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The impact of vertical centrifugation on olive oil quality

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Abstract

Vertical centrifugation is an important step in continuous virgin olive oil production. It is used to clarify the oil, through the separation of water and suspended solids. Despite its effectiveness, the centrifuge can impair quality. In particular, it requires water to work, which reduces the concentration of minor compounds in the oil, and introduces dissolved oxygen. This paper reports the impact of the use of a vertical centrifuge on olive oil quality, with particular respect to minor compounds. Tests were carried out on two common cultivars (*Arbequina* and *Coratina*) 1 month after production and after six months of storage. The vertical centrifuge was found to impair parameters related to oxidation, such as peroxide value and K232. Particularly, the vertical centrifuge was able to increase the peroxide number of about 2 $m_{eq}O_2$/kg. In addition, it oxidizes phenols and consequently reduces the ratio of oxidized and nonoxidized forms of secoiridoids. Furthermore, it removes both hydrophobic (i.e., roughly 25 mg/kg of tocopherols was removed) and hydrophilic antioxidants (biophenolic compounds). Phenols are removed as a function of the oil/water partition coefficient. A total phenols decrease of 47 mg/kg in *Arbequina* and 117 mg/kg in *Coratina* was due to vertical centrifugation. Finally, the vertical centrifuge oxidizes the oils and led to the detection of the rancid defect after six months of storage by an olive oil sensory panel group.

Practical applications

The use of the vertical centrifuge in VOO production is a debated issue. In fact, despite some producers recently started to avoid vertical centrifugation for their top quality products. However, vertical centrifugation is a fundamental step in VOO production, and little is still known on the influence of this centrifuge on VOO quality.

KEYWORDS

biophenols, dissolved oxygen, nozzle centrifuge, secoiridoids, shelf-life

1 | INTRODUCTION

Virgin olive oils (VOOs) are obtained from the fruit of the olive tree by mechanical or other physical means under conditions that avoid altering the oil. The only allowable treatments are washing, decantation, centrifugation or filtration (Regulation EU n 1308/2013). With respect to centrifugation, two steps are involved: horizontal and vertical. These steps are consecutive: horizontal centrifugation separates the oil from most of the water and pomace, while vertical centrifugation (VC) clarifies the oil by removing part of the suspended solids and water. Due to its effectiveness VC is considered as a fundamental step in VOO production. However, it has negative effects on oil quality (EFSA, 2011; Rodis, Karathanos, & Mantzavinou, 2002).

First of all, VC requires the addition of lukewarm tap water. The distribution of phenols between the oily and the aqueous immiscible phases is a function of their partition coefficients and the processing temperature. The partition coefficient (K) is expressed by the following equation:

$$K = [\mathrm{P}]\text{oily phase}/[\mathrm{P}]\text{water phase}$$

where [P] is the concentration of phenol compounds expressed as mg/kg, while the partition coefficient K is dimensionless. The partition equilibrium is strictly valid for individual compounds only, and not for the total phenol content of oil and vegetable water. Therefore, a hydrophobic compound has a K value greater than unity, while the hydrophilic molecules have lower values (Clodoveo et al., 2015). For example, Dammak et al. (2015) calculated the K values during vertical centrifugations for oleuropein ranged from 0.003 to 0.006, while it ranged from 0.68 to 0.77 for hydroxytyrosol. Thus, the added tap water could reduce the hydrophilic phenol content.

Biophenols, which have important nutraceutical properties, are particularly affected (Aparicio & Luna, 2002). These antioxidant compounds (oils made with VC have lower induction time—Di Giovacchino, Solinas, & Miccoli, 1994), have benefits for human health that are recognized by the European Food Safety Authority (EFSA) in the form of the claim that "olive oil polyphenols contribute to the protection of blood lipids from oxidative stress" (EC, 2006; 2012). The conditions for the use of the claim are that the oil "contains at least 5 mg of hydroxytyrosol and its derivatives (e.g., oleuropein complex and tyrosol) per 20 g of olive oil. In order to bear the claim information shall be given to the consumer that the beneficial effect is obtained with a daily intake of 20 g of olive oil" (EC, 2012). Tsimidou and Boskou (2015) notice that not all of the extra virgin olive oils are expected to contain high concentrations of the desirable compounds referred by the claim. Servili (2014) calculates that the 5 mg/day of hydroxytyrosol intake could be obtained from 20 g of extra virgin olive oil with a minimum content of total phenolic compounds of 250–300 mg/kg. In a study on EVOO from the retail market, Caporaso et al. (2015) found a concentration above 250 mg/kg of phenols only on 3 on 32 samples. Thus, since technological factors affect the hydrophilic phenols content, it is important to limit the quantity of water during oil centrifugation in order to safe VOO phenolic compounds (Clodoveo, Hbaieb, Kotti, Mugnozza, & Gargouri, 2014).

Another negative effect of VC on VOO quality is the addition of dissolved oxygen (DO), which is added during production (Parenti, Spugnoli, Masella, & Calamai, 2007). DO leads to the increase in the peroxide value, the spectrophotometric constant K232, and consequently reduces oil quality and shelf-life (Masella, Parenti, Spugnoli, & Calamai, 2009).

Given these effects, attempts have been made to limit VC damage. Altieri et al. (2014) and Guerrini, Masella, Migliorini, Cherubini, and Parenti (2015) replaced VC with a sedimentation device and a filtration system on line with the horizontal centrifuge, respectively. These approaches limit any negative effects related to both the use of water and DO. On the other hand, Masella, Parenti, Spugnoli, and Calamai (2010) used an inert VC to avoid the contact between VOO and air, or immediately removed DO using nitrogen stripping (Masella, Parenti, Spugnoli, & Calamai, 2012). These approaches limit only the oxidative effects of VC.

However, VC is a fundamental step in continuous VOO production, and we argue that there still is a lack of knowledge about its effects, especially on minor compounds and during storage. It is a key issue as the phenolic compounds that are removed by the water and oxidized by the DO are widely understood to be important for VOO stability and shelf life.

The study presented here was carried out on *Arbequina* and *Coratina*. These cultivars were chosen because they are very common and have different phenolic content. Particularly, *Arbequina* is a Spanish olive varieties, known in the international olive oil market for the excellent taste and flavor. *Arbequina*'s phenolic content is usually low (about 100 mg/kg of total phenols) as reported by Criado, Morelló, Motilva, and Romero (2004). *Coratina* is an Italian olive varieties, known for the strong high concentrations of polyphenols, methyl sterols and triterpenic alcohols, and for the low amounts of major sterols and total aliphatic alcohols (Aparicio & Luna, 2002). For example, Caponio, Gomes, and Pasqualone (2001) reported a total phenols concentration higher than 300 mg/kg for *Coratina*.

2 | MATERIALS AND METHODS

Trials were carried out on the cv. *Arbequina* and *Coratina* during April 2013 in Rocha, Uruguay. VOOs were produced in a continuous mill where the olives were washed, crushed (using a disk crusher), and malaxed (in sealed horizontal malaxer). Olive paste was centrifuged in a three-phase decanter, and then, in a vertical centrifuge (UVPX 507, Alfa Laval, Italy). The oils produced with this process constituted the "Control" sample. The process represents the standard way to produce olive oil and, the Control samples were collected in 500 mL dark green bottles. The same residual VOOs were reprocessed with the same VC after one week. The VC operated at 6,500 rpm and was fed with 0.25 L tap water/kg oil. Oils obtained in this way constituted the "Separated" sample, and were collected in the same way as the Control sample. Hence, we compare VOO treated with VC once (Control) with VOO treated twice (Separated). Considering that VOO with high water content cannot be stored for long, as the hydrolytic reactions quickly lead to VOO deterioration (Fortini et al., 2016) we had the need of separate the negative effect of the high water content from the negative effect due to the centrifugation during the storage. Thus, the first vertical centrifugation removed the water in VOO under the limit suggested by the International Olive Oil Council, and the VOOs reached the correct water content. The second vertical centrifugation is suitable for the measurement of the negative effects due to the VC process during the storage.

Half of the bottles were analyzed after 1 month of storage, while the other half was once again divided and stored for 6 months in two storage chambers (one for *Coratina* oils and the other for *Arbequina*). In the first month of storage, bottles were placed into a cardboard box to protect them from light, and covered with 3 cm of polystyrene to insulate them from heat. During this month, the samples were shipped to Italy, where we did the analysis and we stored them. The one-month analysis is considered the "zero point". The following 6 months simulated conditions in a shop. Bottles were exposed for 12 hr/day to neon light (Philips, Master TL-D 90 Graphica, 35 W/390). The wooden light chambers measured 1.30 m × 1.00 m × 0.80 m and the internal walls were covered with reflective material. Bottles were placed in the chamber in random order, while two rows of filled bottles surrounded the samples to limit edge effects.

DO concentration was measured with an oxygen analyzer (InPro 6850i, Mettler Toledo, Italy). Olive oils were tested for free fatty acid content, peroxide value, K232, K270, and ΔK based on methods set out in European Commission Regulation EEC/2568/91. Total and individual biophenol content were recorded according to the method described in IOOC/T.20 Doc. N 29 (IOOC, 2009). Total tocopherols were determined according to the method given in EN ISO 9936:2006

TABLE 1 Comparison of legal parameters and antioxidant compounds for *Arbequina* and *Coratina* cultivars after 1-month of storage

	Arbequina			*Coratina*		
	C	*S*	*p*	*C*	*S*	*p*
Acidity (%)	0.39 (0.01)	0.36 (0.01)	***	0.84 (0.01)	0.78 (0.01)	***
Peroxide number ($meqO_2$/kg)	7.00 (0.79)	8.73 (0.15)	**	3.10 (0.20)	5.53 (0.06)	**
K232	1.94 (0.01)	2.14 (0.01)	**	1.53 (0.02)	1.76 (0.04)	**
K270	0.09 (0.01)	0.09 (0.00)	ns	0.11 (0.01)	0.11 (0.01)	ns
Delta *K*	0.000 (0.000)	0.000 (0.000)	ns	0.000 (0.000)	0.000 (0.000)	ns
Humidity (%)	0.16 (0.01)	0.13 (0.01)	*	0.17 (0.02)	0.14 (0.01)	**
Tocopherols (mg/kg)	222 (7)	199 (4)	*	255 (7)	240 (2)	*
Biophenols (mg/kg)	187 (4)	140 (2)	**	370 (5)	253 (12)	**
Chlorophylls (mg/kg)	8.3 (2.3)	3.0 (0.0)	*	9.0 (1.0)	6.3 (0.6)	*

S represents the separated sample, while *C* represents controls. Significance levels are indicated by an asterisk: $p < 0.05$ is marked as *$p < 0.01$ is marked as **; and $p < 0.001$ is marked as ***

(ISO 9936, 2006). Water content was established using "Karl Fisher" titration.

A panel of eight experts carried out a sensory evaluation of the samples. These experts were trained according to the International Olive Oil Council's method for the organoleptic assessment of VOO as described in EEC regulations 2568/91 and following amendments. The form used for the sensory evaluation was developed following EEC regulation 2568/91 and IOOC/T.20/Doc. No 15/Rev. 8 February 2015 (IOOC, 2015).

Statistical differences were detected using a two-way ANOVA. The factors were the storage time (one and six months) and the treatment (Control and Separated). In the following sections, a significance threshold of 0.05 was adopted.

3 | RESULTS AND DISCUSSION

3.1 | One-month analyses

Differences in VOO quality were found in both the chemical analyses and the panel test. Before the vertical centrifugation (the Control sample) VOOs had a DO content of 1.8 ± 0.3 ppm (*Arbequina*), and 0.7 ± 0.2 ppm (*Coratina*). This compares to after the vertical centrifugation (the Separated sample), where DO content was 6.7 ± 0.4 and 6.3 ± 0.4, respectively. This observation confirms that of Parenti et al. (2007) who found that VC increased DO by about 5 ppm. However, DO is quickly depleted: after one month of storage, when the bottles were opened for the initial analyses, DO concentration was under 1 mg/kg in all samples.

After the vertical centrifugation, there was a mean temperature increase from 18 to 22 °C for the *Arbequina* samples, and from 18 to 21 °C for the *Coratina* samples. These differences are higher than those reported by Altieri et al. (2014), who found an increase of about 1 °C.

Table 1 shows the effect of VC on quality indices. For both cultivars, acidity is lower in the Separated than the Control samples. However, the differences are small: 0.03% for *Arbequina* and 0.06% for *Coratina*. The second VC reduced water content by 0.03% for both cultivars and all samples were below the 0.20% water content threshold suggested by the International Olive Oil Council (IOOC, 2009b).

Peroxide value increased ($p < 0.01$) by 1.73 $m_{eq}O_2$/kg for the *Arbequina* sample, and 2.63 $m_{eq}O_2$/kg for the *Coratina* sample, confirming that contact between atmospheric oxygen and VOO during VC is an important source of oxidation. Similarly, K232 values in the Separated samples were higher than the Control samples in both cultivars ($p < 0.01$—Table 1). This parameter is related to the formation of conjugated dienes, the final products of lipid oxidation (Kanner & Rosenthal, 1992). Hence, changes in this parameter show that VC facilitates the formation of these compounds and promotes oxidation. No significant differences were found for K270 and ΔK.

Lower concentrations of antioxidants and pigments (tocopherols, biophenols, and chlorophylls) were found in the *S* sample for both cultivars. Tocopherols fell ($p < 0.05$) by ~10% for Arbequina and ~6% for Coratina between the C and S samples. These molecules are nonpolar (α-tocopherols octanol–water partition coefficient, $\log_{Kow} = 12$) and they have very low solubility in water. Thus, as well as the increase in the peroxide number and in K232 value, the decrease of tocopherols in the VOO could be almost completely ascribed to the oxygen introduced by VC, which leads to a depletion of antioxidant compounds. More importantly, this is the first observation of tocopherol losses due to VC. Consistent with Altieri et al. (2014), but in contrast to Masella et al. (2009) and (2012), chlorophyll content was higher ($p < 0.05$) in the C sample for both cultivars, suggesting that the loss was due to VC. Biophenol content was significantly lower ($p < 0.01$) in Separated oils, consistent with Di Giovacchino et al. (1994).

Table 2 shows that in the Coratina sample, 12 (32% of the total) phenolic compounds were found at lower concentrations in the Separated samples. This compares to the Arbequina sample where 17 (25% of the total) compounds were found to be at a lower concentration. Higher biophenol losses from fewer compounds in Coratina can be explained by its higher concentrations of tyrosol and hydroxytyrosol (56 and 43 mg/kg). These high levels mean that hydrolytic reactions occur in Coratina oils (Brenes, García, García, & Garrido, 2001). After the vertical centrifugation the concentrations of the two compounds are 15 and 18 mg/kg, respectively. This significant decrease ($p < 0.001$)

TABLE 2 Biophenol concentrations in *Arbequina* and *Coratina* after 1-month of storage

	Arbequina			*Coratina*		
	C	*S*	*p*	*C*	*S*	*p*
Hydroxytyrosol	6.58 (0.15)	1.35 (0.05)	***	55.80 (0.77)	15.24 (1.78)	***
Tyrosol	6.17 (0.07)	2.62 (0.15)	***	43.36 (0.45)	18.26 (1.84)	***
Vanillic acid + caffeic acid	2.59 (0.04)	1.15 (0.02)	***	3.46 (0.05)	1.68 (0.29)	***
Vanillin	2.71 (0.04)	2.17 (0.16)	**	1.19 (0.08)	1.09 (0.12)	ns
Para-Coumaric acid	2.48 (0.17)	2.31 (0.11)	ns	2.36 (0.19)	2.45 (0.12)	ns
Hydroxytyrosyl acetate	5.41 (0.04)	2.77 (0.03)	***	7.06 (0.16)	3.93 (0.40)	***
Ferulic acid	7.08 (0.09)	5.10 (0.06)	***	0.42 (0.35)	0.52 (0.05)	ns
Ortho-Coumaric acid	0.10 (0.02)	0.08 (0.02)	ns	0.07 (0.01)	0.08 (0.01)	ns
Decarboxymethyl oleuropein aglycone, oxidized dialdehyde form	4.10 (0.07)	3.20 (0.17)	***	10.59 (1.00)	8.32 (1.54)	*
Decarboxymethyl oleuropein aglycone, dialdehyde form	26.87 (0.51)	18.31 (0.36)	***	34.77 (0.72)	22.61 (1.42)	***
Oleuropein	1.96 (0.13)	1.57 (0.13)	**	3.72 (0.59)	3.72 (0.56)	ns
Oleuropein aglycone, dialdehyde form	3.49 (1.66)	1.36 (0.22)	*	2.57 (0.30)	3.65 (0.47)	**
Decarboxymethyl ligstroside aglycone, oxidized dialdehyde form	16.96 (0.31)	14.78 (0.28)	***	18.95 (1.70)	17.35 (0.41)	ns
Decarboxymethyl ligstroside aglycone, dialdehyde form	16.70 (0.17)	13.88 (0.11)	***	53.85 (0.92)	43.98 (1.45)	***
Pinoresinol, 1 acetoxy-pinoresinol	43.44 (0.43)	35.33 (0.31)	***	48.61 (0.66)	41.94 (1.77)	**
Cinnamic acid	0.27 (0.05)	0.29 (0.10)	ns	5.19 (0.82)	5.32 (0.24)	ns
Ligstroside aglycone, dialdehyde form	1.95 (0.12)	1.78 (0.27)	ns	1.99 (2.28)	0.57 (0.10)	ns
Oleuropein aglycone, oxidized aldehyde, and hydroxylic form	18.21 (0.57)	15.57 (0.24)	***	20.97 (2.01)	17.94 (1.07)	*
Luteolin	3.16 (0.19)	3.10 (0.18)	ns	1.82 (0.74)	2.12 (0.44)	ns
Oleuropein aglycone, aldehyde, and hydroxylic form	6.36 (0.45)	4.10 (0.26)	***	24.97 (3.65)	13.90 (0.80)	**
Ligstroside aglycone, oxidized aldehyde, and hydroxylic form	3.89 (0.30)	2.84 (0.02)	**	12.38 (0.76)	9.62 (1.77)	*
Apigenin	0.74 (0.13)	0.45 (0.06)	*	5.84 (0.43)	2.90 (2.32)	*
Methyl-luteolin	1.23 (0.16)	0.94 (0.24)	ns	3.77 (0.85)	6.89 (2.87)	ns
Ligstroside aglycone, aldehyde, and hydroxylic form	4.62 (0.07)	4.80 (0.11)	*	9.47 (0.48)	9.23 (1.24)	ns

S represents the separated sample, while *C* represents controls. Significance levels are indicated by an asterisk: $p < 0.05$ is marked as *; $p < 0.01$ is marked as **; and $p < 0.001$ is marked as ***.

is consistent with the oil/water partition ratios of these compounds, since they are more soluble in the water than in the oily phase (Rodis et al., 2002). A similar reduction in tyrosol and hydroxytyrosol was found in the Arbequina sample. Other reductions in biophenolics are shown in Table 2. These losses are also related to the water/oil partition ratio (Rodis et al., 2002) and highlight the washout effect of VC.

On the other hand, the oxidative effect of VC is highlighted by the ratio between the oxidized and nonoxidized forms of secoiridoids (Lerma-García et al., 2009; Rovellini & Cortesi, 2002). Higher ratios mean a more oxidized fraction, while a lower ratio indicates the opposite. In the olive oil phenols profile of the IOOC method (IOOC, 2009a), there are four couple of oxidized/nonoxidized phenols, namely: (i) decarboxymethyl oleuropein aglycone, dialdheide form; (ii) decarboxymethyl ligstroside aglycone, dialdehyde form; (iii) oleuropein aglycone, aldehyde, and hydroxylic form; (iv) ligstroside aglycone, aldehyde, and hydroxylic form. In Arbequina, the two oleuropein aglicones show higher ratios for the S thesis (Figure 1), while in Coratina the higher ratio was for the decarboxymethyl ligstroside aglycone, dialdheide form. Hence, after one month from the production the Separated thesis results more oxidized than the Control thesis.

VC has an effect on VOO taste. For the Control samples the fruity score was 3.6 (Arbequina) and 3.5 (Coratina), while in the Separated samples these scores decreased respectively to 2.7 and to 3.1. Here again, Coratina seems to be more resistant to VC. Furthermore, bitterness is strongly affected by VC. The Arbequina score decreased (from 0.8 to 0.4), as did the Coratina score (from 3.0 to 1.6). Bitterness is related to phenolic composition (Visioli, Poli, & Gall, 2002), thus its reduction is more perceptible in Coratina where phenol losses are higher. On the other hand, pungency only decreased in the Arbequina sample (from 2.3 to 1.2), while there was no change for Coratina.

Coratina oils show muddy defect, which was perceived more clearly in the Control sample (2.8) than the Separated (1.6). Muddy is a characteristic flavor of oil that has been left in contact with sediment and water (Procida, Giomo, Cichelli, & Conte, 2005). Thus, it could be argued that the removal of suspended solids and water reduced its appearance during storage.

3.2 | Six-month analyses

The results of the six-month analyses are shown in Table 3. Higher hydroperoxide content ($p < 0.05$) in the Separated sample was found

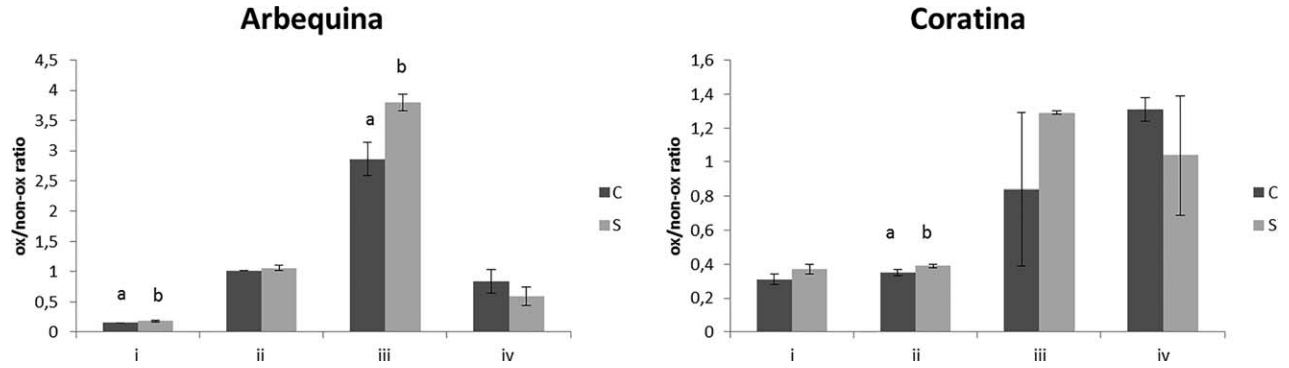

FIGURE 1 Ratio between the oxidized and the nonoxidized form after 1 month of storage of the following biophenols: (i) decarboxymethyl oleuropein aglycone, dialdehyde form; (ii) decarboxymethyl ligstroside aglycone, dialdehyde form; (iii) oleuropein aglycone, aldehyde, and hydroxylic form; (iv) ligstroside aglycone, aldehyde, and hydroxylic form. In the figure, the different letters (a, b) indicates a difference at a *t* test ($p < 0.05$). The error bars represent the standard deviation

for both cultivars. After 6 months from the treatment the differences became 3.64 $m_{eq}O_2$/kg for *Arbequina* and 2.63 $m_{eq}O_2$/kg for *Coratina*, where the Control VOOs show the lower values. Furthermore, in *Arbequina*, a significant interaction between the processing and the storage time have been found. Moreover, the Control samples peroxide number remain stable while the Separated samples peroxide number increase during the storage. The same difference between Separated and Control VOOs was found for K232. Separated oils show higher values ($p < 0.05$ in *Arbequina* and $p < 0.001$ in *Coratina*) of conjugated dienes as result of lipid autoxidation. These two parameters demonstrate the oxidation related to VC use.

Differences in tocopherols, biophenols, and chlorophylls were also found (Table 3). For both cultivars, tocopherol loss was the main observation (an average loss of 9.5 mg/kg). This was due to the storage conditions, which facilitated photooxidation. In olive oil, the α-tocopherol molecule can neutralize the effect of singlet oxygen produced by the action of light (Pirisi et al., 1998). Chlorophylls decreased in both Control and Separated. Higher concentrations were found in Control ($p < 0.05$ in *Arbequina* and $p < 0.001$ in *Coratina*), due to the washout effect highlighted in the first analysis. Total biophenols were stable between the 1- and 6-month analyses. This behavior has been previously described in photo-oxidation studies (Psomiadou & Tsimidou, 2002). Hence, total biophenols still remains higher in Control than Separated ($p < 0.01$ in *Arbequina* and $p < 0.001$ in *Coratina*).

Phenolic compound concentrations are shown in Table 4. Fourteen of the *Arbequina* phenolic compounds were significantly lower ($p < 0.05$) in the Separated than the Control oils. These include phenolic acids, phenolic alcohols, secoiridoid derivatives and lignans and confirm the findings of the first analyses. On the other hand, luteoline levels in Separated oils are higher than in Control oils ($p < 0.05$). Nine *Coratina* phenolic compounds (belonging to the same chemical classes as above) are lower in the Separated samples. Like previous observations, levels of both flavonoids (luteoline and apigenine) and oleuropein were significant lower in the Control sample. Interactions between storage time and VC treatment were not found for *Arbequina*, while for *Coratina* oleuropein, decarboxymethyl oleuropein aglycone, oxidized dialdheide form, and ligstroside aglycone, aldehyde, and hydroxylic form significant interactions were found. In general, we can state that Control VOOs show, after 6 months of storage, higher amounts of biophenols than Control VOOs.

TABLE 3 Comparison of legal parameters and antioxidant compounds for *Arbequina* and *Coratina* cultivars after 6 months in storage

	Arbequina			*Coratina*		
	C	*S*	*p*	*C*	*S*	*p*
Acidity (%)	0.39 (0.02)	0.42 (0.01)	ns	0.92 (0.03)	0.87 (0.01)	ns
Peroxide number ($meqO_2$/kg)	6.66 (0.85)	10.30 (0.75)	*	3.90 (0.44)	6.53 (0.31)	*
K232	1.94 (0.04)	2.17 (0.08)	*	1.54 (0.01)	1.78 (0.01)	***
K270	0.12 (0.01)	0.13 (0.00)	ns	0.13 (0.00)	0.14 (0.01)	ns
Delta *K*	0.002 (0.000)	0.002 (0.000)	ns	0.001 (0.001)	0.002 (0.000)	ns
Humidity (%)	0.16 (0.01)	0.13 (0.01)	*	0.17 (0.02)	0.14 (0.01)	**
Tocopherols (mg/kg)	162 (1)	158 (2)	*	211 (3)	187 (2)	**
Biophenols (mg/kg)	181 (3)	143 (4)	**	355 (2)	253 (4)	***
Chlorophylls (mg/kg)	3.3 (0.6)	2.0 (0.0)	*	6.1 (0.0)	4.3 (0.0)	***

S represents the separated sample, while *C* represents controls. Significance levels are indicated by an asterisk: $p < 0.05$ is marked as *$p < 0.01$ is marked as **; and $p < 0.001$ is marked as ***.

TABLE 4 Biophenol concentrations in *Arbequina* and *Coratina* after 6 months in storage

	Arbequina			*Coratina*		
	C	*S*	*P*	*C*	*S*	*p*
Hydroxytyrosol	7.36 (0.71)	1.80 (0.19)	***	57.97 (1.81)	18.22 (1.78)	***
Tyrosol	6.11 (0.21)	2.69 (0.14)	***	45.33 (1.02)	20.81 (1.84)	***
Vanillic acid + caffeic acid	2.52 (0.11)	0.95 (0.13)	***	3.43 (0.03)	1.77 (0.29)	***
Vanillin	2.47 (0.07)	1.86 (0.05)	***	1.09 (0.08)	1.07 (0.12)	ns
Para-Coumaric acid	7.00 (0.31)	5.38 (0.25)	***	0.16 (0.02)	0.18 (0.12)	ns
Hydroxytyrosyl acetate	0.77 (0.03)	0.91 (0.08)	*	0.73 (0.05)	0.50 (0.40)	**
Ferulic acid	0.82 (0.05)	0.16 (0.02)	***	0.28 (0.14)	0.26 (0.05)	ns
Ortho-coumaric acid	0.28 (0.34)	0.06 (0.02)	ns	0.21 (0.21)	0.12 (0.01)	ns
Decarboxymethyl oleuropein aglycone, oxidized dialdehyde form	3.80 (0.49)	2.71 (0.20)	*	7.47 (0.69)	7.34 (1.54)	ns
Decarboxymethyl oleuropein aglycone, dialdehyde form	23.25 (0.65)	15.27 (0.80)	***	32.14 (0.75)	21.34 (1.42)	***
Oleuropein	0.59 (0.18)	0.51 (0.04)	ns	3.11 (0.20)	4.25 (0.56)	**
Oleuropein aglycone, dialdehyde form	1.25 (0.23)	1.05 (0.02)	ns	2.56 (0.11)	2.98 (0.47)	**
Decarboxymethyl ligstroside aglycone, oxidized dialdehyde form	18.65 (0.74)	19.54 (1.04)	ns	18.03 (1.06)	18.60 (0.41)	ns
Decarboxymethyl ligstroside aglycone, dialdehyde form	15.89 (0.74)	12.42 (0.53)	***	55.08 (0.15)	44.25 (1.45)	***
Pinoresinol, 1 acetoxy-pinoresinol	45.03 (0.82)	37.27 (0.93)	***	49.79 (0.27)	44.95 (1.77)	**
Cinnamic acid	0.96 (0.09)	0.53 (0.34)	ns	4.26 (0.65)	3.82 (0.24)	ns
Ligstroside aglycone, dialdehyde form	1.41 (0.10)	1.23 (0.14)	ns	0.86 (0.19)	0.86 (0.10)	ns
Oleuropein aglycone, oxidized aldehyde, and hydroxylic form	19.50 (0.29)	17.55 (0.59)	**	18.83 (0.86)	17.76 (1.07)	ns
Luteolin	1.15 (0.14)	1.40 (0.06)	*	1.36 (0.36)	2.00 (0.44)	*
Oleuropein aglycone, aldehyde, and hydroxylic form	5.44 (0.30)	3.92 (0.34)	***	23.80 (1.06)	15.31 (0.80)	***
Ligstroside aglycone, oxidized aldehyde, and hydroxylic form	8.14 (0.15)	7.85 (0.12)	*	8.65 (1.10)	9.04 (1.77)	ns
Apigenin	0.90 (0.09)	1.08 (0.29)	ns	1.07 (0.31)	1.60 (2.32)	*
Methyl-luteolin	3.55 (0.35)	3.96 (0.06)	ns	3.75 (1.04)	3.85 (2.87)	ns
Ligstroside aglycone, aldehyde, and hydroxylic form	3.47 (0.40)	2.47 (0.18)	**	14.94 (1.29)	12.08 (1.24)	**

S represents the separated sample, while *C* represents controls. Significance levels are indicated by an asterisk: $p < 0.05$ is marked as *; $p < 0.01$ is marked as **; and $p < 0.001$ is marked as ***.

The ratio of oxidized and nonoxidized secoiridoids was higher in Separated for both cultivars. In *Arbequina* 2 out of the 4 ratios resulted higher in the Separated oils, while the other 2 show no significant differences. In *Coratina*, all the ratios was higher for the Separated VOOs than the Control VOOs (Figure 2). One month after production only 1 biophenol results oxidized by the VC in *Coratina*, while during the storage, the oxidative effect of VC results in a more oxidized secoiridoid fraction. In the oils that were analyzed after the 1-month storage period, the vertical centrifugation effect on the phenolic fraction was due to the washout effect of water and DO oxidation. As no water

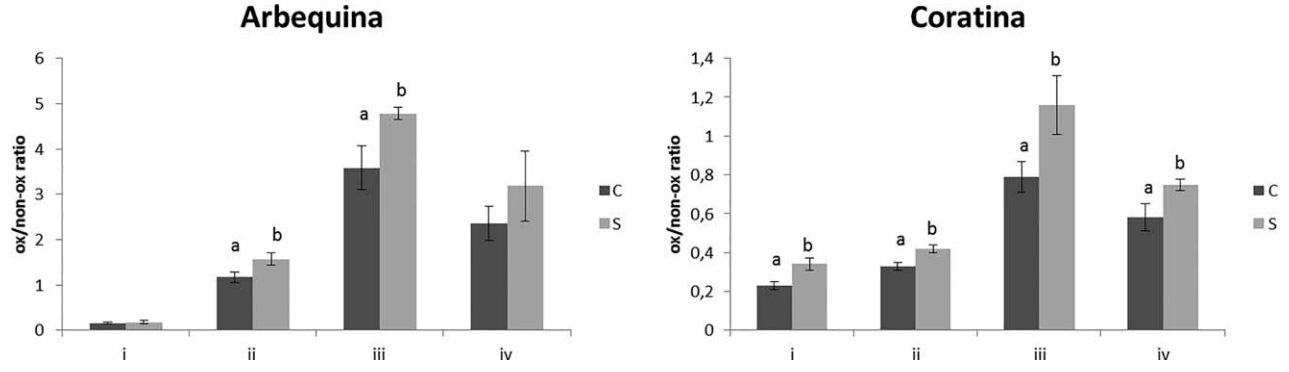

FIGURE 2 Ratio between the oxidized and the nonoxidized form after 6 months of storage of the following biophenols: (i) decarboxymethyl oleuropein aglycone, dialdehyde form; (ii) decarboxymethyl ligstroside aglycone, dialdehyde form; (iii) oleuropein aglycone, aldehyde, and hydroxylic form; (iv) ligstroside aglycone, aldehyde, and hydroxylic form. In the figure the different letters (a, b) indicates a difference at a *t* test ($p < 0.05$). The error bars represent the standard deviation

was added during the 6-month storage period, the differences between samples could be ascribed to oxygen introduced by the vertical centrifugation.

All the samples fall in the commercial category of "virgin olive oil". For both cultivars, confirmation of the poorer oxidative state of the Separated oils was found in as rancid defect at the panel test. The score for *Coratina* was 0.45 for S, while it was not detected in the Control sample. Further, in both tastings the muddy defect was detected. Both *Arbequina* samples were found to be rancid, with the higher score for Separated samples (1.5 for Control and 2.5 for Separated). As for positive attributes, the *Arbequina* Control sample was fruitier (3.5) than the Separated (2.5) sample. For *Coratina*, rancid and muddy defects meant that the panel was unable to assess other parameters.

4 | CONCLUSIONS

It is known that VC has an effect on compounds related to VOO quality. In particular, it increases peroxide values of roughly 2 $m_{eq}O_2$/kg, and K232. Furthermore, it decreases antioxidant compounds such as tocopherols (about 25 mg/kg in our tests) and biophenols. The biophenols reduction in *Arbequina* was on average 47 mg/kg, while in *Coratina* 117 mg/kg. This decrease can be ascribed to two effects: washout and oxidation. Washout is related to the use of water, which decreases the concentration of biophenols as a function of their oil and water partition coefficient. Oxidation is due to oil/air contact, a phenomenon that is related to VC and leads to the oxidation of the VOO minor compounds and to the VOO rancidity.

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