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# Variability in almond oil chemical traits from traditional cultivars and native genetic resources from Argentina

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ABSTRACT

Almond (*Prunus dulcis* (Miller) D.A. Webb) genetic resources (Marcona, Guara, Non Pareil, IXL, AI, Martinelli C, Emilito INTA, Cáceres Clara Chica, Javier INTA) were studied during two consecutive crop years in order to evaluate variations in kernel oil yield and composition, and oil oxidative parameters. Total oil, oleic acid, α-tocopherol and squalene contents were found to range between 48.0% and 57.5%, 65% and 77.5%, 370 and 675 μg/g oil, and 37.9 and 114.2 μg/g oil, respectively. The genotype was the main variability source for all these chemical traits. The α-tocopherol content seems to be the most important contributor to both the radical scavenging capacity and the oxidative stability of almond oils analysed. Results obtained from the local genotypes namely Martinelli C, Emilito INTA and Javier INTA may be of interest for almond breeding focused to improve kernel oil yield and composition.


## 1. Introduction

Almond is a major tree nut crop cultivated mainly in the Mediterranean region and the USA, which is the world's major producer. The kernel is the edible part of the nut and is considered an important snack and confectionary food, with a high nutritional value arising primarily from its high lipid content. Almond kernel mainly contains lipids (45–60%, dry basis); proteins and carbohydrates are present in similar amounts (20% each, in average).

Almond oil (AO) contains a substantial quantity of triacylglycerols (TAG), which are stored as intracellular oil droplets (approximately 1–3 μm in diameter) in the cotyledon tissues of the kernel (Ren, Waldron, Pacy, Brain, & Ellis, 2001). AO is composed predominantly of mono and di-unsaturated fatty acids (FA). The FA composition of AO has been extensively reported for several cultivars from different geographical origins including the USA, Spain, Italy, Tunisia and Turkey (Askin, Balta, Tekintas, Kazankaya, & Balta, 2007; Kodad & Socias i Company, 2008; Martín-Carratalá, Llorens-Jordá, Berenguer-Navarro, & Grané-Teruel, 1999; Piscopo, Romeo, Petrovica, & Poiana, 2010; Prats-Moya, Grané-Teruel, Berenguer-Navarro, & Martín-Carratalá, 1999; Yada, Lapsley, & Huang, 2011). The major FA in AO is oleic acid, representing 50–80% of the total FA content. Linoleic, palmitic and stearic acids are present at levels of 10–26%, 5–9%, and 1.5–4%, respectively. Linolenic acid may be found at very low concentrations (<0.1%). Minor components characterised in AO include: tocopherols (about 450 μg/g oil), sterols (2200 μg/g) and squalene (95 μg/g) (Kornsteiner, Wagner, & Elmadfa, 2006; López-Ortiz et al., 2008; Maguire, O'Sullivan, Galvin, O'Connor, & O'Brien, 2004). The major tocopherol is α-Toc (240–440 μg/g); the sterols are mainly β-sitosterol (95% of the total sterols), and campesterol and stigmasterol in similar amounts.

Freshly extracted AO has low peroxide value (lesser than 0.5 meq $O_2$/kg oil). This means that AO is readily preserved from oxidation. Besides tocopherols, which exert a protective role against lipid oxidation, recent studies have shown that almonds also contain a diverse array of phenolic and polyphenolic compounds. These chemical components are mainly present in the skin

*Abbreviations:* AO, almond oil; AV, acid value; CD, conjugated diene; CT, conjugated triene; CY, crop year; DW, dry basis; FA, fatty acid; HPLC, high-performance liquid chromatography; OC, oil content; O/L, oleic/linoleic acid ratio; OSI, oxidative stability index; PV, peroxide value; RSC, radical scavenging capacity; SQ, squalene; α-Toc, α-tocopherol; $I_2V$, iodine value.

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(seed coat) and they are effective inhibitors of oil oxidative degradation (Bolling, Dolnikowski, Blumberg, & Chen, 2010).

In Argentina, almond cultivation was introduced by European immigrants. Improvement of almond cultivation through breeding was gaining importance and allowed to get some local genotypes such as Emilito INTA, Javier INTA, Cáceres Clara Chica and Martinelli C, which are well adapted to the warm and dry areas of the Argentinean Middle West (provinces of Mendoza and San Juan). Besides giving the morphological and agronomical description of these promising almond genetic resources (Carra de Tolosa & Herrera, 2006), studies should also define their nutritional value. A lot of studies have been carried out on the characterisation of different almond cultivars and criteria for almond kernel quality evaluation, and some works have focused on fatty acid profile, triacylglycerol and tocopherol composition as discriminant parameters in order to differentiate almond genotypes (Askin et al., 2007; García-López, Grané-Teruel, Berenguer-Navarro, García-García, & Martín-Carratalá, 1996; Grane-Teruel, Prats-Moya, Berenguer-Navarro, & Martín-Carratala, 2001; Kodad et al., 2006; López-Ortiz et al., 2008; Martín-Carratalá et al., 1999).

Almond oil content and composition depend primarily on the genotype but may be affected by factors such as the crop year, and the specific environmental conditions of the growing region (Yada et al., 2011). Irrigation has shown to increase almond yields (Sánchez-Bel, Egea, Martínez-Madrid, Flores, & Romojaro, 2008) but appears to have little or no effect on both oil content and composition (Egea et al., 2009). Interestingly, Askin et al. (2007) have reported that kernel weight affects significantly the FA composition of AO showing a positive correlation with oleic acid (OA) content. The different uses of almonds may require kernels with specific physical and compositional characteristics. For oil production, besides high oil content, the FA composition and parameters related to oil oxidative stability should be important criteria for selection.

Almond oil can be extracted easily by screw pressing (Martínez, Penci, Marin, Ribotta, & Maestri, 2013). Employing a pilot plant screw-press, the highest oil recovery (440 g/kg kernel) was achieved at 8 g/100 g kernel moisture and 40 °C pressing temperature.

Increasing worldwide almond production and increasing demand of new specialty oils, encourage screening of new almond genotypes with higher kernel oil content and improved fatty acid (higher OA concentration) profile. This study evaluates some oil chemical parameters of almond genetic resources from Argentina, and compares them with those from some selected commercial cultivars growing under the same agro-ecological conditions.

## 2. Materials and methods

### 2.1. Plant material

Almond fruits (*Prunus dulcis* (Mill.) D.A. Webb, Syn. *Prunus amygdalus* Batsch) were collected during two consecutive crop years (CY) from nine genotypes (Marcona, Guara, Non Pareil, IXL, AI, Martinelli C, Emilito INTA, Cáceres Clara Chica, Javier INTA) growing in an experimental orchard (10-year-old, tree spacing 5 m × 5 m, 400 trees/ha, grafted on "Nemared" peach rootstock) at the Experimental Station (INTA) located at Pocito (San Juan Province, Argentina). Pocito (lat. 31°37′ S, long. 68°32′ W) is located in the Monte phytogeographical province, in arid northwestern Argentina, at 620 m above sea level. The climate in this area represents a typical arid climate with great annual temperature variations (absolute maximum values exceeding 45 °C, and absolute minimum values ranging between 5 °C and 10 °C below zero). The average annual rainfall is below 100 mm concentrated mainly in summer. The region has high heliophany, low cloudiness and intensive solar radiation. The frost-free period comprises about 220–300 days extending from October to May. Table 1 summarises climatic conditions during both 2010 and 2011 CY evaluated. Almonds plants were grown under natural rainfall, plus supplemental irrigation of 1357 mm/year (net irrigation requirement).

From each almond genotype, three fruit samples (1 kg each) were taken from the entire canopy of five selected trees. Fruits were hand-harvested at full maturity and then dried in a vacuum oven (30 °C) until the kernel moisture content reached a value of about 5%.

### 2.2. Dry matter and oil contents

Fruits were cracked and shelled manually, and kernels were ground using a universal cutting mill (model Super Junior, Moulinex, France). Dry matter content was determined after oven drying at 80 °C for 72 h. Lipid extraction for total oil content was performed using Soxhlet devices with *n*-hexane as solvent. The solvent was removed using a rotary vacuum evaporator at 40 °C. The oil content was gravimetrically determined and expressed as weight percent on dry basis (g/100 g kernel, DB) (AOCS, 1998).

### 2.3. Oil analyses

For analytical determinations, oils were extracted by screw-pressing at room temperature. Briefly, kernels containing about 5% moisture (w/w) were ground and particles between 2.4 and 4.8 mm were selected using an automated screen. Oil expression 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 *via* an electrical resistance-heating ring attached around the press barrel, to raise and maintain the screw-press barrel temperature to the desired temperature (25 °C) (Martínez et al., 2013).

Acid (AV), peroxide (PV), conjugated diene (CD) and conjugated triene (CT) values of the oil samples were analysed according to standard methods of AOCS (1998). The oxidative stability indices (OSI) were determined by Rancimat (Metrohm, Herisau, Switzerland) 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.

To evaluate the radical scavenging capacity (RSC), four concentrations (75, 100, 125 and 150 mg of oil in 1 mL toluene) of each AO sample were prepared. Each oil/toluene solution was vortexed (20 s, ambient temperature) with 3.9 mL toluene solution of the free stable DPPH (2,2-diphenyl-1-picrylhydrazyl) radical (DPPH·) at a concentration of $10^{-4}$ mol/L. Against a blank of pure toluene,

**Table 1**
Average monthly temperatures (°C) and rainfall (mm) measured at the Experimental Station (INTA) located at Pocito (San Juan Province, Argentina) during 2010 and 2011 crop years.

| Month | 2010 crop year | | 2011 crop year | |
|---|---|---|---|---|
| | Temperature | Rainfall | Temperature | Rainfall |
| January | 27.5 | 4.6 | 25.9 | 54.0 |
| February | 26.2 | 1.8 | 24.2 | 28.4 |
| March | 24.5 | 0.0 | 22.0 | 9.4 |
| April | 16.7 | 0.0 | 18.2 | 3.8 |
| May | 12.1 | 11.4 | 12.6 | 0.0 |
| June | 9.6 | 0.0 | 8.8 | 0.2 |
| July | 6.8 | 0.0 | 7.8 | 2.8 |
| August | 10.1 | 0.6 | 10.3 | 0.0 |
| September | 14.4 | 5.6 | 15.9 | 0.0 |
| October | 18.6 | 6.2 | 18.5 | 0.2 |
| November | 22.2 | 10.0 | 23.6 | 26.0 |
| December | 25.0 | 15.8 | 25.9 | 0.8 |