On-vine withering process of 'Moscato bianco' grapes: effect of cane-cut system on volatile composition

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Abstract

BACKGROUND: Cane-cut on-vine is a grape dehydration technique used for dry and sweet wines production. The aim of this work was to study the influence of cane-cut applied at harvest on Moscato bianco grapes during on-vine withering process in order to produce dehydrated berries with different chemical composition and volatile profile.

RESULTS: On-vine withering system using cane-cut induced, after 24 days of dehydration, an increase of total volatile content *versus* grape produced with a normal on-vine withering process. This increase was greater in glycosidically-bound volatile compounds than in the free fraction. Bound linalool showed a significant increase of 52% when cane-cut withering system was applied but grapes normally withered appeared to be less prone to the loss of free linalool. A significant increase in the

This article has been accepted for publication and undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process, which may lead to differences between this version and the Version of Record. Please cite this article as doi: 10.1002/jsfa.9281

glycosylated forms of nerol and geraniol was also observed in the two on-vine withering systems at 24th day *vs* control (fresh grape at harvest date).

CONCLUSION: Cane-cut on-vine withering system applied at harvest induced changes in the volatile composition of Moscato bianco grapes increasing total volatile content, mainly bound compounds, at 24th day of dehydration. The grapes partially on-vine dehydrated using this new system also showed significantly greater contents of most free volatile compounds detected.

Keywords: volatile compounds, on-vine partial dehydration, cane-cut system, *Vitis vinifera*

INTRODUCTION

In order to improve the wine quality different canopy techniques, such as training systems, bunch thinning and defoliation, have been developed in the vineyard to increase the content of secondary metabolites in grapes at harvest.[1,2] In recent years, the growing market demand of diversifying enological products has increasingly promoted the use of partially dehydrated grapes for the production of "passito", fortified and reinforced wines.[3]

Grape dehydration, commonly called in the enological field as withering, consists in more or less slow water removal from grapes during which the concentration of sugars and a change of secondary metabolites contained in the pulp and skin occurs.[4,5] The impact of different on- and off-vine dehydration techniques on grape and wine composition, according to the experimental conditions of the process (i.e. temperature,

relative humidity, speed air), has been studied by several authors showing effects on the concentration, synthesis and oxidation of volatile and phenolic compounds.[4,6-10]

In particular, when considering cane-cut on-vine technique, the shoots are generally cut below the clusters before harvest. After the cut, the berries are left on-vine until technological ripeness and/or overripe is reached. The different level of ripeness of the grapes treated with this technique with respect to other normally ripened was technically called double reasoned maturation (DMR).[11-14] Studies on the cane-cut on-vine as overripe technique have demonstrated the capability of this technique to produce changes on soluble solids, organic acids, and phenolic compounds in grape berries.[13] Cane-cut on-vine overripe technique was applied on several cultivars such as Raboso Piave,[13] Istrian Malvasia,[15] Refosk,[14] Rebula and Vitovxka[16] or Merlot[17] showing a positive impact on grape and wine composition, mainly phenolic compounds. However, to our knowledge, studies about the effect of this technique on the volatile composition of grapes have never been performed to date.

Aroma is an important quality factor in white wines. It is well known that the volatile compounds responsible for wine aroma are mainly alcohols, esters, volatile fatty acids, aldehydes and ketones, of which ethyl esters are particularly important.[18] In addition, varietal terpenoids are a group of volatile compounds found in small amounts in wines but, due to low olfactory threshold, they typically contribute to wine aroma. In white aromatic cultivars, such as Muscat, Riesling or Gewürztraminer, monoterpenes are the main compounds responsible for the typical floral aroma and their concentration is influenced by several factors such as grape cultivar and degree of maturity, vintage, climate or vineyard management techniques.[19,20]

The aim of this research was to evaluate the effect of cane-cut on-vine as withering technique, where one-year canes were cut below the clusters at harvest, on grape volatiles concentration and profile during the dehydration process. The results were compared with those of grapes exposed to normal on-vine dehydration (normal late harvest). This study was carried out on the Moscato bianco aromatic white cultivar, grown in Italy to produce different natural sweet dessert wines such as Moscato d'Asti and the sparkling wine Asti DOCG from fresh grapes, as well as *passito* wines from withered grapes.

MATERIALS AND METHODS

Grape samples

This study was performed on white *Vitis vinifera* L. Moscato bianco cv grapes collected in a vineyard located in Calosso (Asti, Italy). The vineyard, sited at 290 m above sea level and grafted onto Kober 5 BB rootstock, was planted in 1979. The vineyard soil is calcareous-clayey, and the vines were trained on a Guyot system with 8-9 buds on the fruit head; the plant density is 3500 vines ha^{-1}, and the average height of the vegetative wall is 1.2 m. At veraison (beginning of August), a thinning was performed with the elimination of about 30% of the bunches, mainly those more distant from the stock.

The experiment was conducted as a randomized block design with four replicates. Each block was composed of two different treatments, a control in which the grapes were left on the vine during the over-ripening process, without manipulation of the clusters, following normal on-vine dehydration (P) and a treatment where one-year canes were cut below the clusters at harvest (T). Samples were randomly collected at different dehydration times from the four replicates: a control (PT-0) was collected at harvest

time on September 4th, then samples on P and T systems were collected 10, 17 and 24 days after PT-0 (T-1 and P-1 on September 14th, T-2 and P-2 on September 21st, and T-3 and P-3 on September 28th).

Climate parameters from the Arpa Piemonte meteorological database (http://www.arpa.piemonte.it/), monitored in the vineyard during the period studied, were very close to those typically found in this growing zone (calculated average of 15 years is presented in parenthesis), specifically average daily minimum temperature of 14.0 ºC (13.8 ºC), average daily maximum temperature of 25.2 ºC (24.9 ºC), average daily mean temperature of 19.1 ºC (19.0 ºC), average daily minimum relative humidity of 46% (47%), average daily maximum relative humidity of 96% (96%), average daily mean relative humidity of 75% (76%), total precipitations of 48.6 mm (46.9 mm), daily maximum precipitations of 39.2 mm (24.2 mm) and average daily air speed of 1.0 m s^{-1} (1.0 m s^{-1}).

Instrumental texture analysis

A Universal Testing Machine (UTM) TAxT2i Texture Analyzer (Stable Micro Systems; Godalming, Surrey, UK) equipped with a HDP/90 platform and a 5 kg load cell was used to determine different mechanical properties of grape berries. For each treatment and date, a total of 20 grape berries were randomly sampled for each test. All data were acquired at 400 Hz and analysed using the Texture Expert Exceed software (Stable Micro Systems). All measurements were performed on the same day as picking to avoid sample modifications. Before analysis, the instrument was calibrated for force and distance, and the berries were placed in a thermally conditioned chamber for 1 h at 20 °C.

For assessing berry skin hardness, a puncture test with a P/2N needle probe (Stable Micro Systems) working at a test speed of 1 mm s^{-1} was used.[21] Each one of the twenty berries were individually punctured in the lateral face, and three parameters were determined: skin break force (N, as F_{sk}), skin break energy (mJ, as W_{sk}) and skin resistance to the axial deformation (N mm^{-1}, as E_{sk}).

The measurement of berry skin thickness (μm, as S_{psk}) required manual separation of a piece of skin from the lateral side of each berry with a razor blade and careful removal of the pulp. The compression test was carried out using a 2-mm P/2 flat cylindrical probe (Stable Micro Systems) and a test speed of 0.2 mm s^{-1}.[22]

The peduncle detachment resistance was assessed by a traction test using the A/PS probe (Stable Micro Systems), modified with a rigid arm, where the peduncle of each berry is anchored through the pliers.[5] The test was carried out at 1 mm s^{-1}, and this resistance was expressed as peduncle detachment maximum force (N, as F_{ped}) and energy (mJ, as W_{ped}).

Standard chemical parameters

For each treatment and date, three replicates of about 100 grape berries were randomly selected. In the juice obtained by manual grape crushing and centrifugation, pH was determined by potentiometry using an InoLab 730 pH meter (WTW, Weilheim, Germany), and titratable acidity (g L^{-1} as tartaric acid) was estimated according to OIV methods.[23] Reducing sugars (as sum of glucose and fructose, g L^{-1}) and organic acids (tartaric acid and malic acid, g L^{-1}) were determined using a high-performance liquid chromatography (HPLC) system (Agilent Technologies, Santa Clara, CA) equipped

with a refractive index detector and a diode array detector (DAD) set to 210 nm, respectively.[24]

Free and glycosylated volatile compounds

Free and glycosylated volatile compounds were determined according to Rolle et al.[25] Samples extraction was performed in duplicate on each sampling point and for each system considered. Briefly, the skins of 200 berries were separated and immediately placed in 20 mL of methanol for 1 h, while the pulps were kept in a beaker in presence of 50 mg of $Na_2S_2O_5$ to avoid oxidations. These two parts were separately homogenized (Waring Laboratory, Torrington, USA) and centrifuged at 7000 × g and 4 °C for 15 min. The pellet was washed and re-suspended with a tartrate buffer (5 g L^{-1} tartaric acid solution of pH 3.20) and centrifuged using the same operating conditions. The resulting extract was adjusted to 250 mL total volume with the tartrate buffer and treated with 100 mg of Rapidase X-Press pectolytic enzyme (DSM, The Nederlands) at 25 °C for 2 h. Then, 100 mL of the extract were joined with 200 µL of 1-heptanol (internal standard, 44 mg L^{-1} in 10% ethanol) and purified using a previously activated Sep-Pak C18 1-g SPE cartridge (Waters Corporation, Milford, MA, USA). The free volatile fraction was eluted using 12 mL of dichloromethane, dried using anhydrous Na_2SO_4 and concentrated prior to injection using a nitrogen stream. The bound fraction was eluted from the cartridge using methanol, the latter dried in a rotary evaporator (Buchi R-210, Flawil, Switzerland) and re-dissolved in a 0.2 mol L^{-1} citrate-phosphate buffer at pH 5. The enzymatic hydrolysis was carried out using 50 mg of Rapidase AR-2000 (DSM) for 24 h at 40 °C. This last fraction was then spiked with the internal

standard solution, purified with the previously described SPE procedure, and concentrated for GC injection.

GC/MS analysis, peak identification and quantitation (in µg L^{-1}) was carried out according to Rolle et al.[25] using a Shimadzu GC-2010 gas chromatograph and a QP-2010 quadrupole mass spectrometer detector (Shimadzu Corporation, Kyoto, Japan).

Statistical analysis

Statistical analyses were performed using Xlstat-Premium statistics software package from Addinsoft SARL (Paris, 2017). Significant differences among samples for each of the parameters determined were assessed by one-way analysis of variance (ANOVA). Fisher's least significant difference (LSD) means comparison test ($p < 0.05$) also was performed. Principal Component Analysis (PCA) was used on the volatile composition of the grape juice to discriminate among on-vine withering systems (P and T) at different dehydration time.

RESULTS AND DISCUSSION

Grape dehydration and mechanical properties

During the grape dehydration process, the berry weight decreased due to water loss in both on-vine P and T systems, even though faster dehydration was observed when the cane-cut system was applied to the vine at harvest (Figure 1). Moscato bianco grapes lost 38% of their weight in 24 days when cane-cut on-vine withering technique (T) was applied whereas normal late harvest grapes (P) lost 18% (Figure 1).

Dehydration conditions play an active role in determining the texture properties of withered grapes.[26] Berry skin texture parameters have been already considered efficient

indicators to assess the wine-grape suitability for on-vine drying.[5,27] In the present work, the influence of on-vine P and T withering systems on the mechanical properties of Moscato bianco grape berries can be observed in Table 1 at different dehydration times. After 17 days of dehydration, the cut of one-year canes at harvest (T-2) caused a significant decrease in the values of the mechanical parameters that define the skin hardness (F_{sk} and W_{sk}), in relation to PT-0 and P-2 samples. Previous studies have reported a decrease in skin hardness when fast water evaporation occurs because of the quick cell turgor loss and texture degradation.[28] In this study, in contrast to on-vine P system, grape berries from on-vine T system reached higher values in F_{sk} and W_{sk} with respect to control (PT-0) at the last dehydration time studied (T-3, 24 days after cane cutting, September 28th), although the differences were significant only for W_{sk}. This change in the trend of skin hardness for the on-vine T system at similar berry weight loss percentage (37 and 38% for T-2 and T-3, respectively) could be due to the combination of grape shrinkage, sugar migration to the skin and cell layers compactness. This could also explain the significant skin hardening of T-3 berries in relation to P-3 ones (38% *vs* 18% weight loss, respectively). These higher values of F_{sk} and W_{sk} are favourable, since they allow the grapes to be more resistant against to fungal diseases and physical damage.[29] In agreement with our results for normal late harvest grapes, these values increased during on-vine drying of Mondeuse and Becuét grapes only after 55th and 90th day, respectively, while no significant trend was observed for Fumin grapes.[5,27]

The values of skin resistance to the axial deformation (E_{sk}) were significantly lower for both P and T systems than those for the control (PT-0), corresponding the lowest values to the T berries at all dehydration times. Therefore, cane-cut on-vine withering

increased skin elasticity. Skin thickness (Sp_{sk}) was not significantly affected by dehydration time or the on-vine withering system. Other studies reported that during the on-vine withering process, E_{sk} values decreased also in Mondeuse, Fumin and Becuét grapes, but the trend of the Sp_{sk} parameter was rather irregular.[5,27]

On the other hand, pedicel detachment resistance, instrumentally defined by F_{ped} and W_{ped}, was lower in on-vine T withering system than in both on-vine P system and the control (PT-0). This aspect could be particularly favourable to the mechanical removal of the berries from the stalk during destemming process. Contrarily, low F_{ped} and W_{ped} values involve a berry detachment risk from the plant and therefore they are not convenient during withering in the case of adverse climatic conditions. This decrease agreed with the reported for other varieties during on-vine grape withering,[5,27] even though the differences were not always significant.

Standard chemical parameters of grapes

The chemical parameters for Moscato bianco grapes exposed to normal dehydration in the plant (on-vine P system) and cane-cut on-vine withering system (T) are shown in Table 2. As expected, the highest content of reducing sugars was found when on-vine T system was applied, in agreement with the highest berry weight loss achieved during dehydration and therefore the greatest concentration effect of pulp components. In comparison to on-vine P system, the berries of Moscato bianco from on-vine T system reached significantly higher sugar contents during dehydration with the highest values at 24 days after cane cutting (T-3).

Regarding the parameters defining the must acidity, pH values were not affected by the withering system (Table 2). On the contrary, titratable acidity decreased at the

beginning of the withering process in relation to control sample (PT-0), and then the values remained practically constant with the exception of T-3 samples where a significant increase was found for on-vine T *vs* P systems only at the end of the process (T-3 *vs* P-3, 24 days after cane cutting). These results demonstrated that cane-cut on-vine withering system (T) was effective to keep the must acidity. Other authors found similar results when this on-vine T withering system was applied before harvest to Raboso Piave grapes.[13]

In the present work, tartaric acid exhibited the highest value for the control sample (PT-0), but its decrease in partially withered grapes was significantly higher in on-vine T system, particularly at the beginning of dehydration (T-1, 10 days after cane cutting). However, malic acid was concentrated due to water loss in the berries from on-vine T system during dehydration period, evidencing little or no depletion as opposite to on-vine P system. Therefore, malic acid responded to cane-cut on-vine withering system with a concentration effect, probably because the fast weight loss masked the decrease of malic acid by respiration as observed for slow weight losses.[5]

Rusjan and Mikulic-Petkovsek[17] observed that Merlot berries from cane-cut vines reached significantly higher soluble acids contents and titratable acidity values in comparison to control berries at harvest. Other studies performed on Refosk,[14] Istrian Malvasia[15] and Rebula[16] grape berries exhibited a significant increase of titratable acidity, tartaric acid and malic acid when cane-cut on-vine technique was applied to the vineyard compared to the control. This behaviour was affected by the season in Istrian Malvasia. Results obtained in Mondeuse grapes also showed that the on-vine withering process induces the reduction of the malic acid content *versus* fresh grape due to malic

respiration. However, titratable acidity and pH trends did not follow those of malic acid content.[5]

Free volatile secondary metabolites

The influence of on-vine dehydration of Moscato bianco grapes on free volatile composition is shown in Table 3. A total of twenty-six compounds were identified and quantified in the free fraction. Among grape-derived free monoterpenoids, linalool that is the principal varietal marker of Moscato bianco grapes exhibited the main decreasing trends in both on-vine P and T systems respect to the control (PT-0). This decrease was confirmed also in another study on Muscat grapes raising under controlled dehydration conditions.[30] In particular, in our work, the on-vine P system appeared to be less sensitive to the decrease of linalool at the end of grape withering (an average of -273.2 μg L^{-1}, i.e. -74%, for P-3 *vs* PT-0) preserving the grape active free aroma, whereas the on-vine T system showed the lower content of linalool with respect to both the initial point (-310.1 μg L^{-1}, i.e. -84%, for T-3 *vs* PT-0) and the on-vine P system (-36.9 μg L^{-1}, i.e. -38% for T-3 *vs* P-3).

On the other hand, in the on-vine T system, the contents of all four linalool oxides (furan and pyran derivatives), α-terpineol and dihydroxylated terpenes (diendiol I and II, hydroxylated linalool and geraniol) and *cis*-rose oxide significantly increased at the final point (T-3), assuming a release of these compounds from the glycosylated forms during on-vine dehydration. Moreover, the concentration effect due to fast water loss could overcome any decrease. Water loss is responsible for important changes in the metabolism of fruits, probably due to increased cell wall enzyme activity and therefore accelerated respiration, ethylene production and also volatiles loss.[4] In our study, free

lilac alcohol stereoisomers (isomer 1 and 2), whose precursor is linalool,[31] were found in Moscato bianco grapes. At the final withering point, the grapes from the on-vine T system presented significantly increased contents of the two isomers. Considering both the decrease of linalool and the increase of its derivative compounds, such as linalool oxides, 8-hydroxylinalool and lilac compounds, linalool fungal biotransformation could be hypothesized, since pH value was not low enough for an acid-catalyzed chemical reaction.[32]

The other representative varietal hydroxylated monoterpenes (nerol and geraniol) did not vary significantly between the two on-vine P and T systems after 24 days of dehydration. It is well established that the synthesis of linalool with a decarboxylation stage is different to the biosynthesis of nerol and geraniol in which this stage is not required.[33]

Diendiol I (3,7-dimethylocta-1,5-dien-3,7-diol) significantly decreased in withered grapes from the on-vine P system, but a significant increase of this molecule was observed in the on-vine T system after 24 days of dehydration (T-3) when compared to PT-0 and P-3 samples. According to Piombino et al.,[34] this terpene is one of the key aromas of Malvasia delle Lipari *passito* wine and, together with linalool and (*E*)-furan linalool oxide, is considered important in other semi-aromatic wines such as Muller Thurgau.

Among C_6 compounds, both on-vine P and T systems showed an increase of 1-hexanol contents in grapes when compared to PT-0 sample without significant differences between systems at the final dehydration point. However, for (*Z*)-3-hexen-1-ol, the increase during withering was only observed for the on-vine T system with a significantly higher value *vs* P in the last period of withering. The amount of free benzyl

alcohol, not present in the fresh grape, significantly increased in the two on-vine systems but more strongly in the on-vine T withering system. Finally, free vanillin did not significantly change in any of two on-vine withering systems.

Glycosidically-bound volatile secondary metabolites

The influence of the on-vine withering systems applied to Moscato bianco vine on grape contents of bound volatile components is shown in Table 4. A total of twenty-eight compounds were identified and quantified in the bound fraction. Fresh Moscato bianco grapes presented a content of about two-fold higher of the principal varietal glycosylated marker and total content of glycosylated compounds with respect to free metabolites in accordance with the literature.[35] During withering, the response of the varietal marker precursors was in general different. In particular, glycosylated linalool contents did not change significantly in the on-vine P system during the dehydration process. Instead, glycosylated linalool showed a significant increase (+407.2 μg L^{-1}, i.e. +52%) in the on-vine T system at the end of the withering process (T-3) in relation to PT-0 samples, indicating a strong stimulus of the cane-cut on the terpenoid potential. This increase was also observed in the on-vine T system for all other bound terpene metabolites, particularly the most distinctive Muscat-like varietal compounds such as linalool oxides, geraniol and nerol, as well as β-citronellol and all the dihydroxylated terpene forms. The content of C_6 compounds also increased significantly in T-3 samples with respect to PT-0 ones. In the on-vine P system, only few bound terpenoids, such as β-citronellol, nerol, geraniol and some hydroxylates (hydroxylinalool and hydroxygeraniol) increased in relation to PT-0 samples, while the other glycosylated metabolites such as linalool decreased or remained stable. In general, the content of

terpenes increases during ripening, but at the overripe stage, the concentration of free terpenes may decrease and that of bound terpenes may increase.[36]

According to the above-mentioned findings, the cane-cut on-vine withering system (T) applied to Moscato bianco grapes increased the wealth of glycosylated terpenic precursors because no significant degradation was observed, and consequently they were accumulated, concentrated or stimulated during withering. Taking into account that these compounds are released during fermentation and/or aging of the resulting wines, the cane-cut on-vine system may contribute to a greater aromatic complexity. Grapes derived from the on-vine T system were richer at the third stage of withering (T-3) in total content of mono- and poly-hydroxylated bound terpenic metabolites compared to the P system.

The response of both free and bound fractions of volatiles to on-vine T and P withering systems is shown in Figure 2. The highest content of total volatile compounds was achieved for T system at the last withering time (T-3) in both free and bound fractions, but the difference was only significant for the bound fraction with respect to the control (PT-0). Moreover, the most abundant volatile compounds in Moscato bianco grapes were found in the bound fraction for control and both withering systems at all dehydration times.

During grape dehydration, water stress can alter the cellular structure of the berry, and therefore affects cell metabolism.[26] Bellincontro et al.[4] also evidenced that fast dehydration increases the content of volatiles in Malvasia and Sangiovese grapes, as occurred in our work for on-vine T withering, in relation to slower dehydration processes. In addition, glycosylation is stimulated by water stress: initially, a high concentration of volatiles is synthetized as a defence mechanism of the plant to the

stress, and then glycosylation occurs because these high concentrations may be toxic to the plant itself.[37] Several studies support the hypothesis that plants may glycosylate volatile compounds as a detoxification strategy since glycosides have been identified in the vacuole of the cell.[38,39] Other studies also showed this effect on the biosynthesis of monoterpenes during dehydration. Off-vine dehydration under ozone atmosphere (combined water and oxidative stress) increased the contents of terpenes, which are the major aromatic markers of Moscato bianco grapes, in the last phases of dehydration.[40] A water loss of 62% in Garnacha tintorera berries during off-vine dehydration induced an increased volatile concentration.[9] In both Moscato bianco and Garnacha tintorera grapes, bound compounds were found in higher concentrations than free volatiles, suggesting that glycosylation occurred during dehydration.[9,40]

For a clearer interpretation of the results, principal component analysis (PCA) was performed (Figure 3). Figure 3a shows a first PCA illustrating the projection of free volatile compounds (Table 3) on the basis of on-vine withering system (P) and cane-cut on-vine withering system (T) applied to Moscato bianco. The two principal components (PC1 and PC2) accounted for 81.13% of the initial variance (60.17% and 20.96%, respectively). Three groups were well differentiated: T-3 (cane-cut on-vine withering system at the last stage of withering) sited in the highly positive side of PC1 and characterized by its greatest richness in most free volatiles. A second group composed of on-vine withering system (P-1, P-2 and P-3) and cane-cut on-vine withering system (T-1 and T-2) was located in the negative side of PC1, and the third group formed by the control sample (PT-0) was located in the positive side of both PC1 and PC2.

The second PCA (Figure 3b) shows the projection of bound volatile compounds (Table 4) on the basis of both on-vine P and T systems. The two principal components

accounted for 79.81% of the total variance (66.25% and 13.56% for PC1 and PC2, respectively). In this second PCA, two groups were exhibited: T-3 (cane-cut on-vine withering system at the last stage of withering) sited in the positive side of PC1 and characterized by the highest contents of most bound volatiles, and a second group composed of the other P and T samples and control sample (PT-0) located in the negative side of PC1.

CONCLUSIONS

The present study highlighted the effect of cane-cut on-vine system applied at harvest on important grape traits of Moscato bianco cultivar. Changes in standard chemical composition, berry skin mechanical properties and volatile compounds during withering have been observed when this technique was applied. A significant increase of parameters that define berry skin hardness and skin elasticity was observed. Cane-cut on-vine system also significantly affected reducing sugars and organic acids in the grape juice, increasing their content with respect to normal on-vine withering. Regarding volatile secondary metabolites, this technique induced the increase of volatile compounds, particularly in the bound fraction. Linalool was influenced by cane-cut on-vine system showing a significant increase in the bound fraction (+52%) when compared to fresh grape. These results demonstrated that the application of this dehydration technique is a good alternative to improve the grape volatile composition and therefore the wine quality.

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FIGURE CAPTIONS

Figure 1. Evolution of berry weight loss percentage in different on-vine withering systems for Moscato bianco grapes: P= normal late harvest, T= cane-cut system.

Figure 2. Total free and bound volatile compounds in Moscato bianco grapes withered using different on-vine withering systems. Significant differences are indicated with different letters (LSD test at $p<0.05$): Capital letters indicate significant differences among PT-0/P-1/T-1; lowercase letters indicate significant differences among PT-0/P-2/T-2; Greek letters indicate significant differences among PT-0/P-3/T3. Normal letters are used for free compounds and bold letters for bound compounds. P= normal late harvest, T= cane-cut system. 0= 4 September, 1= 14 September, 2= 21 September, 3= 28 September.

Figure 3. Principal component analysis (PCA) applied to the volatile composition in the free (a) and bound (b) fraction of Moscato bianco grapes during different on-vine withering treatments: P= normal late harvest, T= cane-cut system. 0= 4 September, 1= 14 September, 2= 21 September, 3= 28 September.

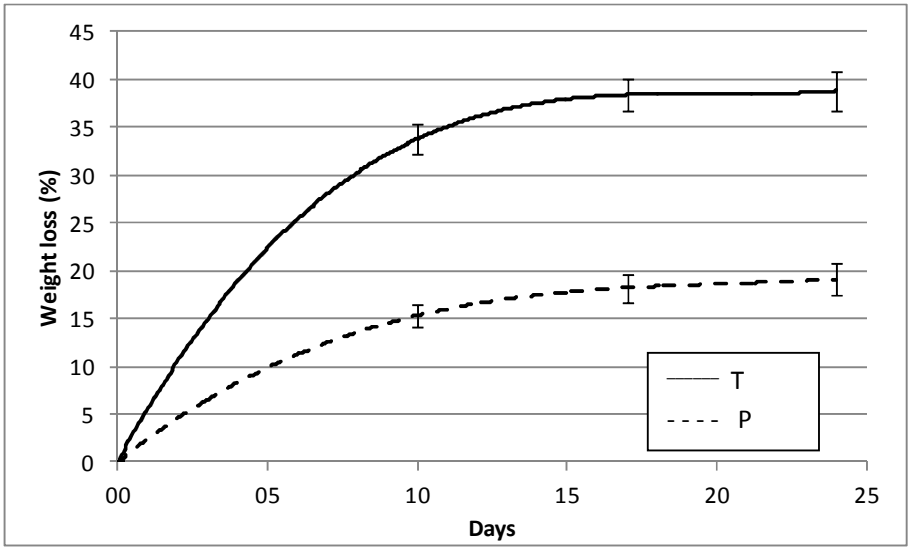


Figure 1.

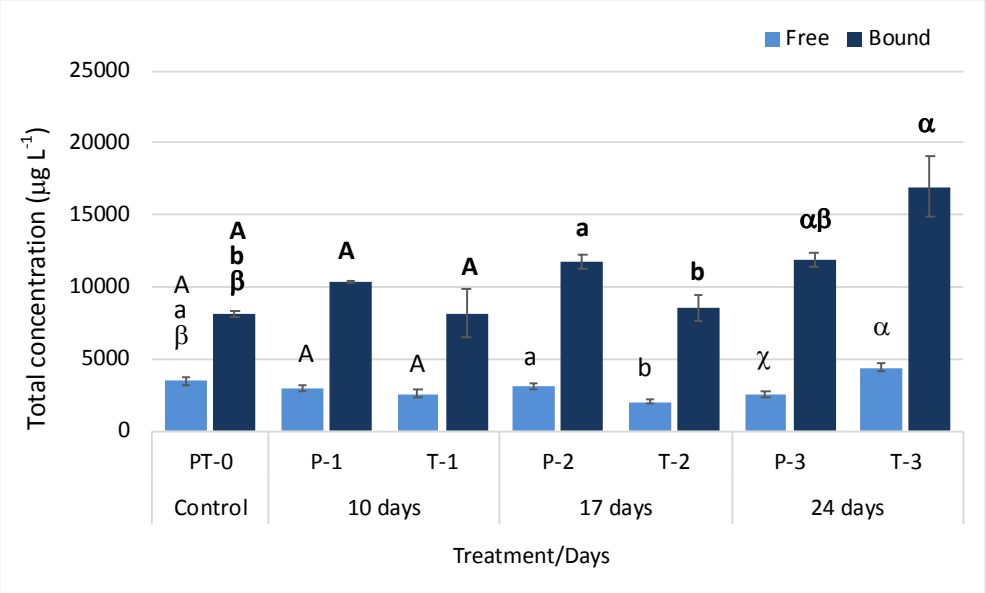
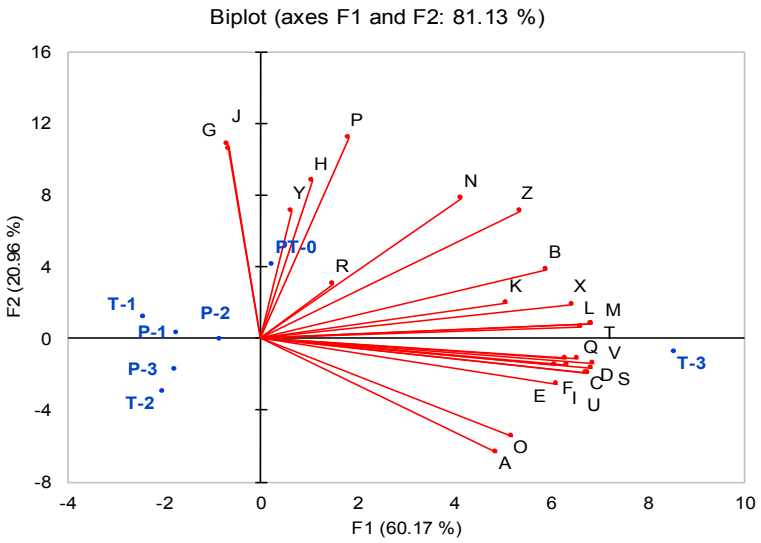


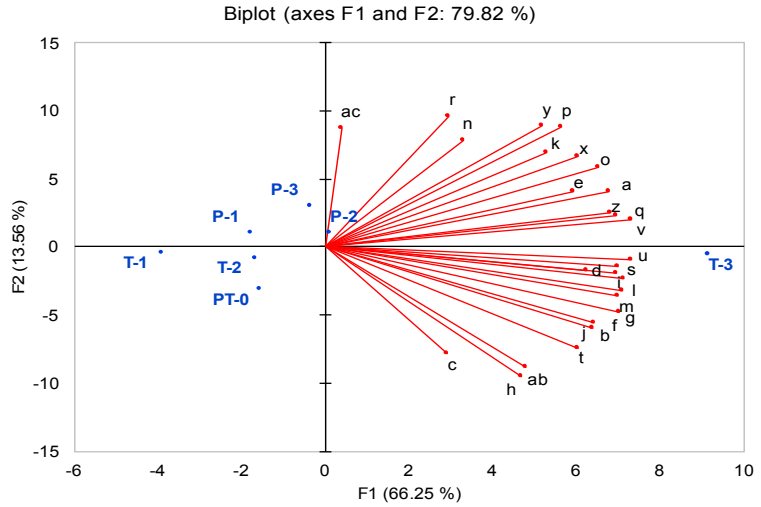
Figure 2.

a)



A:1-Hexanol, B: (Z)-3-Hexen-1-ol , C: cis-Rose oxide, D: (E)-Furan linalool oxide, E: Nerol oxid, F: (Z)- Furan linalool oxide, G: Linalool, H: Ho-trienol, I: α-Terpineol, J: Geranial, K: Ethoxy-diol I, L: (E)-Pyran linalool oxide, M: (Z)-Pyran linalool oxide, N: β -Citronellol, O: Lilac alcohol (isomer 1), P: Nerol, Q: Lilac alcohol (isomer 2), R: Geraniol, S: Benzyl alcohol, T: Diendiol I, U: Diendiol II, V: (E)-8-Hydroxylinalool, X: (Z)-8-Hydroxylinalool, Y: Geranic acid, Z: Vanillin

b)



a: 1-Hexanol, b: (Z)-3-Hexen-1-ol, c: cis-Rose oxide, d: (E)-Furan linalool oxide, e: Nerol oxide, f: (Z)-Furan linalool oxide, g: Linalool, h: Ho-trienol, i: α-Terpineol, j: Geranial, k: Ethoxy-diol I, l: (E)- Pyran linalool oxide, m: (Z)- Pyran linalool oxide, n:β-Citronellol, o: Lilac alcohol (isomer 1), p: Nerol, q: Lilac alcohol (isomer 2), r: Geraniol, s: Benzyl alcohol, t: Diendiol I, u: Diendiol II, v: E)-8-Hydroxylinalool, x: (Z)-8-Hydroxylinalool, y:Geranic acid , z: 3-Hydroxy-β-damascone, ab: Vanillin, ac: 3-Oxo-α-ionol

Figure 3.

Table 1. Berry skin mechanical properties and peduncle detachment resistance behavior during withering in different on-vine systems for Moscato bianco grapes.

	PT-0	P-1	P-2	P-3	*Sig. P*	T-1	T-2	T-3	*Sig. T*	*Sig. 1*	*Sig. 2*	*Sig. 3*
F_{sk} (N)	$0.592\pm0.145^{a,A}$	0.474 ± 0.125^{b}	0.460 ± 0.159^{b}	0.484 ± 0.134^{b}	*	0.435 ± 0.153^{B}	0.274 ± 0.082^{C}	0.605 ± 0.188^{A}	***	ns	***	*
W_{sk} (mJ)	0.513 ± 0.159^{B}	0.574 ± 0.183	0.548 ± 0.187	0.512 ± 0.161	ns	0.592 ± 0.218^{B}	0.407 ± 0.081^{B}	1.111 ± 0.457^{A}	***	ns	**	***
E_{sk} (N mm^{-1})	$0.344\pm0.172^{a,A}$	0.183 ± 0.088^{b}	0.168 ± 0.065^{b}	0.204 ± 0.064^{b}	***	0.133 ± 0.055^{B}	0.074 ± 0.027^{B}	0.127 ± 0.047^{B}	***	*	***	***
Sp_{sk} (µm)	209 ± 38	242 ± 55	224 ± 50	203 ± 66	ns	230 ± 35	201 ± 54	208 ± 46	ns	ns	ns	ns
F_{ped} (N)	$3.49\pm0.93^{a,A}$	2.64 ± 0.66^{bc}	2.28 ± 0.55^{c}	3.13 ± 1.19^{ab}	***	1.74 ± 0.52^{B}	1.30 ± 0.56^{B}	1.30 ± 0.75^{B}	***	***	***	***
W_{ped} (mJ)	$3.21\pm1.98^{ab,A}$	2.87 ± 1.75^{ab}	2.55 ± 1.56^{b}	4.57 ± 3.40^{a}	*	2.12 ± 1.74^{B}	1.47 ± 0.72^{B}	1.61 ± 1.40^{B}	**	ns	**	***

Average value ± standard deviation (n = 20). F_{sk}= skin break force, W_{sk}= skin break energy, E_{sk}= skin resistance to the axial deformation, Sp_{sk}= skin thickness, F_{ped}= peduncle detachment force, W_{ped}= peduncle detachment energy. P= normal late harvest, T= cane-cut system; 0= 4 September, 1= 14 September, 2= 21 September, 3= 28 September. Different lowercase letters indicate significant difference among the normal on-vine withering system (P). Different capital letters indicate significant difference among the cane-cut on-vine withering system (T). Sign: *, **, ***, and ns indicate significance at p<0.05, 0.01, 0.001, and not significant, respectively.

Table 2. Grape technological parameters monitored during withering in different on-vine systems for Moscato bianco grapes.

	PT-0	P-1	P-2	P-3	*Sig. P*	T-1	T-2	T-3	*Sig. T*	*Sig. 1*	*Sig. 2*	*Sig. 3*
Reducing sugars (g L^{-1})	$261\pm1^{d,D}$	314 ± 2^{b}	306 ± 1^{c}	325 ± 2^{a}	***	369 ± 1^{C}	397 ± 1^{B}	433 ± 1^{A}	***	***	***	***
Titratable acidity (g L^{-1})	$5.9\pm0.1^{a,A}$	5.0 ± 0.1^{b}	5.1 ± 0.1^{b}	5.0 ± 0.1^{b}	***	5.0 ± 0.1^{B}	5.1 ± 0.1^{B}	6.1 ± 0.2^{A}	***	ns	ns	*
Tartaric acid (g L^{-1})	$6.5\pm0.1^{a,A}$	4.2 ± 0.1^{c}	3.8 ± 0.1^{d}	4.5 ± 0.1^{b}	***	2.8 ± 0.3^{C}	3.6 ± 0.1^{B}	3.8 ± 0.1^{B}	***	*	ns	***
Malic acid (g L^{-1})	1.8 ± 0.1^{B}	1.2±0.1	1.3±0.1	1.6±0.2	ns	1.7 ± 0.1^{B}	2.2 ± 0.1^{B}	2.8 ± 0.3^{A}	*	*	*	ns
pH	3.34±0.15	3.53±0.04	3.53±0.04	3.54±0.02	ns	3.77±0.11	3.76±0.14	3.66±0.06	ns	ns	ns	ns

Average value ± standard deviation (n = 3). P= normal late harvest, T= cane-cut system; 0= 4 September, 1= 14 September, 2= 21 September, 3= 28 September. Different lowercase letters indicate significant difference among the normal on-vine withering system (P). Different capital letters indicate significant difference among the cane-cut on-vine withering system (T). Sign: *, **, ***, and ns indicate significance at $p<0.05$, 0.01, 0.001, and not significant, respectively.

Table 3. Free volatile compounds (μg L^{-1}) of Moscato bianco grapes monitored during withering in different on-vine systems.

	PT-0	P-1	P-2	P-3	*Sig. P*	T-1	T-2	T-3	*Sig. T*	*Sig.1*	*Sig. 2*	*Sig. 3*
1-Hexanol	45.5±4.9^{d,B}	58.3±0.8^{c}	92.1±0.7^{b}	119.7±6.9^{a}	***	42.7±0.6^{B}	73.8±0.6^{B}	151.1±26.6^{A}	**	**	**	ns
(*Z*)-3-Hexen-1-ol	4.7±0.2^{a,B}	2.7±0.7b	2.1±0.1^{b}	2.6±0.2^{b}	**	1.4±0.3^{C}	1.9±0.2^{C}	5.6±0.3^{A}	***	ns	ns	**
cis-Rose oxide	0.5±0.5^{B}	0.8±0.3	1.2±0.4	0.9±0.1	ns	0.8±0.6^{B}	0.5±0.8^{B}	15.1±1.9^{A}	***	ns	ns	**
(*E*)-Furan linalool oxide	15.2±1.2^{B}	12.4±3.4	17.0±1.2	13.1±1.0	ns	11.5±0.1^{B}	13.7±1.6^{B}	35.3±3.4^{A}	***	ns	ns	*
Nerol oxide	nd	nd	2.3±0.9	nd		1.2±0.1^{B}	nd	12.7±0.7^{A}	***			
(*Z*)- Furan linalool oxide	24.3±0.6^{b,B}	26.4±4.5^{b}	34.3±1.3^{a}	16.1±1.0^{c}	**	17.4±0.1^{C}	26.1±1.1^{B}	49.8±3.3^{A}	***	ns	*	**
Linalool	369.6±17.8^{a,A}	143.5±1.0^{b}	139.6±9.9^{b}	96.4±5.9^{c}	***	102.5±5.5^{B}	29.9±1.0^{D}	59.5±4.2^{C}	***	**	**	*
Ho-trienol	1.4±1.8	nd	nd	0.8±0.9	ns	nd	nd	nd	-			-
α-Terpineol	8.6±0.7^{B}	8.0±0.4	8.6±1.1	8.4±0.7	ns	11.1±0.3^{B}	9.2±0.4^{B}	18.7±2.2^{A}	**	*	ns	*
Geranial	8.6±1.5^{a,A}	5.1±0.1^{b}	4.0±0.2^{b}	4.8±0.7^{b}	*	6.0±0.5^{AB}	3.4±1.8^{B}	4.2±1.9^{B}	ns	ns	ns	ns
Ethoxy-diol I	10.2±0.9^{B}	8.7±1.0	9.5±0.1	12.5±2.0	ns	10.8±0.8^{B}	4.7±0.1^{C}	16.2±2.0^{A}	**	ns	***	ns
(*E*)-Pyran linalool oxide	168.1±32.8^{B}	104.4±6.2	119.3±5.1	108.8±7.8	ns	63.2±3.3^{C}	113.9±8.4^{B}	262.3±35.8^{A}	**	*	ns	*
(*Z*)-Pyran linalool oxide	32.1±3.7^{a,B}	17.5±0.5^{b}	19.0±0.7^{b}	19.1±1.0^{b}	**	12.7±0.1^{C}	18.3±0.8^{B}	59.9±12.0^{A}	**	**	ns	*
β -Citronellol	33.3±0.4^{a,A}	25.7±1.3^{b}	26.1±1.5^{b}	20.4±2.8^{c}	**	34.2±1.6^{A}	18.1±0.6^{B}	36.6±5.5^{A}	**	*	*	ns
Lilac alcohol (isomer 1)	4.2±0.2^{B}	2.9±0.8	5.3±1.9	4.0±0.4	ns	3.5±0.1^{B}	7.9±0.7^{A}	9.9±2.0^{A}	*	ns	ns	ns
Nerol	355.3±12.8^{a,A}	276.9±0.7^{b}	257.2±21.5^{b}	198.3±24.5^{c}	**	273.6±9.5^{B}	162.2±9.0^{C}	272.4±28.3^{B}	**	ns	*	ns
Lilac alcohol (isomer 2)	2.7±0.2^{b,B}	2.4±0.1^{b}	4.2±0.1^{a}	2.3±0.2^{b}	***	2.4±0.1^{B}	2.5±0.1^{B}	6.0±0.2^{A}	***	ns	**	**
Geraniol	471.0±174.3	653.7±4.8	592.7±52.3	421.3±53.5	ns	445.5±20.8	349.8±24.5	453.9±46.3	ns	**	*	ns
Benzyl alcohol	nd	17.5±2.7	8.5±1.0	18.3±1.3	***	13.5±1.3^{B}	17.4±6.8^{B}	50.1±6.1^{A}	**	ns	ns	*
Diendiol I	654.4±52.8^{a,B}	375.0±39.1^{b}	447.7±17.7^{b}	401.9±8.5^{b}	**	361.7±61.4^{C}	439.3±34.3^{C}	1148.2±39.7^{A}	***	ns	ns	**
Diendiol II	155.2±26.5^{B}	124.2±11.6	141.6±0.2	153.9±4.5	ns	101.3±15.2^{C}	134.6±20.2^{BC}	352.5±1.6^{A}	***	ns	ns	***
(*E*)-8-Hydroxylinalool	35.2±13.4^{B}	38.2±0.8	39.8±3.5	31.5±3.1	ns	37.2±7.6^{B}	39.7±2.0^{B}	113.3±6.4^{A}	**	ns	ns	**
(*Z*)-8-Hydroxylinalool + hydroxy-geraniol	482.7±40.9^{B}	477.7±45.9	437.5±40.1	354.4±39.3	ns	320.6±47.6^{C}	339.7±28.1^{C}	697.4±34.0^{A}	**	ns	ns	*
Geranic acid	607.0±186.1^{A}	594.3±112.1	747.9±53.9	528.6±112.8	ns	725.9±90.8^{A}	224.3±7.6^{B}	587.7±40.7^{A}	*	ns	**	ns
Vanillin	15.5±7.4	6.9±0.1	6.2±2.4	3.4±0.4	ns	9.9±1.5	2.6±1.0	18.1±9.4	ns	ns	ns	ns

Average value ± standard deviation (n = 2). nd= not detectable. P= normal late harvest, T= cane-cut system; 0= 4 September, 1= 14 September, 2= 21 September, 3= 28 September. Different lowercase letters indicate significant difference among the normal on-vine withering system (P). Different capital letters indicate significant difference among the cane-cut on-vine withering system (T). Sign: *, **, ***, and ns indicate significance at p<0.05, 0.01, 0.001, and not significant, respectively.

Table 4. Glycosylated volatile compounds (μg L^{-1}) of Moscato bianco grapes monitored during withering in different on-vine systems.

	PT-0	P-1	P-2	P-3	*Sig. P*	T-1	T-2	T-3	*Sig.*	*Sig.1*	*Sig. 2*	*Sig. 3*
1-Hexanol	78.1±8.2^{b,D}	131.9±0.3^{a}	155.4±10.2^{a}	154.2±34.5^{a}	*	96.0±0.8^{C}	157.8±1.2^{B}	268.7±6.6^{A}	***	***	ns	*
(*Z*)-3-Hexen-1-ol	10.2±0.6^{a,B}	5.4±0.8^{b}	6.5±0.6^{b}	6.2±0.9^{b}	*	2.2±0.2^{D}	5.7±1.5^{C}	14.5±0.2^{A}	***	*	ns	**
cis-Rose oxide	5.2±0.1	3.4±0.3	3.4±1.1	3.4±0.4	ns	8.1±6.9	5.1±0.6	8.4±0.7	ns	ns	ns	*
(*E*)-Furan linalool oxide	122.7±3.3^{B}	79.8±3.4	104.5±26.0	90.4±1.6	ns	45.7±1.3^{B}	113.0±20.4^{B}	241.7±64.1^{A}	*	**	ns	ns
Nerol oxide	0.1±0.1^{b,D}	10.3±0.1^{a}	12.8±2.3^{a}	11.3±0.2^{a}	**	7.5±1.4^{C}	16.5±2.3^{B}	26.9±2.1^{A}	***	ns	ns	**
(*Z*)-Furan linalool oxide	40.1±3.3^{B}	26.3±1.0	32.2±8.7	24.7±1.3	ns	14.4±1.9^{B}	35.4±8.0^{B}	87.8±28.8^{A}	*	*	ns	ns
Linalool	775.7±29.8^{B}	594.2±19.2	739.3±147.7	680.6±22.6	ns	469.9±6.8^{B}	657.9±9.2^{B}	1182.9±218.6^{A}	*	*	ns	ns
Ho-trienol	8.6±0.1^{a}	nd	nd	4.9±0.8^{b}	***	nd	8.0±4.0	11.5±4.0	ns			ns
α-Terpineol	78.2±4.8^{a,AB}	61.2±3.0^{b}	77.9±6.4^{a}	73.0±0.8^{ab}	*	45.9±1.8^{B}	65.2±0.6^{B}	112.5±26.3^{A}	*	*	ns	ns
Geranial	20.2±1.1^{a,AB}	14.5±0.3^{b}	12.3±2.8^{b}	12.9±1.4^{b}	*	11.2±0.2^{B}	10.7±0.3^{B}	30.1±9.7^{A}	*	**	ns	ns
Ethoxy-diol I	4.0±0.2^{b,B}	nd	nd	7.8±2.6^{a}	*	nd	nd	11.0±1.6^{A}	***			ns
(*E*)- Pyran linalool oxide	261.6±7.9^{B}	201.9±7.2	256.4±38.0	258.7±29.2	ns	118.8±1.0^{B}	306.0±42.0^{B}	603.4±154.1^{A}	*	**	ns	ns
(*Z*)- Pyran linalool oxide	19.4±2.9^{B}	12.6±0.6	11.9±1.7	15.2±2.8	ns	4.7±4.8^{B}	20.9±1.8^{B}	55.3±15.8^{A}	*	ns	*	ns
β-Citronellol	90.7±0.7^{b,B}	94.7±3.7^{b}	83.3±7.3^{b}	123.6±7.8^{a}	**	91.9±6.9^{B}	53.2±1.0^{C}	113.8±0.5^{A}	***	ns	*	ns
Lilac alcohol (isomer 1)	22.6±1.7^{c,B}	25.5±1.5^{bc}	29.5±1.8^{b}	36.7±1.3^{a}	**	13.7±2.2^{B}	19.4±3.7^{B}	46.3±4.8^{A}	**	*	ns	ns
Nerol	1898.6±28.8^{b,B}	2336.8±8.0^{a}	2357.4±144.0^{a}	2661.0±210.0^{a}	*	1919.8±94.9^{B}	1698.8±65.0^{B}	2919.1±199.0^{A}	**	*	*	ns
Lilac alcohol (isomer 2)	24.8±0.1^{B}	21.1±0.2	26.5±4.3	32.4±3.5	ns	13.8±1.0^{C}	19.8±3.9^{BC}	46.4±4.5^{A}	**	**	ns	ns
Geraniol	1690.8±30.8^{c,B}	2474.3±32.4^{a}	2162.1±136.0^{b}	2177.7±170.5^{ab}	**	1601.6±119.0^{B}	1355.0±55.4^{C}	2202.4±114.2^{A}	**	**	*	ns
Benzyl alcohol	nd	13.1±3.8^{b}	15.2±5.8^{b}	61.9±18.5^{a}	*	8.7±2.2^{B}	9.1±1.7^{B}	194.3±55.3^{A}	**	ns	ns	ns
Diendiol I	668.4±41.2^{a,A}	304.1±8.7^{c}	393.4±31.6^{b}	375.8±33.1^{bc}	**	213.6±82.2^{B}	373.5±28.8^{B}	848.8±132.2^{A}	**	ns	ns	*
Diendiol II	102.1±2.5^{b,B}	80.1±4.9^{c}	132.0±7.3^{a}	108.6±7.8^{b}	**	67.8±27.2^{B}	101.7±26.4^{B}	242.5±55.4^{A}	*	ns	ns	ns
(*E*)-8-Hydroxylinalool	919.0±20.4^{b,B}	947.1±15.4^{b}	1235.0±71.3^{a}	1255.1±24.5^{a}	**	741.7±350.7^{B}	976.6±152.6^{B}	2166.2±288.5^{A}	*	ns	ns	*
(*Z*)-8-Hydroxylinalool + hydroxy-geraniol	185.5±7.0^{c,C}	1291.7±33.7^{b}	1572.1±78.2^{a}	1357.9±120.8^{b}	***	825.0±414.7^{BC}	1354.7±258.6^{B}	2550.4±351.5^{A}	**	ns	ns	*
Geranic acid	1061.3±21.6^{c,B}	1599.6±2.4^{b}	2170.0±107.3^{a}	2240.8±82.7^{a}	***	1768.2±523.0^{B}	1003.5±179.9^{B}	2715.6±309.2^{A}	*	ns	*	ns
3-Hydroxy-β-damascone	13.5±0.2^{c,C}	23.0±0.3^{b}	40.0±3.3^{a}	37.3±0.6^{a}	***	16.9±5.2^{C}	42.8±4.2^{B}	82.2±11.5^{A}	**	ns	ns	*
Vanillin	nd	nd	nd	6.2±3.9	ns	nd	nd	7.0±1.4	***			ns
3-Oxo-α-ionol	61.7±0.3	nd	nd	97.8±44.1	ns	84.0±7.0	112.8±12.5		ns	ns		

Average value ± standard deviation (n = 2). nd = not detectable. P= normal late harvest, T= cane-cut system; 0= 4 September, 1= 14 September, 2= 21 September, 3= 28 September. Different lowercase letters indicate significant difference among the normal on-vine withering system (P). Different capital letters indicate significant difference among the cane-cut on-vine withering system (T). Sign: *, **, ***, and ns indicate significance at $p<0.05$, 0.01, 0.001, and not significant, respectively.