

AperTO - Archivio Istituzionale Open Access dell'Università di Torino

**Influence of different thermohygrometric conditions on changes in instrumental texture properties and phenolic composition during postharvest withering of Corvina winegrapes (*Vitis vinifera* L.).**

**This is the author's manuscript**

*Original Citation:*

*Availability:*

This version is available <http://hdl.handle.net/2318/121951> since 2016-07-05T08:35:08Z

*Published version:*

DOI:10.1080/07373937.2012.745092

*Terms of use:*

Open Access

Anyone can freely access the full text of works made available as "Open Access". Works made available under a Creative Commons license can be used according to the terms and conditions of said license. Use of all other works requires consent of the right holder (author or publisher) if not exempted from copyright protection by the applicable law.

(Article begins on next page)



# UNIVERSITÀ DEGLI STUDI DI TORINO

***This is an author version of the contribution published on:***

*Questa è la versione dell'autore dell'opera:*

***Dry. Technol.,31, 549-564; dx.doi.org/10.1080/07373937.2012.745092***

***The definitive version is available at:***

*La versione definitiva è disponibile alla URL:*

***[<http://www.tandfonline.com/doi/abs/10.1080/07373937.2012.745092#.VImpbnvQP68>]***

**Influence of Different Thermohygrometric Conditions on Changes in Instrumental Texture Properties and Phenolic Composition During Postharvest Withering of Corvina Winegrapes (*Vitis vinifera* L.)**

L. Rolle<sup>#a</sup>, S. Giacosa<sup>#a</sup>, S. Río Segade<sup>a</sup>, R. Ferrarini<sup>b</sup>, F. Torchio<sup>a</sup>, and V. Gerbi<sup>a</sup>

<sup>#</sup> These authors contributed equally to the study.

<sup>a</sup> *Università degli Studi di Torino, Dipartimento di Scienze Agrarie, Forestali e Alimentari, Via Leonardo da Vinci 44, 10095 Grugliasco (TO), Italy.*

<sup>b</sup> *Università degli Studi di Verona, Dipartimento di Biotecnologie, Strada delle Grazie 15, 37100 Verona, Italy.*

**Contact information for Corresponding Author**

Corresponding author: Susana Río Segade

Email: susana.riosegade@unito.it

Tel.: +39 011 6708558

Fax: +39 011 6708549

## Running title: Withering condition affects grape characteristics

### ABSTRACT

Corvina winegrapes were postharvest withered under three controlled thermohygrometric conditions. Sampling was done at different days of withering and the mechanical properties, technological ripeness parameters, phenolic composition and anthocyanin profile were determined. Depending on the condition, skin break force and pedicel detachment force significantly decreased during the dehydration process with a maximum variation of  $-0.258$  and  $-1.306$  N, respectively. Instead, total flavonoids of skin and seeds, and proanthocyanidins and low weight flavanols of seeds increased with a maximum variation of  $+1483$ ,  $+733$ ,  $+1022$  and  $+469$  mg/kg, respectively. The skin hardness was confirmed as an important parameter for the dehydration kinetics.

**Keywords:** Postharvest withering; Phenolic composition; Controlled thermohygrometric conditions; Instrumental texture analysis; cv Corvina (*Vitis vinifera* L.)

## INTRODUCTION

Secondary metabolites that strongly contribute to aroma, taste and color of grape berries are synthesized during ripening, and the quality of grape berries to be dehydrated is highly dependent on the cultivar genotype, environmental conditions and cultural practices.<sup>[1]</sup> In winegrapes, the dehydration process is promoted in the elaboration of dessert wines, either sweet wines (“Passito wines”) or dry wines with special aroma,<sup>[2,3]</sup> which are made with dehydrated berries. Sun exposure is still the most traditional and widely used method for dehydrating winegrapes in sunny Mediterranean regions. However, its typical disadvantages, like unstable weather conditions, environmental contamination, insect infestation, growth of fungi producing toxins, severe embrowning and manual labor requirements,<sup>[4-7]</sup> must be overcome by the use of alternative techniques, like hot air drying<sup>[8,9]</sup> and more recently microwave vacuum drying.<sup>[10]</sup> The epicuticular wax layers of the berry skin act as physical barriers that can delay water loss by evaporation. Chemical pretreatments with ethyl or methyl ester emulsions, and diluted alkaline solutions of sodium hydroxide or potassium carbonate, normally break down this epicuticular wax inducing microstructural changes that increase the skin permeability, the moisture diffusion and therefore the dehydration rates, whereas ethylene induces the cell wall degradation by acting on enzymes.<sup>[4,11-13]</sup> Nevertheless, these grape pretreatments are not always appreciated with winemaking purposes owing to quality and technological reasons.<sup>[14]</sup>

During postharvest grape dehydration, important metabolic changes occur as a consequence of water loss evidencing an active metabolism that affects the chemical composition and the physical properties.<sup>[15]</sup> The extension of these changes mainly depends on the grape cultivar, the maturity stage and the dehydration technique employed.<sup>[2,16]</sup> Withering temperature plays a key role because it affects not only the rate of water evaporation but also the main grape metabolism.<sup>[17-19]</sup> The juice is concentrated within the berry increasing its content in sugars and volatile compounds.<sup>[2,20-23]</sup> Phenol compound families are differentially affected by the management of postharvest grape dehydration,<sup>[17,18,24]</sup> and the volatile profile also changes during the dehydration process depending on the water stress conditions.<sup>[19,20,22,25]</sup> Therefore, the composition of the berries can be partly modulated when the dehydration process is carried

out under a strict control of relative humidity, temperature and ventilation. Many withering metabolic pathways are already activated during ripening, which evidences the added value of grape withering as an industrial practice to make quality wines having unique and appreciated characteristics.<sup>[26]</sup>

In general, winemakers monitor the dehydration process according to water loss and/or the sugar concentration, which could compromise the aromatic and phenolic quality of the grapes.<sup>[27]</sup> In particular, thermally processed biomaterials support a texture degradation closely related to enzymatic and non-enzymatic changes in the cell wall pectin.<sup>[28]</sup> Therefore, the dehydration process induces texture changes in the fruit,<sup>[28-30]</sup> which depend on the dehydration rate.<sup>[17,18,31]</sup> Because the skin acts as a semipermeable membrane that controls the water transfer rate from the fruit to the external medium,<sup>[32]</sup> the skin texture parameters together with the peduncle detachment resistance are already considered efficient indicators of the winegrape suitability for on-vine withering.<sup>[33,34]</sup> However, the evolution of the mechanical properties of winegrapes during postharvest withering under controlled thermohygrometric conditions has been scarcely evaluated. In red winegrape varieties, the quality of the skin is of primary concern because this tissue is undoubtedly one of the main sources of phenolic compounds. Furthermore, the skin hardness of fresh berries is a reliable predictive index of the skin anthocyanin extractability,<sup>[35,36]</sup> affects the extraction kinetics of individual anthocyanins,<sup>[35]</sup> and also influences the grape dehydration rate.<sup>[37,38]</sup>

On the base of all these considerations, the aims of this work were: i) to study the effect of different controlled thermohygrometric conditions of withering on the evolution of the mechanical properties of the pedicel, skin and whole berry; ii) to assess the impact of these conditions on the anthocyanin and tannin composition during the off-vine withering process of red winegrapes; and finally iii) to value the importance of the skin break force of the fresh berries in the dehydration kinetics and in the phenolic profile of the dehydrated grapes.

The study was carried out on the Corvina cultivar (*Vitis vinifera* L.) that is used in Italy for the production of Amarone dry red wine from withered grapes, one of the most important Italian wine commercialized in all the world.<sup>[3]</sup> This work could suppose an important advance in the fast detection of

the metabolic changes occurring during grape dehydration, which can help the winemaker in making decisions on the management of the off-vine withering process to make wines of high phenolic quality.

## **MATERIALS AND METHODS**

### **Grape Sampling and Dehydration Process**

Grape clusters of the Corvina red cultivar (*Vitis vinifera* L.) were randomly sampled from different plants in an experimental vineyard located in the Valpolicella growing zone (Verona, North-East Italy).

In 2008, the sample consisted of about 110 kg of grape berries. The clusters were visually inspected before dehydration, and those with damaged berry skins were discarded. Three batches of clusters (35 kg of grape berries) were randomly selected and placed in perforated boxes (60 × 40 × 15 cm, 5 kg of grape berries in each box) in a single layer for correct aeration. Each batch was subjected to different withering conditions of temperature and relative humidity (RH) in a thermohygrometrically controlled chamber. The first batch was subjected to 15° C and 45% RH (withering condition A). The second batch was treated at 8° C and 45% RH (withering condition B). The third one was dehydrated at 15° C and 80 % RH (withering condition C). In any case, the withering conditions were fixed by the winery, which can be correctly controlled in the chamber. The air speed used was always 0.9m/s.<sup>[37]</sup> For the fresh sample ( $F_0$ ) and for each batch after 15 and 45 days of withering ( $A_{15}$ ,  $A_{45}$ ,  $B_{15}$ ,  $B_{45}$ ,  $C_{15}$ ,  $C_{45}$ ), three sets of 250 berries with attached pedicels were randomly selected and weighed. One subsample of 25 berries was used for the determination of the skin mechanical properties. One subsample of 25 berries was used for the determination of the whole berry mechanical properties. One subsample of 25 berries was used for the determination of the peduncle detachment resistance. Other three subsamples of 10 berries were used for the determination of phenolic compounds. The remaining berries, subdivided in three replicates, were used

for determining the standard physicochemical parameters in the grape must obtained by manual crushing and centrifugation.<sup>[33]</sup>

In 2009, in order to respond to the aim iii), all the berries of each cluster (n = 25) were manually separated from the stalk maintaining attached pedicels, sorted according to their density by flotation in different saline solutions (from 130 to 160 g/L sodium chloride, corresponding to densities comprised between 1082 and 1100 kg/m<sup>3</sup>),<sup>[39]</sup> and those containing 230 ± 8 g/L sugars were selected. This densimetric sorting permits obtaining more homogeneous samples and minimizing the effect of different ripening stages of grape berries. The sorted berries were washed with water and visually inspected; those with damaged skins were discarded. Six sets of 42 densimetric sorted fresh berries each (F<sub>0</sub>), randomly selected, were classified in two groups according to their skin hardness (soft, S and hard, H). Each berry class defined by the skin hardness was placed in the perforated boxes and subjected to the dehydration process in the controlled chamber at the withering condition C. In this case, the weight of 100 berries, phenolic compounds and the standard physicochemical parameters were determined for each berry class before withering (F<sub>0</sub>) and after 10, 20 and 30 days of withering (C<sub>10</sub>, C<sub>20</sub>, C<sub>30</sub>), following the methodology above mentioned.

All fresh grape clusters were weighed before their introduction in the withering cell to determine the average weight of the cluster. The weight was also measured during the withering process at different times by means of a technical balance (Gibertini E1700, Modena, Italy), and the weight loss percentage (WL%) was calculated as  $[100 - (\text{weight of withered samples} \times 100 / \text{weight of fresh sample})]$ .<sup>[37]</sup>

### **Instrumental Texture Analysis**

For instrumental texture analysis, an Universal Testing Machine (UTM) TAxT2i Texture Analyzer (SMS-Stable Micro System, Godalming, Surrey, UK) equipped with a HDP/90 platform was used. All the data were acquired at 400 Hz and evaluated using the Texture Expert Exceed software, version 2.54 for Windows 2000. All measurements were performed in the same day as picking from either the vineyard or

the withering chamber to avoid changes. Before each test session, the instrument was calibrated for force and distance, and each subsample of 25 berries, arranged as a single layer, was thermally conditioned for 1 hour at 20°C in a thermostatically controlled chamber.

The berry skin hardness was assessed by a puncture test using a SMS P/2N needle probe, a 5 kg load cell, a test speed of 1 mm/s and a penetration applied of 3 mm.<sup>[40]</sup> In 2008, each one of the 25 berries was individually punctured in the lateral face and three parameters were measured: skin break force (N, as  $F_{sk}$ ), skin break energy (mJ, as  $W_{sk}$ ) and skin Young's modulus of elasticity (N/mm, as  $E_{sk}$ ). The first variable corresponds to the skin resistance to the needle probe penetration while the second variable is represented by the area under the force/time curve, which is limited between 0 and  $F_{sk}$ .<sup>[40]</sup> The third one is defined as the slope of the stress/strain curve in the linear section and measures the stiffness of the skin to a load applied. The use of needle probe allows separate estimation of this skin mechanical characteristic, minimizing the possible interferences caused by the pulp firmness on the results. For dehydration purposes, the microhole caused by the needle probe penetration was closed with a microdrop of natural resin to avoid interferences in the withering process.<sup>[37]</sup>

The measurement of the berry skin thickness ( $\mu\text{m}$ , as  $Sp_{sk}$ ) required manual separation of a piece of skin (ca. 0.25 cm<sup>2</sup>) from the lateral side of each berry with a razor blade, followed by drying with absorbent paper. The test was carried out using a 2 mm SMS P/2 flat cylindrical probe and a test speed of 0.2 mm/s.<sup>[40]</sup> The berry skin thickness is calculated as the distance between the point corresponding to the probe contact with the berry skin (trigger) and the platform base during the compression test.<sup>[40]</sup> Care was taken when removing the pulp from the skin and when positioning the skin sample on the UTM platform to prevent folding.<sup>[40]</sup> Furthermore, the insertion of an instrumental trigger threshold equal to 0.05 N enabled the plane surface of the probe to adhere completely to the skin sample before the acquisition began. It allowed a reduction or even elimination of the 'tail' effect due to the postponement of the contact point.<sup>[40]</sup>

For the Texture Profile Analysis (TPA) or double compression test, each one of the 25 whole berries was compressed in the equatorial position with a 35 mm SMS P/35 flat cylindrical probe under 25%

deformation, with a waiting time of two seconds between the two bites and a test speed of 1 mm/s.<sup>[40]</sup> Typical berry mechanical parameters that define the whole berry texture characteristics, *i.e.* hardness (N, as BH), cohesiveness (adimensional, as BCo), gumminess (N, as BG), springiness (mm, as BS), chewiness (mJ, as BCh) and resilience (adimensional, as BR), were calculated by the software.<sup>[40]</sup> In this type of compression test, the influence of the pulp and skin properties on the mechanical characteristics of berries is aggregate.<sup>[41]</sup> The berry diameter was calculated as the distance between the whole berry trigger point and the platform base. Since some TPA parameters can be influenced by the berry size, they were also normalized according to the respective berry diameter ( $d_{norm}$ ) expressed in mm.<sup>[42]</sup>

The peduncle detachment resistance was determined by a traction test carried out at 1 mm/s.<sup>[33,43]</sup> In this test, the peduncle is anchored to the pliers of the SMS A/PS probe modified with a rigid arm. During the traction, the peduncle passes through the perforated platform of the UTM (hole diameter of 5 mm), while the berry is blocked permitting the determination of the peduncle detachment maximum force (N, as  $F_{ped}$ ). The peduncle detachment energy (mJ, as  $W_{ped}$ ) is represented by the area under the force/time curve, which is limited between 0 and  $F_{ped}$ .<sup>[43]</sup>

## Chemical Analysis

Reagents and Standards. Solvents of HPLC-gradient grade and all other chemicals of analytical-reagent grade were purchased from Sigma (Milan, Italy). The solutions were prepared in deionized water produced by a Purelab Classic system (Elga Labwater, Marlow, United Kingdom). Phenol standards ((+)-catechin, cyanidin chloride, delphinidin-3-O-glucoside chloride, malvidin-3-O-glucoside chloride, petunidin chloride, peonidin-3-O-glucoside chloride, cyanidin-3-O-glucoside chloride) were supplied from Extrasynthèse (Genay, France). Anthocyanin standards were stored at -20° C away from light before use.

Technological Ripeness Parameters. Total soluble solids concentration (°Brix, as SSC) was measured with an Atago 0–32 °Brix temperature compensating refractometer (Atago Corporation, Tokyo, Japan), and pH was determined by potentiometry using a Crison electrode (Carpi, Italy). Titratable acidity (TA), expressed as g/L tartaric acid, was estimated using the International Organization of Vine and Wine (OIV) method.<sup>[44]</sup> Gluconic acid was determined (as g/L) using an enzymatic test kit from R-Biopharm Italia (Cerro al Lambro, MI, Italy) and an UV-1601 spectrophotometer (Shimadzu, Japan). Organic acids (malic acid and tartaric acid) and glycerol were quantified (as g/L) using a P100-AS3000 HPLC system (Thermo Electron Corporation, Waltham, MA, USA), equipped with an UV detector (UV3000) set to 210 nm. The analyses were performed isocratically at 0.8 mL/min flow-rate and 65° C column temperature with a 300 × 7.8 mm i.d. Aminex HPX-87H cation exchange column and a Cation H<sup>+</sup> Microguard cartridge (Bio-Rad Laboratories, Hercules, CA, USA). The mobile phase was 0.0013 mol/L H<sub>2</sub>SO<sub>4</sub>.<sup>[45]</sup> The data analysis was carried out using the ChromQuest chromatography data system (ThermoQuest, Inc., San Jose, CA, USA).

Phenol Extraction and Determination. The berry skins (<sub>sk</sub>) and seeds (<sub>s</sub>) were manually removed from the pulp using a laboratory spatula and dried with absorbent paper. The berry skins were quickly immersed in 25 mL of a hydroalcoholic buffer at pH 3.2 containing 5 g/L tartaric acid, 2 g/L Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub> and 12% v/v ethanol. Afterwards, the skins were homogenized with an Ultraturrax T25 high-speed homogenizer (IKA Labortechnik, Staufen, Germany) and centrifuged in a PK 131 centrifuge (ALC International, MI, Italy) for 5 min at 3000 × *g* at 20° C. The supernatant was then used for analysis. The berry seeds, after immersion in 10 mL of the same buffer solution used for skins, were placed in a controlled temperature room at 25° C for one week. Spectrophotometric methods were used to determine total anthocyanins (mg malvidin-3-O-glucoside chloride/kg grape, as TA) in the skin, and total flavonoids (mg (+)-catechin/kg grape, as TF), proanthocyanidins (mg cyanidin chloride/kg grape, as PRO) and flavanols reactive to vanillin (mg (+)-catechin/kg grape, as FRV) in the skin and seeds.<sup>[46]</sup> An UV-1800 spectrophotometer (Shimadzu Scientific Instruments Inc., Columbia, MD, USA) was used. The relative standard deviation (RSD) based on repeated analysis (n = 10) of the same sample was 1.14, 0.93, 1.74 and 2.80% for TA, TF, PRO and FRV, respectively.

Anthocyanin Profile. An anthocyanin profile was performed after the berry skin extract had been submitted to solid-phase extraction using a SEP-PAK C<sub>18</sub> cartridge (Waters Corporation, Milford, MA, USA), methanol being the eluent. The chromatography system employed was a P100 pump equipped with an AS3000 autosampler (Spectra Physics Analytical, Inc., San Jose, CA, USA), a 20 µL Reodyne sample loop, a LiChroCART analytical column (25 cm × 0.4 cm i.d.) purchased from Merck (Darmstadt, Germany), which was packed with LiChrospher 100 RP-18 (5 µm) particles supplied by Alltech (Deerfield, IL, USA), and a Spectra Focus diode array detector (DAD, Spectra Physics Analytical, Inc.) operating at 520 nm. The following mobile phases were used: A = formic acid/water (10:90, v/v); B = formic acid/methanol/water (10:50:40, v/v). All of the solvents were filtered through a 0.20 µm filter. The mobile phase flow-rate was 1 mL/min. The following solvent A proportions were used: from 72 to 55%, 15 min; to 30%, 20 min; to 10%, 10 min; to 1%, 5 min; to 72%, 3 min. An equilibrium time of 10 min was selected.<sup>[33]</sup> The data treatment was carried out using the ChromQuest chromatography data system (ThermoQuest, Inc.). The identification of the free forms of anthocyanins in berry skin extracts was performed by comparison with external standards. The acylated forms of anthocyanins were identified by matching the DAD spectrum and retention time of each chromatographic peak, and by comparing these with data available in the literature.<sup>[47]</sup> Individual anthocyanins were expressed in percentages.

### **Statistical Analysis**

Statistical analyses were performed using the SPSS software package version 17.0 for Windows (SPSS Inc., Chicago, IL, USA). The Tukey-b test for  $p < 0.05$  was used in order to establish statistical differences by one-way analysis of variance (ANOVA) in the mechanical properties and the chemical composition during the grape dehydration process. Pearson's correlation coefficients were calculated to determine significant relationships between the parameters determined and the weight loss during grape withering.

## RESULTS AND DISCUSSION

### Dehydration kinetics

Figure 1 showing the evolution of the weight loss percentage (WL%) due to grape dehydration during the postharvest withering process under three controlled environmental conditions (A, B, C). The Corvina cultivar evidenced a WL% of 31.8, 18.5 and 15.9 after 45 days of withering under the environmental conditions A, B and C, respectively, which corresponds to a daily average WL% of 0.71, 0.41 and 0.35, respectively. This agreed with a previously published work, where this grape variety reached a daily average WL% of 0.78 at 16° C and 60% RH.<sup>[38]</sup> At higher temperatures, the daily average WL% was 1.60 (25° C, 53% RH)<sup>[48]</sup>, 0.80 (25° C, 75% RH)<sup>[48]</sup>, 1.73 (28° C)<sup>[49]</sup> and 7.11 (45° C)<sup>[49]</sup>. The moisture diffusion coefficients increase with increasing temperature and decreasing RH, similar to the changes that occur in the moisture content.<sup>[48]</sup> As can be observed in Figure 1, the highest temperature and the lowest RH (A, 15° C, 45% RH) caused the fastest WL% of Corvina grape berries, while the slowest WL% was associated with the withering condition C (15° C, 80% RH).

### Evolution of instrumental mechanical properties during withering

The effect of different controlled thermohygrometric conditions on the evolution of the instrumental texture parameters during the postharvest withering process of red winegrape berries is shown in Table 1. The heterogeneity of the grape berries as a consequence of the inhomogeneous grade of ripeness and/or of dehydration determines the variability of the results obtained. Despite this variability, the evolution was strongly supported. At 15 days of withering, the highest values of the mechanical properties of the berry skin, pedicel and whole berry were found for the environmental condition B<sub>15</sub>. These texture parameters of the whole berry agreed with those obtained using the withering condition C<sub>15</sub>,

excepting for  $BG_{norm}$  and  $BCh_{norm}$  with significantly higher values under the withering condition  $B_{15}$ . No significant difference was evidenced in the values of  $Sp_{sk}$  and  $BS$  for the grapes withered under the three conditions tested. After 45 days of withering, no significant difference was also observed in the parameters defining the skin hardness ( $F_{sk}$ ,  $W_{sk}$ ) and the skin stiffness ( $E_{sk}$ ) among the different withering conditions studied, whereas the values of  $Sp_{sk}$  were significantly lower for the grapes withered under the environmental condition  $A_{45}$ . Among the peduncle mechanical properties, only  $W_{ped}$  showed significant differences, particularly among the withering conditions  $A_{45}$  and  $C_{45}$ . Regarding the texture parameters of the whole berry, the significantly higher values corresponded to the withering condition  $C_{45}$ , excepting for  $BS$ , although they agreed with those obtained using the withering condition  $A_{45}$  for  $B_{Co}$ ,  $BR$  and  $BS_{norm}$ .

In general, the instrumental texture parameters significantly decreased during the withering process under any environmental condition tested, and the differences were more evident for the mechanical properties of the whole berry, particularly for  $BH$ ,  $BG$ ,  $BCh$ ,  $BH_{norm}$ ,  $BG_{norm}$  and  $BCh_{norm}$ . Some mechanical properties were negatively correlated with the  $WL\%$  during withering corresponding the stronger correlations to  $E_{sk}$ ,  $BH$ ,  $BG$ ,  $BH_{norm}$ ,  $BG_{norm}$  and  $BCh_{norm}$  (Pearson's correlation coefficient: 0.884-0.918,  $p < 0.01$ ), although other significant correlations were also found for  $F_{sk}$ ,  $Sp_{sk}$ ,  $BCh$  and  $BR$  (Pearson's correlation coefficient: 0.798-0.869,  $p < 0.05$ ).

Some studies have been recently carried out on the modifications of the mechanical characteristics of Mondeuse, Becuét and Fumin red winegrapes throughout the on-vine drying process in winter season.<sup>[33,34]</sup> The skin hardness and the skin thickness progressively increased during on-vine withering, particularly for the Becuét cultivar ( $F_{sk} +0.148$  N,  $W_{sk} +0.823$  mJ,  $Sp_{sk} +73$   $\mu$ m). Instead, as occurred for Corvina winegrapes, the skin stiffness and the resistance to shattering showed an inverse behaviour ( $E_{sk} -0.300$  N/mm,  $F_{ped} -1.20$  N,  $W_{ped} -0.600$  mJ). Xiao et al.<sup>[31]</sup> evidenced that drying temperature significantly affected the hardness of Monukka seedless grapes during the postharvest drying process in a hot-air impingement dryer. In fact, an increasing trend was observed as drying temperature increased from 55 to 65° C. However, no significant difference was found in the hardness of the grapes dried at different air velocities ranging from 3 to 9 m/s, and constant temperature. This grape hardening could be due to the use

of high drying temperature that involves faster water removal rate from the surface than the water migration rate from the interior of the berry. Therefore, a hard layer, containing previously dissolved solutes, is formed on the surface. Muganu et al.<sup>[1]</sup> also reported an increase in the skin resistance to puncturing during postharvest dehydration of Trebbiano toscano and Rossetto grapes at 20° C and 45% RH. Contrarily, during the off-vine withering process of Corvina winegrapes, the skin and the whole berry tended to soften, but the behaviour of the skin thickness was rather irregular. These results agreed with the postharvest changes in the fruit structure and texture like softening induced by air drying.<sup>[29]</sup>

Water loss causes reduced cell turgor that results in a down-regulation of enzymes involved in the cell wall dynamic depolymerization.<sup>[26]</sup> During the first phase of withering, the biochemical changes affecting cell expansion are inhibited, although a new accumulation of cell wall enzymes is induced in the late withering by mechanical stress factors. These require an adaptive modification as a consequence of tissue tensile strength or flexibility changes.<sup>[26]</sup> Since the berry hardness is basically determined by the vacuole turgidity, reduced cell turgor requires lower rupture force.<sup>[50]</sup> This fact could explain the results obtained for the Corvina cultivar.

Although the texture degradation of thermally processed biomaterials is closely related to enzymatic and nonenzymatic changes in the cell wall pectin,<sup>[26,28]</sup> the main question is whether these changes are varietal dependent and/or withering condition dependent. The withering thermohygro-metric conditions affect the dehydration kinetics, but the same treatment does not induce the same effect on different winegrape varieties. The values of surface/volume ratio and  $F_{sk}$  markedly affected the withering kinetics.<sup>[38,48]</sup> This varietal effect on the dehydration kinetics could be explained by differences in the number of small thick-walled cell layers in the berry skin, their size and volume, which are cultivar specific issues.<sup>[1]</sup>

The berry skin acts as a protective barrier against fungal disease, protects the grape from ultraviolet (UV) light and physical injuries, and regulates the gas exchange between the berry and the surrounding environment.<sup>[51,52]</sup> In addition, the hydrophobic properties of the epicuticular wax coating reduce the

moisture diffusion by transpiration during grape withering. Moisture diffusion coefficients of the withered grapes used for winemaking purposes are lower (1-2 orders of magnitude) than those found in the literature for the dried grapes involved in raisin production processes,<sup>[10,53,54]</sup> where the grapes are chemically or physically pretreated to remove the epicuticular wax layer, and therefore to increase the moisture diffusivity.<sup>[4]</sup> Furthermore, the effective moisture diffusivity is also different for sun dried seeded and seedless grapes with values 1.6 times higher for the last ones.<sup>[55]</sup>

### **Changes in grape chemical composition during withering**

The marked physical changes were accompanied by chemical modification during postharvest dehydration of grape berries, because the berries are also metabolically reactive to water stress after harvest. Regarding the technological ripeness parameters of Corvina winegrapes shown in Table 2, the lowest weight of the berries corresponded to the environmental condition A at 15 and 45 days of withering. This environmental condition was prone to faster grape dehydration (higher temperature and lower RH) enabling a higher concentration of the juice components, excepting for tartaric acid after 45 days of withering. However, the differences found in the technological ripeness parameters determined in the must from the grapes withered under the environmental condition A were not always significant, if compared with B and C conditions. During the postharvest dehydration process, the berry weight decreased, and the richness of the juice components increased, excepting for malic acid that evidenced the inverse trend. This significant decrease in the content of malic acid during grape dehydration was more important for the withering condition B, followed by the C, probably due to the shift from harvest temperature down to 8° C, and from harvest RH up to 80%, respectively.<sup>[19]</sup> Using the environmental condition A, this decrease was not significant. As occurred for Erbaluce grapes,<sup>[37]</sup> no dependence of malic acid pattern on total acidity was observed in this study, but it exists with tartaric acid pattern (Pearson's correlation coefficient: 0.785,  $p < 0.01$ ). It is important to indicate that the grapes dehydrated under the environmental condition B contains the lowest concentration of gluconic acid and glycerol. In any way, the

low content of these two compounds confirmed no presence of *Botrytis cinerea* noble rot in the withered berries. During withering, total acidity and soluble solid content were strongly and positively correlated with the WL% (Pearson's correlation coefficient: 0.974 and 0.985, respectively,  $p < 0.001$ ). Other significant correlation with the WL% was also found for the content of tartaric acid (Pearson's correlation coefficient: 0.794,  $p < 0.05$ ).

### **Modifications in grape phenolic composition during withering**

The effect of different controlled thermohygro-metric conditions on the evolution of the phenolic composition during the postharvest withering process of red winegrape berries is shown in Table 3. Regarding the reached content of phenolic compounds in the berry skin and seeds at different environmental conditions after the same withering time, significant differences were only found in phenolic compounds determined in berry seeds ( $TF_s$ ,  $PRO_s$  and  $FRV_s$ ) after 45 days of withering with significantly higher contents for the environmental condition A. The same behavior was also observed at 15 days of withering, but the differences were not significant. During the postharvest dehydration process, the content of  $TF_{sk}$ ,  $TF_s$ ,  $PRO_s$  and  $FRV_s$  increased at the three environmental conditions tested, excepting for  $FRV_s$  at the withering condition C. This was also evidenced in the significant correlations found among these contents and the WL% (Pearson's correlation coefficient: 0.878-0.936,  $p < 0.01$  for  $TF_{sk}$ ,  $TF_s$ ,  $PRO_s$ , and 0.782,  $p < 0.05$  for  $FRV_s$ ). Instead, the content of  $PRO_{sk}$  and  $FRV_{sk}$ , after an initial decrease at 15 days of withering, increased at 45 days. However, the changes in the phenolic composition during dehydration of Corvina winegrapes were not ever significant, and the environmental condition A led to major changes. At the end of the withering process, phenolic compounds maintained similar or even significantly higher contents in the withered grapes than the fresh ones, excepting for  $FRV_{sk}$ , which may ensure a good protection of the phenolic fraction against strong oxidations.

Little information is available in the scientific literature about the effects of grape dehydration on the secondary metabolites like phenolic compounds. Serratosa et al.<sup>[6]</sup> suggested that the effect induced by

the postharvest dehydration process is a balance between concentration, hydrolysis and oxidation processes, but Mencarelli et al.<sup>[17]</sup> added that this response depends on temperature and water loss. A work showed that the content of flavonoids, anthocyanins, catechins and proanthocyanidins in the Corvina skin slightly decreases under mixed withering (45° C for 36 h, and then uncontrolled conditions for 94 days), whereas it remains almost stable using the other three withering conditions tested (uncontrolled conditions for 100 days, 28° C for 15 days, 45° C for 110 h).<sup>[49]</sup>

Because of high dispersion of data, the postharvest dehydration process of Corvina winegrapes had no effect on the content of  $TA_{sk}$ , which agreed with other works on Raboso piave, Pinot noir and Cesanese grapes.<sup>[18,24,25]</sup> The best temperature for maintaining  $TA_{sk}$  until the berries reach a WL% of 40 % is 10° C.<sup>[17]</sup> Monomeric and oligomeric flavanols of the berry skin usually showed a progressive decrease in their abundance during grape withering, associated with an increase in water loss.<sup>[24,33,56]</sup> In fact, rapid dehydration is generally effective in delaying the reduction in the concentration of flavanols.<sup>[24]</sup> However, the contradictory results reported for different cultivars at the same WL% confirm a genotype effect.<sup>[17,18]</sup> Therefore, these compounds may undergo degradation reactions that overcome the concentration effect resulting from the water evaporation during withering and the hydrolysis of larger oligomers. As occurred in other studies,<sup>[24,33,56]</sup> this decrease in the content of skin low molecular weight flavanols was paralleled by a reduction in the content of skin proanthocyanidins. Contrarily, our results differed from those reported for the content of  $TF_{sk}$ . In overripe Rossetto ("*Roschetto*") and ripe Trebbiano grapes, the content of total flavonoids in the berry skin slightly decreased during the postharvest dehydration process under controlled environmental conditions (18-21° C, 68% RH for 16 days, and 20° C for 9 days, respectively),<sup>[56,57]</sup> whereas the content of these last compounds in berry seeds was similar to that of the fresh grapes.<sup>[56,57]</sup> In the seeds, an increase in both proanthocyanidins and flavanols was also evidenced during the on-vine withering process of Mondeuse grapes.<sup>[33]</sup>

An important aspect to take into account is the increased contribution of tannins from the seeds to total content in the withered grapes, if compared with that in the fresh ones, particularly at the environmental condition A. This fact has a notable influence on the future sensorial properties of red wines

made with maceration, particularly astringency and bitterness. During maceration, phenolic compounds are extracted from the solid parts of the grapes to the must/wine.

Table 4 shows the anthocyanin profile for Corvina winegrapes at harvest and during the postharvest dehydration process at different controlled thermohygrometric conditions. As can be seen, nonacylated glucosides were the most abundant anthocyanin forms in all the fresh and withered samples, particularly malvidin and peonidin forms, followed by cinnamoyl glucosides. At the same withering time, the most significant differences ( $p < 0.001$ ) corresponded to peonidin and malvidin derivatives. In particular, the results show an increase in the percentage of peonidin derivatives and a decrease in that of malvidin derivatives for the environmental condition A. However, no significant correlation was found among the percentages of anthocyanin compounds and the WL%. According to Marquez et al.,<sup>[58]</sup> off-vine withered red grapes led to musts strongly enriched in anthocyanins as a likely consequence of the disruption of the inner skin layers and the anthocyanins diffusion to the pulp. Furthermore, the postharvest withering process modified the membrane permeability of the grapes through the activation of lipoxygenase enzyme (LOX), and involved a change in the intracellular metabolism from aerobic to anaerobic with the consequent activation of alcohol dehydrogenase enzyme (ADH).<sup>[21,22]</sup> The presence of pyruvic acid, acetaldehyde and ethanol in the musts from the dehydrated grapes was explained by the occurrence of enzymatic reactions. These compounds were the precursors in the formation of stable anthocyanin-derived compounds like pyranoanthocyanins and methyldimine bonded anthocyanin-flavanol condensation adducts.

### **Changes in phenol extractability indexes during withering**

In red winemaking, the skin thickness ( $Sp_{sk}$ ) is an useful tool for predicting the anthocyanin extractability from the berry skin to the must/wine.<sup>[59]</sup> The thinner skins seem to be characterized by a greater release of red pigments. Instead, the harder skins have faster extraction kinetics of anthocyanins.<sup>[35]</sup> At the end of the postharvest withering process, the skins of grapes dehydrated under the environmental

condition A were thinner than those of fresh grapes (Table 1), indicating a probably greater release of anthocyanins for Corvina winegrapes after the fastest dehydration tested. However, the skins of dehydrated grapes were softer than those of fresh grapes (Table 1), and therefore slower extraction kinetics of anthocyanins is expected after withering at any environmental condition. In the early stages of maceration, peonidin and cyanidin derivatives are preferentially extracted, which are less protected against oxidation than molecules trisubstituted in the B-ring.<sup>[35]</sup> After 45 days of withering, the withered grapes resulting from the use of the environmental condition C exhibited the lowest percentage of these two anthocyanin compounds (similar to the fresh grapes) (Table 4), which suggests lower degradation of red pigments during the maceration step. The stability could be reinforced as a likely consequence of the lowest percentage of nonacylated glucosides, and the highest one of cinnamoyl glucosides, induced by the use of this last withering condition (Table 4).

An accurate control of the withering environmental conditions provides a key tool to manage the evolution of phenolic compounds. On the basis of the above results, the withering process conducted under the environmental condition C allowed to obtain dehydrated grapes with the best characteristics from the point of view of more stable anthocyanin composition, and lower contribution of seed flavanols giving astringency and bitterness to the resulting wines. Therefore, the environmental condition C was used in the experiments performed in 2009.

### **Influence of skin break force of fresh berries on dehydration kinetics and phenolic profile of Corvina grapes**

Since the dehydration kinetics and the characteristics of the withered grapes depend not only on environmental conditions like temperature, relative humidity and air flow, but also on the physicochemical characteristics of the fresh product,<sup>[4]</sup> the following step was to study the influence of the skin break force ( $F_{sk}$ ) of Corvina fresh winegrapes on the changes in the chemical composition during off-vine withering under the best controlled environmental condition (C, 15° C, 80% RH).

Table 5 shows the average, minimum and maximum values of  $F_{sk}$  determined for the two berry groups used in the withering trial (soft, CS and hard, CH), as well as the average values for each one of the replicates analyzed. The skin hardness of the two groups established for Corvina fresh winegrapes ranged from 0.400 to 0.821 N, and from 0.823 to 1.361 N, respectively. In Figure 2, the evolution of the WL% due to dehydration during the postharvest withering process under the controlled environmental condition C is represented for the two berry groups. Taking into account the linear kinetics, the withering process was shortened to 30 days as usual values of WL% in winery were reached. Significant differences in the WL% values were found among fresh berries with soft and hard skins. The fresh berries with soft skins (CS) were characterized by significantly higher values of the WL% than those with hard skins (CH) from 6 days of withering onwards, and therefore the dehydration rate decreased with increasing the berry skin hardness. Particularly, a WL% of 21.3 was observed at 30 days of withering for the berries with hard skins, whereas it was 25.3 for soft ones.

The effect of the  $F_{sk}$  on the grape dehydration kinetics agreed with the results already reported for white winegrapes varieties by Rolle et al.,<sup>[37]</sup> who suggested that the softer skins of fresh berries facilitate a faster loss of weight when the environmental conditions of the chamber are set to 16° C and 60% RH. In other work conducted on Erbaluce grapes,<sup>[38]</sup> significant differences in the WL% were found among fresh berries having soft and hard skins only at the lowest withering temperature tested (15° C and 55% RH). Taking into account the results published in these two works and the obtained in this study, the grape dehydration kinetics seems to be influenced by the skin hardness at low temperatures, independently on the RH% value.

The chemical parameters that usually define the technological ripeness, the phenolic composition and the anthocyanin profile for Corvina fresh winegrapes with different skin hardness at harvest and during the postharvest dehydration process are shown in Tables 6, 7 and 8, respectively. As can be observed, very few significant differences were found among berries having soft and hard skins at different days of withering. Because of the higher water loss by evaporation, the berries with soft skins evidenced a higher increase in the SSC value at the end of the dehydration process (Table 6). However, the significant

differences found at harvest in the total acidity value (Table 6), the content of  $TA_{sk}$  (Table 7) and the percentage of cyanidin derivative forms (Table 8) among berries with soft and hard skins, and in the content of  $TA_{sk}$  at the end of the dehydration process (Table 7), were probably due to the low variability of the measurements. During withering, significant differences were found in the content of  $TF_{sk}$  and  $FRV_{sk}$  for berries with soft and hard skins (Table 7). The increasing trend was already observed in the 2008 withering trial when grape berries were not sorted according to the density and classified according to the skin hardness, although the differences were not significant for the same environmental condition. The anthocyanin profile corresponding to 2009 (Table 8) was similar to that associated with 2008 (Table 4) because nonacylated glucosides were the most abundant anthocyanin forms in all the fresh and withered samples, particularly malvidin and peonidin forms, followed by cinnamoyl glucosides. During withering, acetyl glucosides increased, but more significantly for hard skins, whereas cyanidin derivatives significantly increased only for hard skins and petunidin derivatives only for soft skins. The major anthocyanin compounds showed no significant differences during grape dehydration as occurred for the environmental condition C in the 2008 withering trial.

## CONCLUSIONS

This work highlighted the need for careful control of the thermohygro-metric conditions during postharvest dehydration of red winegrapes because the physicochemical characteristics of the withered grapes were affected by the dehydration kinetics. Although the instrumental texture parameters values significantly decreased during the withering process under every environmental condition tested, the magnitude of the changes was different. Postharvest dehydration was effective in modifying the chemical composition of red winegrapes. The content of phenolic compounds also appeared to be differentially affected by the three thermohygro-metric conditions tested, corresponding in major changes in the content of total flavonoids of the skin and seeds, as well as of proanthocyanidins and low weight flavanols of the seeds, to the withering condition A. No important phenolic modifications was observed using the

environmental condition C. The anthocyanin profile also evidenced some changes that depended on the withering condition used. These compositional changes could have important consequences on the sensorial properties of the wines made from withered grapes.

The value of the berry weight loss also affected the mechanical properties and the phenolic composition of the withered grapes. In fact, strong negative correlations were found among the weight loss and some mechanical properties like the break force, stiffness and thickness of the skin, and the hardness, gumminess, chewiness and resilience of the whole berry, while positive ones were associated with the content of total flavonoids of the skin and seeds, and that one of proanthocyanidins and low weight flavanols of the seeds.

### **Acknowledgments**

This work was supported by the project “*Contratto di Filiera – Territori DIVINI*” (DM MIPAF 1<sup>st</sup> August 2003 and s.m.i).

### **REFERENCES**

1. Muganu, M.; Bellincontro, A.; Barnaba, F.E.; Paolocci, M.; Bignami, C.; Gambellini, G.; Mencarelli, F. Influence of bunch position in the canopy on berry epicuticular wax during ripening and on weight loss during postharvest dehydration. *American Journal of Enology and Viticulture* **2011**, *62*, 91–98.
2. Ruiz, M.J.; Zea, L.; Moyano, L.; Medina, M. Aroma active compounds during the drying of grapes cv. *Pedro Ximenez* destined to the production of sweet Sherry wine. *European Food Research and Technology* **2010**, *230*, 429–435.

3. Tosi, E.; Fedrizzi, B.; Azzolini, M.; Finato, F.; Simonato, B.; Zapparoli, G. Effects of noble rot on must composition and aroma profile of Amarone wine produced by the traditional grape withering protocol. *Food Chemistry* **2012**, *130*, 370–375.
4. Esmaili, M.; Sotudeh-Gharebagh, R.; Cronin, K.; Mousavi, M.A.E.; Rezazadeh, G. Grape drying: a review. *Food Reviews International* **2007**, *23*, 257–280.
5. Pangavhane, D.R.; Sawhney, R.L. Review of research and development work on solar dryers for grape drying. *Energy Conversion and Management* **2002**, *43*, 45–61.
6. Serratos, M.P.; Lopez-Toledano, A.; Merida, J.; Medina, M. Changes in color and phenolic compounds during the raisining of grape cv. Pedro Ximenez. *Journal of Agricultural and Food Chemistry* **2008**, *56*, 2810–2816.
7. Covarelli, L.; Beccari, G.; Marini, A.; Tosi, L. A review on the occurrence and control of ochratoxigenic fungal species and ochratoxin A in dehydrated grapes, non-fortified dessert wines and dried vine fruit in the Mediterranean area. *Food Control* **2012**, *26*, 347–356.
8. Ramos, I.N.; Silva, C.L.M.; Sereno, A.M.; Aguilera, J.M. Quantification of microstructural changes during first stage air drying of grape tissue. *Journal of Food Engineering* **2004**, *62*, 159–164.
9. Margaris, D.P.; Ghiaus, A.G. Experimental study of hot air dehydration of Sultana grapes. *Journal of Food Engineering* **2007**, *79*, 1115–1121.
10. Clary, C.D.; Mejia-Meza, E.; Wang, S.; Petrucci, V.E. Improving grape quality using microwave vacuum drying associated with temperature control. *Journal of Food Science* **2007**, *72*, E23–E28.
11. Pahlavanzadeh, H.; Basiri, A.; Zarrabi, M. Determination of parameters and pretreatment solution for grape drying. *Drying Technology* **2001**, *19*, 217–226.

12. Botondi, R.; Lodola, L.; Mencarelli, F. Postharvest ethylene treatment affects berry dehydration, polyphenol and anthocyanin content by increasing the activity of cell wall enzymes in Aleatico wine grape. *European Food Research and Technology* **2011**, *232*, 679–685.
13. [Doymaz, I.](#); Altiner, P. Effect of pretreatment solution on drying and color characteristics of seedless grapes. *Food Science and Biotechnology* **2012**, *21*, 43–49.
14. D'Agostino, S.; Riotto, M.; Ciolfi, G. Uva Zibibbo passolata e passa per la produzione dei vini DOC Moscatti-Passiti di Pantelleria. *Industrie delle Bevande* **2002**, *31*, 251–256.
15. Toffali, K.; Zamboni, A.; Anesi, A.; Stocchero, M.; Pezzotti, M.; Levi, M.; Guzzo, F. Novel aspects of grape berry ripening and post-harvest withering revealed by untargeted LC-ESI-MS metabolomics analysis. *Metabolomics* **2011**, *7*, 424–436.
16. Márquez, R.; Castro, R.; Natera, R.; García-Barroso, C. Characterisation of the volatile fraction of Andalusian sweet wines. *European Food Research and Technology* **2008**, *226*, 1479–1484.
17. Mencarelli, F.; Bellincontro, A.; Nicoletti, I.; Cirilli, M.; Muleo, R.; Corradini, D. Chemical and biochemical change of healthy phenolic fractions in winegrape by means of postharvest dehydration. *Journal of Agricultural and Food Chemistry* **2010**, *58*, 7557–7564.
18. Bellincontro, A.; Nicoletti, I.; Valentini, M.; Tomas, A.; De Santis, D.; Corradini, D.; Mencarelli, F. Integration of nondestructive techniques with destructive analyses to study postharvest water stress of winegrapes. *American Journal of Enology and Viticulture* **2009**, *60*, 57–65.
19. Santonico, M.; Bellincontro, A.; De Santis, D.; Di Natale, C.; Mencarelli, F. Electronic nose to study postharvest dehydration of wine grapes. *Food Chemistry* **2010**, *121*, 789–796.
20. Bellincontro, A.; De Santis, D.; Botondi, R.; Villa, I.; Mencarelli, F. Different postharvest dehydration rates affect quality characteristics and volatile compounds of Malvasia, Trebbiano and Sangiovese grapes for wine production. *Journal of the Science of Food and Agriculture* **2004**, *84*, 1791–1800.

21. Costantini, V.; Bellincontro, A.; De Santis, D.; Botondi, R.; Mencarelli, F. Metabolic changes of Malvasia grapes for wine production during postharvest drying. *Journal of Agricultural and Food Chemistry* **2006**, *54*, 3334–3340.
22. Chkaiban, L.; Botondi, R.; Bellincontro, A.; De Santis, D.; Kefalas, P.; Mencarelli, F. Influence of postharvest water stress on lipoxygenase and alcohol dehydrogenase activities, and on the composition of some volatile compounds of Gewürztraminer grapes dehydrated under controlled and uncontrolled thermohygro-metric conditions. *Australian Journal of Grape and Wine Research* **2007**, *13*, 142–149.
23. Piombino, P.; Genovese, A.; Gambuti, A.; Lamorte, S.A.; Lisante, M.T.; Moio, L. Effects of off-vine bunches shading and cryomaceration on free and glycosilated flavours of Malvasia delle Lipari wine. *International Journal of Food Science and Technology* **2010**, *45*, 234–244.
24. Bonghi, C.; Rizzini, F.M.; Gambuti, A.; Moio, L.; Chkaiban, L.; Tonutti, P. Phenol compound metabolism and gene expression in the skin of wine grape (*Vitis vinifera* L.) berries subjected to partial postharvest dehydration. *Postharvest Biology and Technology* **2012**, *67*, 102–109.
25. Moreno, J.J.; Cerpa-Caldero, F.; Cohen, S.D.; Fang, Y.; Qian, M.; Kennedy, J.A. Effect of postharvest dehydration on the composition of Pinot noir grapes (*Vitis vinifera* L.) and wine. *Food Chemistry* **2008**, *109*, 755–762.
26. Di Carli, M.; Zamboni, A.; Pè, M.E.; Pezzotti, M.; Lilley, K.S.; Benvenuto, E.; Desiderio, A. Two-dimensional differential in gel electrophoresis (2D-DIGE) analysis of grape berry proteome during postharvest withering. *Journal of Proteome Research* **2011**, *10*, 429–446.
27. Bellincontro, A.; Cozzolino, D.; Mencarelli, F. Application of NIR-AOTF spectroscopy to monitor Aleatico grape dehydration for passito wine production. *American Journal of Enology and Viticulture* **2011**, *62*, 256–260.

28. Chong, C.H.; Law, C.L.; Cloke, M.; Abdullah, L.C.; Daud, W.R.W. Drying kinetics, texture, color, and determination of effective diffusivities during sun drying of Chempedak. *Drying Technology* **2008**, *26*, 1286–1293.
29. Bolin, H.R.; Huxsoll, C.C. Scanning electron microscope/image analyzer determination of dimensional postharvest changes in fruit cells. *Journal of Food Science* **1987**, *6*, 1649–1650.
30. Rahman, M.S. Dried food properties: challenges ahead. *Drying Technology* **2005**, *23*, 695–715.
31. Xiao, H.-W.; Pang, C.-L.; Wang, L.-H.; Bai, J.-W.; Yang, W.-X.; Gao, Z.-J. Drying kinetics and quality of Monukka seedless grapes dried in an air-impingement jet dryer. *Biosystems Engineering* **2010**, *105*, 233–240.
32. Gabas, A.L.; Telis-Romero, J.; Menegalli, F.C. Thermodynamic models for water sorption by grape skin and pulp. *Drying Technology* **1999**, *17*, 961–974.
33. Rolle, L.; Torchio, F.; Giacosa, S.; Gerbi, V. Modifications of mechanical characteristics and phenolic composition in berry skins and seeds of Mondeuse winegrapes throughout the on-vine drying process. *Journal of the Science of Food and Agriculture* **2009**, *89*, 1973–1980.
34. Rolle, L.; Torchio, F.; Cagnasso, E.; Gerbi, V. Evolution of mechanical variables of winegrapes for icewine production during on-vine drying. *Italian Journal of Food Science* **2010**, *22*, 143–149.
35. Rolle, L.; Torchio, F.; Ferrandino, A.; Guidoni, S. Influence of wine-grape skin hardness on the kinetics of anthocyanin extraction. *International Journal of Food Properties* **2012**, *15*, 249–261.
36. Zouid, I.; Siret, R.; Mehinagic, E.; Maury, C.; Chevalier, M.; Jourjon, F. Evolution of grape berries during ripening: Investigations into the links between their mechanical properties and the extractability of their skin anthocyanins. *Journal International des Sciences de la Vigne et du Vin* **2010**, *44*, 87–99.

37. Rolle, L.; Caudana, A.; Giacosa, S.; Gerbi, V.; Río Segade, S. Influence of skin hardness on dehydration kinetics of wine grapes. *Journal of the Science of Food and Agriculture* **2011**, *91*, 505–511.
38. Giacosa, S.; Torchio, F.; Río Segade, S.; Caudana, A.; Gerbi, V.; Rolle, L. Varietal relationship between skin break force and off-vine withering process for winegrapes. *Drying Technology* **2012**, *30*, 726–732.
39. Rolle, L.; Río Segade, S.; Torchio, F.; Giacosa, S.; Cagnasso, E.; Marengo, F.; Gerbi, V. Influence of grape density and harvest date on changes in phenolic composition, phenol extractability indices, and instrumental texture properties during ripening. *Journal of Agricultural and Food Chemistry* **2011**, *59*, 8796–8805.
40. Letaief, H.; Rolle, L.; Gerbi, V. Mechanical behavior of winegrapes under compression tests. *American Journal of Enology and Viticulture* **2008**, *59*, 323–329.
41. Grotte, M.; Cadot, Y.; Poussier, A.; Loonis, D.; Piétri, E.; Duprat, F.; Barbeau, G. Determination of the maturity status of grape berry (*Vitis vinifera*) from physical measurement: methodology. *Journal International des Sciences de la Vigne et du Vin* **2001**, *35*, 87–98.
42. Santini, D.; Rolle, L.; Cascio, P.; Mannini, F. Modifications in chemical, physical and mechanical properties of Nebbiolo (*Vitis vinifera* L.) grape berries induced by mixed virus infection. *South African Journal of Enology & Viticulture* **2011**, *32*, 183–189.
43. Rolle, L.; Siret, R.; Río Segade, S.; Maury, C.; Gerbi, V.; Jourjon, F. Instrumental texture analysis parameters as markers of table-grape and winegrape quality: a review. *American Journal of Enology and Viticulture* **2012**, *63*, 11–28.
44. OIV. Recueil International des Méthodes d'Analyse des Vins et des Moûts; Paris, France, 2008.
45. Giordano, M.; Rolle, L.; Zeppa, G.; Gerbi, V. Chemical and volatile composition of three Italian sweet white passito wines. *Journal International des Sciences de la Vigne et du Vin* **2009**, *43*, 159–170.

46. Di Stefano, R.; Cravero, M.C. Metodi per lo studio dei polifenoli dell'uva. *Rivista di Viticoltura e di Enologia* **1991**, *44*, 37–45.
47. Pomar, F.; Novo, M.; Masa, A. Varietal differences among the anthocyanin profiles of 50 red table grape cultivars studied by high performance liquid chromatography. *Journal of Chromatography A* **2005**, *1094*, 34–41.
48. Barbanti, D.; Mora, B.; Ferrarini, R.; Tornielli, G.B.; Cipriani, M. Effect of various thermo-hygrometric conditions on the withering kinetics of grapes used for the production of ‘ ‘Amarone’ ’ and ‘ ‘Recioto’ ’ wines. *Journal of Food Engineering* **2008**, *85*, 350–358.
49. Versari, A.; Parpinello, G.P.; Tornielli, G.B.; Ferrarini, R.; Giulivo, C. Stilbene compounds and stilbene synthase expression during ripening, wilting, and uv treatment in grape cv. Corvina. *Journal of Agricultural and Food Chemistry* **2001**, *49*, 5531–5536.
50. De Belie, N.; Tu, K.; Jancsok, P.; De Baerdemaeker, J. Preliminary study on the influence of turgor pressure on body reflectance of red laser light as a ripeness indicator for apples. *Postharvest Biology and Technology* **1999**, *16*, 279–284.
51. Kök, D.; Çelik, S. Determination of characteristics of grape berry skin in some table grape cultivars (*V. vinifera* L.). *Journal of Agronomy* **2004**, *3*, 141–146.
52. Vázquez, G.; Chenlo, F.; Moreira, R.; Costoyas, A. Effects of various treatments on the drying kinetics of Muscatel grapes. *Drying Technology* **2000**, *18*, 2131–2144.
53. Gabas, A.L.; Menegalli, F.C.; Telis-Romero, J. Effect of chemical pretreatment on the physical properties of dehydrated grapes. *Drying Technology* **1999**, *17*, 1215–1226.
54. Dev, S.R.S.; Padmini, T.; Adedeji, A.; Gariépy, Y.; Raghavan, G.S.V. A comparative study on the effect of chemical, microwave, and pulsed electric pretreatments on convective drying and quality of raisins. *Drying Technology* **2008**, *26*, 1238–1243.

55. Doymaz, I. Sun drying of seedless and seeded grapes. *Journal of Food Science and Technology-Mysore* **2012**, *49*, 214–220.
56. Becatti, E.; Chkaiban, L.; Tonutti, P.; Forcato, C.; Bonghi, C.; Ranieri, A.M. Short-term postharvest carbon dioxide treatments induce selective molecular and metabolic changes in grape berries. *Journal of Agricultural and Food Chemistry* **2010**, *58*, 8012–8020.
57. Frangipane, M.T.; Torresi, S.; De Santis, D.; Massantini, R. Effect of drying process in chamber at controlled temperature on the grape phenolic compounds. *Italian Journal of Food Science* **2012**, *24*, 26–31.
58. Marquez, A.; Dueñas, M.; Serratosa, M.P.; Merida, J. Formation of vitisins and anthocyanin–flavanol adducts during red grape drying. *Journal of Agricultural and Food Chemistry* **2012**, *60*, 6866–6874.
59. Río Segade, S.; Giacosa, S.; Gerbi, V.; Rolle, L. Berry skin thickness as main texture parameter to predict anthocyanin extractability in winegrapes. *LWT Food Science and Technology* **2011**, *44*, 392–398.

FIG. 1. Dehydration kinetics for Corvina winegrapes under three different controlled thermohygro-metric conditions.

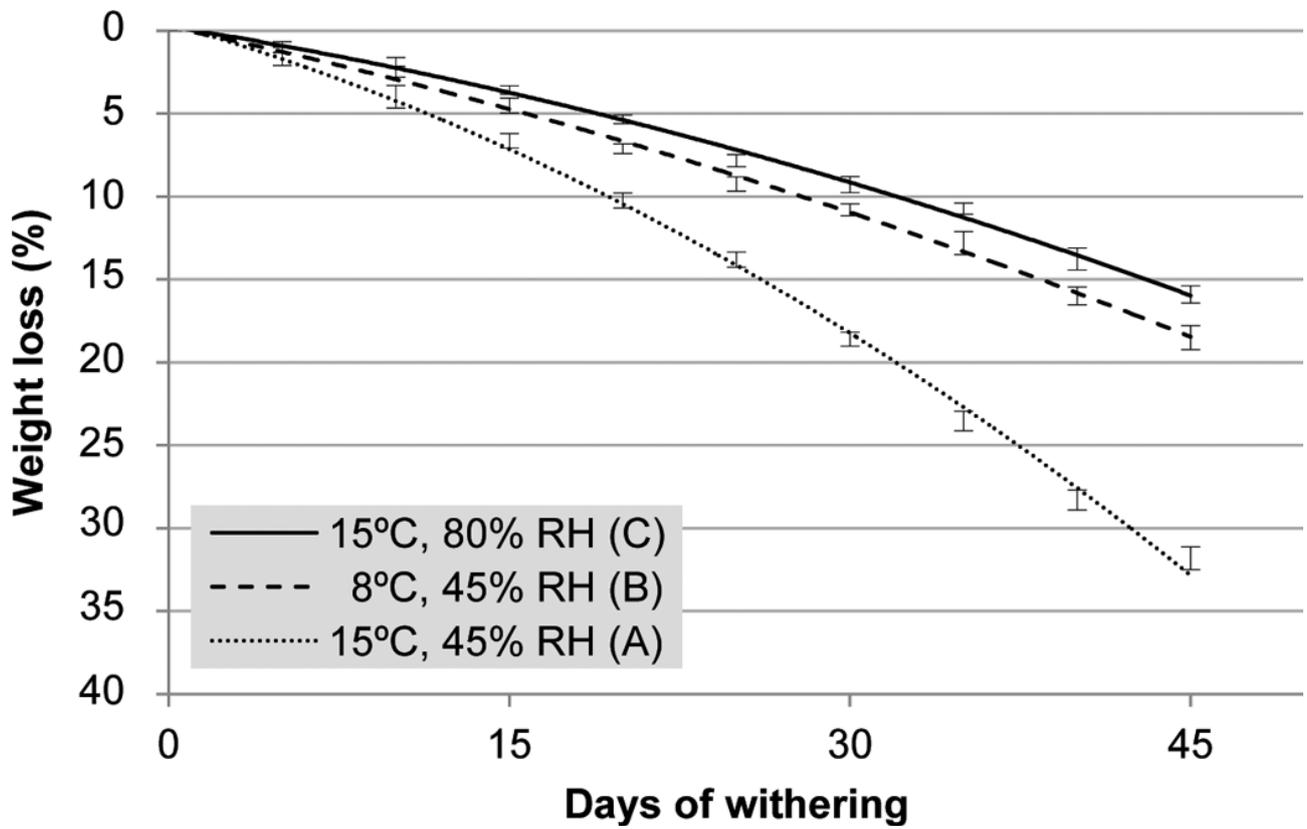


FIG. 2. Dehydration kinetics for Corvina winegrapes with soft and hard skins at 15° C and 80% RH.

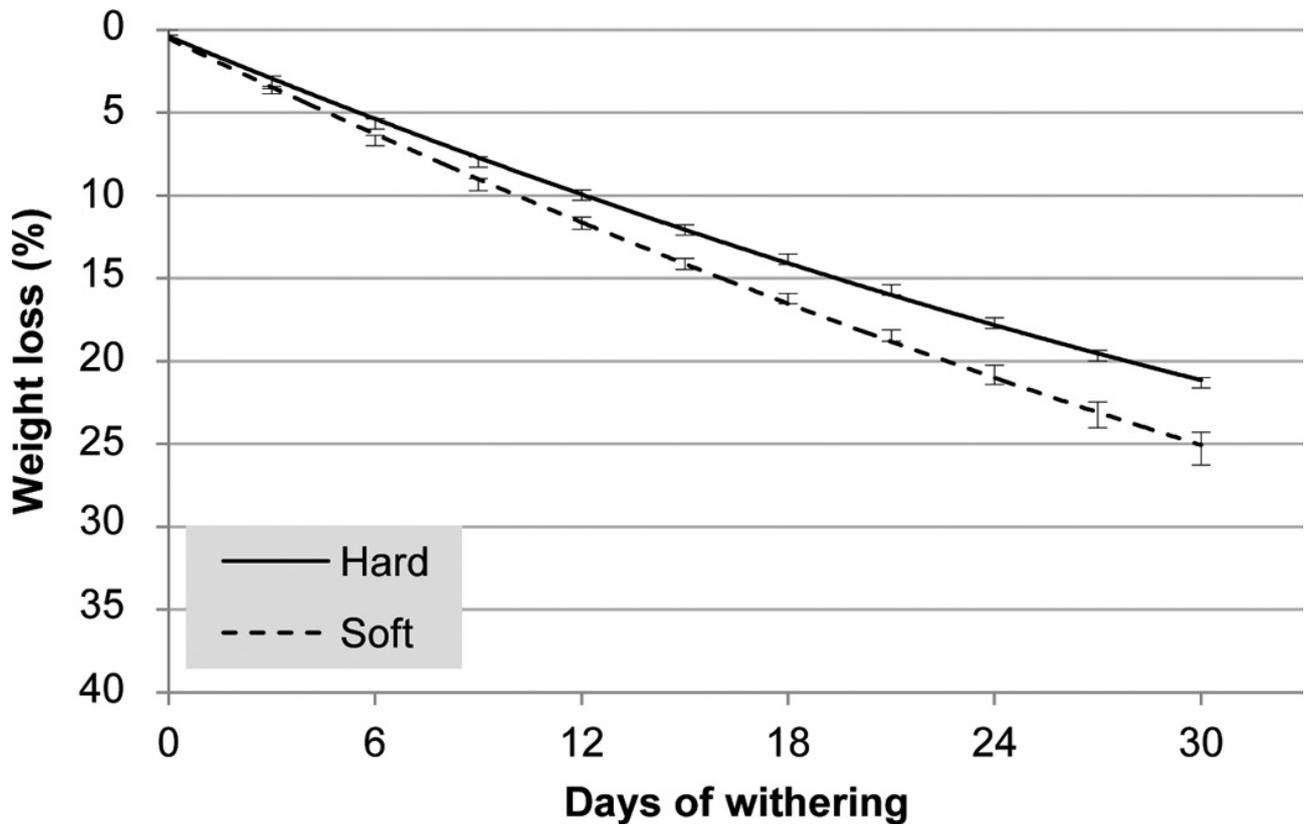


TABLE 1

Instrumental texture parameters for Corvina winegrapes at harvest and during the postharvest dehydration process carried out at different controlled thermohygro-metric conditions in 2008

Mechanical parameter	F <sub>0</sub>	15 days of withering			Sign <sup>a</sup>	45 days of withering			Sign <sup>a</sup>	Sign <sup>b</sup>
		A	B	C		A	B	C		
F <sub>sk</sub> (N)	0.645±0.140 <sup>β,β,β</sup>	0.619±0.176 <sup>a,β</sup>	0.724±0.131 <sup>b,β</sup>	0.594±0.143 <sup>a,β</sup>	**	0.387±0.161 <sup>α</sup>	0.426±0.140 <sup>α</sup>	0.401±0.117 <sup>α</sup>	ns	***,***,***
W <sub>sk</sub> (mJ)	0.606±0.165 <sup>αβ,α</sup>	0.681±0.181 <sup>ab,β</sup>	0.747±0.177 <sup>b,β</sup>	0.605±0.199 <sup>a</sup>	*	0.555±0.195 <sup>α</sup>	0.554±0.138 <sup>α</sup>	0.508±0.142	ns	*,***,ns
E <sub>sk</sub> (N/mm)	0.293±0.060 <sup>γ,β,γ</sup>	0.219±0.068 <sup>a,β</sup>	0.283±0.047 <sup>b,β</sup>	0.238±0.046 <sup>c,β</sup>	***	0.112±0.054 <sup>α</sup>	0.128±0.052 <sup>α</sup>	0.137±0.054 <sup>α</sup>	ns	***,***,***
Sp <sub>sk</sub> (μm)	236±36 <sup>β,α,α</sup>	275±42 <sup>γ</sup>	281±37 <sup>β</sup>	297±38 <sup>β</sup>	ns	194±35 <sup>a,α</sup>	223±34 <sup>b,α</sup>	240±26 <sup>b,α</sup>	**	***,***,***
F <sub>ped</sub> (N)	2.952±0.836 <sup>β,β,γ</sup>	1.849±0.758 <sup>a,α</sup>	2.972±0.854 <sup>b,β</sup>	2.261±0.811 <sup>a,β</sup>	***	1.809±0.718 <sup>α</sup>	1.721±0.485 <sup>α</sup>	1.646±0.629 <sup>α</sup>	ns	***,***,***
W <sub>ped</sub> (mJ)	2.357±0.930 <sup>β,β,β</sup>	1.551±0.923 <sup>a,α</sup>	2.713±1.407 <sup>b,β</sup>	1.674±0.769 <sup>a,α</sup>	**	1.908±0.846 <sup>b,αβ</sup>	1.658±0.764 <sup>ab,α</sup>	1.319±0.624 <sup>a,α</sup>	*	**,*,***
BH (N)	3.214±0.825 <sup>γ,γ,γ</sup>	1.792±0.551 <sup>a,β</sup>	2.466±0.626 <sup>b,β</sup>	2.272±0.526 <sup>b,β</sup>	***	0.473±0.148 <sup>a,α</sup>	0.605±0.290 <sup>a,α</sup>	0.914±0.488 <sup>b,α</sup>	***	***,***,***
BCo (-)	0.738±0.022 <sup>β,β,γ</sup>	0.689±0.046 <sup>a,α</sup>	0.735±0.029 <sup>b,β</sup>	0.719±0.027 <sup>b,β</sup>	***	0.675±0.044 <sup>b,α</sup>	0.632±0.043 <sup>a,α</sup>	0.651±0.037 <sup>ab,α</sup>	***	***,***,***
BG (N)	2.367±0.594 <sup>γ,γ,γ</sup>	1.248±0.417 <sup>a,β</sup>	1.823±0.492 <sup>b,β</sup>	1.638±0.403 <sup>b,β</sup>	***	0.321±0.106 <sup>a,α</sup>	0.388±0.208 <sup>a,α</sup>	0.599±0.331 <sup>b,α</sup>	***	***,***,***
BS (mm)	2.042±0.219 <sup>β,γ,γ</sup>	1.650±0.204 <sup>α</sup>	1.770±0.252 <sup>β</sup>	1.791±0.221 <sup>β</sup>	ns	1.573±0.201 <sup>α</sup>	1.469±0.218 <sup>α</sup>	1.554±0.208 <sup>α</sup>	ns	***,***,***
BCh (mJ)	4.939±1.655 <sup>γ,γ,γ</sup>	2.109±0.822 <sup>a,β</sup>	3.341±1.287 <sup>b,β</sup>	3.014±1.117 <sup>b,β</sup>	***	0.516±0.207 <sup>a,α</sup>	0.587±0.358 <sup>a,α</sup>	0.964±0.617 <sup>b,α</sup>	***	***,***,***
BR (-)	0.379±0.026 <sup>γ,β,γ</sup>	0.309±0.039 <sup>a,β</sup>	0.362±0.033 <sup>b,β</sup>	0.354±0.031 <sup>b,β</sup>	***	0.277±0.039 <sup>b,α</sup>	0.241±0.031 <sup>a,α</sup>	0.272±0.036 <sup>b,α</sup>	***	***,***,***

BH <sub>norm</sub> (N)	0.260±0.053 <sup>γ,γ,γ</sup>	0.156±0.047 <sup>a,β</sup>	0.216±0.041 <sup>b,β</sup>	0.191±0.036 <sup>b,β</sup>	***	0.047±0.015 <sup>a,α</sup>	0.059±0.027 <sup>a,α</sup>	0.084±0.040 <sup>b,α</sup>	***	***,***,***
BG <sub>norm</sub> (N)	0.191±0.037 <sup>γ,γ,γ</sup>	0.108±0.035 <sup>a,β</sup>	0.160±0.033 <sup>c,β</sup>	0.138±0.028 <sup>b,β</sup>	***	0.032±0.011 <sup>a,α</sup>	0.038±0.020 <sup>a,α</sup>	0.055±0.028 <sup>b,α</sup>	***	***,***,***
BS <sub>norm</sub> (mm)	0.166±0.007 <sup>γ,γ,β</sup>	0.144±0.014 <sup>a,α</sup>	0.156±0.012 <sup>b,β</sup>	0.151±0.012 <sup>b,α</sup>	**	0.156±0.016 <sup>b,β</sup>	0.145±0.016 <sup>a,α</sup>	0.147±0.018 <sup>ab,α</sup>	*	***,***,***
BCh <sub>norm</sub> (mJ)	0.032±0.007 <sup>γ,γ,γ</sup>	0.016±0.006 <sup>a,β</sup>	0.025±0.006 <sup>c,β</sup>	0.021±0.006 <sup>b,β</sup>	***	0.005±0.002 <sup>a,α</sup>	0.006±0.003 <sup>a,α</sup>	0.008±0.004 <sup>b,α</sup>	**	***,***,***

All data are expressed as average value ± standard deviation (n = 25). Different Latin letters within the same row indicate significant differences (<sup>a</sup>) among withering conditions at the same withering time (*Tukey-b test*;  $p < 0.05$ ). Different Greek letters within the same row indicate significant differences (<sup>b</sup>) among withering times at the same withering condition (*Tukey-b test*;  $p < 0.05$ ). Sign: \*, \*\*, \*\*\* and ns indicate significance at  $p < 0.05$ , 0.01, 0.001 and not significant, respectively. F<sub>sk</sub>: berry skin break force, W<sub>sk</sub>: berry skin break energy, E<sub>sk</sub>: berry skin Young's modulus, Sp<sub>sk</sub>: berry skin thickness, F<sub>ped</sub>: peduncle detachment force, W<sub>ped</sub>: peduncle detachment energy, BH: berry hardness, BCo: berry cohesiveness, BG: berry gumminess, BS: berry springiness, BCh: berry chewiness, BR: berry resilience. <sub>norm</sub>: normalized according to the respective berry diameter. F<sub>0</sub>: fresh berries, A: 15° C, 45% RH, B: 8° C, 45% RH, C: 15° C, 80% RH.

TABLE 2

Technological ripeness parameters for Corvina winegrapes at harvest and during the postharvest dehydration process carried out at different controlled thermohygro-metric conditions in 2008

Ripeness parameter	F <sub>0</sub>	15 days of withering			Sign <sup>a</sup>	45 days of withering			Sign <sup>a</sup>	Sign <sup>b</sup>
		A	B	C		A	B	C		
SSC (Brix)	18.0±0.1 <sup>α,α,α</sup>	21.2±0.3 <sup>c,β</sup>	19.9±0.0 <sup>b,β</sup>	18.7±0.0 <sup>a,β</sup>	**	29.4±0.1 <sup>c,γ</sup>	25.4±0.3 <sup>b,γ</sup>	22.5±0.0 <sup>a,γ</sup>	***	***,***,***
TA (g/L tartaric acid)	7.50±0.14 <sup>α,α,β</sup>	8.60±0.21 <sup>b,β</sup>	8.15±0.21 <sup>b,α</sup>	6.85±0.00 <sup>a,α</sup>	**	12.20±0.14 <sup>b,γ</sup>	10.00±0.42 <sup>a,β</sup>	9.70±0.14 <sup>a,γ</sup>	**	***,*,***
pH	3.15±0.03	3.16±0.06	3.17±0.06	3.28±0.01	ns	3.25±0.01	3.32±0.04	3.21±0.04	ns	ns, ns,ns
Tartaric acid (g/L)	4.56±0.04 <sup>α,α,α</sup>	5.96±0.09 <sup>b,β</sup>	5.26±0.18 <sup>a,β</sup>	4.93±0.22 <sup>a,α</sup>	*	6.80±0.07 <sup>a,γ</sup>	7.35±0.15 <sup>b,γ</sup>	7.46±0.07 <sup>b,β</sup>	*	***,***,***
Malic acid (g/L)	1.95±0.04 <sup>ν,γ</sup>	1.85±0.12 <sup>b</sup>	1.52±0.09 <sup>a,β</sup>	1.49±0.03 <sup>a,β</sup>	*	1.65±0.06 <sup>c</sup>	0.22±0.05 <sup>a,α</sup>	0.82±0.16 <sup>b,α</sup>	**	ns,***,**
Gluconic acid (g/L)	0.01±0.00 <sup>α,α,α</sup>	0.32±0.02 <sup>b,β</sup>	0.02±0.00 <sup>a,αβ</sup>	0.01±0.01 <sup>a,α</sup>	***	0.42±0.03 <sup>b,γ</sup>	0.05±0.01 <sup>a,β</sup>	0.36±0.01 <sup>b,β</sup>	***	***,*,***
Glycerol (g/L)	0.05±0.01 <sup>α,α,α</sup>	0.52±0.03 <sup>b,β</sup>	0.06±0.01 <sup>a,αβ</sup>	0.48±0.05 <sup>b,β</sup>	**	1.07±0.20 <sup>b,γ</sup>	0.11±0.02 <sup>a,β</sup>	1.41±0.10 <sup>b,γ</sup>	**	**,*,***

All data are expressed as average value ± standard deviation (n = 3). Different Latin letters within the same row indicate significant differences (<sup>a</sup>) among withering conditions at the same withering time (*Tukey-b test*; *p* < 0.05). Different Greek letters within the same row indicate significant differences (<sup>b</sup>) among withering times at the same withering condition (*Tukey-b test*; *p* < 0.05). Sign: \*, \*\*, \*\*\* and ns indicate significance at *p* < 0.05, 0.01, 0.001 and not significant, respectively. SSC: total soluble solids content, TA: titratable acidity. F<sub>0</sub>: fresh berries, A: 15° C, 45% RH, B: 8° C, 45% RH, C: 15° C, 80% RH.

TABLE 3

Phenolic composition for Corvina winegrapes at harvest and during the postharvest dehydration process carried out at different controlled thermohygrometric conditions in 2008

Phenolic compound	F <sub>0</sub>	15 days of withering			Sign <sup>a</sup>	45 days of withering			Sign <sup>a</sup>	Sign <sup>b</sup>
		A	B	C		A	B	C		
TA <sub>sk</sub> (mg malvidin/kg)	961±183	939±146	750±84	981±106	ns	1159±137	877±59	798±251	ns	ns, ns,ns
TF <sub>sk</sub> (mg (+)-catechin/kg)	3277±264 <sup>α,α</sup>	3608±355 <sup>α</sup>	3276±285 <sup>α</sup>	3645±223	ns	4760±305 <sup>β</sup>	4005±83 <sup>β</sup>	4391±842	ns	**,* ,ns
PRO <sub>sk</sub> (mg cyanidin/kg)	1878±170 <sup>β</sup>	1534±239	1375±79 <sup>α</sup>	1750±177	ns	1836±236	1691±133 <sup>β</sup>	1981±306	ns	ns,**,ns
FRV <sub>sk</sub> (mg (+)-catechin/kg)	557±100 <sup>β,β</sup>	302±47 <sup>α</sup>	254±126 <sup>α</sup>	349±27	ns	353±122 <sup>αβ</sup>	266±43 <sup>α</sup>	366±123	ns	*,*,ns
TF <sub>s</sub> (mg (+)-catechin/kg)	395±93 <sup>α</sup>	593±190 <sup>α</sup>	505±61	440±29	ns	1128±183 <sup>b,β</sup>	712±231 <sup>a</sup>	467±39 <sup>a</sup>	**	** , ns,ns
PRO <sub>s</sub> (mg cyanidin/kg)	429±149 <sup>α</sup>	705±356 <sup>α</sup>	597±33	488±45	ns	1451±264 <sup>b,β</sup>	791±324 <sup>a</sup>	520±93 <sup>a</sup>	**	** , ns,ns
FRV <sub>s</sub> (mg (+)-catechin/kg)	214±56 <sup>α</sup>	355±180 <sup>α</sup>	269±38	219±11	ns	683±149 <sup>b,β</sup>	351±168 <sup>a</sup>	167±53 <sup>a</sup>	**	*, ns,ns

All data are expressed as average value ± standard deviation (n = 3). Different Latin letters within the same row indicate significant differences (<sup>a</sup>) among withering conditions at the same withering time (*Tukey-b test*;  $p < 0.05$ ). Different Greek letters within the same row indicate significant differences (<sup>b</sup>) among withering times at the same withering condition (*Tukey-b test*;  $p < 0.05$ ). Sign: \*,\*\* and ns indicate significance at  $p < 0.05$ , 0.01 and not significant, respectively. TA: total anthocyanins, TF: total flavonoids, PRO: proanthocyanidins, FRV: flavanols reactive to vanillin. <sub>sk</sub>: berry skin, <sub>s</sub>: berry seeds. F<sub>0</sub>: fresh berries, A: 15° C, 45% RH, B: 8° C, 45% RH, C: 15° C, 80% RH.

TABLE 4

Anthocyanin profile for Corvina winegrapes at harvest and during the postharvest dehydration process carried out at different controlled thermohygrometric conditions in 2008

Anthocyanin compound	F <sub>0</sub>	15 days of withering			Sign <sup>a</sup>	45 days of withering			Sign <sup>a</sup>	Sign <sup>b</sup>
		A	B	C		A	B	C		
Σ Simple glucosides (%)	90.54±1.08 <sup>β</sup>	91.43±0.27 <sup>b</sup>	89.91±0.33 <sup>a</sup>	91.22±0.71 <sup>b,β</sup>	*	89.91±0.80 <sup>b</sup>	90.03±0.25 <sup>b</sup>	86.22±1.19 <sup>a,α</sup>	**	ns, ns,**
Σ Acetyl glucosides (%)	0.94±0.13 <sup>β</sup>	0.74±0.03 <sup>a,α</sup>	0.93±0.05 <sup>b</sup>	0.85±0.11 <sup>ab</sup>	*	0.70±0.06 <sup>α</sup>	0.85±0.04	0.83±0.26	ns	*, ns,ns
Σ Cinnamoyl glucosides (%)	8.53±0.97 <sup>α</sup>	7.83±0.30 <sup>a</sup>	9.16±0.32 <sup>b</sup>	7.93±0.61 <sup>a,α</sup>	*	9.39±0.77 <sup>a</sup>	9.12±0.22 <sup>a</sup>	12.94±1.25 <sup>b,β</sup>	**	ns, ns,**
Σ Delphinidin derivatives (%)	8.43±1.69 <sup>β,β</sup>	7.22±1.12 <sup>b</sup>	5.30±0.57 <sup>a,α</sup>	8.14±0.70 <sup>b,β</sup>	*	6.72±0.29 <sup>b</sup>	5.13±0.04 <sup>a,α</sup>	5.59±0.73 <sup>a,α</sup>	*	ns,*,*
Σ Cyanidin derivatives (%)	5.78±0.12 <sup>α,α</sup>	9.27±0.27 <sup>b,β</sup>	6.04±0.91 <sup>a,α</sup>	8.04±1.08 <sup>b</sup>	**	9.57±1.06 <sup>b,β</sup>	7.48±0.10 <sup>ab,β</sup>	5.84±1.36 <sup>a</sup>	*	***,*,ns
Σ Petunidin derivatives (%)	7.95±1.12 <sup>β,β</sup>	6.53±0.55 <sup>ab</sup>	5.66±0.30 <sup>a,α</sup>	7.27±0.46 <sup>b,αβ</sup>	*	6.51±0.06 <sup>b</sup>	5.29±0.05 <sup>a,α</sup>	5.97±0.54 <sup>ab,α</sup>	**	ns,**,*
Σ Peonidin derivatives (%)	30.54±2.10 <sup>α,α</sup>	46.23±0.69 <sup>c,β</sup>	38.35±0.59 <sup>b,β</sup>	35.59±1.23 <sup>a</sup>	***	48.32±0.91 <sup>b,β</sup>	44.22±1.61 <sup>b,γ</sup>	35.47±3.28 <sup>a</sup>	***	***,***,ns
Σ Malvidin derivatives (%)	47.30±0.73 <sup>β,β</sup>	30.75±1.26 <sup>a,α</sup>	44.65±2.16 <sup>b,β</sup>	40.97±2.44 <sup>b</sup>	***	28.88±2.16 <sup>a,α</sup>	37.88±1.76 <sup>b,α</sup>	47.13±3.93 <sup>c</sup>	***	***,**,ns

All data are expressed as average value ± standard deviation (n = 3). Different Latin letters within the same row indicate significant differences (<sup>a</sup>) among withering conditions at the same withering time (*Tukey-b test*; *p* < 0.05). Different Greek letters within the same row indicate significant differences (<sup>b</sup>) among withering times at the same withering condition (*Tukey-b test*; *p* < 0.05). Sign: \*, \*\*, \*\*\* and ns indicate significance at *p* < 0.05, 0.01, 0.001 and not significant, respectively. F<sub>0</sub>: fresh berries, A: 15° C, 45% RH, B: 8° C, 45% RH, C: 15° C, 80% RH.

TABLE 5

Average, minimum and maximum values of berry skin break force ( $F_{sk}$ , N) for the two groups of Corvina winegrapes at harvest used in the 2009 withering trial

Sample	Average $\pm$ standard deviation (n = 126)	Minimum	Maximum	Replicates
				average $\pm$ standard deviation (n = 42)
CS	0.667 $\pm$ 0.098	0.400	0.821	0.553 $\pm$ 0.055
				0.677 $\pm$ 0.023
				0.772 $\pm$ 0.032
CH	0.987 $\pm$ 0.120	0.823	1.361	0.868 $\pm$ 0.028
				0.970 $\pm$ 0.037
				1.125 $\pm$ 0.085

Reducing sugars: 230  $\pm$  8 g/L. Withering condition C: 15 $^{\circ}$  C, 80% RH. S: soft, H: hard.

TABLE 6

Technological ripeness parameters at harvest and after postharvest dehydration carried out in 2009 for Corvina fresh winegrapes with different skin hardness

Significance	Days of withering	Sample	SSC (Brix)	TA (g/L tartaric acid)	pH
	0	CS	23.3±0.1	6.58±0.08	3.56±0.02
		CH	23.3±0.2	6.92±0.08	3.50±0.04
Sign <sup>a</sup>			ns	**	ns
	30	CS	29.1±0.1	7.55±0.84	3.60±0.08
		CH	26.9±0.1	7.76±0.73	3.56±0.06
Sign <sup>a</sup>			***	ns	ns
Sign <sup>b</sup>			***,***	ns,ns	ns,ns

All data are expressed as average value ± standard deviation (n = 3). <sup>a</sup>: significant differences among skin hardness at the same withering time. <sup>b</sup>: significant differences among withering times at the same skin hardness. Sign: \*\*, \*\*\* and ns indicate significance at  $p < 0.01$ ,  $0.001$  and not significant, respectively. SSC: total soluble solids content, TA: titratable acidity. Reducing sugars:  $230 \pm 8$  g/L. Withering condition C: 15° C, 80% RH. S: soft, H: hard.

TABLE 7

Phenolic composition at harvest and during the postharvest dehydration process carried out in 2009 for Corvina fresh winegrapes with different skin hardness

Significance	Days of withering	Sample	TA <sub>sk</sub> (mg malvidin/kg)	TF <sub>sk</sub> (mg (+)-catechin/kg)	PRO <sub>sk</sub> (mg cyanidin/kg)	FRV <sub>sk</sub> (mg (+)-catechin/kg)	TF <sub>s</sub> (mg (+)-catechin/kg)	PRO <sub>s</sub> (mg cyanidin/kg)	FRV <sub>s</sub> (mg (+)-catechin/kg)
	0	CS	729±20	4581±328	1248±388	352±46	663±170	549±146	697±102
		CH	620±29	3993±262	1333±135	472±97	503±120	388±122	532±119
Sign <sup>a</sup>			**	ns	ns	ns	ns	ns	ns
	10	CS	725±80	4882±47	1050±94	322±156	599±58	516±54	508±93
		CH	711±123	4606±448	1275±176	244±57	637±59	546±96	548±127
Sign <sup>a</sup>			ns	ns	ns	ns	ns	ns	ns
	20	CS	775±82	5403±214	1250±153	460±73	680±77	557±109	504±101
		CH	685±44	5138±357	1226±94	515±27	721±204	564±208	558±105
Sign <sup>a</sup>			ns	ns	ns	ns	ns	ns	ns
	30	CS	767±38	5676±337	1211±47	638±36	880±96	745±82	651±64
		CH	635±12	5111±200	1220±90	642±32	760±77	631±80	596±30
Sign <sup>a</sup>			**	ns	ns	ns	ns	ns	ns

Sign <sup>b</sup>	ns,ns	**,**	ns,ns	*,***	ns,ns	ns,ns	ns,ns
-------------------	-------	-------	-------	-------	-------	-------	-------

All data are expressed as average value  $\pm$  standard deviation (n = 3). <sup>a</sup>: significant differences among skin hardness at the same withering time. <sup>b</sup>: significant differences among withering times at the same skin hardness. Sign: \*, \*\*, \*\*\* and ns indicate significance at  $p < 0.05$ , 0.01, 0.001 and not significant, respectively. TA: total anthocyanins, TF: total flavonoids, PRO: proanthocyanidins, FRV: flavanols reactive to vanillin. <sub>sk</sub>: berry skin, <sub>s</sub>: berry seeds. Reducing sugars:  $230 \pm 8$  g/L. Withering condition C: 15° C, 80% RH. S: soft, H: hard.

TABLE 8

Anthocyanin profile at harvest and during the postharvest dehydration process carried out in 2009 for Corvina fresh winegrapes with different skin hardness

Significance	Days of withering	Sample	Σ Simple glucosides (%)	Σ Acetyl glucosides (%)	Σ Cinnamoyl glucosides (%)	Σ Delphinidin derivatives (%)	Σ Cyanidin derivatives (%)	Σ Petunidin derivatives (%)	Σ Peonidin derivatives (%)	Σ Malvidin derivatives (%)
	0	CS	90.03±0.97	1.00±0.03	8.97±0.96	5.61±0.30	5.71±0.17	5.73±0.18	48.09±0.58	34.86±0.64
		CH	90.11±0.63	0.92±0.11	8.97±0.53	5.91±0.45	6.43±0.39	5.78±0.52	46.95±2.65	34.93±1.32
Sign <sup>a</sup>			ns	ns	ns	ns	*	ns	ns	ns
	10	CS	89.35±0.58	1.15±0.04	9.51±0.56	5.99±0.84	6.44±0.64	5.89±0.90	47.06±8.06	34.63±6.83
		CH	89.88±0.25	1.12±0.15	9.01±0.30	6.09±0.85	6.96±0.25	5.79±0.88	49.92±4.67	31.24±3.03
Sign <sup>a</sup>			ns	ns	ns	ns	ns	ns	ns	ns
	20	CS	89.92±0.17	1.26±0.10	8.82±0.20	6.66±1.31	7.08±1.13	6.56±0.71	47.17±3.06	32.53±0.17
		CH	89.82±0.23	1.08±0.06	9.09±0.29	7.02±1.57	6.95±0.13	6.86±1.16	47.09±5.35	32.08±2.76
Sign <sup>a</sup>			ns	ns	ns	ns	ns	ns	ns	ns
	30	CS	89.54±0.78	1.28±0.19	9.18±0.67	7.82±0.95	7.18±0.40	7.46±0.51	42.43±4.16	35.12±4.15
		CH	88.94±0.58	1.51±0.08	9.55±0.51	6.65±0.70	7.22±0.16	6.71±0.52	48.98±2.18	30.43±1.11

Sign <sup>a</sup>	ns	ns	ns	ns	ns	ns	ns	ns
Sign <sup>b</sup>	ns,ns	*,***	ns,ns	ns,ns	ns,*	*,ns	ns,ns	ns,ns

All data are expressed as average value  $\pm$  standard deviation (n = 3). <sup>a</sup>: significant differences among skin hardness at the same withering time. <sup>b</sup>: significant differences among withering times at the same skin hardness. Sign: \*,\*\*\* and ns indicate significance at  $p < 0.05$ , 0.001 and not significant, respectively. Reducing sugars:  $230 \pm 8$  g/L. Withering condition C: 15<sup>o</sup> C, 80% RH. S: soft, H: hard.