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Chemical quality and oxidative stability of extra virgin olive oils from San Juan province (Argentina)

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ABSTRACT

This study provides information about the chemical quality (quality indices, fatty acid profile, total polyphenols (PPs), tocopherols and pigments) and oxidative stability index (OSI) of virgin olive oils of Arbequina, Changlot Real and Coratina cultivars (San Juan province, Argentina). The influence of the cultivar and the effect of earlier harvest dates on the yields (OY), quality and OSI of the oils were also evaluated. All the oils were classified as extra virgin. The OY (L/100 kg) averaged: Arbequina = 13.2, Changlot Real = 21.3, Coratina = 18.3. The oleic acid (O) percentage, oleic to linoleic plus linolenic ratio [O / (L + Ln)], PPs and OSI were highly dependent on cultivar (Arbequina < Changlot Real < Coratina). The earlier harvest season associated with lower maturity indices increased the OSI of all the oils (Arbequina: from 6.3–13.8 h up to 10.6–19.0 h, Changlot: from 6.0–12.1 h up to 13.7–36.9 h and Coratina: from 20.5–26.0 h up to 24.6–42.4 h) due to a more favorable O / (L + Ln) ratio and antioxidant composition. Regional producers are recommended to bring forward the harvest season to obtain oils with better chemical and nutritional quality, higher oxidative stability and a fatty acid profile according to the IOC trade standard.

1. Introduction

Argentina produced in average 24,700 t of olive oils between 2010/2011 and 2015/2016 according to the IOC. > 75% of the oils produced in this period were exported, with Argentina ranking fourth after the European Union, Tunisia and Turkey in terms of world exports (IOC, 2016a). Therefore, in the last years, the purchasing countries of olive oils from Argentina (Brazil, USA, Spain, Italy, etc.) and the international organizations such as IOC and Alimentarius Codex have focused their interest on the quality and oxidative stability of these oils. The province of San Juan has increased significantly its export volumes, which represented about 15% of the total olive oil exported by Argentina in the decade 2000/2009 (Antuña, 2010). Owing to its particular soil and climate characteristics and the excellent quality of its irrigation water originated from the thawing snow of the Andes Mountains, the olive oils from the San Juan province are characterized by their excellent quality. However, scarce compositional data for these oils are available (Ceci & Carelli, 2010a; Cobos et al., 2014), and there is great interest in increasing the number of studies that typify, characterize and optimize the quality of these oils.

Oxidation processes are the main cause of olive oil deterioration, and thus of its loss of quality. The main factors affecting the oil shelf life are the glyceride composition and some minor components. Compared to other vegetable oils, olive oil is characterized by its high content of phenolic compounds with recognized antioxidant properties. Studies using purified glyceride matrices from virgin olive oil showed that ortho-diphenolic compounds (hydroxytyrosol or 3,4-DHPEA, hydroxytyrosyl acetate, aldehydic form of oleuropein aglycon, and luteolin) and mixtures thereof exhibited greater antioxidant activities than α-T (Mateos, Trujillo, Pérez-Camino, Moreda, & Cert, 2005). In contrast, tyrosol, squalene and free fatty acids showed low or negligible effects on oil stability. In mixtures of 3,4-DHPEA and α-T, the stability was dependent on the concentration ratio between both antioxidants, and a synergic effect was observed (Baldioli, Servili, Perretti, & Montedoro, 1996).

A multiple linear regression model was developed to study how the

Abbreviations: CARs, carotenoids; CHLs, chlorophylls; EVOO, extra virgin olive oil; FAMEs, fatty acid methyl esters; FA, free acidity; 3,4-DHPEA, hydroxytyrosol; G, gadoleic acid; IOC, International Olive Council; L, linoleic acid; Ln, linolenic acid; MUFAs, monounsaturated fatty acids; OY, oil yield; O, oleic acid; OLLnR, O / (L + Ln) ratio; OSI, oxidative stability index; P, palmitic acid; Po, palmitoleic acid; PV, peroxide value; PPs, polyphenols; PUFAs, polyunsaturated fatty acids; RLV, Reference Labeling Value; S, stearic acid; α-T, α-tocopherol; α-TE, equivalent α-tocopherol; β-T, β-tocopherol; γ-T, gamma-tocopherol; δ-T, delta-tocopherol; TTs, total tocopherols; UFAs, unsaturated fatty acids

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different compositional parameters contribute to the oxidative stability determined by the Rancimat method (Ceci & Carelli, 2010b). By means of this model, it was observed that the oxidative stability of the olive oil depended on its fatty acid composition and the level of natural components, mainly PPs. CARs and β-T also contributed to the oxidative stability as antioxidants, although their contribution was less significant.

In a previous study, samples of EVOO from the San Juan province (Argentina) were evaluated, analyzing the profile and content of total and individual biophenols and their relation to flavor (Ceci, Ramírez, Mussio, Mattar, & Carelli, 2017). The contents of total biophenols, secoiridoids and simple phenols strongly depended on the cultivar, with the highest levels being observed for the Coratina oils, variable levels for the Changlot Real oils, and the lowest levels for the Arbequina oils. By bringing forward the harvest date, oils with enhanced biophenol profiles in terms of quality and concentration were obtained, also being harmonious and complex from a sensory point of view.

The objective of this work was to provide information about the chemical quality of EVOO from the San Juan province (Argentina), evaluating the influence of the cultivar and earlier harvest dates on oil yields, classical quality indices, fatty acid profile, total PPs, tocopherols and pigments. The effect of these parameters on the olive oil oxidative stability determined by the Rancimat method was also analyzed.

2. Materials and methods

2.1. Olive oils

Thirty samples of olive fruits of the Arbequina, Changlot Real and Coratina cultivars were harvested in four departments (25 de Mayo, Sarmiento, Zonda and Ullum) of the San Juan province (Argentina). The coordinates of these departments range 31–32°S and 68–69°W, and their altitudes above sea level are 555–785 m. In 2012, the fruits were harvested at the beginning of the harvest season (late April-early May) and at the end of the season (late May-early June). The maturity indices of the fruits were evaluated by the color of the skin and the flesh using a scale ranging from 0 to 7. The maturity indices obtained in 2012 were: Arbequina (6 samples) = 2.52–5.22, Changlot Real (4) = 4.60–5.06, and Coratina (5) = 1.57–2.97.

In 2013, in order to reduce the maturity indices and avoid processing over-ripe olives, the harvest was brought forward 15–17 days, reaping the fruits in early April and early May. The maturity indices obtained in 2013 were: Arbequina (5 samples) = 1.62–3.27, Changlot Real (6) = 2.53–3.33, and Coratina (4) = 0.33–1.36.

About 100 kg of fruits were processed using OLIOMIO two-phase equipment to extract the oil (temperature = 20.0–27.5 °C, time = 40 min). The oil volume was measured at the centrifuge exit, and the OY was expressed as volume of oil in L/100 kg of processed fresh olives.

2.2. Analytical methods

Classical quality indices such as FA [oleic acid (O) content in g/100 g], PV (peroxide oxygen in mEq/kg) and specific UV extinction coefficients (K268 and K232) were determined according to IOC regulations (IOC, 2016b). The OSI, represented as the induction time in hours, was measured with a Metrohm 679 Rancimat apparatus at 110 °C and 20 L/h airflow.

Fatty acids were determined as FAMEs obtained by trans-esterification with a solution of potassium hydroxide in methanol at room temperature (IOC, 2015). Then, FAMEs were analyzed by Capillary GC with a 4809D series gas chromatograph (Agilent Technologies, Hewlett-Packard, Santa Clara, CA, USA), identified by comparing their retention times with Supelco standards (Supelco 37 Component FAME mix, Supelco, Inc.) and quantified as percentage of fatty acids. FAMEs were separated on a SP2380 capillary column [stabilized poly (90% bicyanopropyl/10% cyanopropylphenylsiloxane)] (30 m length × 0.25 mm i.d., 0.25 μm film thickness; Supelco Inc., Bellefonte, PA, USA) using hydrogen as carrier gas. The column temperature was maintained at 170 °C for 15 min, then increased at 4 °C/min to 210 °C and finally maintained at 210 °C for 10 min. The injector was used in split mode with a ratio of 1:50. The temperatures of the injector and Flame Ionization Detector were 220 °C. Data acquisition and peak integration were performed using EZChromElite 332 data system (Agilent Technologies).

Polyphenolic compounds (PPs) were isolated by three extractions of an oil-in-hexane solution with methanol/water (60%, v/v). The content of PPs was determined spectrophotometrically at 725 nm using Folin-Ciocalteu reagent (Merck, Darmstadt, Germany) and caffeic acid (≥ 99%) provided by Sigma (Sigma Chemical Co., St. Louis, MO, USA) as standard. The content of PPs was expressed as caffeic acid equivalents (mg/kg of oil) (Gutfinger, 1981).

Tocopherol content was determined by HPLC according to AOCS method Ce 8-89 (AOCS, 2009). A standard of α-T (purity > 98%) was obtained from Sigma and used as external standard. The equipment used was a HPLC Varian (Vista 5500) chromatograph equipped with a fluorescence detector and a LiChrosorb Si-60 column (l = 25 cm; i.d. = 4 mm; particle size = 5 μm) (Merck). The mobile phase was filtered and degassed isopropanol:hexane (0.5:99.5, v/v) at a flow rate of 1 mL/min. Peak areas were obtained with Waters Empower 2 software (Waters, Milford, MA, USA). TTs, α-T, β-T, γ-T and δ-T were expressed as mg/kg.

CHLs and CARs were evaluated from the absorption maximum for an oil solution in cyclohexane at 670 and 470 nm, respectively. The absorptivity coefficients of pheophytin “a” and lutein were used for CHLs and CARs, respectively, and the results were expressed as mg/kg (Mínguez-Mosquera, Rejano-Navarro, Gandul-Rojas, Sánchez-Gómez, & Garrido-Fernández, 1991).

2.3. Statistical analysis

Simple ANOVA (software: INFOSTAT 2014, Universidad Nacional de Córdoba, Argentina) was used for all the assays, and Duncan's test ($p \leq 0.05$) was performed to estimate significant differences between cultivars and harvest years. The analyses were carried out in triplicate, except for the fatty acid determinations that were performed in independent duplicates and each one was twice injected onto the gas chromatograph.

3. Results and discussion

3.1. Oil yield and quality indices

The OY was significantly higher for the Changlot Real and Coratina cultivars, being 21.3 and 18.3 L/100 kg olives in average, respectively (Table 1). The fruits from the Arbequina cultivar presented lower OY (average = 13.2 L/100 kg). According to data from a germplasm bank of Spanish varieties, Changlot Real shows higher oil content (77.1% in dry matter) than Arbequina cultivar (66.2%) (Uceda, Aguilera, Giménez, & Beltrán, 2010). On the other hand, Coratina is a variety characterized by high oil content, reaching up to 22.6% of fresh weight in hot regions (Dag, Harlev, Lavee, Zipori, & Kerem, 2014). No significant differences were observed in the OY of the three cultivars between harvest years. Thus, bringing forward the harvest 15–17 days did not affect the oil extractability.

All samples were classified as EVOO taking into account the maximum limits stated by the IOC Trade Standard for this category: FA = 0.8 g/100 g and PV = 20 mEq/kg (Table 1) (IOC, 2016b). No significant differences were detected between cultivars and harvest years for FA, which was < 0.42 g/100 g. As for PV, the Arbequina oils exhibited significantly lower values in the 2013 season when harvest was brought forward (2013 = 3.36, and 2012 = 7.83 mEq/kg in