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The effects of genotype and extraction methods on chemical composition of virgin olive oils from Traslasierra Valley (Córdoba, Argentina)

M.M. Torres, D.M. Maestri *

Instituto Multidisciplinario de Biología Vegetal (IMBIV. CONICET – UNC). Cátedra de Química Orgánica, Facultad de Ciencias Exactas, Físicas y Naturales, Universidad Nacional de Córdoba, Av. Vélez Sarsfield 1611, Ciudad Universitaria, X5016GCA Córdoba, Argentina

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Abstract

This work was carried out to assess the influence of two extration methods (two-phase centrifugation and pressure) on oil quality from four olive varieties cultivated at Traslasierra Valley, Córdoba, Argentina. Analysis of the effect of the extraction system, on the values of analytical determinations, revealed statistically significant differences in some parameters, mainly in free fatty acid and phenol contents, and K_{270} values. Oxidative stability showed a significant positive correlation with phenol content. Most of the quality indices and fatty acid compositions showed significant variations among olive varieties. Nevadillo variety had the highest values of oleic acid, whereas Manzanilla was noteworthy for its higher content of phenolic compounds. Accordingly, pressure-extracted oil from the Manzanilla variety presented better oxidative stability.

Keywords: Virgin olive oil; Genotype; Extraction method; Quality

1. Introduction

The chemical composition of virgin olive oils may be influenced by genotype, and different agronomic, environmental and technological factors (Bruni, Cortesi, & Fiorino, 1994; Caponio, Alloggio, & Gomes, 1999; Di Giovacchino, Solinas, & Miccoli, 1994; Salvador, Aranda, Gómez–Alonso, & Fregapane, 2003).

In Argentina, the commercial production of olive oil is an important economic activity, especially in semi-arid regions that are considered marginal areas for conventional crops. In central Argentina, the olive production is located in the northwest Córdoba province and it accounts for more than 16% of total area planted. The most important olive varieties cultivated in this area are Arbequina, Manzanilla, Nevadillo and Ascolana. The manufacture of virgin olive oil is carried out in small factories which utilize either the dual-phase decanter (centrifugation system) or the older pressure technique which vary not only in the physical forces employed to separate the oil phase but also in the amount of water used. Since the centrifugation system reduces the processing time, which in turn decreases the excessive storage period of the fruits, the oils obtained are frequently of higher quality (Alba, 1997; Nergiz & Unal, 1991).

As occurs in other oil-producing plants, the olive oil industry in Argentina faces the challenge of finding ways to improve the productivity and quality of their products. Although the majority of the production is commercialized as blends of virgin olive oils, there are no

* Corresponding author. Tel./Fax: +54 0351 4334439.
E-mail address: dmaestri@efn.uncor.edu (D.M. Maestri).

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published data on chemical composition of olive oil varieties cultivated in Córdoba.

This work examines the influence of the extraction method on the quality of four monovarietal virgin olive oils produced at Traslasierra Valley, Córdoba, Argentina.

2. Materials and methods

2.1. Oil samples

Olive (*Olea europea* L.) fruits of the varities Arbequina, Manzanilla, Nevadillo and Ascolana, were collected from Traslasierra Valley, Córdoba province, Argentina. Three samples (100 kg each) of each variety were picked by hand at an optimal stage of ripeness. After homogenization and cleaning, each sample from each variety was divided into two portions. One of them was extracted using a centrifugation system (dual-phase decanter), and the other one by a pressure system.

The olive paste was obtained using a metal hammer crusher and then the following experimental procedures were followed:

(a) *Centrifugation*. Olive paste was kneaded for 50 min at 22 ± 2 °C and then diluted with water (10 l/100 kg of olives); oil was extracted with a horizontal centrifugal decanter and liquid obtained was separated with an automated discharge vertical centrifuge.
(b) *Pressure*. Olive paste was kneaded for 50 min at 22 ± 2 °C and then squeezed at 300 bar; the liquid obtained (aqueous and oily) was separated in stainless steel decanters.

All oil samples were filtered through anhydrous Na_2SO_4 and stored at 4 °C in dark glass bottles prior to analyses.

2.2. Analytical methods

Free acidity, peroxide value (PV), and UV absorption characteristics were determined following the analytical methods described in Regulations EEC/2568/91 and later modifications of the European Union Commission (EEC, 1991). All chemicals and solvents used were either of analytical or HPLC grade. Methanol, *n*-hexane and cyclohexane were purchased from Merck (Darmstadt, Germany).

For the determination of fatty acid composition, samples of 0.5 g oil were subjected to alkaline saponification (1 N KOH in methanol). Unsaponificable matter was extracted with *n*-hexane. The fatty acid methyl esters (FAME) of total lipids were obtained using 1 N H_2SO_4 in methanol and analyzed by gas chromatography according to Maestri et al. (1998). A Shimadzu (Kyoto, Japan) gas chromatograph, fitted with a FID detector, was employed. Separations were made on a Supelcowax 10 (Bellefonte, PA, USA) fused-silica capillary column (30 m × 0.25-mm i.d. × 0.25-μm film thickness). Peaks were identified by comparison of their retention times with those of authentic reference compounds (Sigma–Aldrich, St. Louis, MO, USA).

Iodine values (IV) were calculated from fatty acid percentages (Maestri et al., 1998) by using the formula.

$$\mathrm{IV} = (\%\ \text{palmitoleic} \times 1.001) + (\%\ \text{oleic} \times 0.899) + (\%\ \text{linoleic} \times 1.814) + (\%\ \text{linolenic} \times 2.737)$$

Total phenol compounds were extracted from aliquots of 5 ml oil according to Satue, Huang, and Frankel (1995). Oil samples dissolved in 10 ml of *n*-hexane, were extracted three times with 10 ml of a methanol/water mixture (60:40, vol/vol). The pooled extracts were washed with 10 ml of *n*-hexane and solvents were removed with a rotating evaporator (Büchi, Switzerland) under vacuum. To a suitable dilution of the extracts, Folin Ciocalteau (Fluka Co., Buchs, Switzerland) reagent was added and the absorptions of the solutions at 725 nm were measured. Values for total phenols are given as μg of gallic acid/g of oil.

Chlorophyll and carotenoid compounds (mg/kg oil) were determined at 670 and 470 nm, respectively, in cyclohexane using the specific extinction values, by the method of Mínguez-Mosquera, Rejano, Gandul, Sanchez, and Garrido (1991).

Oxidative stability was evaluated at 100 °C, according to Nissiotis and Tasioula-Margari (2002). Briefly, the oil samples (50 ml) were poured into glass beakers (100 ml) and maintained at 100 °C in a conventional oven for 10 days. The samples were removed from the oven (at predetermined time intervals) to determine the PV according to EEC (1991). Three determinations indicated good repeatability of PV determinations, taking into consideration that the accuracy of the titration was 0.05 ml. The results were expressed as induction time, which was considered as the number of hours needed for the peroxide value of the sample to become 70 meq/kg oil (Cinquanta, Esti, & Di Matteo, 2001).

2.3. Statistical analyses

All chemical determinations were done in triplicate. Statistical differences were estimated by ANOVA test at the 5% level ($P = 0.05$) of significance, for all parameters evaluated. Whenever ANOVA indicated a significant difference, a pair-wise comparison of means

Table 1
Quality indices of virgin olive oils from Traslasierra Valley (Córdoba, Argentina)

Quality indices	Arbequina		Ascolana		Manzanilla		Nevadillo	
	P	C	P	C	P	C	P	C
Free fatty acid (% oleic)	0.29^{a1}	0.14^{b1}	1.03^{a4}	0.40^{b2}	0.35^{a3}	0.15^{b1}	0.32^{a2}	0.12^{b1}
Peroxide value (meq/kg)	9.71^{a1}	11.0^{a2}	10.77^{a1}	7.84^{a1}	10.0^{a1}	$9.81^{b1,2}$	9.90^{a1}	9.90^{a2}
K_{232}	1.86^{a1}	1.90^{a3}	1.82^{a1}	1.77^{a2}	1.76^{a1}	1.93^{a3}	1.71^{b1}	1.61^{a1}
K_{270}	0.10^{a1}	0.15^{b3}	0.12^{a1}	0.13^{b2}	0.07^{a1}	0.15^{b3}	0.08^{a1}	0.11^{a1}
Chlorophylls (mg/kg)	$2.77^{a1,2}$	$5.15^{b2,3}$	2.46^{a1}	5.92^{b3}	6.38^{a3}	$4.45^{a1,2}$	3.55^{a2}	3.54^{a1}
Carotenoids (mg/kg)	2.15^{a2}	2.21^{a1}	1.55^{a1}	2.10^{b1}	2.68^{a3}	2.72^{a2}	3.61^{a4}	2.29^{a1}
Total phenols (mg/kg)	373^{b2}	223^{a3}	178^{b1}	99.2^{a1}	588^{b3}	$171^{a2,3}$	188^{a1}	$144^{a1,2}$
Oxidative stability (h)	89^{a1}	80^{a1}	$80^{a1,2}$	68^{a2}	117^{a3}	90^{b3}	$80^{a1,2}$	88^{a3}

P, pressure system; C, centrifugation system (dual-phase decanter). Mean values ($n = 3$).
Values in each row with different superscript letters present significant differences ($P < 0.05$) between extraction systems for each variety.
Values in each row with different superscript numbers present significant differences ($P < 0.05$) between olive varieties for each extraction system.

by least significant difference (LSD) was carried out. Correlation analysis was performed employing Pearson's test.

3. Results and discussion

The quality indices of virgin olive oils revealed statistically significant differences among varieties and extraction systems (Table 1). The free fatty acid content of all analyzed samples was below 1 and fell within the accepted value for extra virgin olive oils (EEC, 1991). Ascolana variety had the highest acidity value in both, pressure and centrifugation systems. The acidity of oils from the pressure system was higher than that from the dual-phase decanter system. In the former, the oils are extracted with the vegetable water (aqueous phase plus solid wastes) and remain together until they are separated by decanting. This fact may favour the hydrolysis of triglycerides, resulting in an increase of free fatty acid concentration.

Peroxide values (PV) in pressure-extracted oils varied from 9.71 to 10.8 meq/kg; centrifuge-extracted oils were in the range 7.84–11.0 meq/kg. In the varieties Ascolana and Manzanilla, the highest PV were observed in oils obtained by the pressure system, whereas in the varieties Arbequina and Nevadillo there were no statistically significant differences between extraction systems. On the other hand, when the oils from all varieties were compared for each extraction system, there were no significant differences in pressure-extracted oils. However, in the oils extracted with the centrifugation system, Ascolana variety had a PV significantly lower than the other varieties.

With respect to the UV absorption characteristics, K_{232} and K_{270}, all samples analyzed had values that did not exceed the established limits (EEC, 1991). Values of K_{232} showed minor differences between varieties and extraction systems. Differences in K_{270} were more marked. Oils from the centrifugation system were higher in their K_{270} values than those from the pressure system.

The total pigment content of olive oils is an important quality parameter because it correlates with colour, which is a basic attribute for evaluating olive oil quality. Furthermore, pigments are also involved in autoxidation and photooxidation mechanisms (Mínguez-Mosquera et al., 1991). Fakourelis, Lee, and Min (1987) have demonstrated that chlorophylls act as prooxidants under light storage, whereas β-carotene minimizes lipid oxidation by its light-filtering effect. Chlorophyll pigment content varied from 2.46 mg/kg (Ascolana) to 6.38 mg/kg (Manzanilla) in the pressure-extracted oils. Oils from the centrifugation system had values between 3.54 mg/kg (Nevadillo) and 5.92 mg/kg (Ascolana). With the exception of Ascolana variety, there were no statistically significant differences between extraction systems in the concentration of carotenoid pigments.

The oils from the pressure system had higher total phenol contents than those from the centrifugation system. Similar results have been reported by Di Giovacchino et al. (1994). However, contradictory results have been reported in other studies (Salvador, Aranda, & Fregapane, 1998, 2003). The differences in phenol contents, due to the extraction systems employed, have been attributed to the many variables involved in the process of extraction, such as the olive crushing machinery, the temperatures applied and the total volume of water used (Boskow, 1996; Caponio et al., 1999; Gimeno, Castellote, Lamuela-Raventos, De la Torre, & López-Sabater, 2002). In the present work, the olive pastes were obtained under the same conditions for both, centrifugation and pressure systems, therefore the differences in phenolic compounds may be better explained by their water solubility. Phenols present in olive paste are soluble in water and oil, depending on their partition coefficients and extraction temperatures. Addition of water to the paste alters the partition equilibrium between liquid phases and causes a reduction of phenol concentration through dilution of the aqueous phase (Gimeno et al.,

Table 2
Fatty acid composition (% of total fatty acids) and iodine values of virgin olive oils from Traslasierra Valley (Córdoba, Argentina)

Fatty acids	Arbequina		Ascolana		Manzanilla		Nevadillo	
	P	C	P	C	P	C	P	C
Palmitic	17.6^{a3}	17.8^{a3}	13.0^{a1}	16.7^{b2}	15.2^{a2}	16.9^{b2}	13.6^{a1}	13.7^{a1}
Palmitoleic	2.53^{a3}	2.98^{b4}	1.37^{a1}	1.69^{b2}	1.97^{a2}	2.21^{a3}	1.51^{a1}	1.34^{a1}
Stearic	1.51^{a1}	1.39^{b1}	1.90^{a2}	1.93^{a2}	1.43^{a1}	1.43^{a1}	2.70^{a3}	2.02^{b3}
Oleic	63.0^{a1}	61.3^{b1}	71.0^{a2}	66.5^{b2}	$72.2^{a2,3}$	66.04^{b2}	73.4^{a3}	74.6^{a3}
Linoleic	14.8^{a3}	15.8^{b3}	11.2^{a2}	13.4^{a2}	8.34^{a1}	12.5^{b2}	8.76^{a1}	7.73^{a1}
Linolenic	0.66^{a2}	0.70^{b1}	0.89^{a3}	0.61^{a1}	0.85^{a3}	0.75^{b1}	0.60^{a1}	0.64^{b1}
SFA	19.1^{a3}	19.2^{a3}	14.9^{a1}	$18.7^{b2,3}$	16.6^{a2}	18.4^{b2}	16.3^{a2}	15.7^{a1}
MUFA	65.5^{b1}	64.3^{a1}	72.3^{b2}	68.2^{a2}	74.2^{b3}	68.3^{a2}	74.9^{a3}	75^{a3}
PUFA	15.4^{a3}	16.5^{b3}	12.1^{a2}	14.0^{b2}	9.19^{a1}	13.4^{b2}	9.35^{a1}	8.37^{a1}
Iodine value	87.7^{a2}	88.7^{b3}	88.0^{a2}	$87.5^{a2,3}$	84.3^{a1}	86.6^{b2}	85.0^{a1}	84.2^{a1}

P, pressure system; C, centrifugation system (dual-phase decanter).
Mean values ($n = 3$).
Values in each row with different superscript letters present significant differences ($P < 0.05$) between extraction systems for each variety.
Values in each row with different superscript numbers present significant differences ($P < .05$) between olive varieties for each extraction system.
SFA, saturated fatty acids; MUFA, monounsaturated fatty acids; PUFA, polyunsaturated fatty acids.

2002). Higher water/paste ratios are used in the centrifugation system, and therefore larger amounts of phenols are eliminated with water wastes.

Analyses of fatty acid composition are shown in Table 2. Mean values of fatty acids differed slightly, depending on the extraction system employed, although the differences were statistically significant in most cases. The differences were mainly remarkable for oleic acid, the most abundant fatty acid in olive oil, which appeared to be higher with the pressure system than with the centrifugation system. The variability of fatty acid composition covered the normal range expected for virgin olive oils (Uceda & Hermoso, 1999). The oleic acid content in Arbequina variety was at lower concentration (less than 63%); Nevadillo was the variety with the greatest value (>73%). Current biochemical evidence indicates that, in olive and other plant species, the polyunsaturated fatty acids (C18:2 and C18:3) are produced by the consecutive desaturation of oleic acid (Gutierrez, Jimenez, Ruiz, & Albi, 1999). Accordingly, Arbequina and Nevadillo varieties had the highest and the lowest linoleic acid levels, respectively.

Virgin olive oils are known to be more resistant to oxidation than other edible oils because of their contents of natural antioxidants and lower unsaturation levels; the higher the number of double bonds in fatty acids, the shorter is the induction period for oil autoxidation. The data from the oxidative stability test showed a significant positive correlation between oxidative stability and total phenol content ($r = 0.52$). Furthermore, a significant negative correlation ($r = -0.56$) was found to exist between phenol content and K_{270}, an indicator of oil autoxidation. The antioxidant potential of olive phenolic compounds has been analyzed previously (Caponio et al., 1999; Sifi, Ben Hamida, & Amamou, 2001; Uceda & Hermoso, 1999). Thus, phenolic extracts from fruits of different olive varieties were able to extend the induction period, or the time during which an oil can effectively resist oxidation. However, the significance of these findings also depends on the fatty acid composition. For example, Manzanilla was the variety with the highest phenol content and the best oxidative stability. Ascolana, a variety with similar concentration of oleic acid but minor amount of phenol compounds, had poorer oxidative stability. Finally, Arbequina, a variety with higher phenol content but lower oleic acid content, showed a resistance to oxidation which was between those of the varieties mentioned above. Although there were no significant correlations between oxidative stability and any particular fatty acid, the following significant correlations were found between K_{270} values and individual fatty acids: negative with oleic acid ($r = -0.52$) and positive with linoleic acid ($r = 0.59$). In agreement with these findings, iodine values of the oils correlated positively with K_{232} and K_{270} values.

4. Conclusions

The results of the present investigation, and other related (Torres, Orecchia, & Maestri, in press) studies, confirm the general judgement that virgin olive oils produced by the mills located in the northwest of Córdoba (Argentina) are of good quality.

Contradictory results have been found in some studies with respect to differences in virgin olive oil composition due to the extraction systems employed. Some authors have reported that the extraction method affects chemical characteristics related to oxidative stability of oils, but others have concluded that there are no such differences between olive oils obtained by pressure and centrifugation systems (Caponio et al., 1999; Gimeno et al., 2002; Salvador et al., 2003).

The chemical data, from virgin olive oils of the most important varieties cultivated at Traslasierra Valley, show that differences among cultivars were, in general, stronger than differences among extraction systems. However, the amount of total phenols was strongly affected by the extraction method. The concentration of phenolic substances usually ranges from 50 to 400 ppm, but oils can be found with concentrations of up to 600 ppm, expressed as caffeic acid. Thus, the content of total phenol compounds in pressure-extracted oils from Manzanilla variety, is among the highest found in Spanish varieties (Uceda & Hermoso, 1999). Since the extraction systems employed slightly affected the values of the main fatty acids, and the microclimate and other environmental conditions of Traslasierra Valley are sufficiently homogeneous, their influences on fatty acid composition are negligible with respect to influence of the genotype. Hence, the data set from fatty acid composition are useful for distinguishing the monovarietal olive oils belonging to particular cultivars.

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