‘Fortified’ wines volatile composition: Effect of different postharvest dehydration conditions of wine grapes cv. Malvasia moscata (Vitis vinifera L.)

‘Fortified’ wines volatile composition: effect of different postharvest dehydration conditions of winegrapes cv. Malvasia moscata (*Vitis vinifera* L.)

Delia Elena Urcan[1,2], Simone Giacosa[2], Fabrizio Torchio[3], Susana Río Segade[2], Stefano Raimondi[4], Marta Bertolino[2], Vincenzo Gerbi[2], Nastasia Pop[1], Luca Rolle[2,4]*

[1] University of Agricultural Sciences and Veterinary Medicine, Calea Mănăştur 3-5, 400372 Cluj-Napoca, Romania.

[2] Università degli Studi di Torino, Dipartimento di Scienze Agrarie, Forestali e Alimentari, Largo Paolo Braccini 2, 10095 Grugliasco, TO, Italy.

[3] Università Cattolica del Sacro Cuore, Istituto di Enologia e Ingegneria Agro-Alimentare, Via Emilia Parmense 84, 29122 Piacenza, Italy.

[4] Consiglio Nazionale delle Ricerche, Istituto per la Protezione Sostenibile delle Piante, Unità Grugliasco, Largo Paolo Braccini 2, 10095 Grugliasco, TO, Italy.

*Corresponding author: luca.rolle@unito.it, Tel.: +39 011 6708558; Fax: +39 011 6708549

ABSTRACT

The impact of postharvest dehydration on the volatile composition of Malvasia moscata grapes and fortified wines produced from them was assessed. The ripeness effect of fresh grapes on volatile compounds of dehydrated grapes was evaluated for the first time in this study. Fresh grape berries were densimetrically sorted, and more represented density classes were selected. Dehydration of riper berries (20.5 ºBrix) led to volatile profiles richer in terpenes, particularly linalool and geraniol. The effect of dehydration rate on the volatile composition of dehydrated grapes and fortified wines was also evaluated. Fast dehydration grapes were richer in total free terpenes, and the resulting wines contained greater amounts of volatile compounds. The predominant compounds were free esters, but linalool, rose oxide, citronellol and geraniol can also contribute to wine aroma, particularly for fast dehydration. β-damascenone can be an active odorant, although its contribution was greater in wines made from slow dehydrated grapes.

Keywords: fortified wines, volatile compounds, berry density, postharvest dehydration, wine grapes, terpenes.

1. Introduction

In the last years, the growing market demand of diversifying enological products has promoted the use of partially dehydrated grapes for the production of fortified and reinforced wines. Fortified wines are sweet wines produced from fresh or dehydrated grapes by adding alcohol or spirits, whereas reinforced wines are dry wines made with partially dehydrated grapes (weight loss less than 25% of initial fresh weight; Mencarelli & Tonutti, 2013). Famous wines for their particular and differentiated aroma are produced in many viticultural areas of the world from postharvest dehydrated grapes.

Postharvest dehydration is a dynamic process of water loss from the berries occurring under more or less controlled environmental conditions. Off-vine grape dehydration can be performed by direct exposure of grapes to sun in regions with favorable climatic conditions (Ruiz, Zea, Moyano, & Medina, 2010), and indoors in naturally ventilated rooms (Rolle, Giordano et al., 2012) or in chambers with thermohygrometric control (Bellincontro, De Santis, Botondi, Villa, & Mencarelli, 2004; Chkaiban, Botondi, Bellincontro, De Santis, Kefalas, & Mencarelli, 2007; Torchio et al., 2016). This process induces changes in the chemical composition and in the physical properties of grape berries. In addition to increased sugar content, postharvest dehydration plays an important role in the concentration, synthesis and oxidation of volatile and phenolic compounds (Bellincontro et al., 2004; Costantini, Bellincontro, De Santis, Botondi, & Mencarelli, 2006; Mencarelli, Bellincontro, Nicoletti, Cirilli, Muleo, & Corradini, 2010; Noguerol-Pato, González-Álvarez, González-Barreiro, Cancho-Grande, & Simal-Gándara, 2013). Moreover, changes are produced in the composition and structure of fruit surface tissues, which affect the color and texture of the berry skin (Rolle, Giordano et al., 2012; Rolle, Giacosa, Río Segade, Ferrarini, Torchio, & Gerbi, 2013).

During grape dehydration, water stress can alter the cellular structure of the berry, and therefore affects cell metabolism (Ramos, Silva, Sereno, & Aguilera, 2004). Generally, a first

metabolic stress response occurs involving changes in membrane permeability by activation of lipoxygenase (LOX), followed by a drastic change in basal cell metabolism from aerobic to anaerobic related to alcohol dehydrogenase (ADH) activity (Costantini et al., 2006). The increased activity of LOX and ADH during the dehydration process promotes the formation of different volatile compounds (Chkaiban et al., 2007; Costantini et al., 2006). Dehydration time is an important commercial parameter, but weight loss by water evaporation and dehydration rate are key factors in the changes occurred in the metabolism of wine grapes (Cirilli et al., 2012). The metabolic response to water stress is faster in grapes dehydrated under uncontrolled environmental conditions, whereas the accurate control of thermohygrometric conditions permits to delay water stress even at higher weight loss (Chkaiban et al., 2007). Dehydration temperature affects the critical weight loss. The higher the temperature, the faster the water stress (Nicoletti et al., 2013). Nevertheless, the critical water loss for grape metabolism depends on the variety (Chkaiban et al., 2007; Costantini et al., 2006). Therefore, a careful control of the environmental conditions is of great importance for the evolution of volatile compounds during the grape dehydration process.

The volatile composition of grapes contributes greatly to the varietal aroma and quality of wines. In white aromatic cultivars, such as Muscat, Riesling and Gewürztraminer, monoterpenes are the main compounds responsible for the typical floral aroma (Strauss, Wilson, Gooley, & Williams, 1986). Few studies have evaluated the changes in volatile compounds of grapes throughout the dehydration process and of the resulting wines. In both aromatic and non-aromatic wine grape cultivars, alcohols, esters and terpenes with positive odor descriptors are synthesized during the postharvest dehydration process (Serratosa, Marquez, Moyano, Zea, & Merida, 2014). Therefore, the wines made from postharvest dehydrated grapes are richer in terpenes than those made from the fresh fruit (Moreno, Cerpa-Calderón, Cohen, Fang, Qian, & Kennedy, 2008). C6 volatile compounds providing herbaceous notes are also formed (Costantini et al., 2006). Although postharvest dehydration influences the volatile composition of grapes, the

significance of the changes depends on weight loss (Moreno et al., 2008; Santonico, Bellincontro, De Santis, Di Natale, & Mencarelli, 2010), dehydration rate (Bellincontro et al., 2004) and also temperature (Santonico et al., 2010). Most of these studies were performed on non-aromatic wine grapes.

Vitis vinifera L. cv. Malvasia moscata is an aromatic white wine grape variety. In Italy, Malvasia grapes are used for the production of fortified wines, but no work has been published to date on the aromatic potential of Malvasia moscata grapes to produce this type of wines. Malvasia moscata is a local cultivar probably originated in Piedmont (North-west Italy). Several vines of this cultivar were identified and recovered in different (often distant) areas of this region, namely in the surroundings of Alessandria, Asti, Chieri, Pinerolo and even in the northern part of the region. This widespread presence indicates a relevance of its culture in the past. While declining in Piedmont, this variety (likely introduced by immigrants from Piedmont) moderately developed in California, where accounts today more than 500 ha under the name of Malvasia bianca (Robinson, Harding, & Vouillamoz, 2012). The evaluation of the ampelographic features and of the agronomic and productive behavior, carried out in the Piedmontese grape collection of Grinzane Cavour (Cuneo), led to the enrolling of Malvasia moscata in the Italian National Register of grape varieties (in 2012). An ampelographic and agronomic presentation of this grape variety is available at http://www.vitisdb.it/varieties/show/1013 (Raimondi, Ruffa, & Schneider, 2014).

The increasing interest of grape producers and winemakers in improving the aromatic quality of fortified wines requires further effort in understanding the effect of the dehydration process on the aromatic composition of Malvasia moscata wine grapes and the resulting wines. Therefore, the main purpose of this work was to investigate the influence of maturity on free and glycosylated volatile compounds of fresh and partially dehydrated grapes. To our knowledge, this is the first time that the effect of maturity on the aroma profile of dehydrated grapes was studied. Furthermore, in a second year, the impact of dehydration conditions (fast and slow

processes) was evaluated on the volatile composition of dehydrated grapes and the fortified wines made from them.

2. Material and methods

2.1. Grape samples and dehydration

White grapes of the Malvasia moscata (*Vitis vinifera* L.) cultivar were picked in a commercial vineyard located in Lu–Monferrato (Province of Alessandria, Piedmont, North-West Italy). In 2013, the sample was collected from different vines when a total soluble solids content (SSC) of about 18 °Brix was reached. A set of healthy whole clusters was selected and used for subsequent analysis and dehydration (unsorted berries). In another set of healthy clusters, all the berries were manually separated from the stalk maintaining attached short pedicels. All single berries were sorted according to their density by flotation in saline solutions of eight different concentrations (from 90 to 160 g/L NaCl, corresponding to densities comprised between 1057 and 1107 kg/m^3) (Rolle, Torchio, Giacosa, Río Segade, Cagnasso, & Gerbi, 2012). After washing with water, the berries belonging to the three more represented classes were selected (1075, 1081 and 1088 kg/m^3). In order to assess the effect of ripeness on the chemical and volatile composition of partially dehydrated grapes, the berries belonging to the three density classes selected (3 kg of grape berries for each class) were separately placed in a single layer in perforated boxes and then dehydrated at 25 ºC and 45% relative humidity (RH) for 10 days.

In 2014, two batches of whole clusters (about 300 kg of grape berries), picked from the same vineyard of the 2013 with a SSC of 19.1 °Brix, were placed in perforated boxes (60 cm × 40 cm × 15 cm, 5 kg of grape berries per box) in a single layer for correct aeration. Each batch was subjected to different environmental conditions of dehydration in a thermohygrometrically controlled chamber. The first batch was treated at 28 ºC and 40% RH (fast withering, 8 days), and the second batch was subjected to 18 ºC and 40% RH (slow withering, 29 days). For all

trials, air speed was always 0.9 m/s. These conditions were previously used for slow and fast dehydration of several wine grape varieties (Torchio et al., 2016).

All fresh clusters and densimetrically sorted berries were weighed before their introduction into the dehydration chamber (fresh samples). The achieved final weight loss (WL) was about 20%, which is usually used to produce fortified wines.

For each trial, three samples of 200 berries were used for the determination of free and glycosylated volatile compounds in fresh and dehydrated grapes. Other three samples of 100 berries were used for the determination of the technological ripeness parameters in the grape juice resulting from their manual crushing and centrifugation.

2.2. Winemaking

The wines were made in the experimental cellar of the University of Turin from grapes partially dehydrated by the fast and slow processes. For each dehydration process, the clusters were subdivided in three replicates, and they were separately destemmed and crushed. Cold soak was carried out for one day at 4±1 °C in presence of 20 mg/L sulphur dioxide added. Then, for each replicate, the grape pomace was pressed using a small pneumatic press (PMA 4, Velo SpA, Italy) operating at a maximum pressure of 1.20 bar, and free-run juice and press juice were mixed. The grape juice was clarified by spontaneous settling at 14±1 ºC for 18 h. The juice was racked and inoculated with *Saccharomyces cerevisiae* (Fermol CH, AEB Group, Brescia, Italy) commercial yeast (20 g/hL). The alcoholic fermentation was performed in a 100 L stainless steel tank at 20±1 °C and stopped when the residual sugar content was about 120 g/L by the addition of 100 mg/L sulfur dioxide and 95% food-grade ethanol up to a total alcohol content of 15% v/v. The wines obtained were stored at 0 ºC for 2 weeks (cold stabilization), filtered (Seitz KS grade filter sheet, Pall Corporation, Washington, NY, USA), supplied again with free sulphur dioxide up to 50 mg/L and then bottled.

2.3. Chemical analysis

2.3.1. Reagents and standards

All chemicals of analytical-reagent grade and standards of volatile compounds were purchased from Sigma (Milan, Italy). Standard solutions of volatile compounds were prepared in 10% v/v ethanol. Deionized water was produced by a Milli-Q system (Merck Millipore, Darmstadt, DE).

2.3.2. Standard chemical parameters

In the grape juice obtained, total soluble solids content (ºBrix, as SSC) was measured using an Atago 0–32 ºBrix temperature compensating refractometer (Atago Corporation, Tokyo, Japan). In the grape juice and in the resulting wine, pH was determined by potentiometry using an InoLab 730 pH meter (WTW, Weilheim, Germany), and titratable acidity (g/L tartaric acid) was estimated according to the International Organization of Vine and Wine methods (OIV, 2008). Reducing sugars (glucose and fructose) (g/L), organic acids (citric acid, tartaric acid, malic acid, acetic acid and lactic acid) (g/L), glycerol (g/L) and ethanol (% v/v) were determined using a high performance liquid chromatography (HPLC) system (Agilent Technologies, Santa Clara, CA, USA) equipped with a refractive index detector and a diode array detector (DAD) set to 210 nm (Giordano, Rolle, Zeppa, & Gerbi, 2009).

2.3.3. Free and glycosylated volatile compounds

Free and glycosylated volatile compounds were determined by head space solid phase microextraction (HS-SPME) coupled with gas chromatography-mass spectrometry (GC-MS). The grape berries were treated according to the method used by Rolle, Torchio, Giacosa, & Río Segade (2015). They were crushed under a nitrogen atmosphere with a laboratory blender (Waring Laboratory, Torrington, USA) for 1 min. After centrifugation (7000 x g, 15 min, 4 °C), a 5-mL aliquot of the supernatant was diluted with 5 mL of deionized water, adjusted at pH 5 and transferred to a 20 mL glass headspace sampling vial containing 2 g of sodium chloride. The

internal standard used was 1-heptanol (200 µL of 1.55 mg/L solution in 10% v/v ethanol). In the case of wines, the same treatment was used replacing the supernatant by 5 mL of the wine sample.

Glycosylated volatile compounds were extracted following the method proposed by Wang, Kang, Xu, & Li (2011) slightly modified. Briefly, 10 mL of the supernatant or 10 mL of the wine were submitted to reversed-phase solid phase extraction using a 1 g Sep-Pak C18 cartridge (Waters Corporation, Milford, MA, USA). After eluting the free fraction with 10 mL of dichloromethane, the cartridge was washed with 10 mL of deionized water. The glycosylated fraction was then recovered with 10 mL of methanol. In all steps, the flow rate was about 2 mL/min. The methanolic extract was evaporated to dryness using a vacuum rotavapor (Buchi R–210, Switzerland) at 35 °C. The dried glycosidic extract obtained was dissolved in 5 mL of 0.2 M citrate-phosphate buffer (pH 5). For the enzymatic hydrolysis, 50 mg of an AR–2000 commercial preparation with glycosidase side activity (DSM Oenology, The Netherlands) were used with incubation at 40 °C for 24 h. Finally, the extract was diluted with an equal volume of deionized water and placed into a 20 mL glass headspace sampling vial containing 2 g of sodium chloride. In this case, 1-heptanol was also added as internal standard (200 µL of 1.55 mg/L solution in 10% v/v ethanol).

A 50/30 µm divinylbenzene-carboxen-polydimethylsiloxane (DVB/CAR/PDMS) fiber from Supelco was exposed to the headspace of the capped vial for 20 min at 40 ºC (Sánchez-Palomo, Díaz-Maroto, & Pérez-Coello, 2005). This three-phase fiber allows high extraction efficiency for a wide range of volatile compounds having different chemical functionalities and polarities with good repeatability (Barros et al., 2012; Rebière, Clark, Schmidtke, Prenzler, & Scollary, 2010). Prior to analyses, the fiber was conditioned following the manufacturer's recommendations. All SPME injections were carried out in the splitless mode at 250 ºC for 5 min for the thermal desorption of analytes from the fiber.

GC-MS analyses were performed using an Agilent 7890C gas chromatograph (Little Falls, DE, USA) coupled to an Agilent 5975 mass selective detector. The chromatographic and MS conditions were previously described by Sánchez-Palomo et al. (2005) and slightly modified by Rolle et al. (2015). The DB-WAXETR capillary column (30 m x 0.25 mm, 0.25 µm, J&W Scientific Inc., Folsom, CA, USA) was used. Volatile compounds were identified according to retention indices and mass spectra of pure standards and the NIST database (http://webbook.nist.gov/chemistry/). Semiquantitative determinations (µg/kg of berries, or µg/L of wine, respectively) were carried out by the internal standard method.

2.4. Wine color parameters

The wine color was evaluated from absorbance at 420 nm (A_{420}) and the CIELab parameters (OIV, 2008) including lightness (L*), red/green color coordinate (a*), yellow/blue color coordinate (b*) and hue angle (H*). A UV-1800 spectrophotometer (Shimazdu Corporation, Kyoto, Japan) was used with cuvettes of 10 mm path length.

2.5. Statistical analysis

Statistical analyses were performed using the SPSS Statistics software package, version 19.0 (IBM Corporation, Armonk, NY, USA). The Tukey-b test for $p<0.05$ was used in order to establish significant differences by one-way analysis of variance (ANOVA).

3. Results and discussion

3.1. Maturity effect on the composition of fresh and dehydrated grape berries

Table 1 shows the standard chemical parameters, which define the technological maturity of Malvasia moscata grapes. In fresh grape berries, significant differences were observed in all the parameters quantified among the three different ripeness levels (i.e. density classes), except for

citric acid content. As expected, the value of SSC increased significantly whereas glucose/fructose ratio decreased with increasing berry density. The value of pH increased significantly and titratable acidity decreased due to the decrease of malic acid content. In fact, malic acid content was highly correlated with berry density in Nebbiolo wine grapes whereas tartaric acid content was not affected by the berry classification based on density (Rolle, Torchio et al., 2012). The chemical composition of unsorted berries was similar to that of berries belonging to the density class of 1075 kg/m^3. The only exception was for tartaric acid, whose content was significantly higher in unsorted berries in relation to sorted berries.

For each density class, the sugar content of grape berries increased significantly after postharvest dehydration according to the value of SSC, showing higher contents of fructose than glucose as it can be deduced from the decrease of glucose/fructose ratio. Tartaric acid content also increased significantly resulting in an increase of titratable acidity because no significant difference was found in malic acid content among fresh and partially dehydrated berries. This higher richness in the grape juice components is due to the concentration effect by water loss. Nevertheless, the increase in malic acid content might have been overturned by increased respiration as a consequence of postharvest water stress and even gluconeogenesis (Centioni, Tiberi, Pietromarchi, Bellincontro, & Mencarelli, 2014). In turn, the dehydrated berries belonging to the density class of 1088 kg/m^3 had the highest content of sugars, particularly fructose, and the lowest contents of tartaric and malic acids. Acetic acid and glycerol were only detected in dehydrated grapes at relatively low contents. During grape dehydration, the cell metabolism shift from aerobic to anaerobic and the strong osmotic potential due to higher sugar contents promote the synthesis of acetic acid and glycerol (Chkaiban et al., 2007; Cirilli et al., 2012).

The free volatile composition of fresh and dehydrated grape berries sorted according to density is shown in Table 2. Fifteen free volatile compounds were identified and quantified, which belong to the chemical classes of aldehydes, alcohols, aromatic alcohols, esters and

terpenes. In fresh and partially dehydrated grapes, the most five abundant compounds were *E*-2-hexenal, hexanol, linalool, *E*-2-hexen-1-ol and geraniol. C6 compounds were also the main free volatile compounds in white cultivars, particularly *E*-2-hexenal, 1-hexanol and *E*-2-hexen-1-ol, followed by monoterpenes in aromatic cultivars (Vilanova, Genisheva, Bescansa, Masa, & Oliveira, 2012). Table 2 shows that unsorted fresh berries were richer in total free aldehydes and alcohols than in terpenes. *E*-2-hexenal was the predominant compound and represented about 32.5% of total free volatile compounds. However, significant differences were found in the contents of *E*-2-hexenal and linalool among unsorted berries and berries belonging to the three density classes selected due to different ripeness levels. When berry density increased, *E*-2-hexenal content decreased significantly (accounting for 30.8, 13.7 and 4.8% of total free volatile compounds for the berries of 1075, 1081 and 1088 kg/m^3, respectively), whereas linalool content increased (accounting for 28.0, 46.2 and 66.8% of total free volatile compounds for the berries of 1075, 1081 and 1088 kg/m^3, respectively). In fact, *E*-2-hexenal reached the minimum content in the ripest fresh berries, which corresponded to the density class of 1088 kg/m^3, but they were also the richest berries in linalool with a content exceeding those of all other free volatile compounds detected. Other authors reported a decrease of free *E*-2-hexenal content and an increase of free linalool content throughout ripening in Blanco lexítimo and Muscat Hamburg aromatic cultivars (Fenoll, Manso, Hellín, Ruiz, & Flores, 2009; Vilanova et al., 2012). The detection lack of *Z*-3-hexenal could be attributed to its isomerization to *E*-2-hexenal and, therefore, the decrease of *E*-2-hexenal could be related to lower isomerization or higher reduction to *E*-2-hexen-1-ol through ADH activity (Kalua & Boss, 2010). Terpenes are accumulated until the optimum sugar content is achieved (Vilanova et al., 2012). In the present work, for all density classes, linalool was the predominant free monoterpene detected in the Malvasia moscata cultivar, followed by geraniol. The total content of free terpenes increased progressively with maturity representing from 43.1% of total free volatile compounds at 17.7 ºBrix (1075 kg/m^3) to 68.3% at 19.5 ºBrix (1081 kg/m^3) and 79.9% at 20.5 ºBrix

(1088 kg/m^3). In other studies performed on Muscat cultivars, such as Muscat Hamburg, Moscatuel and Bimeijia, high contents of linalool and geraniol were found (Fenoll, Martinez, Hellin, & Flores, 2012; Yang, Wang, Wu, Fang, & Li, 2011), becoming the major free monoterpenes in grape berries with SSC values higher than 19.4 ºBrix (Fenoll et al., 2009; Rolle et al., 2015). Terpenes are responsible for the characteristic varietal aroma of Muscat cultivars (Selli, Canbas, Cabaroglu, Erten, & Gunata, 2006).

For all the three density classes, the total contents of free volatile compounds, particularly aldehydes, alcohols and terpenes, increased after dehydration, albeit did not always significantly (Table 2). Synthesis reactions occurred during the postharvest dehydration process because the increase exceeded the concentration effect by water loss. Regarding individual free volatile compounds, hexanol and *E*-2-hexen-1-ol contents were significantly higher in the berries after postharvest dehydration. Furthermore, partially dehydrated berries were richer in free *E*-2-hexenal, citronellol, nerol and geraniol than fresh berries, although the differences were not significant for the density class of 1081 kg/m^3 because of high standard deviations in dehydrated berries. Increased contents were also found for free 2-phenyl ethanol in dehydrated berries in relation to those of fresh berries, but the differences were only significant for the density class of 1088 kg/m^3. The trend of free linalool content with the dehydration process depended on the density class. When the berries were dehydrated at 20% WL, those belonging to the density class of 1075 kg/m^3 showed lower linalool content, those of the density class of 1081 kg/m^3 had an increased content of this terpenol, and those of the density class of 1088 kg/m^3 showed no significant variation with respect to fresh berries. Less dense berries could be more prone to the degradation or transformation of linalool into other compounds during postharvest dehydration, whereas the concentration effect overcame the decrease resulting from these reactions in denser berries.

In dehydrated berries, alcohols were the predominant free volatile compounds for all the density classes accounting for 36.8-46.5% of total free volatile compounds, particularly hexanol.

A high presence of *E*-2-hexenal was also observed for the density classes of 1075 and 1081 kg/m^3, whereas linalool was for the density class of 1088 kg/m^3 (Table 2). When the free volatile composition of berries dehydrated at 20% WL was compared among density classes, significant differences were found in *E*-2-hexen-1-ol and linalool contents. The dehydrated berries belonging to the density class of 1088 kg/m^3 showed the highest free *E*-2-hexen-1-ol content, whereas those of 1075 kg/m^3 had the lowest free linalool content. This contributed to a progressive decrease in C6 compounds with herbaceous notes in favor of terpenes with floral nuances when berries with increasing density were dehydrated (total free terpenes representing 22.2, 35.0 and 38.8% of total free volatile compounds for 1075, 1081 and 1088 kg/m^3, respectively). The partial dehydration of Malvasia moscata grape berries belonging to the density class of 1075 kg/m^3 caused an increase of free geraniol content but a decrease of linalool content, resulting in a terpene profile with predominance of geraniol. Instead for the other two density classes, free linalool was the predominant free monoterpene detected in dehydrated berries, followed by geraniol.

Other authors reported that controlled grape dehydration decreased substantially the contents of free hexanol, hexanal, *E*-2-hexenol and *E*-2-hexenal, although the effect was variety dependent (Bellincontro et al., 2004; Serratosa, Lopez-Toledano, Merida, & Medina, 2014). Costantini et al. (2006) showed that C6 compounds, such as 1-hexenol, hexanal and *E*-2-hexenal, reached the highest contents at 11.7% WL. Chkaiban et al. (2007) also confirmed a slight increase in the contents of some free C6 compounds (hexanal, *E*-2-hexenal, hexanol) at 13% WL, but the highest increase was observed at 32% WL. These differences may be due to cell sensitivity to water stress and the enzymatic activity of LOX during postharvest dehydration.

The glycosylated volatile composition of fresh and dehydrated berries sorted according to their density is shown in Table 3. A total of 19 compounds were detected. Hexanal, 3-methyl-2-buten-1-ol, *Z*-3-hexen-1-ol, benzyl alcohol, methyl salicylate, *trans*-furanic-linalool oxide, hotrienol and 3,7-dimethyl-2,6-octadienal were found only in the bound fraction. Most of these

glycosylated volatile compounds were also detected in other grape varieties (Fenoll et al., 2009; Noguerol et al., 2013; Rolle, Giordano et al., 2012). Nevertheless, some volatile compounds detected in the free fraction, such as *E*-3-hexenal, *E*-2-hexenal, 2-ethyl hexanol and ethyl dodecanoate, were not found in the bound fraction. In general, the contents of glycosylated volatile compounds were higher than those of free compounds, particularly terpenes (Mateo & Jiménez, 2000). In the present work, a higher presence of aromatic alcohols (benzyl alcohol and 2-phenyl ethanol) was also observed in the glycosidically-bound fraction.

Terpenes were the most abundant glycosylated volatile compounds in fresh and dehydrated berries, specifically geraniol (representing between 37.9% and 43.9% of total glycosylated volatile compounds) followed by nerol and linalool (accounting for 19.9-27.8% and 14.4-23.4%, respectively) independently on the density class (Table 3). In fresh berries, the contents of these three compounds and 3,7-dimethyl-2,6-octadienal, as well as those of total terpenes and total glycosylated volatile compounds, increased significantly with increasing berry density, and the maximum contents of all terpene compounds determined were reached in the berries belonging to the density class of 1088 kg/m^3 (accounting for 88.9, 84.3, 88.8 and 93.4% of total glycosylated volatile compounds for unsorted berries and berries with a density of 1075, 1081 and 1088 kg/m^3, respectively). This significant increase was reported by other authors during grape maturation (Fenoll et al., 2009). Furthermore, in the present work, other glycosylated volatile compounds such as methyl salicylate decreased significantly with increasing berry density.

When the contents of glycosylated volatile compounds were compared among fresh and partially dehydrated berries for each density class, no significant difference was observed for the berries belonging to the density class of 1081 kg/m^3 probably due to the high standard deviations associated with this sample (Table 3). For the other two density classes (1075 and 1088 kg/m^3), total contents increased significantly after dehydration exceeding the concentration effect by water evaporation, particularly for alcohols and terpenes. Considering individual glycosylated

volatile compounds, berries dehydrated at 20% WL were significantly richer in hexanol, *trans*-furanic-linalool oxide, linalool, 3,7-dimethyl-2,6-octadienal, nerol and geraniol than fresh berries. The increase was also significant in the berries with a density of 1075 kg/m^3 for glycosylated *E*-2-hexen-1-ol and 2-phenyl ethanol, and in those of 1088 kg/m^3 for glycosylated 1-octanol and citronellol. Regarding glycosylated C6 compounds (alcohols and aldehydes), Noguerol-Pato et al. (2013) reported that they increased through dehydration, although 1-hexanol did in higher proportion. Table 3 shows that, in berries dehydrated at 20% WL, the effect of berry density was only significant on the contents of glycosylated *trans*-furanic-linalool oxide, linalool, methyl salicylate and geraniol. The berries belonging to the density class of 1088 kg/m^3 were richer in *trans*-furanic-linalool oxide, linalool and geraniol. Therefore, in agreement with the results for fresh grapes, the highest total content of glycosylated terpene compounds corresponded to dehydrated berries belonging to the density class of 1088 kg/m^3 (representing 89.2, 90.9 and 92.4% of total glycosylated volatile compounds for berries with a density of 1075, 1081 and 1088 kg/m^3, respectively). This contributed positively to the higher richness in total glycosylated volatile compounds of the dehydrated berries belonging to the density class of 1088 kg/m^3.

In general, the water loss associated with the dehydration process promoted an increase of the content of volatile compounds. The dehydration of the riper berries (density class of 1088 kg/m^3) permitted to obtain volatile profiles richer in free terpene compounds, which are directly involved in varietal aroma, but also in glycosylated terpenes, which being odorless can release free volatiles by acid and enzymatic hydrolysis during winemaking, enhancing the floral nuances of the resulting wines (Günata et al., 1986). Although rose oxide has been detected in Muscat grapes and was proposed as an useful indicator of Muscat flavor (Ruiz-García, Hellín, Flores, & Fenoll, 2014), in the present work quantifiable contents of free *cis*-rose oxide and *trans*-rose oxide were only found in dehydrated berries, whereas the highest contents of the two glycosylated isomers were observed in fresh berries.

3.2. Effect of dehydration rate on the composition of grapes

Table 4 shows the standard chemical parameters of the musts obtained from grapes dehydrated at 20% WL by the fast and slow processes. The results obtained for grapes dehydrated by the fast process agreed with those of Table 1, with the exception of glycerol, because of the similarity of the thermohygrometric conditions used. As can be observed in Table 4, the effect of dehydration rate on the chemical composition of musts was not significant, excepting for ethanol. The significantly higher ethanol content in fast dehydrated grapes might be likely due to the metabolic response to the rapid water stress occurred at 28 ºC. Ethanol content also increased significantly when the temperature of controlled postharvest dehydration rose from 20 ºC to 30 ºC for WL% between 10 and 30 (Cirilli et al., 2012). At dehydration temperatures of about 30 ºC, an immediate shift in metabolism is induced from aerobic to anaerobic, involving the activation of enzymes responsible for the increase in ethanol (Costantini et al., 2006).

The volatile composition of Malvasia moscata grape berries dehydrated at different rates is shown in Table 5. In agreement with the results obtained for grape berries dehydrated under similar environmental conditions to those corresponding to the fast dehydration process (Tables 2 and 3), *E*-2-hexenal, geraniol and hexanol were the predominant free volatile compounds, followed by *E*-2-hexen-1-ol and linalool, whereas geraniol, nerol and linalool were the most abundant glycosylated volatile compounds.

When the volatile composition was compared among grapes dehydrated by the fast and slow processes, very few significant differences were found (Table 5). Regarding free volatile compounds, the content of geraniol increased, but that of hexanol and 2-phenyl ethanol decreased with increasing dehydration rate. One advantage of the fast process was the higher total content of free terpenes in partially dehydrated grapes (accounting for 27.1% of total free volatile compounds for the slow process and 36.7% for the fast process), but a lower total content of free alcohols was achieved (accounting for 31.1% of total free volatile compounds for

the slow process and 18.7% for the fast process). For glycosylated compounds, a significant decrease in the contents of *cis*-rose oxide, *Z*-3-hexen-1-ol and nerol was observed, when the dehydration process slowed down, while those of hexanol, geraniol and methyl salicylate increased significantly. This resulted in total contents of glycosylated terpenes and alcohols that remained practically unchanged with dehydration rate. In fact, no significant differences were found in the total content of free or glycosylated volatile compounds between the slow and fast dehydration processes.

Other authors reported that the contents of free C6 compounds and terpenes decreased significantly with increasing dehydration temperature from 20 ºC to 30 ºC at 45% RH (therefore increasing dehydration rate), particularly for WL% between 10 and 40 (Cirilli et al., 2012). They pointed out that the initial formation of C6 compounds and their subsequent loss is linked to ADH activity. Chkaiban et al. (2007) observed that grape berries dehydrated under controlled thermohygrometric conditions (fast process) had lower contents of free C6 compounds than control berries (uncontrolled environmental conditions, slow process) for WL% between 13 and 23, although the differences were not significant. As a general tendency, in the present work, grape fast dehydration also caused the decrease of alcohols but the increase of terpenes in relation to the slow process.

3.3. Effect of grape dehydration rate on the composition of fortified wines

The standard chemical parameters of the wines made from grapes dehydrated by the slow and fast processes are shown in Table 4. The wines made from slow dehydrated grapes showed significantly higher contents of the compounds involved in titratable acidity (citric acid, tartaric acid and malic acid) and volatile acidity (acetic acid), and therefore lower value of pH. The results obtained were in the range of other liqueur/fortified wines, although the contents of tartaric acid and malic acid were relatively high (Jelén, Majcher, Dziadas, Zawirska-Wojtasiak, Czaczyk, & Wąsowicz, 2011).

Regarding chromatic characteristics, significant differences were observed in A_{420} and CIELab parameters among the two fortified wines (Table 4). The wines made from fast dehydrated grapes showed significantly higher values of A_{420} than those made from slow dehydrated grapes. This parameter is widely used as a browning marker, and the values obtained indicated moderate browning (0.2-0.5 A.U.) according to the categories proposed by Fernández-Zurbano, Ferreira, Escudero, & Cacho (1998). Grape drying causes the formation of brown compounds by oxidation of phenolic compounds (Serratosa et al., 2008). As a consequence of higher browning of fortified wines, the fast dehydration process resulted also in significantly higher values of a* and b* coordinates, suggesting wines with more red and yellow color components, when compared with the slow dehydration process. Furthermore, fast dehydration led to significantly lower values of L* and H*, indicating that fortified wines were darker and exhibited more reddish hue. ΔE* parameter (OIV, 2008) was calculated from the average values of L*, a* and b* coordinates to show the overall colorimetric difference between the fortified wines resulting from fast and slow grape dehydration. The calculated value of ΔE* was 7.14, confirming differences in color over the perceptibility threshold among the wines made from fast and slow dehydrated grapes.

Table 6 shows the influence of grape dehydration rate on the volatile composition of Malvasia moscata fortified wines. With the exception of *Z*-3,7-Dimethyl-2,6-octadienal, nerol, geraniol and benzyl alcohol, free volatile compounds were found at higher contents than glycosylated compounds. A total of 42 free volatile compounds were identified and quantified. Esters of fatty acids and acetates were the predominant free volatile compounds in the two fortified wines (representing around 90% of total free volatile compounds), particularly ethyl octanoate (50.5-54.8% of total free volatile compounds), ethyl decanoate (18.1-19.8%), ethyl hexanoate (6.6-8.1%) and ethyl acetate (5.3-5.6%). Esters are the main markers of fermentative aroma, and they provide pleasant nuances of fruit. The contents of the main esters exceeded the olfactory threshold (Ferreira, López, & Cacho, 2000), and therefore they might contribute to the

aroma of Malvasia moscata fortified wines. Significantly higher contents of total esters and many individual esters were observed in the free volatile fraction of the wines made from fast dehydrated grapes. Most free esters detected in other sweet fortified wines were also found in the wines analyzed in the present work. Ethyl decanoate, ethyl hexanoate and ethyl 2-methylbutanoate were identified as key odorants in the Jutrzenka wine (Jelén et al., 2011), but ethyl octanoate, ethyl hexanoate, ethyl 2-methylbutanoate and ethyl 3-methylbutanoate were in the Garnacha tintorera wine (Noguerol-Pato, González-Álvarez, González-Barreiro, Cancho-Grande, & Simal-Gándara, 2012). Furthermore, 3-methylbutyl acetate, ethyl hexanoate, ethyl octanoate and ethyl decanoate can contribute sensorially to the aroma of sweet monovarietal wines made from Muscat and Malvasia grapes (Del Caro, Fanara, Genovese, Moio, Piga, & Piombino, 2012).

In Malvasia moscata fortified wines, aliphatic and aromatic alcohols represented 5.7–7.3% of total free volatile compounds, 2-phenyl ethanol and 2-methyl-1-butanol being the most abundant free alcohols (Table 6). Nevertheless, their contents were below the corresponding odorant thresholds. Although the wines made from fast dehydrated grapes showed a significantly higher content of free 2-methyl-1-butanol, it has no direct effect on the aroma but interactions with odorants cannot be discarded. In other studies, isoamyl alcohols (2+3-methyl-1-butanol) and 2-phenyl ethanol were the main alcohols in sweet fortified wines, but they also do not contribute to the aroma profile (Noguerol-Pato el al., 2012).

In the present work, terpenes accounted for 2.8-3.1% of total free volatile compounds. Linalool, hotrienol, 3,7-dimethyl-1,5,7-octatriene and geranyl ethyl ether were the most abundant free terpenes. Nevertheless, according to the olfactory threshold, linalool, rose oxide, citronellol and to a lesser extent hotrienol and geraniol can contribute actively to the aroma of the wines made from fast and slow dehydrated grapes with floral notes. Therefore, significantly higher contents of *trans*-rose oxide, geranyl ethyl ether, linalool and 2,6-dimethyl-2,6-octadiene, and therefore of total terpenes, in the free volatile fraction of the wines made from fast dehydrated

grapes could enhance the varietal aroma. Linalool was also identified as a key odorant in sweet fortified wines of aromatic white Jutrzenka grapes (Jelén et al., 2011) and even linalool, geraniol and citronellol were in sweet wines of Muscat grapes (Del Caro et al., 2012).

Only three free fatty acids (hexanoic acid, octanoic acid, decanoic acid) were detected in Malvasia moscata fortified wines (Table 6). However, their contents were lower than the olfactory threshold. Hexanoic acid and octanoic acid were found as active odorants in sweet fortified wines (Noguerol-Pato el al., 2012), hexanoic acid in monovarietal Muscat and Malvasia sweet wines, and octanoic acid in Malvasia sweet wines (Del Caro et al., 2012). Regarding free norisoprenoids, β-damascenone can be considered an active floral odorant because of the low olfactory threshold. The wines significantly richer in free norisoprenoids (β-damascenone and TDN) were those made from slow dehydrated grapes. β-damascenone was also a key odorant in other sweet fortified wines (Jelén et al., 2011; Noguerol-Pato el al., 2012). It is important to highlight that the contents of the three predominant esters, linalool and β-damascenone in the fortified wines made from fast and slow dehydrated Malvasia moscata grapes were higher than those found for other sweet fortified wines, whereas alcohols and fatty acids were less abundant. Despite C6 aldehydes were present in Malvasia moscata grapes dehydrated using the two different dehydration conditions (Table 5), these compounds were not detected in the resulting fortified wines (Table 6) in agreement with other previously published work on a naturally sweet wine made from Garnacha grapes dehydrated under controlled thermohygrometric conditions (Noguerol-Pato et al., 2012, 2013).

Fourteen glycosylated volatile compounds were detected in the wines (Table 6), mainly alcohols and terpenes. The predominant glycosylated compounds were geraniol (43.1-45.0%) and nerol (28.6-33.6%), followed by hexanol (7.5-8.4%) and linalool (5.1-7.5%). Geraniol, nerol, linalool and 2-phenyl ethanol were also the most abundant volatile compounds of the bound fraction for Muscat sweet wines (Del Caro et al., 2012). In the present work, some significant differences were observed among wines made from fast and slow dehydrated grapes.

Glycosylated hexanol, nerol and geraniol were significantly more abundant in the wines made from fast dehydrated grapes, whereas 2-phenyl ethanol and *Z*-3,7-dimethyl-2,6-octadienal were in those made from slow dehydrated grapes. As a general tendency, the wines made from fast dehydrated grapes were richer in total volatile compounds (free and glycosylated), particularly in alcohols, esters and terpenes, although poorer in norisoprenoids, when compared with those from slow dehydrated berries.

4. Conclusions

This study contributes to the knowledge of the effect of berry maturity and dehydration rate under controlled thermohygrometric conditions on the volatile composition of dehydrated Malvasia moscata wine grapes and the fortified wines made from them. This was the first time that the effect of berry maturity was studied for free and glycosylated volatile compounds in dehydrated Malvasia moscata grapes. The ripeness level of fresh berries at harvest affected significantly the volatile composition of dehydrated berries. In fact, the dehydration of the riper berries increased the contribution of terpenes to the volatile profile, favoring the greater presence of pleasant nuances. Therefore, berry densimetric sorting could be advantageous from the qualitative and quantitative point of view in order to promote the concentration and synthesis of key positive odorant compounds in wine grapes during postharvest dehydration.

Dehydration rate also had a strong impact on the volatile composition of Malvasia moscata wine grapes and fortified wines. In general, faster dehydrated grapes were richer in volatile compounds, particularly in free terpenes. Malvasia moscata grapes were suitable for the production of fortified wines, although the volatile composition and chromatic characteristics depended on dehydration rate. In fact, the wines made from fast dehydrated grapes showed a higher total content of free and glycosylated volatile compounds, mainly many free esters and terpenes that probably contribute actively and positively to the aroma of fortified wines. Instead, the wines made from slow dehydrated grapes were richer in free norisoprenoids and showed less

browning. Thus, it is possible to reduce the time involved in the postharvest dehydration process and in turn to increase the content of volatile compounds that potentially could contribute to improve the aromatic quality of fortified wines, which is an important aspect from an economic point of view, but the expense of higher browning.

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Table 1. Chemical parameters of fresh and dehydrated berries of Malvasia moscata sorted according to their initial density (Year 2013).

Grape must composition[a] (g/L unless specified)	Whole sample (unsorted in density classes)	**Initial selected density class**								
		1075 kg/m^3	1081 kg/m^3	1088 kg/m^3	1075 kg/m^3	1081 kg/m^3	1088 kg/m^3	1075 kg/m^3	1081 kg/m^3	1088 kg/m^3
%WL[e]	0[b]	0	0	0	20[c]	20	20	*Sign.*[d]		
Brix (°)	18.0 ± 0.1 A	17.7 ± 0.1 A	19.5 ± 0.6 B	20.5 ± 0.1 C	24.8 ± 0.6 α	26.0 ± 0.4 α	27.9 ± 0.1 β	**	**	***
pH (-)	3.12 ± 0.01 A	3.14 ± 0.03 A	3.21 ± 0.01 B	3.23 ± 0.01 C	3.24 ± 0.05	3.27 ± 0.06	3.35 ± 0.01	ns	ns	**
Titratable acidity[g]	5.9 ± 0.2 B	5.3 ± 0.2 B	4.6 ± 0.1 A	4.4 ± 0.1 A	6.2 ± 0.2	6.0 ± 0.2	5.1 ± 0.4	*	*	ns
Glucose/Fructose ratio	0.920 ± 0.001 C	0.914 ± 0.006 BC	0.908 ± 0.002 AB	0.906 ± 0.001 A	0.862 ± 0.003 α	0.867 ± 0.006 α	0.885 ± 0.004 β	**	*	*
Citric acid	0.17 ± 0.01	0.16 ± 0.01	0.14 ± 0.01	0.15 ± 0.02	0.18 ± 0.04	0.22 ± 0.01	0.19 ± 0.01	ns	**	ns
Tartaric acid	5.16 ± 0.13 B	4.55 ± 0.23 A	4.38 ± 0.06 A	4.56 ± 0.03 A	7.58 ± 0.17 β	7.06 ± 0.14 β	6.19 ± 0.19 α	**	**	**
Malic acid	2.38 ± 0.02 C	2.21 ± 0.10 BC	2.01 ± 0.01 AB	1.89 ± 0.07 A	2.18 ± 0.05 β	1.78 ± 0.15 αβ	1.59 ± 0.12 α	ns	ns	ns
Acetic acid	nd[f]	nd	nd	nd	0.08 ± 0.11	0.16 ± 0.02	0.04 ± 0.06	-	-	-
Glycerol	nd	nd	nd	nd	0.62 ± 0.08	0.64 ± 0.42	0.46 ± 0.06	-	-	-

[a]All data are expressed as average value ± standard deviation (n = 3). [b]Different Latin letters within the same row indicate significant differences among density classes at 0% WL (Tukey-b test; $p<0.05$). [c]Different Greek letters within the same row indicate significant differences among density classes at 20% WL (Tukey-b test; $p<0.05$). [d] (1075, 1081, 1088)*Sign.*: *, **, *** and ns indicate significance at $p<0.05$, 0.01, 0.001 and not significant, respectively, among fresh and dehydrated berries belonging to the same density class. [e]WL=weight lost, [f]nd = not detected. [g]Titratable acidity expressed in g/L as tartaric acid.

Table 2. Free volatile compounds of fresh and dehydrated berries of Malvasia moscata sorted according to their initial density (Year 2013).

Free aroma compounds[a]			**Initial selected density class**								
(µg/kg berries)		Whole sample (unsorted in density classes)	1075 kg/m^3	1081 kg/m^3	1088 kg/m^3	1075 kg/m^3	1081 kg/m^3	1088 kg/m^3	1075 kg/m^3	1081 kg/m^3	1088 kg/m^3
%WL[e]	*Kovats index*	0[b]	0	0	0	20[c]	20	20	*Sign.*[d]		
Aldehydes											
E-3-Hexenal	1158	8.5 ± 11.9	0.8 ± 1.2	0.6 ± 0.9	0.3 ± 0.4	3.9 ± 5.5	5.2 ± 7.3	1.0 ± 1.2	ns	ns	ns
E-2-Hexenal	1230	181.7 ± 9.9 C	41.0 ± 5.6 B	17.0 ± 11.3 AB	8.0 ± 1.4 A	118.3 ± 24.5	166.4 ± 50.2	70.3 ± 18.0	*	ns	*
Σ Aldehydes		190.1 ± 21.9 B	41.8 ± 4.4 A	17.6 ± 12.1 A	8.4 ± 1.9 A	122.2 ± 30.0	171.6 ± 42.9	71.3 ± 19.2	ns	*	*
Alcohols											
Hexanol	1375	145.8 ± 104.6	18.1 ± 0.5	9.0 ± 12.6	15.4 ± 2.6	116.6 ± 18.0	162.3 ± 23.5	128.3 ± 4.8	*	*	**
E-2-Hexen-1-ol	1423	72.9 ± 42.4	8.4 ± 0.3	8.1 ± 1.0	6.8 ± 1.1	43.1 ± 7.6 α	52.9 ± 7.8 α	79.1 ± 1.2 β	*	*	***
2-Ethyl hexanol	1516	2.1 ± 2.6	3.5 ± 0.0	1.4 ± 1.9	0.8 ± 1.2	1.6 ± 2.2	2.9 ± 3.9	2.7 ± 1.1	ns	ns	ns
1-Octanol	1574	0.3 ± 0.1	0.1 ± 0.1	0.2 ± 0.3	0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.1	0.2 ± 0.2	ns	ns	ns
2-Phenyl ethanol	1895	1.4 ± 0.3	3.0 ± 4.3	2.4 ± 0.8	1.4 ± 0.0	8.6 ± 2.5	7.7 ± 2.3	15.6 ± 2.5	ns	ns	*
Σ Alcohols		222.5 ± 150.0	33.2 ± 3.7	21.1 ± 12.8	24.6 ± 4.7	169.9 ± 30.4	225.8 ± 29.8	225.9 ± 7.1	*	*	***
Esters											
Ethyl dodecanoate	1846	0.4 ± 0.2	0.7 ± 0.1	0.5 ± 0.1	0.7 ± 0.3	0.1 ± 0.1	1.1 ± 1.6	0.1 ± 0.1	**	ns	ns
Terpenes											
c-Rose oxide	1369	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	3.0 ± 4.2	3.7 ± 0.3	-	-	-
t-Rose oxide	1380	0.1 ± 0.1	< 0.1	< 0.1	< 0.1	0.1 ± 0.1	0.5 ± 0.7	0.3 ± 0.5	-	-	-
Linalool	1556	108.1 ± 16.3 B	37.3 ± 0.1 A	57.2 ± 9.1 A	111.9 ± 15.8 B	17.9 ± 5.1 α	121.2 ± 10.9 β	128.5 ± 11.7 β	*	*	ns
α-Terpineol	1720	0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.2	0.2 ± 0.2	0.4 ± 0.6	0.5 ± 0.7	ns	ns	ns
Citronellol	1785	1.1 ± 0.5	0.8 ± 0.4	1.0 ± 0.1	0.7 ± 0.6	4.3 ± 0.7	6.5 ± 3.7	4.7 ± 1.1	*	ns	*
Nerol	1814	4.3 ± 3.1	1.9 ± 1.0	4.1 ± 0.6	2.8 ± 0.9	15.4 ± 2.4	19.7 ± 5.6	11.4 ± 0.4	*	ns	**
Geraniol	1848	31.9 ± 10.0	17.4 ± 0.6	22.1 ± 2.4	18.3 ± 3.3	45.2 ± 6.9	63.6 ± 22.9	39.0 ± 1.5	*	ns	*
Σ *Terpenes*		145.6 ± 28.9 B	57.4 ± 0.2 A	84.5 ± 12.1 AB	133.9 ± 19.0 B	83.2 ± 5.3 α	214.8 ± 48.5 β	188.2 ± 15.3 αβ	*	ns	ns
Σ *Volatile compounds*		558.6 ± 200.6 B	133.1 ± 7.9 A	123.8 ± 12.8 A	167.6 ± 25.2 A	375.4 ± 65.7	613.4 ± 122.8	485.4 ± 41.6	*	*	*

[a]All data are expressed as average value ± standard deviation (n = 3). [b]Different Latin letters within the same row indicate significant differences among density classes at 0% WL (Tukey-b test; $p<0.05$). [c]Different Greek letters within the same row indicate significant differences among density classes at 20% WL (Tukey-b test; $p<0.05$). [d] (1075, 1081, 1088)*Sign.*: *, **, *** and ns indicate significance at $p<0.05$, 0.01, 0.001 and not significant, respectively, among fresh and dehydrated berries belonging to the same density class. [e]WL=weight lost.

Table 3. Glycosylated volatile compounds of fresh and dehydrated berries of Malvasia moscata sorted according to their initial density (Year 2013).

Glycosylated aroma compounds[a]			**Initial selected density class**								
(μg/kg berries)		Whole sample (unsorted in density classes)	1075 kg/m^3	1081 kg/m^3	1088 kg/m^3	1075 kg/m^3	1081 kg/m^3	1088 kg/m^3	1075 kg/m^3	1081 kg/m^3	1088 kg/m^3
%WL[e]	*Kovats index*	0[b]	0	0	0	20[c]	20	20	*Sign.* [d]		
Aldehydes											
Hexanal		2.9 ± 0.1	3.4 ± 0.5	1.2 ± 0.7	3.9 ± 3.3	1.8 ± 1.9	1.6 ± 0.3	2.1 ± 2.2	ns	ns	ns
Alcohols											
3-Methyl-2-buten-1-ol	1343	14.4 ± 9.4	21.4 ± 0.3	10.9 ± 15.3	10.5 ± 14.8	15.3 ± 21.6	8.1 ± 11.3	17.1 ± 24.0	ns	ns	ns
Hexanol	1375	104.5 ± 6.4	94.3 ± 0.8	107.5 ± 4.1	110.4 ± 4.5	188.3 ± 1.5	155.1 ± 37.9	239.9 ± 21.2	***	ns	*
Z-3-Hexen-1-ol	1402	2.1 ± 0.1	1.5 ± 0.3	2.0 ± 2.8	2.3 ± 0.2	5.2 ± 3.9	2.8 ± 0.3	1.6 ± 2.2	ns	ns	ns
E-2-Hexen-1-ol	1423	6.0 ± 3.3	9.1 ± 0.2	4.8 ± 6.7	6.0 ± 2.7	17.2 ± 0.8	8.8 ± 5.5	16.2 ± 3.2	**	ns	ns
1-Octanol	1574	6.6 ± 9.3	4.8 ± 6.8	11.9 ± 1.0	0.1 ± 0.1	20.8 ± 3.6	5.8 ± 8.2	24.5 ± 0.1	ns	ns	***
Benzyl alcohol	1847	51.9 ± 24.3	54.1 ± 0.3	40.5 ± 4.5	19.9 ± 8.5	41.3 ± 13.3	30.7 ± 2.3	23.5 ± 1.7	ns	ns	ns
2-Phenyl ethanol	1895	43.1 ± 1.3	40.2 ± 0.3	42.5 ± 3.2	43.4 ± 3.5	52.8 ± 2.7	29.2 ± 11.4	57.1 ± 11.1	*	ns	ns
Σ Alcohols		228.6 ± 35.4	225.4 ± 7.9	220.1 ± 6.3	192.5 ± 2.9	341.0 ± 2.8 αβ	240.7 ± 9.8 α	379.9 ± 55.8 β	**	ns	*
Esters											
Methyl salicylate	1790	56.3 ± 0.2 C	26.4 ± 0.1 B	18.3 ± 1.4 B	5.1 ± 7.2 A	45.2 ± 11.1 β	14.2 ± 5.0 α	20.3 ± 2.2 αβ	ns	ns	ns
Terpenes											
c-Rose oxide	1369	< 0.1	1.6 ± 0.3	1.6 ± 0.8	4.2 ± 6.0	< 0.1	< 0.1	< 0.1	-	-	-
t-Rose oxide	1380	0.3 ± 0.4	5.8 ± 2.1	11.5 ± 4.4	12.5 ± 17.6	1.2 ± 1.3	0.1 ± 0.1	1.4 ± 1.1	ns	ns	ns
Linalool	1465	590.9 ± 34.5 B	235.7 ± 78.0 A	336.3 ± 94.5 A	622.2 ± 3.0 B	516.4 ± 36.6 α	512.8 ± 113.8 α	1241.0 ± 115.1 β	*	ns	*
t-Furanic-linalool oxide	1565	16.5 ± 8.0	7.0 ± 1.2	9.0 ± 3.9	20.2 ± 0.1	22.0 ± 0.2 α	26.6 ± 5.9 α	48.7 ± 5.0 β	**	ns	*
Hotrienol	1627	5.1 ± 0.1	5.8 ± 1.0	6.8 ± 3.5	12.5 ± 6.4	11.1 ± 3.2	11.2 ± 5.9	8.7 ± 4.8	ns	ns	ns
Z-3,7-Dimethyl-2,6-octadienal	1699	62.2 ± 2.1 BC	43.2 ± 1.1 A	57.8 ± 2.3 B	67.5 ± 3.2 C	96.9 ± 13.6	67.2 ± 12.2	120.7 ± 16.1	*	ns	*
α-Terpineol	1720	23.4 ± 0.3	12.3 ± 5.8	17.8 ± 0.3	18.8 ± 0.5	31.7 ± 3.3	22.2 ± 6.0	18.9 ± 26.6	ns	ns	ns
Citronellol	1785	42.3 ± 0.6	27.8 ± 0.9	36.8 ± 1.5	40.3 ± 19.0	83.9 ± 19.9	69.1 ± 19.5	132.1 ± 10.0	ns	ns	*
Nerol	1814	525.1 ± 5.5 C	322.9 ± 14.9 A	486.4 ± 11.2 B	792.1 ± 0.8 D	995.6 ± 130.6	764.8 ± 210.9	1315.8 ± 63.5	*	ns	**
Geraniol	1848	1041.8 ± 10.1 C	705.4 ± 31.8 A	942.2 ± 3.1 B	1249.6 ± 35.3 D	1438.4 ± 179.8 αβ	1087.4 ± 287.1 α	2006.1 ± 67.8 β	*	ns	**
Σ Terpenes		2307.7 ± 21.1 C	1367.6 ± 130.1 A	1906.2 ± 87.6 B	2839.9 ± 2.4 D	3197.2 ± 385.7 α	2561.3 ± 661.3 α	4893.5 ± 2.9 β	*	ns	***
Σ Volatile compounds		2595.6 ± 14.4 C	1622.8 ± 122.6 A	2145.9 ± 91.7 B	3041.5 ± 3.4 D	3585.2 ± 395.9 α	2817.8 ± 666.4 α	5295.8 ± 52.9 β	*	ns	***

[a]All data are expressed as average value ± standard deviation (n = 3). [b]Different Latin letters within the same row indicate significant differences among density classes at 0% WL (Tukey-b test; $p<0.05$). [c]Different Greek letters within the same row indicate significant differences among density classes at 20% WL (Tukey-b test; $p<0.05$). [d] (1075, 1081, 1088)*Sign.*: *, **, *** and ns indicate significance at $p<0.05$, 0.01, 0.001 and not significant, respectively, among fresh and dehydrated berries belonging to the same density class. [e]WL=weight lost.

Table 4. Chemico-physical parameters of Malvasia moscata grapes dehydrated using two different dehydration conditions. and of the fortified wines produced from them (Year 2014).

		Musts obtained from dehydrated grapes			Fortified wines obtained from dehydrated grapes		
Parameter[a]	units	**Fast dehydration**	**Slow dehydration**	*Sign.*[b]	**Fast dehydration**	**Slow dehydration**	*Sign.*[b]
°Brix	°Bx	26.5 ± 0.7	26.6 ± 1.8	ns	-	-	-
pH	-	3.32 ± 0.05	3.34 ± 0.11	ns	3.67 ± 0.02	3.57 ± 0.02	*
Titratable acidity	g/L as tartaric acid	6.3 ± 0.4	6.0 ± 0.8	ns	5.3 ± 0.1	6.2 ± 0.1	*
Glucose/fructose ratio	-	0.926 ± 0.010	0.893 ± 0.007	ns	0.508 ± 0.002	0.502 ± 0.001	ns
Ethanol	% v/v	0.33 ± 0.02	0.06 ± 0.05	*	15.2 ± 0.2	15.2 ± 0.1	ns
Citric acid	g/L	0.24 ± 0.05	0.26 ± 0.05	ns	0.12 ± 0.01	0.18 ± 0.01	**
Tartaric acid	g/L	7.02 ± 0.84	7.96 ± 0.43	ns	1.75 ± 0.01	1.98 ± 0.01	***
Malic acid	g/L	2.55 ± 0.72	2.88 ± 0.48	ns	2.36 ± 0.01	2.50 ± 0.02	*
Acetic acid	g/L	nd[c]	nd	-	0.10 ± 0.01	0.23 ± 0.01	***
Lactic acid	g/L	-	-	-	nd	nd	-
Glycerol	g/L	nd	0.13 ± 0.12	-	7.89 ± 0.04	7.76 ± 0.06	ns
L*	-	-	-	-	90.0 ± 0.3	93.9 ± 0.2	**
a*	-	-	-	-	2.03 ± 0.13	-1.89 ± 0.08	***
b*	-	-	-	-	30.35 ± 0.28	25.86 ± 0.39	**
H*	-	-	-	-	3.52 ± 0.08	4.92 ± 0.04	**
A_{420} (O.P. 10 mm)	A.U.[d]	-	-	-	0.56 ± 0.01	0.44 ± 0.01	***

[a]All data are expressed as average value ± standard deviation (n = 3). [b]*Sign.*: *, **, *** and ns indicate significance at $p<0.05$, 0.01, 0.001 and not significant, respectively, among fast and slow dehydration processes (grapes or wines obtained from them). [c]nd = not detected. [d]A.U. = absorbance units.

Table 5. Volatile composition of Malvasia moscata grapes dehydrated using two different dehydration conditions (Year 2014).

Compound[a] (μg/kg berries)	*Kovats index*	**Free compounds**			**Glycosylated compounds**		
		Fast	**Slow**	*Sign.*[b]	**Fast**	**Slow**	*Sign.*[b]
Aldehydes							
Hexanal	1098	nd[c]	nd	-	< 0.1	0.1 ± 0.1	-
E-2-Hexenal	1230	189.7 ± 38.9	158.7 ± 88.9	ns	nd	nd	-
Σ Aldehydes		189.7 ± 38.9	158.7 ± 88.9	ns	< 0.1	0.1 ± 0.1	-
Alcohols							
3-Methyl-2-buten-1-ol	1343	nd	nd	-	22.6 ± 3.7	13.7 ± 3.4	ns
Hexanol	1375	50.0 ± 6.1	75.9 ± 2.6	*	89.4 ± 2.5	109.1 ± 2.5	*
Z-3-Hexen-1-ol	1402	nd	nd	-	8.8 ± 0.4	4.2 ± 1.0	*
E-2-Hexen-1-ol	1423	26.7 ± 3.4	33.9 ± 2.6	ns	nd	nd	-
2-Ethyl hexanol	1516	< 0.1	< 0.1	-	nd	nd	-
1-Octanol	1574	0.3 ± 0.1	0.3 ± 0.1	ns	13.9 ± 6.7	15.2 ± 1.0	ns
Benzyl alcohol	1847	nd	nd	-	35.6 ± 7.6	23.2 ± 0.1	ns
2-Phenyl ethanol	1895	2.6 ± 0.2	7.7 ± 0.2	**	24.5 ± 15.3	40.1 ± 0.6	ns
Σ Alcohols		79.6 ± 9.3	117.9 ± 5.1	*	194.8 ± 22.7	205.4 ± 8.6	ns
Esters							
Methyl salicylate	1790	nd	nd	-	28.5 ± 1.2	36.0 ± 1.6	*
Terpenes							
c-Rose oxide	1369	3.6 ± 2.0	5.0 ± 2.0	ns	44.9 ± 1.4	19.6 ± 3.0	**
t-Rose oxide	1380	0.4 ± 0.1	0.4 ± 0.3	ns	13.2 ± 4.1	6.5 ± 0.9	ns
t-Furanic-linalool oxide	1465	nd	nd	-	17.0 ± 7.4	12.5 ± 5.1	ns
Linalool	1565	38.2 ± 1.4	31.9 ± 2.3	ns	727.8 ± 172.0	548.7 ± 41.4	ns
Hotrienol	1627	nd	nd	-	7.8 ± 1.2	4.1 ± 1.0	ns
Z-3,7-Dimethyl-2,6-octadienal	1699	nd	nd	-	22.1 ± 2.3	19.4 ± 1.9	ns
α-Terpineol	1720	1.1 ± 0.1	0.7 ± 0.5	ns	25.4 ± 11.4	14.2 ± 4.9	ns
Citronellol	1785	4.7 ± 0.7	2.3 ± 0.5	ns	99.2 ± 3.7	90.0 ± 2.9	ns
Nerol	1814	17.8 ± 25.1	11.7 ± 6.6	ns	1081.6 ± 9.3	843.0 ± 30.4	**
Geraniol	1848	90.0 ± 8.3	50.6 ± 3.0	*	1329.9 ± 3.0	1412.8 ± 26.9	*
Σ Terpenes		155.8 ± 13.9	102.5 ± 8.7	*	3368.9 ± 205.9	2970.8 ± 91.3	ns
Σ Volatile compounds		425.1 ± 34.2	379.0 ± 75.1	ns	3592.2± 181.9	3212.3 ± 101.7	ns

[a]All data are expressed as average value ± standard deviation (n = 3). [b]*Sign.*: *, ** and ns indicate significance at $p<0.05$, 0.01 and not significant, respectively, among fast and slow dehydration processes. [c]nd = not detected.

Table 6. Volatile composition of fortified wines produced with Malvasia moscata grapes dehydrated using two different dehydration conditions (Year 2014).

Compound[a] (µg/L wine)	*Kovats index*	Olfactory threshold (µg/L)	**Free compounds**			**Glycosylated compounds**		
			Fast	**Slow**	*Sign.*[b]	**Fast**	**Slow**	*Sign.*[b]
Alcohols								
2-Methyl-1-propanol	1121	40000[d]	41.7 ± 36.0	51.7 ± 52.5	ns	nd	nd	-
2-Methyl-1-butanol	1237	30000[d]	1059.1 ± 98.4	727.8 ± 134.9	*	7.0 ± 2.8	5.4 ± 1.1	ns
3-Methyl-1-butanol	1363	30000[d]	21.7 ± 10.4	25.1 ± 7.5	ns	nd	nd	-
Hexanol	1375	8000[d]	128.4 ± 45.3	135.0 ± 4.1	ns	101.7 ± 2.2	77.4 ± 3.1	*
(R,R-levo)-2,3-Butanediol	1559	150000[e]	332.0 ± 43.1	302.1 ± 69.5	ns	nd	nd	-
(R,S-meso)-2,3-Butanediol	1596	150000[e]	67.6 ± 36.1	84.3 ± 15.9	ns	nd	nd	-
Benzyl alcohol	1874	200000[e]	0.9 ± 0.5	1.8 ± 2.5	ns	21.4 ± 7.2	16.2 ± 7.1	ns
2-Phenyl ethanol	1895	14000[d]	3989.7 ± 105.6	3720.2 ± 193.3	ns	15.4 ± 0.9	34.0 ± 1.5	**
Σ Alcohols			5641.1 ± 89.7	5047.9 ± 283.7	*	145.5 ± 5.6	133.0 ± 13.4	ns
Esters								
Ethyl acetate	nd	7500[f]	5535.2 ± 240.3	3687.0 ± 177.4	***	nd[c]	nd	-
Methyl butanoate	1048	-	161.9 ± 3.8	144.3 ± 8.4	*	nd	nd	-
Ethyl 2-methyl butanoate	1064	18[d]	13.1 ± 3.7	12.2 ± 2.6	ns	nd	nd	-
Ethyl 3-methyl butanoate	1082	3[d]	13.6 ± 2.2	7.8 ± 1.6	*	nd	nd	-
3-Methyl-butyl acetate	1138	30[d]	1253.5 ± 28.1	737.6 ± 37.1	***	nd	nd	-
Ethyl hexanoate	1257	14[d]	6484.9 ± 207.5	5585.9 ± 331.6	*	nd	nd	-
Hexyl acetate	1294	1500[d]	285.1 ± 8.3	87.4 ± 6.1	***	nd	nd	-
Ethyl heptanoate	1352	-	13.2 ± 0.3	20.3 ± 3.9	*	nd	nd	-
Ethyl octanoate	1453	5[d]	53796.4 ± 1789.3	34818.2 ± 2891.1	***	nd	nd	-
Ethyl nonanoate	1553	-	61.2 ± 19.2	43.9 ± 14.8	ns	nd	nd	-
Methyl decanoate	1611	-	24.8 ± 7.6	16.8 ± 10.1	ns	nd	nd	-
Ethyl decanoate	1655	200[d]	17801.5 ± 2708.5	13697.3 ± 1411.8	ns	nd	nd	-
3-Methyl-butyl octanoate	1674	125[d]	127.0 ± 12.4	52.3 ± 17.8	**	nd	nd	-
Diethyl succinate	1700	200000[e]	689.2 ± 224.1	965.9 ± 54.8	ns	nd	nd	-
Ethyl-9-decenoate	1710	-	2449.7 ± 90.7	1336.2 ± 83.9	***	nd	nd	-
Ethyl phenyl acetate	1804	250[d]	69.1 ± 19.5	18.0 ± 4.6	*	nd	nd	-
Ethyl dodecanoate	1846	-	199.0 ± 33.4	142.3 ± 128.1	ns	nd	nd	-
Σ Esters			88978.3 ± 1981.6	61373.4 ± 4721.9	***	-	-	-
Acids								
Hexanoic acid	1850	420[d]	26.5 ± 23.1	71.3 ± 37.1	ns	nd	nd	-
Octanoic acid	2000	500[d]	542.2 ± 295.1	119.1 ± 31.0	ns	nd	nd	-
Decanoic acid	2155	1000[d]	123.8 ± 13.0	53.6 ± 54.5	ns	nd	nd	-
Σ Acids			692.5 ± 304.4	244.0 ± 118.3	ns	-	-	-
Terpenes								
t-Rose oxide	1369	0.2[f]	50.8 ± 18.5	18.9 ± 7.1	*	6.8 ± 1.7	9.5 ± 2.9	ns
t-Linalool oxide	1465	>3000[g]	33.1 ± 8.9	22.4 ± 6.3	ns	0.1 ± 0.1	0.1 ± 0.1	ns
Geranyl ethyl ether	1528	-	459.8 ± 17.7	267.2 ± 23.7	***	nd	nd	-

Linalool	1565	25.2[d]	937.0 ± 51.5	607.8 ± 46.9	**	68.5 ± 3.9	69.0 ± 3.8	ns
Hotrienol	1627	110	460.3 ± 32.0	449.4 ± 48.0	ns	15.0 ± 1.5	9.1 ± 2.9	ns
2,6-Dimethyl-2,6-octadiene	1680	-	20.4 ± 7.5	3.8 ± 4.2	*	nd	nd	-
Z-3,7-Dimethyl-2,6-octadienal	1699	-	0.3 ± 0.1	0.3 ± 0.1	ns	8.6 ± 4.9	18.4 ± 1.0	***
α-Terpineol	1720	250[d]	134.7 ± 116.8	118.2 ± 11.1	ns	5.8 ± 0.1	2.5 ± 3.3	ns
3,7-Dimethyl-1,5,7-octatriene	1750	-	460.5 ± 32.0	449.6 ± 47.9	ns	15.0 ± 1.5	9.1 ± 3.0	ns
Citronellol	1785	100[f]	135.7 ± 48.2	177.9 ± 17.1	ns	23.6 ± 12.7	9.2 ± 1.7	ns
Nerol	1814	300[g]	9.1 ± 8.4	11.1 ± 9.5	ns	453.8 ± 30.7	262.0 ± 12.2	*
	1848	30[d]						
Geraniol			38.7 ± 5.4	36.0 ± 22.1	ns	606.7 ± 41.8	394.7 ± 18.8	*
Σ Terpenes			2740.4 ± 283.5	2162.6 ± 180.5	*	1203.9 ± 91.5	783.6 ± 68.7	*
Norisoprenoids								
TDN	1764	-	33.2 ± 4.2	84.8 ± 11.2	**	nd	nd	-
β-Damascenone	1830	0.05[d]	34.3 ± 8.7	92.3 ± 10.0	**	nd	nd	-
Σ Norisoprenoids			67.5 ± 9.9	177.2 ± 20.0	**	-	-	-
Σ Volatile compounds			98119.8 ± 1822.3	69005.1 ± 4978.8	***	1349.4 ± 97.5	916.6 ± 55.7	*

[a]All data are expressed as average value ± standard deviation (n = 3). [b]*Sign.*: *, **, *** and ns indicate significance at $p<0.05$, 0.01, 0.001 and not significant, respectively, among fast and slow dehydration processes. [c]nd = not detected. [d]Ferreira et al. (2000), [e]Etiévant (1991), [f]Guth (1997), [g]Fenoll et al. (2009).