Phenolic Compounds and Fatty Acid Content of Some Extra Virgin Olive Oils from North-West of Argentina (La Rioja)

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Summary

Extra virgin olive oil (EVOO) is one of the most important vegetable oils from an economic and nutritional point of view. The health properties and oxidative stability of this oil depend on its chemical composition. However, these attributes are affected by the type of cultivar and the climate in which the olive trees are grown. This study was carried out to determine the fatty acid composition (FA) and the amount of polyphenols (PT) including hydroxytyrosol (HT) in 4 EVOO obtained from 'Coratina', 'Arbequina', 'Barnea' and oil blend ('Barnea' and 'Arbequina') varietals grown in a semi-arid region of northwestern Argentina. The 'Coratina' variety had a high oleic acid content (72.875%), and a higher monounsaturated and polyunsaturated fatty acids (MUFA/PUFA) ratio. PT values were significantly higher for the blend (280 mg/kg) than for 'Arbequina' (268 mg kg^{-1}), 'Barnea' (248 mg kg^{-1}) and 'Coratina' (210 mg kg^{-1}). The HT content ranged from 3 mg kg^{-1} oil ('Arbequina') to 0.6 mg kg^{-1} oil (Blend). It is evident that all the oils analyzed contain nutritionally important elements which are determined by the varietal component of each one of them, and to a lesser extent by the soil and climatic conditions of the production region. These data could be useful to facilitate the selection of olive varieties planted in this semi-arid region, capable of producing EVOO with distinctive signs and better food quality.

Key words

extra virgin olive oil, fatty acid, hydroxytyrosol, La Rioja - Argentina

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Received: January 17, 2024 | Accepted: March 8, 2024 | Online first version published: May 1, 2024

Introduction

Argentina's production of olives (*Olea europaea* L) has now reached over 1 million tonnes. Of this production, approximately 60% is destined for oil production and the remaining percentage is destined for table olives. It is worth noting the contribution of La Rioja as one of the producing provinces with 25,000 hectares planted, out of a total of 81,269 in the country, positioning it as the main producer of table olives and the second largest producer of olive oil in the country. These oils are recognized for their quality and stand out for their fruity character and low acidity. Likewise, in recent years there has been an increase in the production of olives and olive oil in the Province, highlighting the 'Arbequina', 'Coratina' and 'Barnea' varieties among others (PROCAL, 2016). Therefore, this genetic variability that characterizes olive cultivation in La Rioja, associated with special means of production, can result in obtaining olive oils with a chemical composition characteristic of the variety and place of origin (Asheri et al., 2015). It is particularly seen in the content of fatty acids and polyphenols, components that are related to their sensory attributes, authenticity and health benefits (Kiritsakis, 2020), although in the bibliography there are works that address different aspects on the importance of olive cultivars on oil characteristics in the main olive growing regions of Argentina (Rondanini et al., 2011a; Ceci et al., 2017). No current studies are found that have analyzed the content of fatty acids and total phenolics in EVOO, particularly those obtained from the 'Arbequina', 'Coratina' and 'Barnea' varieties grown in the producing region of the province of La Rioja (Gilbert-López et al., 2014). It is therefore important to determine the applicability of these results by assessing the performance of these introduced cultivars in this new producing region, i.e. outside the Mediterranean region, in order to strengthen the identity of the regional product and position it in the market (Rondanini et al., 2014b; Bajoub et al., 2016). In this context, this preliminary work aimed to characterize the fatty acid profile and determine the amount of total polyphenols, including hydroxytyrosol, in 4 EVOO samples of 'Arbequina', 'Coratina', 'Barnea' and a blend of 'Barnea' and 'Arbequina' oils from the 2023 harvest in La Rioja (Argentina). This was also done to find out which cultivars would be superior under similar climatic conditions and to highlight the impact of cultivars on EVOO attributes in a hot, semi-arid region such as La Rioja.

Materials and Methods

All reagents were analytically graded and HPLC graded. Standards were purchased from Fluka (Fluka, Switzerland).

Samples

In this study, 4 samples of EVOO from different cultivars corresponding to the 2023 harvest were analyzed, from establishments located in the Capital department of the province of La Rioja, where similar processes are applied in accordance with the regulations of the International Olive Oil Council (IOC) and the Argentinean Food Code (CAA). The oil samples analyzed belong to the commercial category "extra virgin" and the varieties analyzed were: 'Coratina', 'Arbequina', 'Barnea' and Mixture ('Arbequina' and 'Barnea'). These oils were kept until analysis which was carried out in the first months after production due to their higher nutritional potential.

Determination of the Composition of Phenolic Compounds

The determination of phenolic compounds was carried out by means of specific internal procedures implemented by INTI. PE 64.0 R02 based on C.O.I/ T20/ Doc No. 29. Rev.1 (2017). High-performance ternary gradient liquid chromatograph (HPLC- PerkinElmer), equipped with C18 reverse-phase column (4.6 mm x 25 cm), type Spherisorb ODS-2 5µm, 100 A°, with spectrophotometric UV detector at 280 nm and integrator was used. Spectral recording for identification purposes was facilitated by using a photodiode detector with a spectral range from 200 nm to 400 nm. Ternary linear elution gradient: water 0.2% $H3PO4$ (V/V) (A), methanol (B), acetonitrile (C). Elution solvents should be de-gassed. The results were expressed as percentage and milligrams per kilogram.

Determination of Fatty Acid Composition

The characterisation of the fatty acid profile was determined by gas chromatography (GC PerkinElmer). This method gives general guidance for the application of capillary column gas chromatography (carrier gas, hydrogen) to determine the qualitative and quantitative composition of a mixture of fatty acid methyl esters obtained in accordance with the steps specified for this method COI/T.20/Doc. No 33/Rev.1 (2017). Fatty acids were identified individually according to retention times and in comparison with fatty acid standards and are expressed as percentage of methyl esters.

Statistical Analysis

The results obtained represent mean values of three repetitions ± SD. Data were analysed by one-way ANOVA (* $P \leq 0.05$) and mean separation was performed with Tukey's HSD test.

Results and Discussion

The fatty acid profile is one of the chemical markers used to distinguish and classify EVOO from other vegetable oils. As shown in Table 1, the cultivars studied showed some differences in oleic acid content with respect to the IOC limits for EVOO. A significant effect of variety on the fatty acid profile of samples was observed ($P < 0.05$). The oil obtained from the 'Coratina' variety presented the highest amount of oleic acid (72.8 ± 0.52%) and the lowest amount was detected in the oil obtained from 'Arbequina' and the Blend (54.27±0.35 and 53.73±0.56% respectively), these differences being significant. These results are similar to those reported in literature for 'Coratina', 'Barnea' and 'Arbequina' oils from various producing regions of Argentina, Iran and Pakistan (Rondanini, et al., 2011a; Rondanini, et al., 2014b; Asheri et al., 2015; Ceci, et al., 2017; Rizwan et al., 2019). Although the oleic acid content in both 'Arbequina' and Blend oils was lower than the IOC standards (Table 1), they are within the limits set by the Argentinean food code (CAA). However, the amounts could be adjusted to facilitate compliance with the minimum IOC requirements for extra virgin olive oil. In any case, both oils present positive characteristics for their valorisation, and also for new possible blends of oils that are declassified but still have interesting attributes. From this point of view, it is of scientific and practical interest in meeting the growing demand for sustainability and reduction of food waste.

Table 1. Fatty acid composition of extra virgin olive oils studied

Fatty Acids (%)	Samples			
	Coratina	Barnea	Arbequina	Blend
Myrístic	<0.01 ± 0.00	<0.01 ± 0.00	0.02 ± 0.00	<0.01 ± 0.00
Palmític	11.1 ± 0.16[c]	13.61 ± 0.30[b]	19.36 ± 0.29[a]	15.99 ± 0.35[a]
Palmitoleic	0.49 ± 0.02[d]	0.92 ± 0.017[c]	2.84 ± 0.06[a]	2.06 ± 0.04[b]
Heptadecanoic	0.04 ± 0.01[b]	0.04 ± 0.03[b]	0.1 ± 0.02[a]	0.08 ± 0.01[c]
Heptadecenoic	0.05 ± 0.04[b]	0.06 ± 0.01[b]	0.2 ± 0.019[a]	0.17 ± 0.03[a]
Stearic	2.45 ± 0.02[a]	2.47 ± 0.04[a]	1.61 ± 0.01[b]	2.34 ± 0.01[a]
Oleic	72.8 ± 0.52	65.84 ± 0.70	54.27 ± 0.35	53.73 ± 0.56
Ác. Linoleic	10.81 ± 0.1[c]	15.4 ± 0.22[b]	19.94 ± 0.31[a]	14.0 ± 0.39[b]
Linolénic	0.76 ± 0.04[b]	0.8 ± 0.07[a]	0.8 ± 0.05[a]	0.92 ± 0.03[a]
Arachídic	0.46 ± 0.03[a]	0.45 ± 0.05[a]	0.37 ± 0.04[b]	0.42 ± 0.02[a]
Gadoleic	0.46 ± 0.04[a]	0.24 ± 0.03[b]	0.23 ± 0.04[b]	0.24 ± 0.02[b]
Behénic	0.11 ± 0.01	0.13 ± 0.09	0.11 ± 0.06	0.10 ± 0.05
MUFA/PUFA ratio	2.90	2.04	1.30	1.62

Note: Significant differences according to Tukey's HSD test in the same column are shown by different letters ($P < 0.05$)

In general, palmitic, oleic and linoleic acids were present at high levels, suggesting a genotype effect on content between cultivars (Table 1). Linoleic acid is the predominant PUFA in EVOO and has been shown to be more susceptible to oxidation than MUFA. The lowest values of linoleic acid were found in 'Coratina' EVOO, but the differences were not significant when compared with the other samples analysed. Therefore, it is possible to suggest a similar stability of all EVOOs against oxidation. Nevertheless, the data indicated that all EVOOs investigated had lower, but within the expected range, amounts of palmitoleic, linolenic, stearic and arachidic acids. This is interesting because linolenic acid, although a bioactive compound, is a polyunsaturated acid with three double bonds that influences the instability and rancidity of the oil. With the exception of miristic and behenic acid, all fatty acid amounts varied significantly between the oil samples analysed. Consequently, the ratio between MUFA/PUFA was influenced, being lower than in oils from the Mediterranean region. In particular, 'Arbequina' had the lowest values of this parameter compared to other EVOOs analysed, suggesting a lower stability and resistance to oxidation (Table 1). In the same vein, several studies have reported significant reductions in the MUFA/PUFA ratio in varieties grown in warm regions or during growing cycles with higher average temperatures (Lémole et al., 2018). These findings are in line with previous studies suggesting that the fatty acid composition of olive oil may be due to a complex interaction between genetic and soil and climatic factors during the ripening process (El Riachy et al., 2023). One of the main phenolic alcohols in olive oil is hydroxytyrosol, also known as 3,4-dihydroxyphenyl ethanol (3,4 DHPEA). This compound is found in low concentrations in fresh oils, and concentrations generally increase during the storage period as a consequence of the hydrolysis of secoiridoids (El Riachy et al., 2023). As can be seen in table 2, total HT contents ranging from 0.6 to 3.06 mg/kg of AVOE were found, with 0.6 mg kg^{-1} belonging to the oil blend and 3 mg/kg to the 'Coratina' variety sample. Except for the oil Blend, the amounts detected in this work are within the range reported by other studies in which the HT content varied between 1 and 9.97 mg/kg in EVOO from other production areas such as Italy and Algeria (El Riachy et al., 2023), although they are below these values reported for EVOOs of the cultivar 'Coratina' or 'Barnea' from Pakistan and Brazil (Rizwan et al., 2019; Freitas-Filoda et al., 2020). This indicates that they fall short of the recommended amount of hydroxytyrosol, 5 mg of hydroxytyrosol per serving of olive oil, necessary to have an antioxidant effect in a balanced diet (Pedan et al., 2018). It is likely that the concentration of HT in EVOO varies not only according to the cultivar, but also to the management practices adopted, the level of ripening of the fruit and the geographical region. Thus, this work constitutes the first report on the HT content of EVOO from the region studied. Table 2 shows the variation in the amount of total polyphenols in the oil samples analysed. The amount of polyphenols in olive oil is not regulated; however, the determination of their amounts is important because it is related to the oxidative stability and shelf life of virgin olive oil and amounts between 50 and 1000 mg/kg have been reported (Gilbert-López et al., 2014). The PT content varied greatly between 280 (blend) and 210 mg kg^{-1} ('Coratina'). Thus, the oil obtained from the blend of the 'Barnea' and 'Arbequina' cultivar had the highest PT and was higher than the values obtained for the oils extracted from the individual varietals.

Table 2. Concentrations of phenolic compounds and hydroxytirosol in extra virgin olive oils studied

Phenolic compounds	Samples			
	Coratina	Barnea	Arbequina	Blend
TP (mg kg^{-1})	210 ± 0.81^{d}	248 ± 0.73^{c}	268 ± 0.56^{b}	280 ± 0.77^{a}
TP (%)	0.21	0.25	0.27	0.28
Hydroxytirosol (mg kg^{-1})	3.06 ± 0.091^{a}	1.8 ± 0.03^{b}	3.0 ± 0.03^{a}	0.6 ± 0.03^{c}
Hydroxytirosol (%)	0.003	0.002	0.003	0.001

Note: Significant differences to Tukey's HSD test in the same column are shown by different letters ($P < 0.05$)

The results reveal a strong influence of the variety on the PT content of the oils (Torres and Maestri, 2006). Any comparison with similar studies in the literature has been difficult because the methods of analysis, the equipment used and the type of oil analysed were different from those used in this work (Torre and Maestri, 2006; Ceci et al., 2017; Lémole et al., 2018). However, the differences observed in relation to other studies could also be attributed to the ripening rates of the olives and the soil and climatic conditions in each study (Bajoub et al., 2016).

In conclusion, in this study the four EVOO samples studied showed an interesting chemical-nutritional composition in terms of fatty acids and phenolic compounds and provided information on the quality of olive oils produced by the olive industry in the province of La Rioja (Argentina). Quantitatively, all the oils studied have different fatty acid contents meeting the standards established by the IOC and the CAA. Oleic acid is the dominant fatty acid, with all the oils studied having proportions above 53%. The highest value was recorded for 'Coratina' oil with 72.80%. The 'Arbequina' variety showed low values of oleic acid, in relation to other productive regions, probably due to a low plasticity in the adaptation to the local soil and climatic conditions. The amount of PT is different between the samples, which makes it possible to distinguish between the oils. In contrast to previous studies, 'Coratina' oil is distinguished from other varieties by the lower polyphenol content (210.0 mg kg^{-1}), but however, it contains a similar amount of HT as 'Arbequina'. In this respect, higher levels of hydroxytyrosol seem to characterise the oils of the 'Coratina' and 'Arbequina' cultivars.

Conclusion

From all the results obtained, it seems that the variety is an important factor influencing the amounts of PT and fatty acids in the different EVOO samples. However, it is not possible to rule out the edaphic factors of the region of production of the olives, which could also influence these compositions. However, samples of EVOO from different harvests are needed to ratify these results, especially in terms of improving oils for higher quality and health attributes.

Acknowledgements

This research was funded by Foundation Barceló. We would like to express our sincere gratitude to Ricardo Guzzonato for his assistance during the sampling stage. We thank INTI for their constructive comments.

CRediT Authorship Contribution Statement

Maria Rosana Ramirez and Agostina Lorena Guzzonato: Conceptualization, Methodology. **Maria Rosana Ramirez and Federico Nowakowski:** Software. **Federico Nowakowski:** Validation. **Maria Rosana Ramirez, Agostina Lorena Guzzonato and Federico Nowakowski:** Formal analysis. **Federico Nowakowski:** Investigation. **Maria Rosana Ramirez:** Resources. **Maria Rosana Ramirez and Agostina Lorena Guzzonato:** Data curation. **Maria Rosana Ramirez and Agostina Lorena Guzzonato:** Writing—Original draft preparation. **Maria Rosana Ramirez and Agostina Lorena Guzzonato:** Writing—review and editing, **Maria Rosana Ramirez:** Visualization, Supervision. Project administration. **Maria Rosana Ramirez and Agostina Lorena Guzzonato:** Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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aCS89_18