay. A factorial arrangement was conducted, in pressing experiments, in order to study the combined effects of seed moisture content (4, 6, 8, 10 and 12% (w/w)) and pressing temperature (20, 40 and 60 °C) on oil recovery and quality parameters. Oil recovery increased significantly as moisture content raised. The highest oil recovery (79.3%) was obtained at 8% (w/w) seed moisture content and 40 °C pressing temperature. All extraction conditions employed were compatible with an acceptable chemical oil quality.

Although in the accelerated assay of thermo-oxidation, the TBHQ became the most effective antioxidant, considering natural alternatives, rosemary extract and ascorbyl palmitate combination showed additional protective effect on the AO preservation.

1. Introduction

Almonds (*Prunus dulcis* (Miller) D.A. Webb) are a highly nutritious vegetable food. There is an increasing interest in them as healthy foodstuff because many health benefits have been reported related to their regular consumption (Ahmad, 2010).

The fruit (nut) is used as shelled and peeled kernels and packed nuts, or as an ingredient for many food products such as bakery products and confectionary, and as flavoring agent in beverages and ice creams.

Almond kernels are known as source of high lipid content (48–67%). The major fatty acid is oleic, representing 50–70% of the total fatty acid content. Linoleic, palmitic and stearic acids are present at levels of 10–26%, 5–9%, and 1.5–4%, respectively. Linolenic and myristic acids may be found at very low concentrations (<0.1%). Minor components characterized in AO include sterols (about 2000 μg/g), tocopherols (about 450 μg/g oil), and squalene (95 μg/g) (Cherif et al., 2004; Maguire et al., 2004; Kodad and Socias, 2008; Moayedi et al., 2010). The seed also contains proteins (12–22%) and carbohydrates (20%) (Ahmad, 2010; Ozcan et al., 2011).

Although, the current Committee on Fats and Oils of the Codex Alimentarius does not describe AO, it is produced at a small scale in many countries such as France, Spain and USA. The oil is used for edible purposes, mainly as a salad dressing. It is also used in the cosmetic industry, as a component of dry skin creams, anti-wrinkle and anti-aging products.

Fresh AO is low in free FA, peroxides and phosphatides, which is why it may be consumed directly, without refining.

The increase of worldwide almond production and the demand of new specialty oils, encourages the research for appropriate methods to enhance the AO production. The quantitative and qualitative extraction of AO is imperative to determine the feasibility of turning it into a commercial production.

Screw pressing is experiencing renew interest as an alternative process to solvent extraction, especially for specialty oils. Mechanical screw presses usually recover 75 to 95% of the oil from oilseeds. Screw – press performance with a given oilseed depends

* Corresponding author. Address: Instituto Multidisciplinario de Biología Vegetal (IMBIV, CONICET – UNC), Instituto de Ciencia y Tecnología de los Alimentos (ICTA), Facultad de Ciencias Exactas, Físicas y Naturales (FCEFyN – UNC), Av. Vélez Sarsfield 1611, X5016GCA Córdoba, Argentina. Tel.: +54 0351 4334141; fax: +54 0351 4334439.
E-mail addresses: marcelamartinez78@hotmail.com, mmartinez@efn.uncor.edu (M.L. Martínez).

0260-8774/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.jfoodeng.2013.05.010

on the method of preparing the raw material, which may consist of a number of unit operations, such as cleaning, conditioning, decorticating, cracking, flaking, cooking, extruding. One of the most important parameter is the optimal moisture content. The seed moisture content at the time of pressing is a key process variable, as reported by various researchers who used either hydraulic or screw presses with various oilseeds (Singh and Bargale, 1990, 2000; Fils, 2000; Wiesenborn et al., 2001; Singh et al., 2002; Martínez et al., 2008a, 2012). The moisture content was reported as the most important factor affecting residual oil content in the cake, and 7.5% moisture was reported to be optimal in screw pressing of walnut fruit (Martínez et al., 2008a). Screw pressing of soaked and sun-dried flaxseed showed that the oil recovery increased from 78 to 88% as moisture content increased from 5 to 7%, and thereafter it decreased to 76% at 9% moisture content. Singh and Bargale (1990) suggested that higher moisture content increased plasticity and thereby reduced the level of compression and contributed to poor oil recovery. It was also suggested that moisture acted as a lubricant in the barrel; therefore, higher moisture content resulted in insufficient friction during pressing.

Considering the relevance of seed moisture content at the time of pressing, a systematic study was deemed necessary to determine the effects of this parameter on pressing process and almond oil quality.

The large content of both mono and di unsaturated fatty acids of almonds, make them highly susceptible towards oxidation reactions induced by environmental factors such as humidity, temperature, light and oxygen content at storage atmosphere. These are exogenous factors that promote oxidation processes but there are also endogenous factors such as oxidizing enzymes produced in these natural foods as the lipoxygenase (LOX); its activation normally takes place when a disruption of plant tissue occurs (Salcedo et al., 2010). The oxidation reactions start to produce undesirable flavors, rancid odours, discoloration and other forms of spoilage. The primary autoxidation products are hydroperoxides, that have no taste and flavor, but their degradation products (aldehydes, ketones) are very potent taste and flavor modifiers (Frankel, 2005).

Antioxidants can increase shelf life of food products by slowing lipid oxidation, a typical free radical chain process. Although synthetic antioxidants, such as butylated hydroxyanisole (BHA), butylated hidroxytoluene (BHT), di-tert-butyl hydroquinone (TBHQ) and propyl gallate (PG), are extensively used as food additives, food safety related to their use has been questioned the search and evaluation of naturally occurring compounds with antioxidant properties have been stimulated. As a result, there is a great interest in obtaining and utilizing the antioxidants from natural sources as ascorbyl palmitate and spice extracts because they are presumed to be safe since they occur in plants. Naturally-occurring antioxidants from herbs and spices have been extensively studied for their antioxidative activity (Economou et al., 1991; Madsen et al., 1998). The greatest level of attention among herbs and spices has been focused on rosemary. Many studies have been made to examine the antioxidative activities of crude rosemary and different rosemary extracts (Rezzoug et al., 2005; Atungulu et al., 2007; Rodríguez-Rojo et al., 2012). Many rosemary extracts, for use in food systems, are today available in the market (Rizner Hras et al., 2000). Ascorbyl palmitate is a synthetically-derived oil-soluble ester of ascorbic acid and the later occurs widely in the vegetable world.

The objectives of this study were: (a) to study the combined effects of seed moisture content and pressing temperature on oil recovery and quality parameters of almond oil and (b) to evaluate the effectiveness of natural (rosemary extract and ascorbyl palmitate) and synthetic antioxidants (TBHQ) on the oxidative stability of AO by analyzing chemical changes during storage.

2. Materials and methods

2.1. Materials

Almond fruits (*Prunus dulcis* Miller – Guara variety) D.A. Webb) were collected from commercial plantations at Mendoza Province, Argentina. After cleaning, the fruits were dried at 30 ± 2 °C in a day's time and then were shelled manually. Seeds contained about 53% oil (dry basis) and 4.5% moisture (w/w).

All chemicals and solvents used were either analytical or HPLC grade.

2.2. Methods

2.2.1. Almond kernel composition

Samples were analyzed according to standards AACC (AACC, 2003) and AOCS (AOCS, 2009) for total oil content, fatty acid profile, total protein, total carbohydrates and ashes. The activity of LOX was determined following the procedure described by Meriles et al. (2000).

2.2.2. Screw-press extraction

Almond seeds were conditioned to reach 4, 6, 8, 10 and 12% (w/w) of moisture content. They were milled and sifted through an automatic sieve to achieve 2.4 to 4.8 mm particle size. Particles were then sprinkled with fresh water to reach 6, 8, 10 and 12% (w/w) of moisture content, according to Singh and Bargale (2000). The water-sprinkled samples were then packed in air-tight metal containers and stored for about 48 h for equilibration. The containers were shaken at regular intervals to distribute moisture uniformly throughout the sample. To adjust moisture content to 4% (w/w) level, samples were kept in a vacuum oven at 25 °C until the desired moisture was reached.

Pressing was carried out at three different temperatures, 20, 40 and 60 °C. Oil extraction was carried out with a Komet screw press (Model CA 59 G, IBG Monforts, Mönchengladbach, Germany), with a 5 mm restriction die and a screw speed of 20 rpm. The screw press was first run for 15 min without seed material but with heating means, an electrical resistance-heating ring, attached around the press barrel to raise the screw-press barrel temperature to the desired temperature. Running temperature was checked with a digital thermometer inserted into the restriction die. Each treatment (consisting of a combination of seed moisture content and pressing temperature) was run in triplicate. After each run, all press devices were cleaned and dried.

2.2.3. Total seed oil content

Three samples (10 g each) of dry, finely chopped almonds were used to determine total oil content in accordance with AOCS, 2009.

2.2.4. Oil recovery (OR)

The oil recovery (OR) was calculated considering the initial oil content in the incoming material and the residual oil content in the cake. Both were determined according to AOCS, 2009.

2.2.5. Fines content in oil (FCO)

Screw-pressed oils were centrifuged at 11,000 g for 30 min. The precipitated solids were recovered, washed with cyclohexane, dried and weighed. Solid content was expressed as g solids/100 g extract (oil + solid).

2.2.6. Oil analysis

Hydroperoxide (HV), acid (AV) and K_{232} values were determined according to standard methods of AOCS, 2009. The antioxidant activity (AA) was measured according to Martínez and Maestri,

Table 1
Treatments used for almond oil (AO) storage stability test.

Code	Treatment
C	Control (AO without additives)
TBHQ	TBHQ 100 ppm
AP	AP 100 ppm
RE	RE 400 ppm
TBHQ + AP	TBHQ 100 ppm + AP 100 ppm
TBHQ + RE	TBHQ 100 ppm + RE 400 ppm
AP + RE	AP 100 ppm + RE 400 ppm

TBHQ (tert-butylhidroquinone).
AP (ascorbyl palmitate).
RE (rosemary extract).

2008b. An aliquot of 100 mg of oil was dissolved in 1 mL toluene and then 3.9 mL of a DPPH radical solution (0.004 g DPPH·/100 mL) were added. The absorbance values were measured after 30 min of incubation. Total tocopherols content (TTC) was determined by high pressure liquid chromatography (HPLC) according to Pocklington and Dieffenbacher, 1988. Fatty acid composition was analyzed by gas chromatography (Martínez et al., 2006). Chlorophyll and carotenoid compounds were determined at 670 and 470 nm, respectively, in cyclohexane via specific extinction values using the method of Minguez-Mosquera et al., 1991. To determine the carnosic acid content in rosemary extract (RE), HPLC and UV spectrophotometric analyses were carried out according to the procedures employed by Visentin et al., 2011).

The protection factor (PF) was calculated using the oxidative stability indexes (OSI). OSI was determined using the Rancimat analysis, and corresponded to the break points in the plotted curves. Air flow rate was set at 20 L/h and temperature of the heating block was maintained at 110 °C.

2.2.7. Schaal oven test

Almond oil (AO) samples were put into 50 mL glass bottles, were stored at 60 °C ± 1 °C according to AOCS, 2009 for 12 days. Samples of each treatment were removed periodically from storage for evaluation of lipid oxidation. Samples were also evaluated on day "zero". The following additives were added to AO samples: 100 ppm TBHQ (Sigma Aldrich); 100 ppm ascorbyl palmitate (Grindox, DANISCO); and 400 ppm rosemary extract (Guardian, DANISCO) or their combinations (Table 1). The Schaal oven tests were carried out with AO sample obtained considering the best oil recovery conditions and chemical quality. Each treatment was prepared in duplicate (consisting of a combination from oil plus additive). For the control treatments, AO samples without added antioxidants were used.

2.2.8. Statistical analysis

Statistical differences among treatments were estimated from ANOVA test at the 5% level ($p \leqslant 0.05$) of significance, for all parameters evaluated. Whenever ANOVA indicated a significant difference, a pair-wise comparison of means by least significant difference (LSD) was carried out.

3. Results and discussion

3.1. Almond fruit composition

Almond kernel composition is shown in Table 2. The oil content was consistent with reported values (Cherif et al., 2004; Kodad and Socias, 2008; Moayedi et al., 2010; Ozcan et al., 2011). Abundance order of fatty acids was as follows: oleic (71%) > linoleic (20%) > palmitic (7%) > stearic (2%) > palmitoleic acid (0.4%). The almond seeds used in the present study had higher protein and ash contents that those reported by Ozcan et al., 2011 (12, 71 and 2.74%, respectively) (Table 2). The tocopherol content mean value was higher than those informed by Kodad et al. (2011) (216 to 569 μg/g oil). Regarding pigments, AO showed low carotenoid and chlorophyll contents (1659 and 0163 μg/g oil, respectively).

3.2. Pre-treatments of almond seed for extraction

In some almonds varieties the hull seed affects negatively the material size reduction process. After milling the particles which remain attached to the hull could affect the sieving and the oil extraction. In this study, scalding (water at 100 °C during 20, 25, 30, 35, 40, 45 and 50 s) and heating treatments (air at 50 °C during 5, 10, 15, 20 min) were evaluated. Even though a total seed coat removal was possible by almond scalding, an increase in plasticity and seed moisture were observed in all the cases, which affected negatively the milling operation. On the other hand, all heat treatments produced a tegument stiffening that allowed grinding the material without difficulty (data not shown). Among all the above mentioned studies, heat treatment at 50 °C during 10 min was selected. Regarding to LOX activity, it was not detected in Guara variety.

3.3. Screw press extraction

OR by screw pressing of almond seeds at different moisture and temperature conditions are shown in Table 3 and Figs. 1 and 2. Heat pre-treatment and moisture conditioning did not affect the oil quality as measured by HV and AV. Increasing seed moisture content from 4 to 8% (w/w) increased OR, but a further increase of moisture content from 8 to 12% (w/w) produced a slight decreased of OR. Similar trends were reported by Singh and Bargale (1990, 2000). These authors, working in a moisture content range of 5 to 12% (w/w), have observed a maximum in OR at 7% (w/w) and at 7.5% (w/w) moisture content for water-soaked linseed and rapeseed, respectively. Martínez et al., 2008a obtained the highest OR at 7.5% (w/w) moisture content for walnut seed in the moisture content range of 2.5 to 7.5% (w/w). They also observed that moistening was more beneficial than heating in terms of OR in the range of conditions used. Furthermore, Li et al. (1999) demonstrated that thermal treatments and water addition before pressing caused an expansion and breaking of cell structure, that made it more permeable and, consequently, improved the oil yield. In this work, the highest OR (79.3%) was obtained at 8% (w/w) moisture and 40 °C

Table 2
Almond kernel composition.

Parameter	Value[a]
Moisture content (w.b.)%	4.50 ± 0.13
Lipids (d.b.)%	53.11 ± 0.20
Proteins (d.b.)%	25.56 ± 0.21
Ashes (d.b.)%	3.28 ± 0.01
Carbohydrates (d.b.)%[b]	13.55
Fatty acid distribution (relative abundance)	
Palmitic acid (16:0)	6.74 ± 0.06
Palmitoleic acid (16:1)	0.4 ± 0.01
Stearic acid (18:0)	1.84 ± 0.58
Oleic acid (18:1)	71.24 ± 0.36
Linoleic acid (18:2)	19.77 ± 0.14
Minor lipid components	
Total Tocopherols (μg/g oil)	591 ± 15.6
Carotenoids (μg/g oil)	1.659 ± 0.002
Chlorophylls (μg/g oil)	0.163 ± 0.001

[a] Mean ± standard deviation ($n = 3$).
[b] By difference.

Table 3
Effect of treatments combining seed moisture content and pressing temperature on pressing yields and quality parameters.

Parameter		Treatments															
SMC		4			6			8			10			12			
T		20	40	60	20	40	60	20	40	60	20	40	60	20	40	60	
Physical	OR	$22.8^{j} \pm 0.6$	$31.1^{i} \pm 1.0$	$32.7^{i} \pm 0.5$	$36.4^{h} \pm 0.6$	$50.9^{g} \pm 2.5$	$55.5^{f} \pm 0.7$	$74.6^{b} \pm 0.9$	$79.3^{a} \pm 0.9$	$71.3^{c} \pm 1.1$	$73.7^{b} \pm 0.5$	$73.8^{b} \pm 0.4$	$68.4^{d} \pm 1.0$	$69.5^{d} \pm 0.7$	$71.7^{c} \pm 0.3$	$64.9^{e} \pm 1.4$	
	CRO	$70.1^{a} \pm 1.3$	$62.8^{b} \pm 2.7$	$59.4^{c} \pm 0.4$	$58.0^{c} \pm 0.4$	$36.7^{d} \pm 0.8$	$34.6^{d} \pm 0.8$	$19.0^{fg} \pm 3.6$	$17.6^{g} \pm 0.8$	$21.3^{ef} \pm 1.5$	$22.8^{e} \pm 1.7$	$22.6^{e} \pm 0.7$	$20.5^{ef} \pm 0.9$	$20.3^{ef} \pm 2.0$	$21.7^{e} \pm 0.6$	$21.9^{e} \pm 1.1$	
	FCO	$28.6^{d} \pm 2.1$	$23.4^{b} \pm 2.1$	$22.4^{b} \pm 0.5$	$16.4^{e} \pm 0.4$	$8.74^{d} \pm 1.5$	$8.60^{d} \pm 1.2$	$6.17^{e} \pm 1.96$	$2.56^{h} \pm 1.23$	$2.63^{gh} \pm 0.27$	$4.28^{fg} \pm 0.28$	$4.14^{fgh} \pm 0.59$	$4.13^{fgh} \pm 0.58$	$6.35^{e} \pm 0.09$	$5.59^{ef} \pm 0.26$	$5.55^{ef} \pm 0.40$	
Chemical	AV	$0.12^{d} \pm 0.02$	$0.12^{d} \pm 0.01$	$0.12^{cd} \pm 0.01$	$0.12^{d} \pm 0.0$	$0.12^{d} \pm 0.00$	$0.12^{d} \pm 0.01$	$0.16^{ab} \pm 0.02$	$0.15^{b} \pm 0.01$	$0.15^{ab} \pm 0.01$	$0.14^{bc} \pm 0.01$	$0.15^{b} \pm 0.01$	$0.15^{b} \pm 0.01$	$0.15^{b} \pm 0.01$	$0.16^{ab} \pm 0.01$	$0.17^{a} \pm 0.01$	
	k_{232}	$1.04^{b} \pm 0.1$	$1.07^{b} \pm 0.01$	$1.08^{b} \pm 0.02$	$1.04^{b} \pm 0.0$	$1.05^{b} \pm 0.03$	$1.05^{b} \pm 0.03$	$1.06^{b} \pm 0.01$	$1.22^{ab} \pm 0.29$	$1.36^{a} \pm 0.27$	$1.08^{b} \pm 0.03$	$1.06^{b} \pm 0.01$	$1.07^{b} \pm 0.03$	$1.07^{b} \pm 0.03$	$1.08^{b} \pm 0.03$	$1.09^{b} \pm 0.02$	
	TTC	$571^{c} \pm 20$	$578^{c} \pm 6$	$579^{c} \pm 12$	$572^{c} \pm 10$	$579^{c} \pm 12$	$579^{c} \pm 10$	$594^{b} \pm 11$	$608^{ab} \pm 3$	$611^{a} \pm 3$	$607^{ab} \pm 4$	$600^{ab} \pm 2$	$607^{ab} \pm 4$	$599^{ab} \pm 1$	$604^{ab} \pm 3$	$600^{ab} \pm 3$	
	HV	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	
	DPPH·r (%)	$29.5^{a} \pm 0.4$	$28.5^{ab} \pm 0.3$	$29.2^{a} \pm 0.3$	$28.4^{ab} \pm 2.0$	$26.6^{bc} \pm 2.2$	$25.8^{cd} \pm 0.5$	$26.8^{bc} \pm 1.3$	$25.1^{cde} \pm 0.6$	$25.7^{cd} \pm 1.3$	$22.5^{g} \pm 0.2$	$22.7^{fg} \pm 0.2$	$22.6^{g} \pm 0.1$	$22.2^{g} \pm 0.3$	$24.6^{def} \pm 1.6$	$23.6^{efg} \pm 1.9$	

Abbreviations and units: SMC, seed moisture content (%, w.b.); T, temperature (°C); OR, oil recovery (d.b.,%); CRO, cake residual oil (d.b.,%); FCO, fines content in oil (%, d.b.); AV, acid value (% oleic acid); TTC, total tocopherol content (μg/g oil); HV, hydroperoxide value (meq/kg oil); DPPH·r, remanent DPPH at 30 min incubation (%).
Mean values (±standard deviation) were the averages of three independent measurements, Values in each row with different superscript letters, present significant differences ($p \leqslant 0.05$) among treatments. ND: not detected.

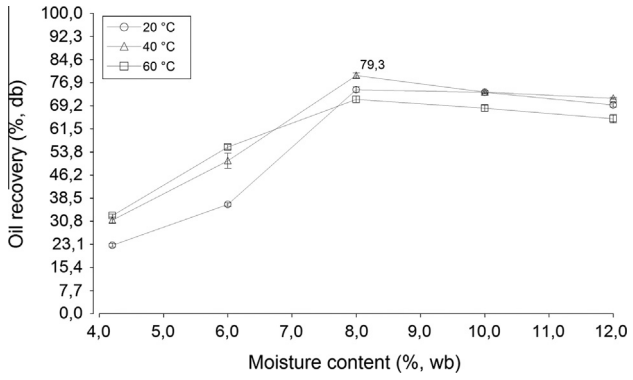

Fig. 1. Relationship between oil recovery and seed moisture content in screw pressing of almond seeds at different pressing temperature.

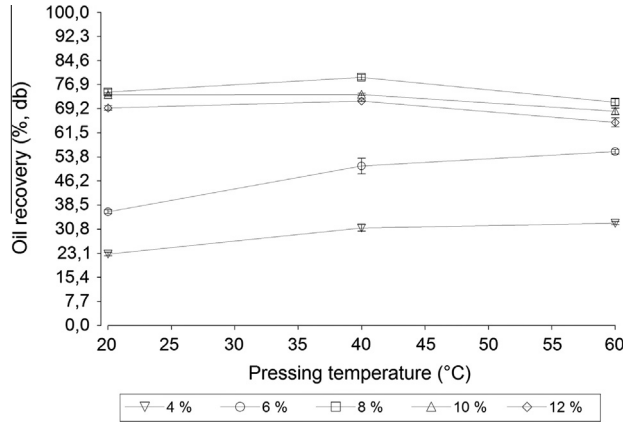

Fig. 2. Relationship between oil recovery and pressing temperature in screw pressing of almond seeds at different moisture contents.

temperature. At this moisture content, an increase of temperature from 20 to 40 °C produced a significant increase in OR.

The fines content in oil (FCO) ranged from 2.56 to 28.60% (d.b.). The lowest FCO was obtained at 8% (w/w) moisture content and 40 °C pressing temperature. At these conditions, the press-cake became compact and darker, and lesser amount of sediments diverted to the barrel openings. The two-way ANOVA test applied to data set allowed to see that variations among treatments in OR and FCO may be explained, mainly, by differences in seed moisture content (Table 4). The oil quality data from almond seeds pressed at different moisture and temperature conditions indicated significant variations for all parameters evaluated. The most outstanding feature was the slightly increase of AV, TTC and

Table 4
Variability expressed as percentage of total sum of squares for oil recovery, solid content in oil and chemical parameters from screw-pressed almond oil.

Parameter	Moisture content (MC)	Pressing temperature (PT)	MC × PT**
Oil recovery	93.18*	1.78*	4.83*
Fines content in oil	91.93*	4.28*	2.78*
Acid value	67.57*	0.88	5.20
Total tocopherol content	72.10*	3.36	4.44
DPPH·r (%)	79.31*	0.64	7.57*

* Significant at $p \leqslant 0.05$.
** MC × PT is the interaction among MC and PT determinated by a two-way ANOVA test.

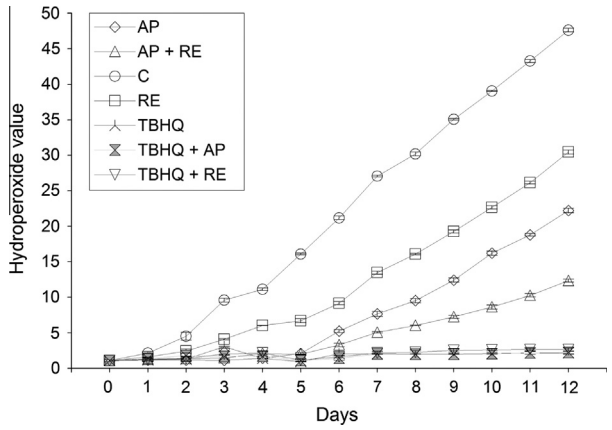

Fig. 3. Kinetic curves of hydroperoxide (meq O_2/kg oil) accumulation from almond oil alone or with added antioxidants, under thermo-oxidation conditions. Plotted values are means of two independent determinations.

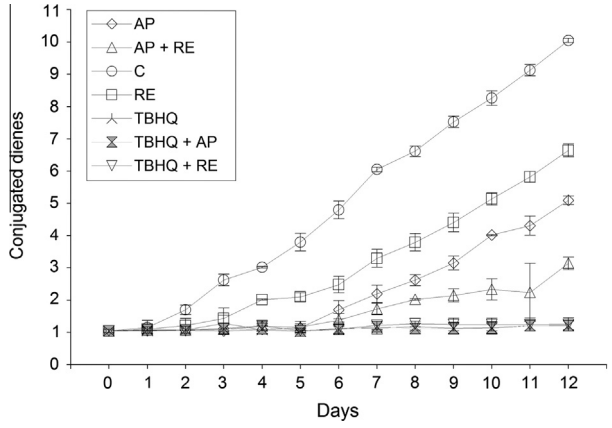

Fig. 4. Kinetic curves of conjugated dienes values (K_{232}) from almond oil alone or with added antioxidants, under thermo-oxidation conditions. Plotted values are means of two independent determinations.

antioxidant activity with increasing moisture content. These trends were confirmed by two-way ANOVA test, where the main variability source was the moisture content rather than the pressing temperature (Table 4). The acid and specific extinction coefficient k_{232} values were lower than 0.17 (% oleic acid) and 1.09, respectively; while, HV was not detected, indicating that the increase of seed moisture and pressing temperature did not affect negatively AO quality. The TTC varied between 571 and 611 μg/g oil. These values are slightly higher than those reported by Kodad and Socias, 2008 (400 and 500 μg/g oil). Antiradical activity varied between 78 and 70% and it can be attributed mainly to the tocopherol content.

3.4. Thermo-oxidation experiment

Food regulations worldwide recognize the rosemary extracts as GRAS ("generally recognized as safe") additives. There are no regulations that border their use yet. Rosemary extract (RE) used in this work contained 3.25% carnosic acid as the main active antioxidant component. A preliminary assessment of the antioxidant capacity of RE was carried out using Rancimat method. The oxidative stability of almond oil (Control) was 21.80 h ± 0.05 h. The RE concentration was selected based on previous experiences of the authors in walnut oil (Martinez et al., 2013). All RE concentrations tested significantly protected AO. The protection factors were 1.72 ± 0.01, 1.97 ± 0.05 and 2.13 ± 0.04 for 400 ppm RE, 600 ppm RE and 800 ppm RE, respectively. Considering that doubling the concentration of RE is not duplicated the PF, a concentration of 400 ppm RE was used for AO schaal oven test.

Table 5
Regression coefficients and R^2 for HV from AO during the storage stability test.

Treatment	β_0	β_1	β_2	R^2	
Natural antioxidants					Day (HV_{15}) foretold
Control	0.082	3.122	−0.535	0.99	5
RE	0.161	0.558	0.982	0.99	8
AP	0.193	−0.493	1.150	0.99	10
AP + RE	0.091	−0.157	1.287	0.99	13
With artificial antioxidants					Day (HV_3) foretold
TBHQ	−0.010	0.160	1.160	0.96	23
TBHQ + RE	−0.010	0.260	1.210	0.95	14
TBHQ + AP	−0.004	0.130	1.320	0.91	27

Regression equations: $y = \beta_0 + \beta_1 x + \beta_2 x^2$, where '$y$' is the dependent variable (hydroperoxide value); β_0 is a constant that it is equal the value of 'y ' when the value of 'x' = 0; β_1 is the coefficient of 'x'; β_2 is the coefficient of 'x^2'; 'x' is an independent variable (time) and R^2 is the determination coefficient.

Table 6
Mean values and standard deviations of % inhibition DPPH·r from almond oil during the storage stability test, Different superscript letters in each column indicate significant differences between treatments ($p \leqslant 0.05$).

Treatment	% Inhibition DPPH·r		
	Day 0	Day 6	Day 12
C	$76.21^{a} \pm 0.08$	$68.69^{a} \pm 0.65$	$49.47^{a} \pm 1.00$
RE	$79.32^{a} \pm 0.57$	$76.84^{c} \pm 0.32$	$68.23^{b} \pm 0.59$
AP	$84.51^{b} \pm 0.13$	$75.75^{b} \pm 0.73$	$69.88^{c} \pm 0.59$
TBHQ	$95.97^{c} \pm 0.08$	$95.64^{e} \pm 0.00$	$95.50^{ef} \pm 0.17$
AP + RE	$85.48^{b} \pm 0.00$	$79.13^{d} \pm 0.00$	$77.28^{d} \pm 0.17$
TBHQ + RE	$96.14^{c} \pm 0.08$	$95.18^{e} \pm 0.00$	$94.50^{e} \pm 0.42$
TBHQ + AP	$96.43^{c} \pm 0.00$	$95.93^{e} \pm 0.08$	$95.80^{f} \pm 0.08$

During the thermo-oxidation assay major changes were detected in HV (Fig. 3) and conjugated dienes (k_{232}) (CD) (Fig. 4), indicating that AO was susceptible to degradation. Control sample (AO without additive) reached a HV and CD around 48 meq/kg oil and 10.10, respectively. The addition of TBHQ, alone or in combination, presented the highest oxidative stability, followed by AP + RE, AP and RE. The combination AP + RE showed an additional protective effect on AO, while the treatments with TBHQ resulted equally effective in inhibiting the formation of primary oxidation products in AO.

The complete HV data set (0–12 days) was used to perform a polynomial regression between HV and time (Table 5) with acceptable determination coefficients (0.91–0.99). According to Codex (FAO/WHO, 1981), the end point for rancidity or acceptability limit for general vegetable virgin and cold press fats and oils corresponds to a HV of 15 meq/kg oil. Under the storage conditions used, this end-point was reached at 8, 10 and 13 days of storage for RE, AP and AP + RE treatments respectively (Table 5). Since for TBHQ treatments the major HV was around 2.3 meq/kg oil after 12 days storage, the criteria for data presented in Table 5 was HV of 3.0 meq/kg oil.

The various combinations among the antioxidants tested reduced appreciably the AO oxidation rate during storage. These findings indicate that: (a) RE could be used in combination with AP (100 ppm) for preserving AO from oxidation at least for 13 months (Abou-Gharbia et al., 1996; Evans et al., 1973); (b) the antioxidant effectiveness of TBHQ may be achieved by using the 50% of the maximum concentration (200 ppm) allowed by worldwide food regulations for synthetic antioxidants in oils (Frankel, 2005).

The scavenger activity assay (Table 6, DPPH·r %) showed a strong influence of the antioxidant instead of storage time. The assessment of the antiradical capacity allowed determining that:

Table 7
Fatty acid composition (relative %) control simple.

Fatty acids (relative %)	Day 0	Day 12
Palmitic acid (16:0)	$6.74^{a} \pm 0.06$	$6.82^{a} \pm 0.04$
Palmitoleic acid (16:1)	$0.40^{b} \pm 0.01$	$0.43^{b} \pm 0.00$
Stearic acid (18:0)	$1.84^{c} \pm 0.58$	$2.37^{c} \pm 0.03$
Oleic acid (18:1)	$71.24^{d} \pm 0.36$	$70.96^{d} \pm 0.04$
Linoleic acid (18:2)	$19.77^{e} \pm 0.14$	$19.43^{e} \pm 0.04$

Mean values (±standard deviation) were the averages of two independent measurements. Values with different superscript letters, present significant differences ($p \leqslant 0.05$) among treatments.

(a) an additional antioxidant activity with AP + RE combination was observed; (b) TBHQ was an effective inhibitor of free radicals in AO; (c) AP and RE were less successful than TBHQ and did not demonstrate an additive effect on the activity of TBHQ.

The fatty acid composition of the control sample did not evidence changes during storage time (Table 7).

In view that AO is a non-traditional expensive edible oil due to the raw materials cost, it is important to preserve their chemical and nutritional quality. Since synthetic antioxidants are extensively used as food additives, their safety has been questioned stimulating the search and evaluation of naturally occurring compounds with antioxidant properties like ascorbyl palmitate and rosemary extract. Although in the accelerated assay of thermo-oxidation, the TBHQ was the most effective antioxidant, considering natural alternatives, the combination of ascorbyl palmitate and rosemary extract showed extra protective effect on the AO preservation.

4. Conclusions

Oil recovery from almonds seeds by pressing could be enhanced by adjusting seed moisture at 8% (w/w) and pressing temperature at 40 °C. Moistening was more beneficial than heating in terms of OR for the range of conditions used in this study. The lowest FCO was obtained at the same processing conditions (8% moisture content and 40 °C pressing temperature) because the press-cake became more compact and darker, and lesser amount of sediments diverted to the barrel openings. All the extraction conditions employed were compatible with good quality of oil chemistry.

Although in the accelerated assay of thermo-oxidation, the TBHQ resulted in the most effective antioxidant, considering natural alternatives, rosemary extract and ascorbyl palmitate combination showed additional effect on the AO preservation.

Acknowledgements

This work was financed with grants from CONICET, SeCyT – UNC and Ministerio de Ciencia y Tecnología de la Provincia de Córdoba (Argentina).

References

AACC, 2003. Approved methods of AACC, 10th ed. American Association of Cereal Chemist's, St. Paul Min.
Abou-Gharbia, H.A., Shahidi, F., Shehata, A.A.Y., Youssseff, M.M., 1996. Oxidative stability of extracted sesame oil from raw and processed seeds. J. Food Lipids 3, 59–72.
Ahmad, 2010. The uses and properties of almond oil. Zeeshan Complementary Therapies Clin. Pract. 16, 10–12.
AOCS, 2009. Official methods and recommended practices of the american oil chemists' society, fifth ed. AOCS Press, Champaign.
Atungulu, G., Miura, M., Atungulu, E., Satou, Y., Suzuki, K., 2007. Activity of gaseous phase steam distilled propolis extracts on peroxidation and hydrolysis of rice lipids. J. Food Eng. 80 (3), 850–858.
Cherif, A., Sebei, K., Boukhchina, S., Kallel, H., Azul, J., 2004. Kernel fatty acid and triacylglycerol composition for three almond cultivars during maturation. J. Am. Oil Chem. Soc. 81 (10), 901–905.
Economou, K.D., Oreopoulou, V., Thomopoulos, C.D., 1991. Antioxidant activity of some plant extracts of the family labiatae. J. Am. Oil Chem. Soc. 68, 109–113.
Evans, C.D., List, G.R., Moser, H.A., Cowan, J.C., 1973. Long term storage of soybean and cottonseed salad oils. J. Am. Oil Chem. Soc. 50 (2), 18–222.
Fils, J.M., 2000. The production of oils. In: Hamm, W., Hamilton, R.J. (Eds.), Edible Oil Processing. Sheffield Academic Press, Sheffield, England, pp. 47–78.
Frankel, E.N., 2005. Lipid oxidation, second ed. The oily Press, P.J. Barnes and Associates, England.
Kodad, O., Socias, I.C.R., 2008. Variability of oil content and of major fatty acid composition in almond (*Prunus amygdalus* Batsch) and its relationship with kernel quality. J. Agric. Food Chem. 56, 4096–4101.
Kodad, O., Estopañán, G., Juan, T., Mamouni, A., Socias, R., 2011. Tocopherol concentration in almond oil: genetic variation and environmental effects under warm conditions. J. Agric. Food Chem. 59, 6137–6141.
Li, M., Bellmer, D.D., Brusewitz, G.H., 1999. Pecan kernel breakage and oil extracted by supercritical CO_2 as affected by moisture content. J. Food Sci. 64, 1084–1088.
Madsen, H.L., Sorensen, B., Skibsted, L.H., Bertelsen, G., 1998. The antioxidative activity of summer savory (*Satureja hortemis* L.) and rosemary (*Rosmarinus officinalis* L.) in dressing stored exposed to light or in darkness. Food Chem. 63, 173–180.
Maguire, L.S., O'Sullivan, S.M., Galvin, K., O'Connor, T.P., O'Brien, N.M., 2004. Fatty acid profile, tocopherol, squalene and phytosterol content of walnuts, almonds, peanuts, hazelnuts and the macadamia nut. Int. J. Food Sci. Nutr. 55 (3), 171–178.
Martínez, M.L., Mattea, M.A., Maestri, D.M., 2006. Varietal and crop year effects on lipid composition of walnut (*Juglans regia* L.) genotypes. J. Am. Oil Chem. Soc. 83, 791–796.
Martínez, M.L., Mattea, M.A., Maestri, D.M., 2008a. Pressing and supercritical carbon dioxide extraction of walnut oil. J. Food Eng. 88, 399–404.
Martínez, M.L., Maestri, D.M., 2008b. Oil chemical variation in walnut (*Juglans regia* L.) genotypes grown in Argentina. Eur. J. Lipid Sci. Technol. 110, 1183–1189.
Martínez, M.L., Marín, M.A., Salgado Faller, C.M., Revol, J., Penci, M.C., Ribotta, P.D., 2012. Chia (*Salvia hispanica* L.) oil extraction: study of processing parameters. Food Sci. Technol. 47, 78–82.
Martinez, M.L., Penci, M.C., Ixtaina, V., Ribotta, P.D., Maestri, D., 2013. Effect of natural and synthetic antioxidants on the oxidative stability of walnut oil under different storage conditions. Food Sci. Technol. 51, 44–50.
Meriles, J.M., Guzmán, C.A., Maestri, D.M., 2000. Lipoxygenase-1 activity of soybean genotypes grown in Argentina. Molecules 5, 475–478.
Minguez-Mosquera, M.I., Rejano, L., Gandul, B., Sánchez, A., Garrido, J., 1991. Color-pigment correlation in virgin olive oil. J. Am. Oil Chem. Soc. 68, 332–336.
Moayedi, A., Rezae, K., Moini, S., Keshavarz, B., 2010. Chemical compositions of oils from several wild almond species. J. Am. Oil Chem. Soc. 88 (4), 503–508.
Ozcan, M.M., Unver, A., Erkan, E., Arslan, D., 2011. Characteristics of some almond kernel and oils. Scientia Horticulturae 127, 330–333.
Pocklington, W.D., Dieffenbacher, A., 1988. Determination of tocopherols and tocotrienols in vegetable oils and fats by high-performance liquid chromatography. Pure Appl. Chem. 60, 877–892.
Salcedo, C.L., López de Mishima, B., Nazareno, M.A., 2010. Walnuts and almonds as model systems of foods constituted by oxidisable, pro-oxidant and antioxidant factors. Food Res. Int. 43, 1187–1197.
Singh, J., Bargale, P.C., 1990. Mechanical expression of oil from linseed. J. Oilseeds Res. 7, 106–110.
Singh, J., Bargale, P.C., 2000. Development of a small capacity double stage compression screw press for oil expression. J. Food Eng. 43 (2), 75–82.
Singh, K.K., Wiesenborn, D.P., Tostenson, K., Kangas, N., 2002. Influence of moisture content and cooking on screw pressing of crambe seed. J. Am. Oil Chem. Soc. 79 (2), 165–170.
Rezzoug, S.A., Boutekedjiret, C., Allaf, K., 2005. Optimization of operating conditions of rosemary essential oil extraction by a fast controlled pressure drop process using response surface methodology. J. Food Eng. 71 (2), 229–233.
Rizner Hras, A., Hadolin, M., Knez, Z., Bauman, D., 2000. Comparison of antioxidative and synergistic effects of rosemary extract with α-tocopherol, ascorbyl palmitate and citric acid in sunflower oil. Food Chem. 71 (1), 9–17.
Rodríguez-Rojo, S., Visentin, A., Maestri, D., Cocero, M.J., 2012. Assisted extraction of rosemary antioxidants with green solvents. J. Food Eng. 109 (1), 98–103.
Visentin, A., Cismondi, M., Maestri, D., 2011. Supercritical CO_2 fractionation of rosemary ethanolic oleoresins as a method to improve carnosic acid recovery. Innovative Food Sci. Emerging Technol. 12, 142–145.
Wiesenborn, D., Doddapaneni, R., Tostenson, K., Kangas, N., 2001. Cooking indices to predict screw-press performance for crambe seed. J. Am. Oil Chem. Soc. 78 (5), 467–471.