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Effect of harvest time on table grape quality during on-vine storage

Francesca Piazzolla, Sandra Pati, Maria Luisa Amodio* and Giancarlo Colelli

Abstract

BACKGROUND: Postponing the harvest of grapes is a common practice in southern Italy, in order to delay harvest up to Christmas and make higher income from their sale. The aim of this work was to evaluate the effect of harvest time (over almost 3 months) on the quality of table grapes (cv. Italia). The experiment was repeated for two years (2010 and 2011). In 2010, grapes were harvested starting from 8 October and after 11, 27 and 48 days. In 2011, five harvest times were compared over a period of 56 days. Respiration rate, firmness, colour, sensory attributes, total soluble solids (TSS), pH, titratable acidity (TA), phenols and antioxidant activity were measured. In addition, in the second year, volatile compounds were evaluated.

RESULTS: For both years, harvest time influenced most parameters, which indicated that metabolic changes took place in the plants. In 2010, harvest time influenced respiration rate, cluster and berry appearance scores, colour attributes, crunchiness, pH, TA, total phenol content and antioxidant activity. In 2011, harvest time influenced respiration rate, colour attributes, most sensory attributes, TSS and TA. Generally, late harvested grapes showed higher firmness, berry appearance score, sweetness, fruity taste, overall sensory evaluation score and TSS. Regarding volatile compounds, terpene content decreased during ripening, while C6 compounds showed a nonlinear trend.

CONCLUSION: The results showed that table grape sensory quality could be increased by delaying harvest up to a certain time of the season, while excessive delay could reduce final grape quality.

Keywords: harvest time; sensory attributes; volatiles; maturity

INTRODUCTION

Grape is a non-climacteric fruit and does not ripen further after harvest, so harvesting at the proper stage of maturity is essential for optimal grape quality in terms of soluble solids, berry weight, titratable acidity and overall sensory characteristic. Grape ripening is a physiological period that starts at the moment of veraison and lasts until the fruit is harvested. This is a very important period that influences grape composition and determines varietal characteristics.[1] Grapes undergo many changes during the ripening process that involve a number of physical and biochemical modifications, including weight, sugar, acidity, colour and aroma.

The full-bodied aroma of grapes is one of the most important factors that attracts consumers and is essential for the highly competitive market and food industry.[2] Although several studies have focused on the evolution of volatile compounds during wine grape ripening,[3–6] with the aim of optimizing wine flavour, only a few have concentrated on table grapes.[2] For the consumer, the acceptability of table grapes depends on different attributes. Visual attributes such as colour, size and shape of the berry are primary characteristics that consumers observe.[7,8] In addition to visual characteristics, physicochemical properties are involved in sensory and quality evaluation.[7,9–14] Sensory descriptors such as skin friability, skin thickness and flesh firmness have been proposed to characterize commercial table grape cultivars.[7,15]

Degree of ripeness, type of soil, climatic conditions, cultural practices and growing location are important factors affecting the physical properties and chemical composition of table grapes, but the phenolic composition depends strongly on the table grape variety.[16,17] In addition, cultural practices[18] and postharvest conditions,[19] as also the variety,[20,21] may affect textural parameters of grape berries such as skin friability, skin thickness and flesh firmness that have been proposed to characterize commercial table grape cultivars.[7,15]

In the literature, there are recent works evaluating the effects of agronomic practices on the chemical composition of table grapes ('Italia', 'Superior Seedless' and 'Red Globe') using nuclear magnetic resonance (NMR) spectroscopy[22] and the effects of potassium- and calcium-based salts applied before and after harvest[23] and calcium in pre- and post-veraison to control decay and maintain table grape fruit quality during cold storage,[24] but very few regarding the effect of harvest time on table grape quality. In southern Italy (i.e. Apulia Region where about 80% of Italian table grapes are produced), the harvest season, especially for 'Italia' and 'Red Globe' varieties, is commonly extended by leaving the product on the vines from early October (when harvest season typically starts) up to the end of November or well into December. This allows growers to have freshly harvested produce for the

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season's holiday market, when prices are higher and demand is stronger. Towards this aim, vine canopies are appositely covered with plastic film in order to prevent damage to the fruits during the autumnal rainy period. This forced 'storage' of table grapes on the plant also allows one to maintain a fully hydrated, green stalk (which is very difficult to obtain after harvest) and, last but not least, to apply fungicides, which cannot be used during postharvest storage; to the best of our knowledge, there is little or no scientific support for the effect of this practice on quality and storability of the grapes as compared with the product regularly harvested from the end of September to the end of October, which has typically been the normal harvest season for these varieties in this region.

The plastic cover, made of low-density polyethylene (LDPE), is placed over the canopy during the veraison stage (late semi-forced storage) when the fruit becomes more susceptible to *Botrytis* attack; in addition, the coverage induces delayed maturation in terms of a gradual increase in total soluble solids (TSS) and decrease in titratable acidity (TA).[25] The same authors reported that the 'late' forced growing system (unlike the 'early' one consisting of covering the canopy with plastic film in early spring with the purpose to advance bud shooting by 10–40 days depending on the cultivar) has the aim to delay the harvest for up to 3 months. Therefore this technique of table grape storage on the plant supposedly slows down grape ripening in order to meet the demand for high-quality fresh produce in the late season, for a higher economic profitability of the market.

A study on the influence of growing season (winter *versus* summer) on phenolic compound synthesis/accumulation and antioxidant properties in five grape cultivars found that the total phenol content was significantly higher in seeds and skins of grapes grown in winter than in those grown in summer.[26] Other authors reported that seasonal variations in phenolic compounds and antioxidant properties of grapes berries were also caused by climatic factors such as variations in solar radiation, rainfall and hydrothermic coefficient between different growing seasons.[27,28]

A recent study by Río Segade *et al.*[29] evaluated the effect of different ripening stages with the aim of characterizing mechanical proprieties of berries of 'Red Globe' and 'Crimson Seedless' grapes; in particular, they found that berry cohesiveness could be a good predictor of ripening stage of table grapes, since its variation during ripening was not dependent on berry size.

Starting from these considerations, the objective of this work was to study the effect of harvest time on table grape quality, in order to give to producers more information for the management of postharvest handling.

MATERIAL AND METHODS

Plant material

The experiment was repeated for two years, 2010 and 2011, in two growing areas of southern Italy, Bari (41° 00′ 55.4″ N, 16° 56′ 27.0″ E) and Foggia (41° 28′ 39.2″ N, 15° 36′ 04.3″ E). Table grapes (cv. Italia) were cultivated with the 'Apulia tendone' system, covered with netting and plastic film (LDPE, thickness 170 μm).

In 2010, table grapes were harvested starting from 8 October (HT 1) and after 11 (HT 2), 27 (HT 3) and 48 (HT 4) days. In 2011, five harvest times were compared (the first on 7 October and the following after 14, 28, 42 and 56 days, corresponding to HT 1, HT 2, HT 3, HT 4 and HT 5 respectively).

At each harvest time, 45 clusters (three bunches from 15 plants) were harvested and transported to the Postharvest Laboratory of the University of Foggia. The three bunches from each plant were considered as an experimental replicate, for a total of 15 replicates.

For both years and for each harvest date, the following quality parameters were analysed on fresh samples: respiration rate, firmness and colour parameters (L^*, a^*, b^*, hue angle, chroma). In addition, the following sensory attributes were evaluated: aroma, flavour, crunchiness, sweetness, acidity, cluster appearance score, berry appearance score, overall quality and, for the second year only, resistance to berry detachment, skin peelability, fruity taste, green taste and seed astringency.

Samples were then frozen and stored at −80 °C for chemical analysis. On frozen samples, TSS, pH, TA, total phenol content and antioxidant activity were measured. For samples of the second year, analysis of volatile compounds was also carried out.

Respiration rate

Respiration rate (mL CO_2 kg^{-1} h^{-1}) was measured using a static system,[30] evaluating the amount of CO_2 accumulated in the headspace of sealed poly(vinyl chloride) (PVC) containers (5 L) containing one cluster per plant. Carbon dioxide concentration was measured using a gas chromatograph (model 17A, Shimadzu, Jiangsu, China) equipped with a thermal conductivity detector (TCD, 200 °C). Separation of CO_2 was achieved on a Carboxen 1006 PLOT column (30 m × 0.53 mm; Supelco, Bellefonte, PA, USA). Per cent CO_2 was then referred to the weight of the sample, to the volume of the headspace and to the elapsed time.

Firmness

Firmness was determined on 15 berries from each cluster, for a total of 45 berries per replicate, and defined as the force (N) required to compress each berry by 3 mm between two parallel plates (diameter 10 cm) using an Instron Universal Testing Machine (model 3343, Canton, MA, USA) at a speed of 50 mm min^{-1}. The deformation limit was defined after preliminary tests to compare methods with a fixed load and at fixed deformation. The method at fixed deformation had the advantage of preventing excessive deformation and eventual overpassing of the elastic limit, even for the unknown samples we were going to analyse over a period of 2 months.

Visual quality

Clusters were evaluated by a trained panel of five judges and individually scored using the following five-point subjective scale: 5 = excellent, fresh appearance, compact cluster (well filled), green–golden yellow and turgid berries, green stalk and pedicels; 4 = very good, fresh appearance but with slight browning of pedicels and stalk, and berries with occasional dark coloration; 3 = fair, less compact cluster, with some dehydration of stalk and pedicels, less turgid berries, of which less than 15% presented dark coloration; 2 = poor, not compact cluster, dehydrated stalk and pedicels, soft berries, of which less than 30% presented dark coloration; 1 = very poor or inedible, with completely dehydrated stalk and pedicels, very soft and browned berries, presence of moulds. A score of 3 was considered as the limit of marketability and a score of 2 as the limit of edibility.[31]

Colour analysis and volume of berries

Colour was measured by elaborating images acquired with a Spectral scanner (DV Srl, Padova, Italy) equipped with a Spectral imaging spectrometer (V10 type, 400–1000 nm, 25 μm slit, resolution

5 nm). One scan per sample of 10–15 berries was acquired at an acquisition speed of 3 mm s^{-1} in a dark room with a stabilized halogen light source (150 W). On each berry, a region of interest (ROI) corresponding to the maximum inscribed rectangle was manually selected, allowing the determination in reflectance mode of the CIE L^*, a^*, b^* scale colour parameters. From the primary L^*, a^* and b^* values, the following indices were calculated:

$$\text{hue angle } H^\circ = \tan^{-1}(b^*/a^*)$$

$$\text{chroma} = \left(a^{*2} + b^{*2}\right)^{1/2}$$

The volume of berries (cm^3) was determined from the perpendicular diameters of 10–15 berries for each cluster measured using digital callipers.

Sensory evaluation

In 2010, a trained panel of five judges evaluated sensory attributes of the berries. The judges tasted one berry with pedicel from each sampling replicate for each harvest time. Judges were asked to assess berry appearance score, aroma, flavour, crunchiness, sweetness, sourness and overall evaluation using a five-point scale, where 5 = excellent, 4 = very good, 3 = good, 2 = bad and 1 = not edible (not tasted). In 2011, a five-judge panel evaluated sensory attributes of the berries according to a method reported by Rousseau.[32] Panellists were asked to assess berry appearance score, firmness, resistance to berry detachment, aroma, skin peelability, sweetness, acidity, fruity, taste, green taste, seed astringency and overall evaluation using a four-point scale, where 4 indicates a quality feature of ripe and 1 of non-ripe grapes.

TSS, pH and TA

Fresh juice samples (4 g) from ten berries for each replicate were used to determine TSS, pH and TA. TSS was measured using a digital refractometer (PR-32 Palette, Atago, Tokyo, Japan). TA and pH were measured with an automatic titrator (TitroMatic 1S, Crison, Toledo, Spain) by titrating the juice samples with 0.1 mol L^{-1} NaOH up to pH 8.1; TA was expressed as g tartaric acid L^{-1}.

Total phenol content and antioxidant activity

The following extraction procedure was used for both total phenol and antioxidant activity determinations. Berry samples (5 g) without seeds were homogenized in an Ultra-Turrax (T18 Basic, IKA, Wilmington, NC, USA) after the addition of 3 mL g^{-1} methanol plus 30 mL L^{-1} formic acid, then the extracts were centrifuged at $3622 \times g$ for 10 min at 5 °C. Total phenols were determined according to the method of Singleton and Rossi.[33] Each extract (100 µL) was mixed with 1.58 mL of water, 100 µL of Folin–Ciocalteu reagent and 300 µL of 200 g L^{-1} sodium carbonate solution. After the solution had stood for 2 h in darkness, the absorbance at 725 nm was read against a blank using a spectrophotometer (UV-1700, Shimadzu, Kyoto, Japan). The content of total phenols was calculated on the basis of a calibration curve of gallic acid and expressed as g gallic acid (GA) kg^{-1} fresh weight. The antioxidant assay was performed by the procedure of Brand-Williams *et al.*[34] with minor modifications. The diluted sample (50 µL) was pipetted into 0.95 mL of 0.12 mmol L^{-1} DPPH (diphenylpicrylhydrazyl) solution to initiate the reaction; the absorbance at 515 nm was read after 24 h. Trolox (6-hydroxy-2,5,7,8-tetramethylchromane-2-carboxylic acid) was used as standard and the antioxidant activity was expressed as mg Trolox equivalent (TE) kg^{-1} fresh weight

Extraction and gas chromatography/mass spectrometry (GC/MS) analysis of volatile compounds for table grapes of vineyard 2011

The extraction of volatile compounds was carried out by headspace solid phase microextraction (SPME) using an 85 µm carboxen/polydimethylsiloxane fibre (Supelco) according to the method of Yang *et al.*[2] with some modifications. At first use, the fibre was preconditioned in the injection port of the gas chromatograph according to the manufacturer's instructions. For headspace sampling, grapes were defrosted at 5 °C and pedicels and seeds were removed from the berries. Then 100 g of berries along with 2 g of $CaCl_2$, 20 g of NaCl and 100 µL of internal standard solution (100 µg g^{-1} 2-methylpentanol methanolic solution) were homogenized using a commercial blender. For each measurement, 8 g of puree was transferred into a 15 mL capped SPME vial. After 20 min of sample stirring at 40 °C, the fibre was exposed to the capped vial headspace for 30 min. Then the fibre was inserted manually into the gas chromatograph in splitless mode (injection port temperature 250 °C) for 4 min to allow for the desorption of volatile compounds.

Volatile determination was carried out using a 6890 N gas chromatograph (Agilent Technologies, Palo Alto, CA, USA) equipped with a 5975C mass spectrometer (Agilent Technologies). Analytes were separated on a DB-WAX capillary column (60 m × 250 µm × 0.25 µm; J&W Scientific Inc., Folsom, CA, USA) by applying the following temperature programme: 40 °C for 4 min, 40–180 °C at 3 °C min^{-1}, with a total run of 51 min. The transfer line temperature was 280 °C. Mass detector conditions were electronic impact mode at 70 eV, source temperature 230 °C, scanning rate 2.88 scans s^{-1} and mass scanning range m/z 30–400. The carrier gas was helium at 1 mL min^{-1}. Identification of detected volatile compounds was achieved by comparing their mass spectra with reference spectra contained in a library (NIST 02) of reference data (with probability of matching $P > 80$) and by comparing their retention times and mass spectra with those obtained by standard injections when pure compounds were available. All compounds were quantified as µg 2-methylpentanol equivalent g^{-1}.

Statistical analysis

The effect of harvest time on quality attributes, including volatiles, was evaluated by one-way analysis of variance (ANOVA). Sensory attributes and volatiles were subjected to principal component analysis (PCA), excluding after a first screening all variables with scores lower than 0.3. The data were analysed using Statistica Version 7 (StatSoft, Tulsa, OK, USA).

RESULTS AND DISCUSSION

In general, many physicochemical parameters have been correlated with sensory descriptors and used as predictors of consumer acceptability of products,[35] such as TSS, TA and TSS/TA ratio.[12,36] Texture is also an important attribute in consumer acceptance of foods;[37] in particular, the firmness of the berry is considered as an indicator of its freshness.[15]

Table 1 shows the effect of harvest time on quality parameters. Harvest time affected respiration, colour parameters, TA, berry volume and TSS (the latter only in 2011), phenol content and antioxidant activity (only in 2010). Regarding sensory parameters, for grapes of 2010, cluster and berry appearance, crunchiness and sourness were significantly affected by harvest time. In 2011, more attributes were evaluated, many of them proving significant, such

Table 1. Effect of harvest time on quality attributes of 'Italia' table grapes on 2010 and 2011.

Quality attribute	2010	2011
Respiration rate (mL CO_2 kg^{-1} h^{-1})	*	**
Firmness (N)	NS	NS
L^*	**	**
a^*	****	****
b^*	****	****
Hue angle (°)	****	****
Chroma	****	****
Total soluble solids (°Brix)	NS	*
pH value	****	NS
Titratable acidity (g tartaric acid L^{-1})	****	***
Phenol content (mg per 100 g)	***	NS
Antioxidant activity (mg per 100 g)	****	NS
Berry volume (cm^3)	****	****
Sensory scores		
Cluster appearance	****	NS
Berry appearance	**	*
Aroma	NS	****
Berry detachment	–	****
Flavour	NS	–
Crunchiness	**	*
Sweetness	NS	****
Sourness	****	NS
Fruity taste	–	****
Green taste	–	*
Skin peelability	–	NS
Seed astringency	–	**
Overall evaluation	NS	****

Significance levels:
*$P \leq 0.05$;
**$P \leq 0.01$;
***$P \leq 0.001$;
****$P \leq 0.0001$; NS, not significant.

as fruity taste, green taste, berry detachment and seed astringency. Since for many quality parameters the results of both years were in accordance, we present below only figures of the second year with a longer harvest season and which also included the analysis on volatiles.

Figure 1 shows the effect of harvest time on respiration rate, berry volume, TA, TSS, a^* and $H°$ of table grapes.

In particular, with progression of the harvest date, it is possible to observe that the respiration rate increased and the colour turned from green to light yellow, as described by changes in a^* and $H°$ values. These results are in agreement with those of the first year and with results reported by other authors, albeit for wine grapes.[38]

The respiration rate and the berry volume increased significantly starting from HT 3 (respiration rate of about 6 mL CO_2 kg^{-1} h^{-1} and volume of 6.3 cm^3), whereas grapes of HT 1 presented a volume (4.03 cm^3) significantly lower than grapes of later HTs (about 6.3 cm^3 from HT 3 on) and respiration of about 3 mL CO_2 kg^{-1} h^{-1}.

These results are again in accordance with those of the first year and suggest that the increase in respiration rate, measured as CO_2 production, may be due to the increase in volume. During grape maturation, the increase in volume of the berry becomes rapid, not for cell multiplication, such as in the early stages after veraison, but usually for magnification of the cells. The increase in the volume of the berries is also due to distension of the cells under the influx of sugar and water.[39,40]

In many plants, cell enlargement is accompanied by an increase in protein content per cell and in respiration, which rise to a maximum when the cell reaches full size.[41] Moreover, Harris *et al.*[42] found that respiratory quotient, contrarily to oxygen uptake, increased in four varieties of grapes during the cell expansion phase. This may be explained by the metabolism of organic acids, particularly malate, one of the most prevalent acids in grapes, which releases more CO_2 per molecule of O_2 consumed than do the sugars or starch used during ripening of climacteric fruits.[43] Once grapes reach veraison, hexose sugars are accumulated,[44] therefore reassuming the role of major carbon source for energy metabolism and biosynthesis.

From a compositional point of view, and with regard to maturity indices, a decrease in acidity was observed. In particular, the decrease in acidity for grapes of 2011 is shown in Fig. 1; grapes of HT 1 presented a higher value (0.37% tartaric acid) than grapes of later HTs (about 0.30% tartaric acid from HT 3 on), whereas an intermediate result was observed for grapes of HT 2 (0.34% tartaric acid). This trend can be related to progression of maturation, as reported by Watson[39] and Coombe.[45]

TSS for the same year did not follow a linear trend with progression of the season, and no statistical differences were observed in 2010. The initial level of TSS was the same in both years, corresponding to about 18.3 °Brix. In 2011, grapes of HT 3 presented a higher value (19.26 °Brix) than grapes of HT 2 (17.95 °Brix), whereas intermediate results were observed for grapes of the other harvest dates. It can be speculated that grapes from the first two harvests were not completely ripe and that accumulation of sugars continued up to at least HT 3, considering that not only sugars but also organic acids and other minor solid constituents, e.g. amino acids and minerals, contribute to TSS, which decreased slightly in absolute value at the following harvest dates.

Figure 2 shows visual appearance and other sensory parameters, including green taste, aroma, sweetness, berry detachment score and firmness. Berry appearance clearly improved with progression of the season, with grapes from HT 5 showing the highest score, probably because of colour evolution. Sensory firmness and berry detachment score increased with progression of the harvest, as also did sweetness, green taste and fruity taste (data not shown), with higher scores being attributed to riper fruits and therefore to less firm berries with lower herbaceous taste and lower resistance to berry detachment. Berry appearance score was higher for HT 5 compared with HT 2 grapes; grapes of the first harvest were discriminated from the following ones for green taste and fruity taste, receiving the lowest scores. Moreover grapes of HT 1 were crunchier and showed a lower score relating to berry detachment (high resistance, typical of non-ripe fruits) compared with grapes of HT 4 and HT 5, as well as the lowest score for sweetness. Regarding aroma, the trend was not linear; grapes from HT 3 were more appreciated, receiving a score (2.40) higher than grapes of HT 1 (1.96), HT 2 (2.16) and HT 5 (2.00), confirming that at this time grapes reached the highest organoleptic properties, whereas intermediate results were observed for the remaining harvest dates. Grapes at this time, in fact, already reached the maximum berry volume and, starting from HT 2 the highest sweetness and green taste scores, confirming that ripening was complete, most likely with the optimal sensory quality and the highest accumulation of aromatic compounds and their precursors.

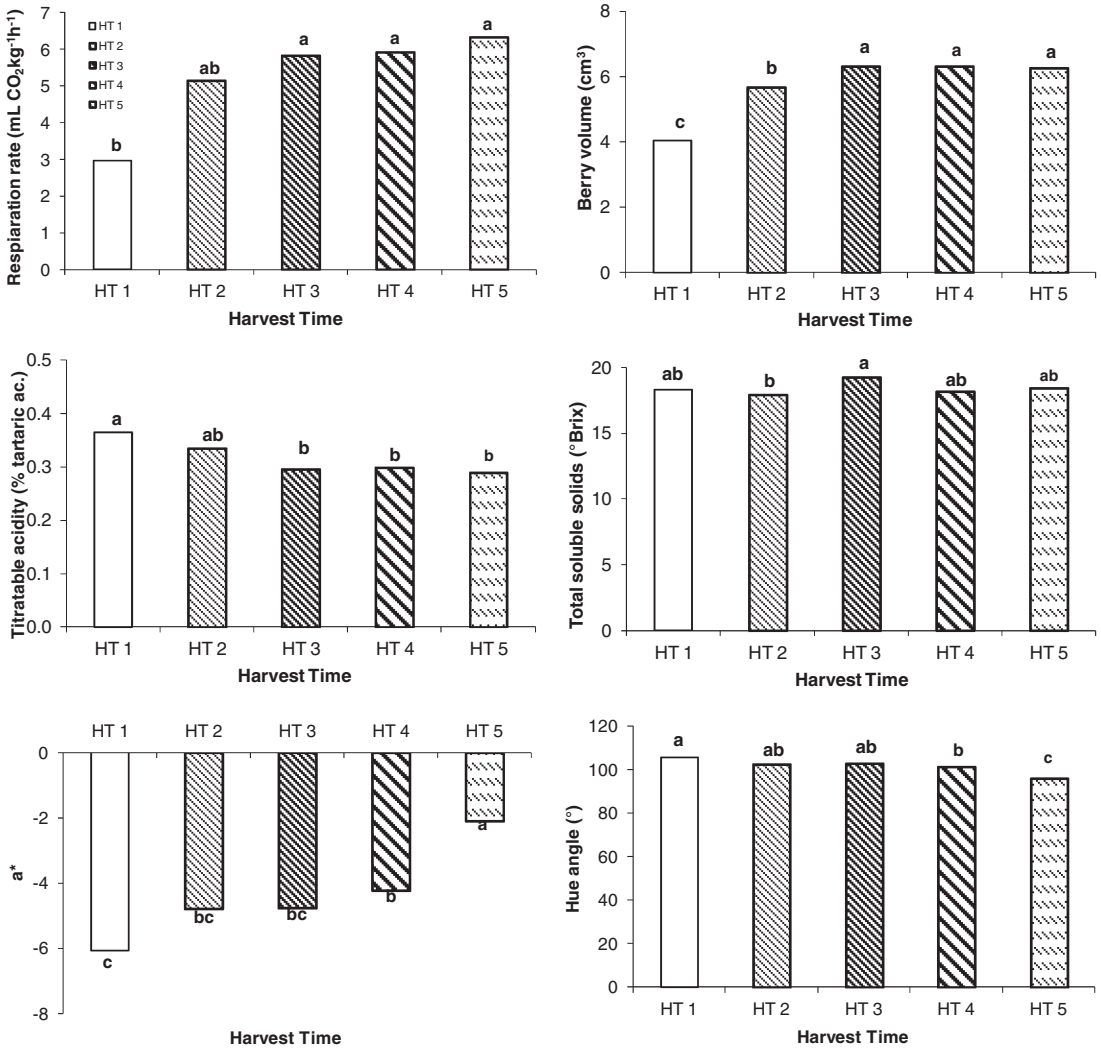

Figure 1. Effect of harvest time on respiration rate, berry volume, titratable acidity, total soluble solids, *a** and hue angle of 'Italia' table grapes (2011). Mean values with different letters are significantly different at $P \leq 0.05$.

Evolution of volatile compounds and relation to sensory quality

The formation of aroma involves over 300 compounds and occurs during grape ripening. Yang *et al.*[2] studied the evolution of volatile compounds in 'Jingxiu', 'Bimeijia' and 'Jingya' table grapes during and after maturation. In particular, terpenoids, responsible for floral flavour in berries, increased until maturation, while C6 compounds with a 'green' flavour increased until the early period of maturation, then decreased. However, the evolution of terpenes during grape maturation seems to be largely variety-dependent.[5,46,47]

In this study a total of 30 volatile compounds, including aldehydes, alcohols, esters, terpenes, furan derivatives and acids, were found in table grapes at the tested harvest times (Table 2).

Among these compounds, four aldehydes (acetaldehyde, 2-butenal, hexanal and (*E*)-2-hexenal), two alcohols (ethanol and 2-methyl-3-buten-2-ol), three terpenes (D-limonene, (*E*)-3,7-dimethylocta-1,6-dien-3-ol and *p*-menth-1-en-8-ol), one ester (ethyl acetate) and one furan derivative (3-methylfuran) were statistically affected by the time of harvest. In particular, the contents of *p*-menth-1-en-8-ol, also known as α-terpineol, and (*E*)-3,7-dimethylocta-1,6-dien-3-ol, commonly known as linalool, which are recognized to give typical floral notes, decreased from HT 1 to HT 2 and then remained constant at a total level greater than sensory thresholds reported elsewhere (some tens of µg L^{-1}). These results are in accordance with previous studies[3,47] on wine grapes which showed that the highest concentration of free terpenols is reached some days before maximum sugar levels.

A PCA with volatile compounds as variables and HTs as factors was performed in order to facilitate the interpretation of volatile analysis results, helping to identify the key compounds that best discriminated among samples analysed. Figure 3a shows the distribution of the 12 main volatiles according to the first two principal components (PCs), which accounted for 78.4% of the total variance (45.6 and 32.8% for PC1 and PC2 respectively). PC1 was characterized by ethyl acetate, acetaldehyde, ethanol and 2-methyl-3-buten-2-ol on the positive side and by *p*-menth-1-en-8-ol, (*E*)-3,7-dimethylocta-1,6-dien-3-ol and hexanal on the negative side. For PC2, *p*-menth-1-en-8-ol and (*E*)-3,7-dimethylocta-1,6-dien-3-ol mainly accounted for the positive axis and (*E*)-2-hexenal and 2-butenal for the negative axis. Figure 3b shows the discrimination of the samples at harvest according to the first two PCs. In particular, HT 1 and HT 2 grapes

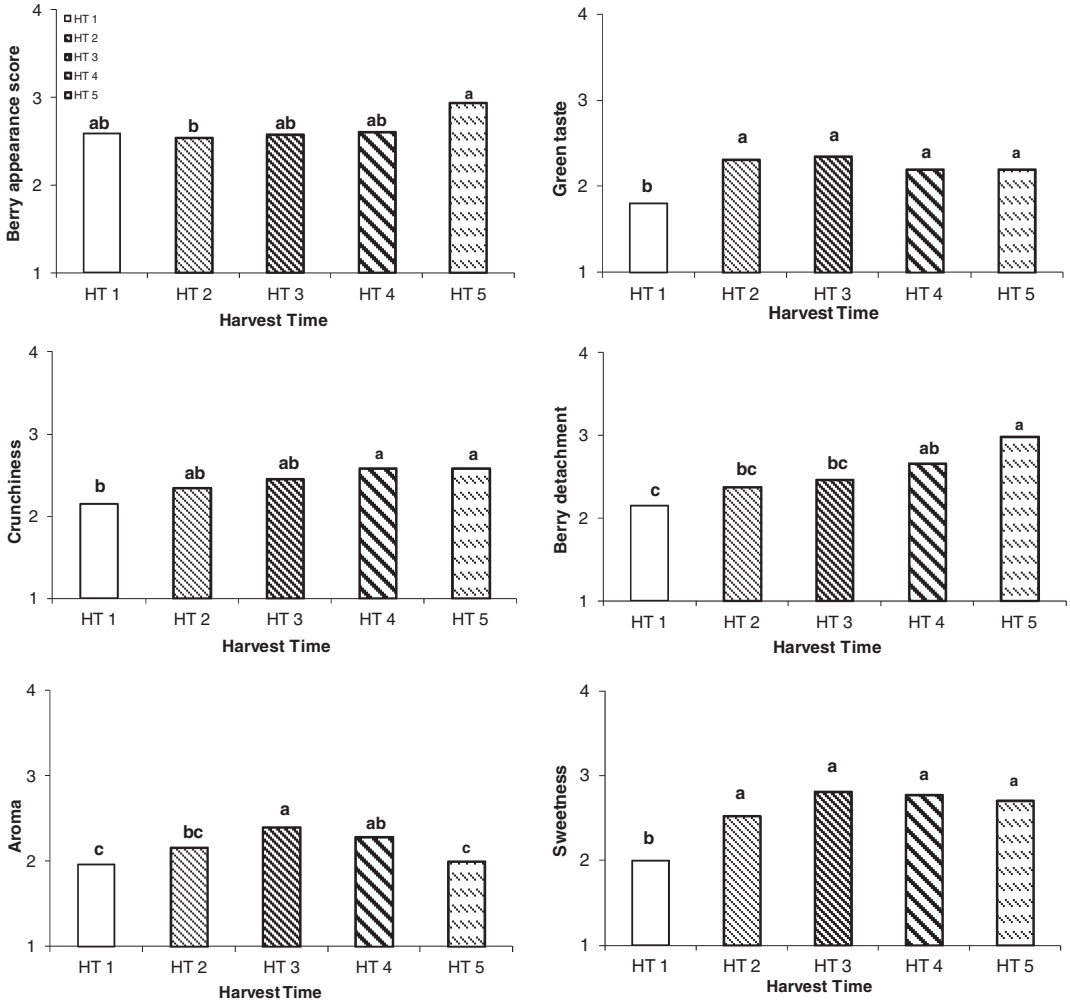

Figure 2. Effect of harvest time on berry appearance score, green taste, crunchiness, berry detachment, aroma and sweetness of 'Italia' table grapes (2011). Mean values with different letters are significantly different at $P \leq 0.05$.

could be discriminated from HT 3 and HT 4 grapes on PC1, while HT 5 grapes could be discriminated from all other grapes on PC2.

The discrimination among these groups is characterized by the evolution of volatile compounds at different harvest times. In particular, the group formed by HT 1 and HT 2 is characterized by terpenes (linalool and α-terpineol), which give a typical fruity and floral odour; also, HT 1 and HT 2 are characterized by high concentrations of hexanal exceeding its olfactory threshold (4.5 µg L^{-1}), responsible for green notes. Grapes of HT 3 and HT 4 were characterized by the presence of linalool and α-terpineol, like HT 1 and HT 2 samples, as well as by other compounds associated with fermentative and biochemical changes induced by progressive maturation, namely ethyl acetate, acetaldehyde and ethanol. However, these compounds showed rather low concentrations and have relatively high sensory thresholds (according to Etievant,[48] all higher than 10 mg L^{-1}), so their individual flavour impacts were unlikely to be large. Also, grapes of HT 3 and HT 4 showed the lowest amounts of C6 compounds, mainly aldehydes and alcohols, which are derived from C18 fatty acids via the lipoxygenase and alcohol dehydrogenase pathways and are known to give a herbaceous aroma. Finally, the third group formed by HT 5 grapes was characterized by hexanal and (*E*)-2-hexenal C6 compounds; the high amount of C6 aldehydes could be attributed in this case to intensified enzyme activity caused by gradual disintegration of the cell structure. Yang *et al.*[2] also reported that both hexanal and (*E*)-2-hexenal increased during maturation of 'Jingxiu', 'Bimeijia' and 'Jinya' table grapes.

The volatile results can explain the sensory quality of grape berries as assessed by panellists at different harvest times (Figs 3c and 3d).

In particular, Fig. 3c shows the distribution of the ten sensory attributes according to the first two PCs, which accounted for 75.7% of the total variance (49.1 and 26.6% for PC1 and PC2 respectively). PC1 was characterized by aroma, seed astringency, fruity taste, skin peelability, sweetness, crunchiness, berry detachment and overall evaluation on the positive side and sourness on the negative side. For PC2, aroma, seed astringency, fruity taste and sweetness accounted for the positive axis and crunchiness, overall evaluation, berry detachment, green taste and berry appearance for the negative axis. Figure 3d shows the discrimination of the samples at harvest according to the first two PCs. Also in this case, as seen in Fig. 3b for volatiles, HT 1 and HT 2 grapes could be discriminated from HT 3 and HT 4 grapes on PC1, while HT 5 grapes could be discriminated from all other grapes on PC2.

The discrimination among these groups is characterized by the changes in sensory quality of table grapes at different harvest times during ripening. In particular, the group formed by HT 1 and HT 2 is characterized only by sourness, confirming that

Table 2. Volatile compounds detected in 'Italia' table grapes of 2011 from different harvest times.

Volatile compound	Retention time (min)	Harvest time HT 1	HT 2	HT 3	HT 4	HT 5	Odour descriptor
Aldehydes							
Acetaldehyde	5.14	0.452b	0.359b	1.898a	1.804a	0.534b	Pungent
Propanal	6.09	0.042	0.051	0.073	0.048	0.043	Sharp, pungent
2-Methylpropanal	6.73	0.087	0.082	0.057	0.011	0.021	Green, pungent, burnt, malty, toasted
Butanal	7.73	0.017	0.030	0.068	0.033	0.022	Fruity, meaty, ethereal
2-Butenal	7.83	0.028c	0.039bc	0.040bc	0.044b	0.066a	
2-Methylbutanal	8.71	0.078	0.077	0.066	0.178	0.057	
3-Methylbutanal	8.84	0.258	0.201	0.174	0.386	0.105	
Pentanal	1.89	0.071	0.123	0.108	0.123	0.108	Woody, vanilla, fruity, nutty
C6 compounds							
Hexanal	15.12	5.708c	9.631a	0.465c	2.342b	10.072a	Fatty, green, grassy
(*Z*)-2-Hexenal	20.76	0.031	0.061	0.050	0.050	0.077	Grassy, green
(*E*)-2-Hexenal	21.56	3.433b	7.329a	1.110b	3.390b	8.887a	Green
Hexanol	27.93	0.586	0.561	0.313	0.829	0.457	
(*Z*)-3-Hexenol	29.35	0.161	0.145	0.144	0.377	0.113	Green, bitter, fatty
(*E*)-2-Hexenol	30.30	0.157	0.148	0.182	0.239	0.322	Leafy, green wine-like, fruity
Hexanoic acid	47.59	0.435	0.408	0.324	0.650	0.402	Sickening, sweaty, rancid, sour, sharp
Esters and alcohols							
Ethyl acetate	8.01	0.064c	0.039c	0.366a	0.201b	0.068c	Pineapple, ethereal
Ethanol	9.54	7.069b	3.773b	21.264a	22.964a	9.606b	
2-Methyl-3-buten-2-ol	13.45	0.915b	0.939b	1.330ab	1.976a	1.753a	Herbaceous, earthy
Pentanol	23.19	0.068	0.131	0.170	0.164	0.091	Mild green, fusel oil
Furan derivatives							
3-Methylfuran	8.21	0.025c	0.058ab	0.040c	0.178ab	0.146a	
Terpenes							
2,3-Dehydro-1,8-cineole	20.30	0.058	0.030	0.034	0.032	0.055	
D-Limonene	20.54	0.065a	0.066a	0.012b	0.006b	0.025b	Mild, citrus, sweet, orange, lemon
cis-Linaloxide	31.98	1.217	0.742	1.121	1.396	1.154	Floral
trans-Linaloxide	33.22	0.277	0.125	0.191	0.151	0.181	Floral
(*E*)-3,7-Dimethylocta-1,6-dien-3-ol	36.24	21.694a	9.839b	7.972b	7.764b	6.949b	Floral, citrus, fragrant, orange, sweet
(*E*)-3,7-Dimethylocta-1,5,7-trien-3-ol	38.75	0.201	0.117	0.164	0.152	0.186	
p-Menth-1-en-8-ol	42.35	0.362a	0.197b	0.164b	0.118b	0.118b	
-cis-2,2,6-Trimethyl-6-ethynyltetrahydro-2*H*-pyran-3-ol	43.91	0.592	0.421	0.493	0.477	0.464	Floral
trans-2,2,6-Trimethyl-6-ethynyltetrahydro-2*H*-pyran-3-ol	44.74	0.284	0.189	0.184	0.199	0.154	Floral
(*E*)-3,7-Dimethylocta-2,6-dien-1-ol	47.77	0.291	0.300	0.185	0.275	0.101	Sweet, floral, rose, fruity

Data are means of three replicates and expressed as μg internal standard equivalent per 100 g grapes. Within a row, mean values with different letters are significantly different ($P < 0.05$).

acidity is high at the first two harvests and then decreases during maturation.[39] Grapes of HT 3 and HT 4 were clearly characterized by their aroma, lower seed astringency (data not shown), fruity taste and sweetness. In particular, aroma, fruity taste and sweetness increased during ripening and progression of the harvest time, confirming again the volatile results shown in Fig. 3a. Finally, the third group formed by grapes of HT 5 was mainly influenced by berry detachment and overall evaluation. The high score for berry detachment (meaning a ripe behaviour for this attribute) is in accordance with the results obtained for volatile compounds, indicating more advanced senescence and gradual disintegration of the cell structure, which may have induced the formation of C6 aldehydes and alcohols through the action of lipoxygenase and alcohol dehydrogenase on C18 fatty acids. Besides all these considerations, grapes of HT 5 received the highest overall evaluation, most likely owing to the colour change, which also influenced the berry appearance score, since for most other sensory parameters no differences among these grapes and early harvested ones were detected, and in the case of aroma a lower score was assigned by panellists to these grapes.

In general, delaying the harvest increased the sensory quality of table grapes, improving their colour without compromising the berry appearance score. For grapes tested in 2011, where forced storage was longer than in 2010, some negative changes in sensory quality were detected, including increased susceptibility to berry detachment and loss of aroma. For the volatile profile, in fact, grapes of HT 3 and HT 4 developed higher quality compared with grapes of HT 1 and HT 2 as well as grapes of HT 5, even though

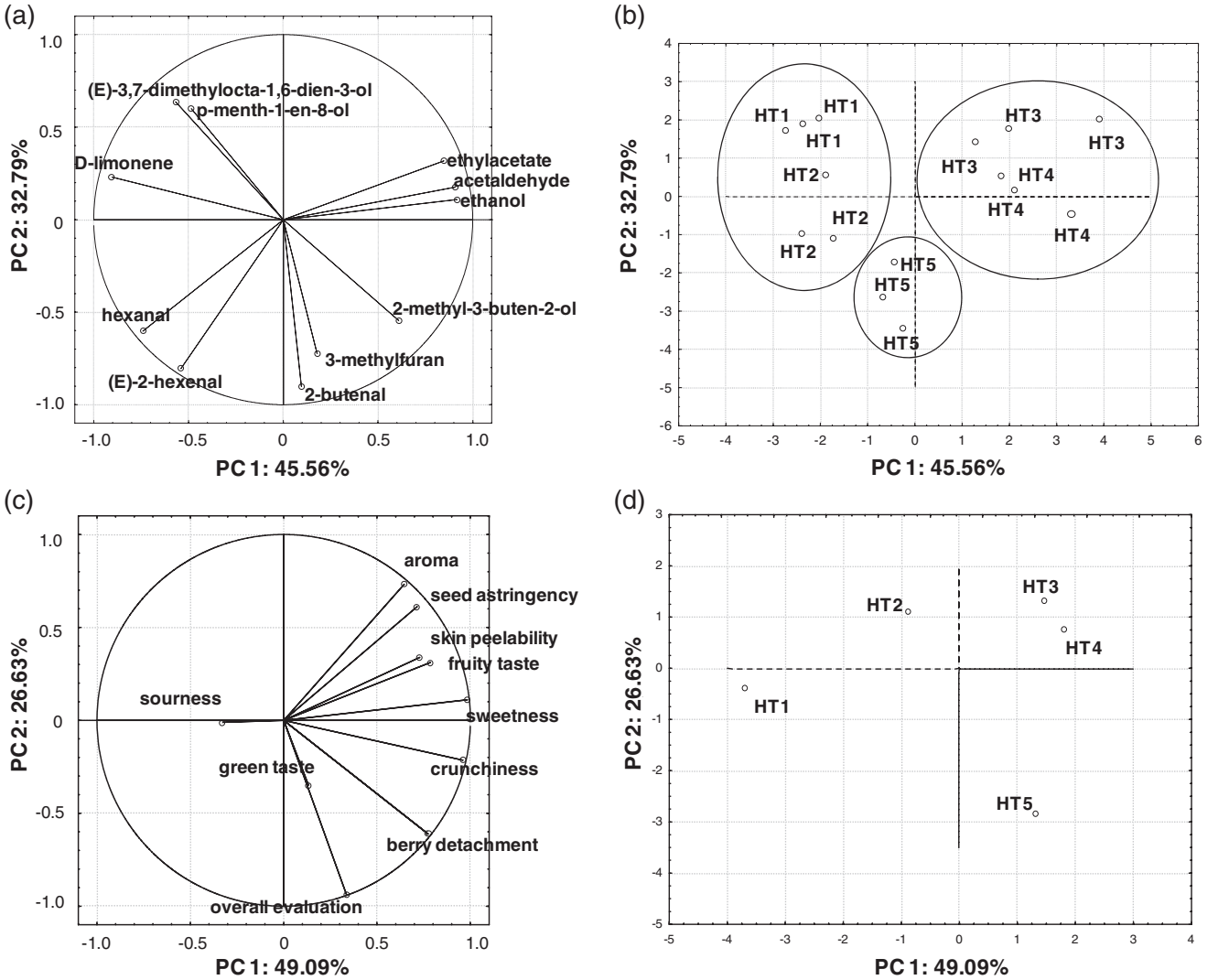

Figure 3. PCA biplots of (a, b) volatile compounds and (c, d) sensory attributes of table grapes at harvest: (a, c) variables; (b, d) discrimination among grapes from different harvest times (2011).

these grapes were perceived as the sweetest. The physicochemical attributes at harvest suggest that ripening continued up to HT 3 and that grapes maintained the same quality characteristics up to HT 4, then decreased in quality at HT 5.

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REFERENCES

1 Gómez E, Martínez A and Laencina J, Changes in volatile compounds during maturation of some grape varieties. *J Sci Food Agric* **67**:229–233 (1995).
2 Yang C, Wang Y, Wu B, Fang J and Li S, Volatile compounds evolution of three table grapes with different flavour during and after maturation. *Food Chem* **128**:823–830 (2011).
3 Kalua CM and Boss PK, Evolution of volatile compounds during the development of Cabernet Sauvignon grapes (*Vitis vinifera* L.). *J Agric Food Chem* **57**:3818–3830 (2009).
4 Fenoll J, Manso A, Hellín P, Ruiz L and Flores P, Changes in the aromatic composition of the *Vitis vinifera* grape Muscat Hamburg during ripening. *Food Chem* **114**:420–428 (2009).
5 Gunata YZ, Bayonove C, Baumes RL and Cordonnier R, The aroma of grapes. 1. Extraction and determination of free and glycosidically bound fractions of some grape aroma components. *J Chromatogr* **331**:83–90 (1985).
6 Park SK, Morrison JC, Adams DO and Noble AC, Distribution of free and glycosidically bound monoterpenes in the skin and mesocarp of Muscat of Alexandria grapes during development. *J Agric Food Chem* **39**:514–518 (1991).
7 Cliff MA, Dever MC and Reynolds AG, Descriptive profiling of new and commercial British Columbia table grape cultivars. *Am J Enol Vitic* **47**:301–308 (1996).
8 Zeppa G, Rolle L and Gerbi V, Valutazione mediante consumer test dell'attitudine al consumo diretto di un'uva a bacca rossa. *Ind Alim* **38**:818–824 (1999).
9 Crisosto CH and Crisosto GM, Understanding American and Chinese consumer acceptance of 'Redglobe' table grapes. *Postharv Biol Technol* **24**:155–162 (2002).
10 Liu HF, Wu BH, Fan PG, Li SH and Li LS, Sugar and acid concentrations in 98 grape cultivars analyzed by principal component analysis. *J Sci Food Agric* **86**:1526–1536 (2006).
11 Peppi MC, Fidelibus MW and Dokoozlian N, Abscisic acid application timing and concentration affect firmness, pigmentation, and color of 'Flame Seedless' grapes. *HortScience* **41**:1440–1445 (2006).
12 Jayasena V and Cameron I, Brix/acid ratio as a predictor of consumer acceptability of Crimson seedless table grapes. *J Food Qual* **31**:736–750 (2008).

13 Jayasena V and Cameron I, The effect of ethephon and clone on physical characteristics and sensory quality of Crimson Seedless table grapes after 1 month storage. *Int J Food Sci Technol* **44**:409–414 (2009).
14 Piva CR, López Garcia JJ and Morgan W, The ideal table grapes for the Spanish market. *Rev Bras Frutic* **28**:258–261 (2006).
15 Vargas A, Pérez J, Zoffoli JP and Pérez A, Comparacion de variables de textura en la medición de firmeza de bayas de uva Thompson seedless. *Ciencia Invest Agraria* **28**:37–42 (2001).
16 Baiano A and Terracone C, Varietal differences among the phenolic profiles and antioxidant activities of seven table grape cultivars grown in the South of Italy based on chemometrics. *J Agric Food Chem* **59**:9815–9826 (2011).
17 Revilla E, Escalona JM, Alonso E and Kovac V, The phenolic composition of table grapes. *Dev Food Sci* **37**:1579–1596 (1995).
18 Sato A, Yamada M, Iwanami H and Mitani N, Quantitative and instrumental measurements of grape flesh texture as affected by gibberellic acid application. *J Jpn Soc Hort Sci* **73**:7–11 (2004).
19 Deng Y, Wu Y and Li Y, Effects of high O_2 levels on postharvest quality and shelf life of table grapes during long-term storage. *Eur Food Res Technol* **221**:392–397 (2005).
20 Rolle L, Giacosa S, Gerbi V and Novello V, Comparative study of texture properties, color characteristics, and chemical composition of ten white table-grape varieties. *Am J Enol Vitic* **62**:49–56 (2011).
21 Rolle L, Giacosa S, Gerbi V, Bertolino M and Novello V, Varietal comparison among the chemical, physical and mechanical properties of five colored table grape cultivars. *Int J Food Prop* **16**:589–612 (2013).
22 Gallo V, Mastrorilli P, Cafagna I, Nitti GI, Latronico M, Longobardi F *et al*, Effects of agronomical practices on chemical composition of table grapes evaluated by NMR spectroscopy. *J Food Compos Anal* **35**:44–52 (2014).
23 Youssefa K and Roberto SR, Applications of salt solutions before and after harvest affect the quality and incidence of postharvest gray mold of 'Italia' table grapes. *Postharv Biol Technol* **87**:95–102 (2014).
24 Ciccarese A, Stellacci AM, Gentilesco G and Rubino P, Effectiveness of pre- and post-veraison calcium applications to control decay and maintain table grape fruit quality during storage. *Postharv Biol Technol* **75**:135–141 (2013).
25 De Palma L, Novello V, Tarricone L, Lopriore G and Tarantino A, Semiforzatura precoce e tardiva del vigneto a uva da tavola. *Spec Vitic Tavola* **13**:9–16 (2005).
26 Xu C, Zhang Y, Zhu L, Huang Y and Lu J, Influence of growing season on phenolic compounds and antioxidant properties of grape berries from vines grown in subtropical climate. *J Agric Food Chem* **59**:1078–1086 (2011).
27 Downey MO, Dokoozlian NK and Krstic MP, Cultural practice and environmental impacts on the flavonoid composition of grapes and wine. *Am J Enol Vitic* **57**:257–268 (2006).
28 Guidoni S, Ferradino A and Novello V, Effect of seasonal and agronomical practices on skin anthocyanin profile of Nebbiolo grapes. *Am J Enol Vitic* **59**:22–29 (2008).
29 Río Segade S, Giacosa S, Torchio F, de Palma L, Novello V, Gerbi V *et al*, Impact of different advanced ripening stages on berry texture properties of 'Red Globe' and 'Crimson Seedless' table grape cultivars (*Vitis vinifera* L.). *Sci Hort* **160**:313–319 (2013).
30 Kader AA, Modified atmospheres during transport and storage, in *Postharvest Technology of Horticultural Crops. Publication 3311* , 2nd edition, ed. by Kader AA. University of California, Oakland, pp. 85–92 (1992).
31 Amodio ML, Cabezas-Serrano AB, Rinaldi R and Colelli G, Implementation of rating scales for visual quality evaluation of various vegetable crops, in *Produce Quality Rating Scales and Colour Charts. Postharvest Horticulture Series No. 23*, ed. by Kader AA and Cantwell M. University of California, Davis, Appendix 1 (2007).
32 Rousseau J, *Institut Cooperatif du Vin (ICV) – Département Vigne & Vins*, Montpellier, France. Handout of training course on sensorial analysis by Vinidea, Italy, (2011).
33 Singleton SL and Rossi JA, Colorimetry of total phenolics with phosphomolybdic–phosphotungstic acid reagents. *Am J Enol Vitic* **16**:144–158 (1965).
34 Brand-Williams W, Cuvelier ME and Berset C, Use of a free radical method to evaluate antioxidant activity. *LWT – Food Sci Technol* **28**:25–30 (1995).
35 Abbott JA, Quality measurement of fruits and vegetables. *Postharv Biol Technol* **15**:207–225 (1999).
36 Dokoozlian N, Luvisi D, Moriyama M and Schrader P, Cultural practices improve color, size of 'Crimson Seedless'. *Calif Agric* **49**(2):36–40 (1995).
37 Tunick MH, Food texture analysis in the 21st century. *J Agric Food Chem* **59**:1477–1480 (2011).
38 Kontoudakis N, Esteruelas M, Fort F, Canals JM and Zamora F, Use of unripe grapes harvested during cluster thinning as a method for reducing alcohol content and pH of wine. *Aust J Grape Wine Res* **17**:230–238 (2011).
39 Watson B, Evaluation of wine grape maturity, in *Oregon Viticulture*, ed. by Hellman EW. Oregon State University Press, Corvallis, pp. 235–245 (2003).
40 Hellmann E, How to judge grape ripeness before harvest. *Southwest Regional Vine & Wine Conf.*, Albuquerque, 50 pp. (2004).
41 Heyes JK and Brown R, Cytochemical change in cell growth and differentiation in plants, in *Encyclopedia of Plant Physiology*, Vol. **15**, ed. by Ruhland W. Springer, Heidelberg, pp. 187–212 (1965).
42 Harris JM, Kriedemann PE and Possingham JV, Grape berry respiration: effects of metabolic inhibitors. *Vitis* **9**:291–298 (1971).
43 Sweetman C, Deluc LG, Cramer GR, Ford CM and Soole KL, Regulation of malate metabolism in grape berry and other developing fruits. *Phytochemistry* **70**:1329–1344 (2009).
44 Ruffner HP and Hawker JS, Control of glycolysis in ripening berries of *Vitis vinifera*. *Phytochemistry* **16**:1171–1175 (1977).
45 Coombe BG, Research on development and ripening of the grape berry. *Am J Enol Vitic* **43**:101–110 (1992).
46 Park SK and Noble AC, Monoterpenes and monoterpene glycosides in wine aromas. *ACS Symp Ser* **536**:98–109 (1993).
47 Carballeira Lois L, Cortés Diéguez S, Gil de la Peña ML and Fernández Gómez E, SPE-GC determination of aromatic compounds in two varieties of white grape during ripening. *Chromatographia* **53**(Suppl. 1):S350–S355 (2001).
48 Etievant P, Wine, in *Volatile Compounds in Food and Beverages*, ed. by Maarse H. TNOCIVO Food Analysis Institute, Zeist, pp. 486–546 (1991).