

AperTO - Archivio Istituzionale Open Access dell'Università di Torino

Physico-mechanical evaluation of the aptitude of berries of red winegrape varieties to resist the compression in carbonic maceration vinification.

This is the author's manuscript

Original Citation:

Availability:

This version is available <http://hdl.handle.net/2318/118829> since 2016-07-05T08:32:53Z

Published version:

DOI:10.1111/ijfs.12032

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 the accepted version of the following article:

[Giacosa S., Torchio F., Río Segade S., Gaiotti F., Tomasi D., Lovat L., Vincenzi S., Rolle L. (2013) - Physico-mechanical evaluation of the aptitude of berries of red winegrape varieties to resist the compression in carbonic maceration vinification. *Int. J. Food Sci. Technol.*, 48, 817-825.

],

which has been published in final form at

[<http://onlinelibrary.wiley.com/doi/10.1111/ijfs.12032/pdf>]

**PHYSICO-MECHANICAL EVALUATION OF THE APTITUDE OF BERRIES OF RED WINEGRAPE VARIETIES TO
RESIST THE COMPRESSION IN CARBONIC MACERATION VINIFICATION**

Simone Giacosa^a#, Fabrizio Torchio^a#, Susana Río Segade^a, Federica Gaiotti^c, Diego Tomasi^c, Lorenzo Lovat^c,
Simone Vincenzi^b & Luca Rolle^{a,*}

^a University of Turin, Dipartimento di Scienze Agrarie, Forestali e Alimentari, Via L. da Vinci 44, 10095 Grugliasco (TO), Italy.

^b University of Padova, Centro Interdipartimentale per la Ricerca in Viticoltura ed Enologia, 35020, Legnaro (PD), Italy.

^c CRA-VIT Centro di Ricerca per la Viticoltura, Via XXVIII Aprile 26, 31015 Conegliano (TV), Italy.

*Corresponding author: luca.rolle@unito.it, Tel.: +39 11 6708558; Fax: +39 11 6708549

Running Title: Winegrapes resistance to the compression

These authors contributed equally to the study.

ABSTRACT

By texture analysis tests, the berry aptitude to resist the rupture under compression load supported during intracellular fermentation was studied for twenty-three red winegrape varieties. The softest berries were associated with Ancellotta (1.72 N), Dolcetto (1.79 N), Gamay (2.26 N) and Schiava gentile (2.29 N) cultivars. The hardest berries corresponded to Franconia and Bonarda cultivars (4.02-4.03 N). High resistance to splitting was also detected for Grenache, Raboso, Marzemino, Negramaro, Montepulciano and Croatina cultivars (3.50-3.95 N).

The differentiating power of the mechanical variables of the whole berry and skin was assessed by univariate and multivariate analysis. Relationships among the instrumental berry hardness and other physical and mechanical properties were also investigated.

The results obtained suggest that the manufacture of carbonic macerated wines should be planned considering the berry hardness, and it represents a new variable that should be considered in selecting which is the most appropriate winegrape variety to elaborate these wines.

Keywords: carbonic maceration; red winegrape varieties; berry hardness; instrumental texture parameters; varietal differentiation.

1. Introduction

Described for the first time by Flanzy in 1934 (Tesniere and Flanzy, 2011), carbonic maceration winemaking technique exploits the metabolic phenomena that happen spontaneously in the uncrushed winegrape berries when placed in anaerobiosis. Under anaerobic atmosphere, intracellular fermentation occurs and a series of internal transformations are promoted by the activity of endogenous enzymes present in the grapes (partial degradation of malic acid, limited alcohol production), as well as part of phenolic compounds diffuse from the skin to the pulp. The intact grape clusters, introduced into a closed tank, are kept under carbon dioxide atmosphere for one week or longer before pressing and the juice completes the alcoholic fermentation without skins (Tesniere and Flanzy, 2011). The final product is somewhat softer (lower alcohol degree, **malic acid content** and total acidity, reduced astringency owing to the lesser contribution of grape seeds to the proanthocyanidin composition) than a conventional wine, and it is characterized by a less colour intensity and more intense fruity aromas (Castillo-Sánchez *et al.*, 2006; Rizzon *et al.*, 1999; Spranger *et al.*, 2004). Traditionally, the wines obtained by carbonic maceration are early consumed, they being better appreciated as young wines and commonly recommended for consumption within few months after winemaking.

The carbonic macerated grapes are richer in volatile compounds than the traditionally treated grapes (Dourtoglou *et al.*, 1994; Fondville-Bagnol *et al.*, 1999). These compounds persist after alcoholic fermentation and, therefore, the wines produced by carbonic maceration are by far richer in them providing a distinctive aroma (Flanzy, 2003; Lőrincz and Vas, 1998) with red berry notes (Ducruet, 1984; Etaio *et al.*, 2008; Versini and Tomasi, 1983). The volatile compounds contributing to the flavour of carbonic macerated grapes are largely independent on the grape variety, and they can be attributed to specific biochemical pathway regarding specific amino acids (Dourtoglou *et al.*, 1994). In fact, an increase in the amino acid content was also observed when the grapes were kept under carbon dioxide atmosphere (Dourtoglou *et al.*, 1994). The anaerobic metabolism of grape berries also influences the phenolic composition. If compared with conventional young wines, the carbonic macerated ones are characterized by a combination of higher contents of B-type vitisins and ethyl-bridged anthocyanins-flavanol adducts (Chinnici *et al.*, 2009), probably resulting from the high amount of acetaldehyde produced by the anaerobic metabolism (Amati *et al.*, 1973; Carnacini and Del Pozzo, 1985), with lower contents of total anthocyanins and monomeric anthocyanins (Castillo-Sánchez *et al.*, 2006; Castillo-Sánchez *et al.*, 2008; Gómez-Míguez and Heredia, 2004; Spranger *et al.*, 2004; Sun *et al.*, 2001). The grape variety, the ripeness of berries, the differences in the ethanol content reached and in the length and temperature of maceration could explain

the contradictory results found in the scientific literature about the proanthocyanidin content (Castillo-Sánchez *et al.*, 2008; Spranger *et al.*, 2004; Sun *et al.*, 2001) and, therefore, about total phenolic content in carbonic macerated wines (Gómez-Míguez and Heredia, 2004; Pellegrini *et al.*, 2000; Spranger *et al.*, 2004; Sun *et al.*, 2001).

Anaerobic metabolism occurs whenever the oxygen concentration is low in either gaseous or liquid environment, but the intensity of the phenomena diminishes in liquid environment (Ribéreau-Gayon *et al.*, 2000). Therefore, whole grapes immersed in the must, produced by berries splitting (generally those placed in the lower part of the tank), undergo a less intense anaerobic metabolism than the same grapes placed in carbon dioxide atmosphere (Ribéreau-Gayon *et al.*, 2000). These aspects indicate that the mechanical characteristics of the whole berry and skin could play a key role to decide if a certain grape variety is adequate to support the crushing/compression that the berries withstand in the tank.

The aim of this work was to compare the instrumental texture parameters of the whole berry and of the berry skin for different red winegrape varieties because of their incidence on the berry resistance to the burst/splitting after compression and, therefore, to differentiate these cultivars on their suitability to carbonic maceration winemaking technique. Furthermore, a relationship was established among the berry hardness and different physical and mechanical parameters of the whole berry and skin.

2. Materials and methods

2.1. Grape samples

Grape samples of 23 red cultivars, all of them belonging to *Vitis vinifera* L., were harvested in the same collection-experimental vineyard of 1.2 ha located in Susegana – TV, Veneto Region (North-East Italy) in 2010. The vines had the same age (15 years), were grafted on SO4 rootstock and were planted at 3.0 m between rows and 1.5 m between vines. The vines were Sylvoz pruned with three canes of 10/12 buds each one and shoots were vertically positioned upward between three pairs of catch wires.

To minimize the possible ripening effect among berries, the grape samples (about 1000 berries picked randomly up from ten plants) were harvested for each variety when the soluble solid content was about 21 °Brix. Moreover, once in the laboratory, the grape berries were separated according to their density by flotation in different saline solutions (from 100 to 190 g L⁻¹ sodium chloride, corresponding to densities comprised between 1069 and 1125 kg m⁻³) (Rolle *et al.*, 2011a). The comparative study was carried out on berries with a density of 1088 kg m⁻³ so that all of them contain a similar sugar content of 202 ± 8 g L⁻¹ (Rolle *et al.*, 2011a). The sorted berries were washed with water, visually inspected before analysis and those with damaged skins were discarded. For each variety studied, a sub-sample of 35 sorted berries was used for the determination of the physical and mechanical properties (Maury *et al.*, 2009).

2.2. Physical and mechanical properties

For each variety studied, the grape berries were singularly weighed. The length between top and bottom sides (L), and the length between both lateral sides at middle of the berry height (ℓ) were measured using a calliper, which had an accuracy of 0.1 mm. The volume was then calculated comparing the berry form to an ellipsoid, following the equation (Río Segade *et al.*, 2011a):

$$\text{Volume (cm}^3\text{)} = V_b = 4 \pi a b c / 3$$

where $a = b = \ell / 2$, $c = L / 2$.

For instrumental texture analysis, a 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.

For the Texture Profile Analysis (TPA) or double compression test, each one of the 35 whole berries weighed and measured for each cultivar studied was compressed in the equatorial position with a SMS

P/35 flat probe under 25% deformation, with a waiting period of two seconds between the two bites and using a speed test of 1 mm s^{-1} (Letaief *et al.*, 2008). The 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 (Le Moigne *et al.*, 2008; Letaief *et al.*, 2008; Maury *et al.*, 2009). In this type of compression test, the influence of the pulp and skin properties on the mechanical characteristics of berries is aggregate (Grotte *et al.*, 2001). The hardness variable was calculated as the first maximum compression force and used as marker for the berry resistance to the compression.

The berry skin hardness of the same berries used in TPA test, defined as the resistance to probe penetration, was assessed by a puncture test using a SMS P/2N needle probe, a 5 kg load cell and a speed test of 1 mm s^{-1} (Letaief *et al.*, 2008). The berries were individually placed on the metal plate of the UTM with the pedicel in a horizontal plane in order to be consistently punctured in the lateral face. The skin hardness was expressed in terms of the skin break force (N, as F_{sk}), skin break energy (mJ, as W_{sk}) and skin resistance to axial deformation (N mm^{-1} , as E_{sk} or Young's modulus). 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} . 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 measurement of the berry skin thickness (μm , as Sp_{sk}) required manual separation of a piece of skin (ca. 0.25 cm^2) from the lateral side of each berry using a razor blade, followed by drying with absorbent paper. The test was carried out using a P/2 flat probe and a speed test of 0.2 mm s^{-1} (Letaief *et al.*, 2008). The berry skin thickness is given by the distance between the point corresponding to the probe contact with the berry skin (trigger) and the platform base during the compression test (Río Segade *et al.*, 2011a). Care was taken in removing the pulp from the skin and in positioning the skin sample on the UTM platform to prevent folding (Río Segade *et al.*, 2011a). Furthermore, it was convenient to insert an instrumental trigger threshold equal to 0.05 N that enabled the plane surface of the probe to adhere completely to the skin sample before the acquisition started. This allowed a reduction or elimination of the 'tail' effect due to the postponement of the contact point (Letaief *et al.*, 2008).

Before each test, the instrument was calibrated for force and distance.

2.3. Statistical analysis

Statistical analyses were performed using the statistical software package SPSS version 17.0 (SPSS Inc., Chicago, IL, USA). The Tukey-b test for $p < 0.01$ was used to evaluate the existence of significant differences by one-way analysis of variance (ANOVA). Pearson's correlation coefficients (R) were calculated to determine significant relationships among the whole berry hardness and all remaining instrumental texture parameters. A cluster analysis was performed to classify red winegrape varieties according to their mechanical properties using the average linkage between groups and Euclidean distance. Principal component analysis (PCA) was also used to try the varietal differentiation. The criterion used for the selection of the principal component was higher variance with a confidence level of 95 %. The effects of the physical and mechanical parameters on the berry hardness were assessed by means of multiple linear regression.

3. Results and discussion

3.1. Characterization and differentiation of red winegrape varieties according to berry hardness

Figure 1 shows the values of the whole berry hardness determined at harvest in the sorted berries selected for all of the red winegrape varieties studied. It is important to emphasize that this comparative study was performed on grape berries harvested in the same vineyard to minimize also the possible variations related to environmental effects (Sato *et al.*, 2000). As can be observed, the softest berries were associated with Ancellotta (1.72 N) and Dolcetto (1.79 N) cultivars, whose values of the whole berry hardness agreed with those ones obtained for Gamay and Schiava gentile cultivars (2.26 and 2.29 N, respectively), and were significantly lower if compared with the remaining winegrape varieties. The hardest berries corresponded to the Franconia cultivar (4.03 N) and its values of the whole berry hardness agreed with those ones obtained for Bonarda, Grenache, Raboso, Marzemino, Negramaro, Montepulciano and Croatina cultivars (3.50-4.02 N). The remaining winegrape varieties showed intermediate values of this berry mechanical parameter.

The differences observed in the hardness of the berry among the red winegrape varieties studied confirm that this double compression parameter is likely to be varietal dependent at harvest. Its contribution to the varietal differentiation has been previously assessed for red Spanish winegrape varieties, **in which cv Merenzao showed highest values of the berry hardness (4.32 N) in comparison with Brancellao (3.45 N) and Mencía (3.33 N)** (Río Segade *et al.*, 2011b), and **for white table-grape varieties** (Rolle *et al.*, 2011b).

The berry hardness, also called firmness by some authors (Rolle *et al.*, 2012a), is basically determined by the vacuole turgidity. De Belie *et al.* (1999) also reported that a high cellular turgor requires a higher rupture force. Since an increase in the membrane permeability allows that water leaves the cell, thereby resulting in a decrease in the cellular and tissue turgor, a decreased turgor may be attributed to the degradation of biological membranes. This fact has a paramount importance in the elaboration of carbonic macerated wines because the entire berries suffer a strong compression by others located on them, this effect being more accused for the berries located in the lower part of the maceration tank. Therefore, the whole berry hardness could play a key role in the selection, at harvest, of the more adequate grape varieties to elaborate wines by carbonic maceration technique, with the aim of reducing the risk of the berry rupture and of promoting the intracellular fermentation step. Within the same variety, the values of the berry hardness can be influenced by the ripeness grade (Le Moigne *et al.*, 2008), growing location (Letaief *et al.*, 2008; Torchio *et al.*, 2010; Río Segade *et al.*, 2011c), agronomic management of the vineyard (Porro *et al.*, 2010) and also by clone (Rolle *et al.*, 2012c) and virus infection of the vine (Santini *et al.*, 2011). Consequently, the selection of the more appropriate vineyard must be executed taking into account all these factors.

3.2. Skin instrumental texture parameters

The skin mechanical properties determined at harvest for all of the red winegrape varieties studied are shown in Table 1. Regarding the parameters that characterize the skin hardness (F_{sk} and W_{sk}) and the one that determines the skin rigidity or stiffness (E_{sk}), the Schiava gentile cultivar is characterized by the softest and springiest skins (0.322 N, 0.282 mJ, and 0.179 N mm⁻¹, respectively), followed by Ancellotta grapes (0.433 N, 0.364 mJ, and 0.216 N mm⁻¹, respectively). The values of these three skin texture parameters agreed between the two winegrape cultivars. Furthermore, the Ancellotta cultivar presented the thickest skins (259 μm). Conversely, the hardest skins corresponded to the Malbech cultivar, whose

values of the break force and energy of the berry skin (0.873 N and 1.049 mJ) agreed with those obtained for the Barbera cultivar (0.827 N and 0.913 mJ). Nevertheless, this last cultivar is also characterized by the thinnest skins (153 μm). However, no correlation was found between F_{sk} and Sp_{sk} , in accordance with data reported in literature (Río Segade *et al.*, 2011a). The Raboso cultivar showed significantly higher values of the Young's modulus (0.427 N mm^{-1}) if compared with the remaining winegrape varieties and, therefore, its skins were the stiffer.

On the basis of the results showed in Table 1, the skin mechanical properties allow the differentiation of red winegrape varieties. In particular, the skin break force has been previously proposed as a varietal marker (Letaief *et al.*, 2008; Río Segade *et al.*, 2011b; Sato *et al.*, 1997). Furthermore, the instrumental texture parameters characterizing the skin hardness are little influenced by the ripeness grade of the grape. In fact, a previously published work highlighted that the changes observed in the mechanical parameters through the ripening process are more related to the berries density than to the harvest date (Rolle *et al.*, 2011a). In addition, no significant changes were reported in the hardness and stiffness of berry skins during the sugar accumulation (Río Segade *et al.*, 2011a, 2011b; Torchio *et al.*, 2010).

For a better visualization of the differentiating power of the skin mechanical properties and to globally evaluate the results showed in Table 1, the red winegrape varieties studied were classified by cluster analysis (Figure 2). There are two main clusters well separated, one composed of those varieties having values of the skin thickness higher than 200 μm and another of those with values less than 200 μm . In fact, the varieties resulted to be clustered mainly attending to this skin mechanical parameter. It agrees with the role of the skin thickness in the differentiation of Italian wine and table-grapes (Letaief *et al.*, 2008; Rolle *et al.*, 2011b, 2012b).

The thickness and toughness of the skin are factors that contribute to the resistance of grapes against fungal pathogens and handling injury during harvest and transport (Kök and Çelik, 2004). Therefore, the skin thickness may also contribute to the resistance of grapes against rupture during the intracellular fermentation stage in the elaboration of carbonic macerated wines. In addition, it has already been reported that in a traditional "red winemaking", the skin thickness is an useful tool for predicting the anthocyanin extractability from the berry skin to the must/wine (Río Segade *et al.*, 2011a). The thinner skins seem to be characterized by a greater release of red pigments. Instead, the harder skins have faster extraction kinetics of anthocyanins (Rolle *et al.*, 2012c). Therefore, in the carbonic maceration technique

the grape skin texture parameters may also be taken into account to predict the colour extraction from the berry skin to the must/wine.

All instrumental texture parameters of the berry skin were significantly correlated with the whole berry hardness but Pearson's correlation coefficients were low, which were comprised between 0.085 at $p < 0.05$ for the skin thickness and 0.690 at $p < 0.001$ for the skin Young's modulus. Pearson's correlation coefficients were 0.425 and 0.177 ($p < 0.001$) for the skin break force and energy, respectively.

3.3. Berry instrumental texture parameters

The double compression parameters of the whole berry determined at harvest for all of the red winegrape varieties studied are shown in Table 2. If compared with the winegrape varieties studied, Ancellotta and Dolcetto cultivars are characterized not only by the softest berries, but also by the less gumminess and chewiness ones (1.37 and 1.36 N, 2.44 and 3.01 mJ, respectively). In the case of the berry springiness, the values obtained for the Ancellotta cultivar (1.76 mm) were significantly lower than those associated with all of the remaining varieties. The Pinot nero and Malbech cultivars showed values significantly lower of the berry cohesiveness (0.67 and 0.70, respectively), when compared with the other cultivars. On the other hand, Bonarda and Montepulciano cultivars presented the higher values of the berry chewiness (8.15 mJ), whereas the higher values of the berry hardness and gumminess were associated with Bonarda and Franconia cultivars (4.02 and 4.03 N, 3.23 and 3.07 N, respectively). This last winegrape variety also showed the lower berry resilience (0.358), followed by the Raboso cultivar (0.363). The highest values of the berry cohesiveness, springiness and resilience corresponded to Barbera (0.87), Montepulciano and Malvasia nera (2.78-2.79 mm), and Merlot cultivars (0.476), respectively.

In red winegrape varieties, the berry hardness, gumminess, springiness, chewiness and resilience are helpful varietal discriminating factors, the berry chewiness being the most representative one for other Italian and Spanish varieties (Letaief *et al.*, 2008; Río Segade *et al.*, 2011b). White and colored table-grape varieties were also discriminated attempting to the double compression parameters of the whole berry. Gumminess, chewiness and resilience seem to be the best mechanical properties to characterize/differentiate table-grape varieties (Rolle *et al.*, 2011b, 2012b). It is important to take into

account that the double compression parameters enable the discrimination of the two grape types. In fact, the instrumental flesh texture of table-grapes is harder than that of wine-grapes (Sato and Yamada, 2003).

For a better visualization of the differentiating power of the whole berry mechanical attributes and to globally evaluate the results showed in Table 2, the red winegrape varieties studied were classified by cluster analysis (Figure 3). The varieties studied were well differentiated in two main clusters mainly according to the berry chewiness and gumminess. The smaller one included those varieties having values of the berry chewiness lower than 3.10 mJ and of the berry gumminess lower than 1.40 N, and another composed of other well separated two sub-clusters that classify the varieties according to values of the berry chewiness (discriminating value of 6.00 mJ), and the berry gumminess (discriminating value of 2.40 N). This agrees with the representative role of the berry chewiness and gumminess in the differentiation of Italian red winegrape varieties (Letaief *et al.*, 2008).

A correlation study among the berry hardness and all remaining instrumental texture parameters of the whole berry was performed. The berry springiness was positively correlated with the berry hardness (coefficient = 0.490, $p < 0.001$), whereas the berry cohesiveness (coefficient = -0.108, $p < 0.01$) and resilience (coefficient = -0.219, $p < 0.001$) presented negative coefficients. As observed for the berry skin mechanical parameters, Pearson's correlation coefficients were also low. Gumminess and chewiness were calculated from the berry hardness and, therefore, their coefficients are not shown.

3.4. Global evaluation of data

Principal Component Analysis (PCA) was performed for a global evaluation of the results, and better understanding of the differences found among red winegrape varieties at harvest on the basis of the physical (berry weight and volume, data not shown) and instrumental texture parameters of the whole berry, and of the skin mechanical properties. Four principal components explained 91.4% of the variability in the original data. Table 3 shows the loadings for each variable in the four principal components. Component 1 accounted for 37.6% of the total variance, it being mainly associated with the berry chewiness (coefficient = 0.946), gumminess (coefficient = 0.939) and hardness (coefficient = 0.935). Component 2 accounted for 28.9% of the total variance, it being mainly associated with the berry springiness (coefficient = 0.809) and weight (coefficient = 0.807). Component 3 accounted for 14.0% of the

total variance, it being mainly associated with the skin thickness (coefficient = -0.838). Figure 4 shows the distribution of the red winegrape varieties studied in the plane defined by the first and third principal components. The separation along the first principal component agreed with that obtained by cluster analysis performed from the berry double compression parameters (Figure 3). The cultivars included in the first cluster (from Grenache to Raboso) are located in the right side, which would be more adequate to favour the processes involved in the anaerobic metabolism. Ancellotta and Dolcetto cultivars that correspond to the third cluster are located in the more negative side and less prone to the elaboration of carbonic macerated wines. On the other hand, with very few exceptions, the distribution of the winegrape varieties along the principal component 3 agreed with cluster analysis performed on the skin mechanical parameters (Figure 2). The cultivars included in the first cluster (from Bonarda to Cabernet franc) are located in the lower side, whereas all of the remaining ones belonging to the other cluster are located in the upper side.

To achieve a more accurate evaluation of the correlation among the berry hardness (N) and other instrumental texture and physical parameters of the berry, and the skin mechanical properties, multiple linear regression was performed. Therefore, the effects of independent variables like the berry weight (W_b , g), berry volume (V_b , cm^3), F_{sk} (N), W_{sk} (mJ), E_{sk} (N mm^{-1}), Sp_{sk} (μm), BCo, BG (N), BS (mm), BCh (mJ) and BR on BH (N, dependent variable) were described by the following equation ($R^2 = 0.995$, $p < 0.001$):

$$\text{BH} = (2.502 \pm 0.062) + (-0.034 \pm 0.013) W_b + (0.021 \pm 0.016) V_b + (0.536 \pm 0.101) F_{sk} + (-0.360 \pm 0.053) W_{sk} + (-0.371 \pm 0.143) E_{sk} + (8.105 \text{E-}05 \pm 0.000) Sp_{sk} + (-3.387 \pm 0.052) \text{BCo} + (1.332 \pm 0.029) \text{BG} + (0.138 \pm 0.026) \text{BS} + (-0.028 \pm 0.011) \text{BCh} + (-0.274 \pm 0.063) \text{BR}$$

The berry volume, skin break force, skin thickness, berry gumminess and springiness showed positive coefficients, whereas the berry weight, skin break energy and Young's modulus, berry cohesiveness, chewiness and resilience presented negative coefficients. This indicates that an increase in the first variables, induced by environmental or agronomic factors, results in an increased berry hardness, and therefore favourable to the carbonic maceration process. With the exception of the berry volume and skin thickness, all of the remaining variables had a significant correlation with the berry hardness ($p < 0.05$), the correlation significance even being less than 0.001 for the skin hardness, and the berry cohesiveness, gumminess, springiness and resilience. The skin break force is likely to be a new variable that should be considered in the estimation of the aptitude of a variety for the elaboration of carbonic macerated wines.

4. Conclusions

The elaboration of carbonic macerated wines requires grape berries with appropriate hardness with the aim of minimizing risks of skin tissue degradation and berry rupture during intracellular fermentation causing a lower effect on the phenomena of the anaerobic metabolism. Since the harder berries could permit to extend this winemaking step, red winegrape varieties were characterized and differentiated in terms of the berry hardness. Univariate analysis of the instrumental texture parameters of both the skin and the whole berry revealed that all of these parameters are powerful tools to differentiate the varieties studied according to their attitude to carbonic maceration techniques. Cluster analysis performed separately for the mechanical parameters of skins showed that the most discriminating ones are the skin thickness, and the berry chewiness and gumminess. Principal component analysis applied to all of the instrumental texture parameters studied confirmed that those of the whole berry more strongly contribute to the varietal differentiation.

Finally, multiple linear regression showed that the mechanical parameters that characterize the skin hardness were strongly and significantly correlated with the berry hardness. Therefore, the skin break force should be considered in the evaluation of a variety for aiming carbonic macerated wines.

This work represents the first approach to characterize the berry hardness as a tool for the selection of winegrapes for the elaboration of carbonic macerated wines, but further research would be required on the real correlation between the berry hardness and the phenolic, aromatic and sensory quality of this young wine typology.

References

- Amati, A., Donati, A.M., Galassi, S. & Pallotta, U. (1973). Esperimenti di vinificazione tramite macerazione carbonica di uve Romagnole. II. Caratteristiche chimiche e fisico-chimiche di vini Sangiovese, Merlot e Cagnina ottenuti mediante macerazione carbonica. *Scienza e Tecnologia degli Alimenti*, **3**, 357–361.
- Carnacini, A. & Del Pozzo, A. (1985). Characteristics of wines obtained by carbonic maceration. *L'Enotecnico*, **21**, 1115–1119.

- Castillo-Sánchez, J.J., Mejuto, J.C., Garrido, J. & García-Falcón, S. (2006). Influence of wine-making protocol and fining agents on the evolution of the anthocyanin content, colour and general organoleptic quality of Vinhao wines. *Food Chemistry*, **97**, 130–136.
- Castillo-Sánchez, J.X., García-Falcón, M.S., Garrido, J., Martínez-Carballo, E., Martins-Dias, L.R. & Mejuto, X.C. (2008). Phenolic compounds and colour stability of Vinhao wines: Influence of wine-making protocol and fining agents. *Food Chemistry*, **106**, 18–26.
- Chinnici, F., Sonni, F., Natali, N., Galassi, S. & Riponi, C. (2009). Colour features and pigment composition of Italian carbonic macerated red wines. *Food Chemistry*, **113**, 651–657.
- De Belie, N., Tu, K., Jancsok, P. & De Baerdemaeker, J. (1999). 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*, **16**, 279–284.
- Dourtoglou, V.G., Yannovits, N.G., Tychopoulos, V.G. & Vamvakias, M.M. (1994). Effect of storage under CO₂ atmosphere on the volatile, amino acid, and pigment constituents in red grape (*Vitis vinifera* L. var. Agiorgitiko). *Journal of Agricultural and Food Chemistry*, **42**, 338–344.
- Ducruet, V. (1984). Comparison of the headspace volatiles of carbonic maceration and traditional wine. *Lebensmittel-Wissenschaft and Technologie*, **17**, 217–221.
- Etaio, I., Elortondo, F.J.P., Albisu, M., Gaston, E., Ojeda, M. & Schlich, P. (2008). Effect of winemaking process and addition of white grapes on the sensory and physicochemical characteristics of young red wines. *Australian Journal of Grape and Wine Research*, **14**, 211–222.
- Flanzy, C. (2003). Vinificación por maceración carbónica. Enología: Fundamentos científicos y tecnológicos, 2ª edición. A. Madrid Vicente and Mundi-Prensa, Madrid.
- Fondville-Bagnol, A., Sarris, J., Bayonove, C.L., Robin, J.P., Berger, J.L., Cottureau, P., Pradal, M., Nicol, M.Z. & Flanzy, C. (1999). Effects des vapeurs d'un moût en fermentation sur les composés volatils de baies de raisin en métabolisme anaérobie. *Sciences des Aliments*, **19**, 215–234.
- Gómez-Míguez, M. & Heredia, F.J. (2004). Effect of the maceration technique on the relationships between anthocyanin composition and objective color of Syrah wines. *Journal of Agricultural and Food Chemistry*, **52**, 5117–5123.
- Grotte, M., Cadot, Y., Poussier, A., Loonis, D., Piétri, E., Duprat, F. & Barbeau, G. (2001). Determination of the maturity status of grape berry (*Vitis vinifera*) from physical measurement: methodology. *Journal International des Sciences de la Vigne et du Vin*, **35**, 87–98.

- Kök, D. & Çelik, S. (2004). Determination of characteristics of grape berry skin in some table grape cultivars (*V. vinifera* L.). *Journal of Agronomy*, **3**, 141–146.
- Le Moigne, M., Maury, C., Bertrand, D. & Jourjon, F. (2008). Sensory and instrumental characterisation of Cabernet Franc grapes according to ripening stages and growing location. *Food Quality and Preference*, **19**, 220–231.
- Letaief, H., Rolle, L. & Gerbi, V. (2008). Mechanical behavior of winegrapes under compression tests. *American Journal of Enology and Viticulture*, **59**, 323–329.
- Lőrincz, G., & Vas, G. (1998). Examination of volatile components in carbonic macerated red wines. *Viticulture and Enology Science*, **53**, 18–21.
- Maury, C., Madieta, E., Le Moigne, M., Mehinagic, E., Siret, R. & Jourjon, F. (2009). Development of a mechanical texture test to evaluate the ripening process of Cabernet Franc grapes. *Journal of Texture Studies*, **40**, 511–535.
- Pellegrini, N., Simonetti, P., Gardana, C., Brenna, O., Brighenti, F. & Pietta, P. (2000). Polyphenol content and total antioxidant activity of vini novelli (young red wines). *Journal of Agricultural and Food Chemistry*, **48**, 732–735.
- Porro, D., Tomasi, T., Ramponi, M., Rolle, L. & Poni, S. (2010). Nutritional implications of water stress in grapevine and modifications of mechanical properties of berries. *Acta Horticulturae*, **868**, 73–80.
- Ribéreau-Gayon, P., Dubourdieu, D., Donèche, B.J. & Lonvaud, A. (2000). Handbook of Enology. Volume 1. The microbiology of wine and vinification. John Wiley & Sons Ltd., Chichester, UK.
- Río Segade, S., Giacosa, S., Gerbi, V. & Rolle, L. (2011a). Berry skin thickness as main texture parameter to predict anthocyanin extractability in winegrapes. *LWT Food Science and Technology*, **44**, 392–398.
- Río Segade, S., Orriols, I., Giacosa, S. & Rolle, L. (2011b). Instrumental texture analysis parameters as winegrapes varietal markers and ripeness predictors. *International Journal of Food Properties*, **14**, 1318–1329.
- Río Segade, S., Soto Vázquez, E., Orriols, I., Giacosa, S. & Rolle, L. (2011c). Possible use of texture characteristics of winegrapes as markers for zoning and their relationship with anthocyanin extractability index. *International Journal of Food Science and Technology*, **46**, 386–394.
- Rizzon, L.A., Miele, A., Meneguzzo, J. & Zanuz, M.C. (1999). Effect of three processes of vinification on chemical composition and quality of Cabernet Franc wine. *Pesquisa Agropecuária Brasileira*, **34**, 1285–1293.

- Rolle, L., Giacosa, S., Gerbi, V. & Novello, V. (2011b). Comparative study of texture properties, color characteristics, and chemical composition of ten white table-grape varieties. *American Journal of Enology and Viticulture*, **62**, 49–56.
- Rolle, L., Giacosa, S., Gerbi, V., Bertolino, M. & Novello, V. (2012b). Varietal comparison among the chemical, physical and mechanical properties of five colored table grape cultivars. *International Journal of Food Properties*, in press, DOI: 10.1080/10942912.2011.558231.
- Rolle, L., Río Segade, S., Torchio, F., Giacosa, S., Cagnasso, E., Marengo, F. & Gerbi, V. (2011a). 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*, **59**, 8796–8805.
- Rolle, L., Siret, R., Río Segade, S., Maury, C., Gerbi, V. & Jourjon, F. (2012a). Instrumental texture analysis parameters as markers of table-grapes and winegrapes quality: a review. *American Journal of Enology and Viticulture*, **63**, 11–28.
- Rolle, L., Torchio, F., Ferrandino, A. & Guidoni, S. (2012c). Influence of wine-grape skin hardness on anthocyanin extraction kinetic. *International Journal of Food Properties*, **15**, 249–261.
- Santini, D., Rolle, L., Cascio, P. & Mannini, F. (2011). Modifications in chemical, physical and mechanical properties of Nebbiolo (*Vitis vinifera* L.) grape berries induced by mixed virus infection. *South African Journal of Enology and Viticulture*, **32**, 183–189.
- Sato, A. & Yamada, M. (2003). Berry texture of table, wine, and dual-purpose grape cultivars quantified. *HortScience*, **38**, 578–581.
- Sato, A., Yamada, M., Iwanami, H. & Hirakawa, N. (2000). Optimal spatial and temporal measurement repetition for reducing environmental variation of berry traits in grape breeding. *Scientia Horticulturae*, **85**, 75–83.
- Sato, A., Yamane, H., Hirakawa, N., Otobe, K. & Yamada, M. (1997). Varietal differences in the texture of grape berries measured by penetration tests. *Vitis*, **36**, 7–10.
- Spranger, M.I., Clímaco, M.C., Sun, B., Eiriz, N., Fortunato, C., Nunes, A., Leandro, M.C., Avelar, M.L. & Belchior, A.P. (2004). Differentiation of red winemaking technologies by phenolic and volatile composition. *Analytica Chimica Acta*, **513**, 151–161.

- Sun, B., Spranger, I., Roque-do-Vale, F., Leandro, C., & Belchior, P. (2001). Effect of different winemaking technologies on phenolic composition in Tinta Miùda red wines. *Journal of Agricultural and Food Chemistry*, **49**, 5809–5816.
- Tesniere, C. & Flanzky, C. (2011). Carbonic maceration wines: characteristics and winemaking process. *Advances in Food and Nutrition Research*, **63**, 1–15.
- Torchio, F., Cagnasso, E., Gerbi, V. & Rolle, L. (2010). Mechanical properties, phenolic composition and extractability indices of Barbera grapes of different soluble solids contents from several growing areas. *Analytica Chimica Acta*, **660**, 183–189.
- Versini, G. & Tomasi, T. (1983). Confronto tra i componenti volatili dei vini rossi ottenuti con macerazione tradizionale e macerazione carbonica. Importanza differenziante del cinnamato di etile. *L'Enotecnico*, **9**, 595–600.
- Yang, D.Y., Kakuda, Y. & Subden, R.E. (2006). Higher alcohols, diacetyl, acetoin and 2,3-butanediol biosynthesis in grapes undergoing carbonic maceration. *Food Research International*, **39**, 112–116.

Figure 1. Berry hardness at harvest of the red winegrape varieties studied.

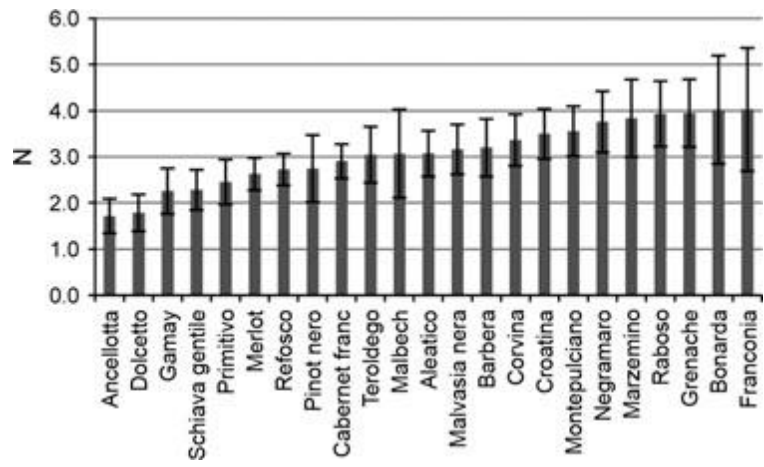


Figure 2. Dendrogram of red winegrape varieties by applying the average linkage between group and Euclidean distance for hierarchical cluster analysis according to their skin mechanical properties at harvest.

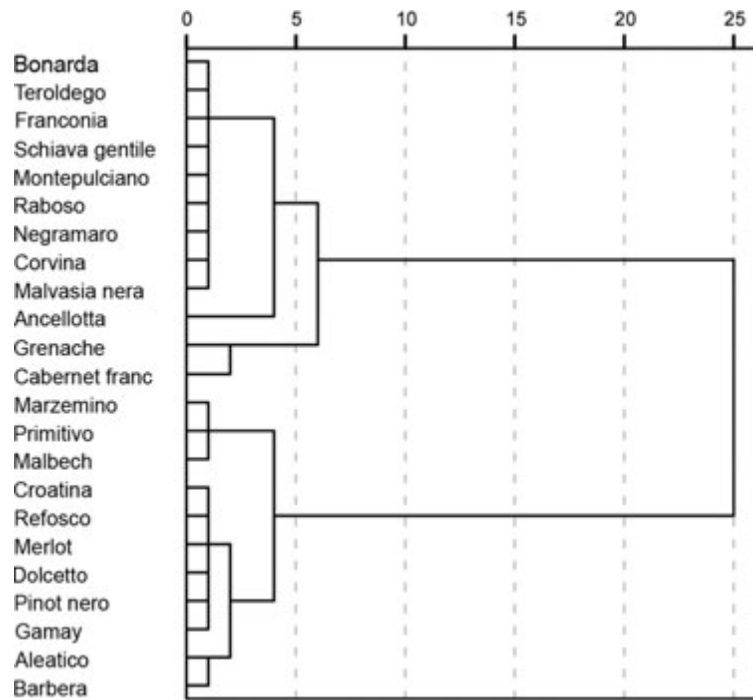


Figure 3. Dendrogram of red winegrape varieties by applying the average linkage between group and Euclidean distance for hierarchical cluster analysis according to their whole berry mechanical properties at harvest.

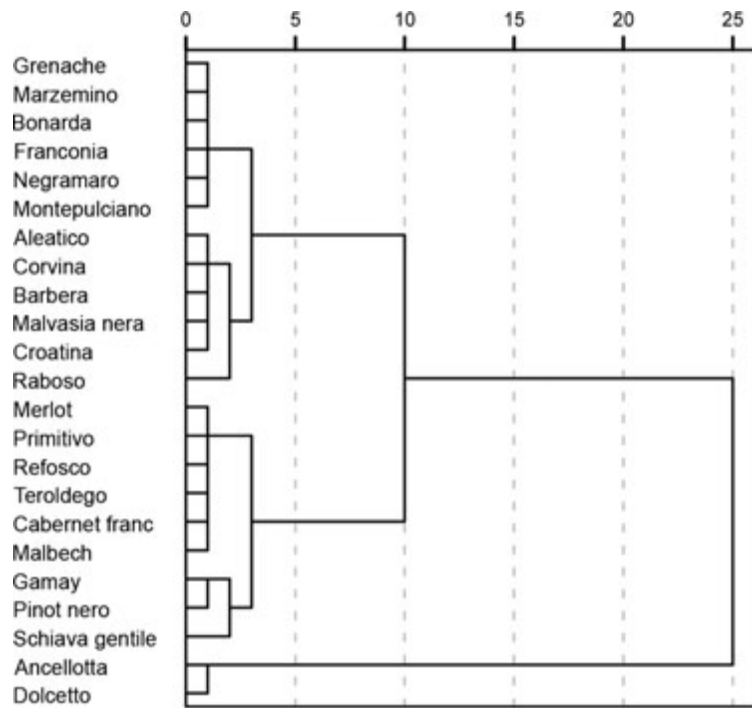


Figure 4. Projection of red winegrape varieties in the plane defined by the first and third principal components.

