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Original research article

Modeling of the evolution of phenolic compounds in berries of "Italia" table grape cultivar using response surface methodology

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ABSTRACT

The aim of this work was to determine the phenolic profile of *Vitis vinifera* L. cv. "Italia" table grapes during ripening, as influenced by the harvest date and berry heterogeneity. The results showed that this cultivar is rich in phenolic compounds with health-promoting properties, particularly at early harvest stage (341 and 178 mg/kg berries of total phenols in the skin and pulp, respectively). Caftaric acid was the most abundant compound in the skin (28.95–51.93 mg/kg), while *p*-coumaroyl-glucose was the highest in the pulp (6.39–17.18 mg/kg). Low levels of resveratrol (0.11–0.29 mg/kg) were found in the skin starting from day 14 of the harvest. Response surface methodology (RSM) was used to model the evolution of phenolic compounds in berries during ripening. The regression models were highly significant for protocatechuic acid, catechin, epicatechin and *t*-resveratrol in the skin, and total hydroxycinnamoyl tartaric acids in the pulp ($R \geq 0.80$). This modeling could be a tool that would permit better exploitation of maximum accumulation of phenolic compounds in the vineyard by selecting the most suitable combination of sampling date and berry density. An adequate sampling strategy could be implemented to increase the content of specific bioactive phenolic compounds according to consumer preference, thus promoting the health-promoting quality of fresh table grapes and ready-to-eat fruit salads.

1. Introduction

Table grapes are among the most valuable sources of phenolic compounds (Brat et al., 2006). These compounds are probably responsible for most of the beneficial effects of grapes with respect to a number of chronic diseases, including atherosclerosis, cardiovascular diseases, neurodegenerative disorders and aging (Iriti and Faoro, 2009; Xia et al., 2010; Pezzuto, 2008). Recently, Carrieri et al. (2013) studied selected table grape varieties and showed that the ability of the grape skin extracts to inhibit the synthesis of the tissue factor involved in the pathogenesis of thrombotic diseases is correlated to the phenolic composition.

The main phenolic classes found in table grapes are phenolic acids, anthocyanins, proanthocyanidins and stilbenes, each distributed differently within the grape tissues (Liang et al., 2008; Iriti and Faoro, 2009). In particular, hydroxycinnamic acids are located mainly in the grape skin and flesh, whereas anthocyanins and resveratrol only in the skin, and proanthocyanidins in both skin and seeds (Iriti and Faoro, 2009). Anthocyanins and resveratrol are reported to be the most bioactive grape compounds (Xia et al., 2010). Several studies on the health-promoting properties of table grapes have already compared the phenolic composition of different cultivars using grapes purchased from the market or harvested at maturity, whereas others have examined the effect of in-field and/or postharvest treatments on the phenolic profile (Baiano and Terracone, 2011; Cantos et al., 2002; Lago-Vanzela et al., 2011; Capriotti et al., 2012; Crupi et al., 2013; Rolle et al., 2013). In most of the cited cases, polyphenols were determined by using liquid chromatography coupled with UV and mass spectrometric detection systems, providing useful structural information for the identification of these compounds.

The phenolic content changes during grape ripening according to the different regulation of the enzyme activity involved in the mevalonate pathway, as is the case of resveratrol, whose concentration seems to decrease from veraison to harvest (Singh Brar et al., 2008; Iriti and Faoro, 2009). As already pointed out by other authors, berry maturity stage at harvest can greatly affect the overall quality of table

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grape berries in terms of texture, color and chemical composition (Baiano and Terracone, 2011; Parpinello et al., 2013; Rolle et al., 2015). However, in the vineyard the grapes do not ripen homogeneously. Each cluster of the vine and also each berry of the cluster can ripen at different rates depending on the position, environmental factors, and management of viticultural practices. As a consequence, a high berry heterogeneity can be found from the beginning of the ripening process until the moment of the harvest (Kontoudakis et al., 2011; Río Segade et al., 2013). All the quality traits are strongly linked to the in-field berry variability, which can have a great influence on the consumer acceptance (Rolle et al., 2015). Recently, it has been shown that berry densimetric sorting and size can be applied to separate berries with different chromatic characteristics, texture parameters, aromatic profiles and phenolic composition (Rolle et al., 2015; Río Segade et al., 2013). Gallo et al. (2014) also highlighted that the agronomical practices can influence the composition of primary metabolites of table grapes and proposed the NMR spectroscopy (an advanced analytical technique) in complement or as an alternative to traditional determination of Brix, titrable acidity, and so on to discriminate among the applied practices.

Table grape berries can be consumed fresh, processed as juice or added to salads, drinks and desserts. Because of their many uses and increased consumer demand, the presence of table grapes in the market should last as long as possible (if not all year round), while care is taken to preserve their quality attributes.

Given that the health-promoting properties of table grapes play a significant role in determining their overall quality, and also increasingly influence the consumer choices, the main aim of this work was to investigate when the highest content of phenolic compounds in *Vitis vinifera* cv. “Italia” table grape berries is reached, particularly for the production of ‘ready-to-eat’ fruit salad. For this aim, not only the evolution of phenolic compounds during ripening of the berries was studied, but also a model was developed to assess the combined effect of grape density and harvest date using response surface methodology (RSM). The selection of the most suitable harvest time and berry density to achieve the maximum accumulation of phenolic metabolites during ripening is a novel aspect with relevance for the fresh-cut industry. The study was carried out on cv. Italia, one of the most popular Italian seeded white table grape varieties, originally bred in 1911 by crossing Bicane and Muscat Hamburg (Baiano and Terracone, 2011).

2. Materials and methods

2.1. Grape sampling and selection

Vitis vinifera L. cultivar “Italia” (Italia, hereafter) table grapes were harvested in 2012 from a vineyard located in Trinitapoli (BT province, Puglia region, Southern Italy, N 41.1872, E 16.0079). The vineyard was established in 2007 on a clay loam soil high in mineral elements and with moderate organic matter content; 6% Ca^{++}; and pH 8.1. Cv. Italia was grown on 140 Ru stock and trained onto an overhead “tendone” trellis (Apulia type). Vines were pruned to 4 canes and spurs, with average number of 35 shoots per vine and 1.7 clusters per shoot. The vineyard was managed according to viticultural practices common for the growing area, including winter mineral nutrition with guanito (6 q/ha), shoot and bunch positioning, basal leaf removal, spring-summer fertigation, and irrigation with seasonal volume of about 2000 m^3/ha by drip irrigation.

Grapes were harvested for five consecutive weeks, from August 22 to September 18. Single berries and small groups of three to five berries were randomly taken from all parts of the clusters. Once in the lab, broken berries were discarded and the single berries with attached short pedicels were densimetrically sorted by flotation in different saline solutions, ranging from 190 to 80 g/L sodium chloride (NaCl) concentration, following the procedure described by Rolle et al. (2012). Afterwards, the respective berry groups were weighed to obtain the distribution percentages of berries into density classes (Fig. 1). In order to evaluate grape heterogeneity and model the compositional differences, the most represented (according to weight percentage) five density classes were considered. The berry groups corresponding to different density classes and sampling points were treated separately for all subsequent analyses.

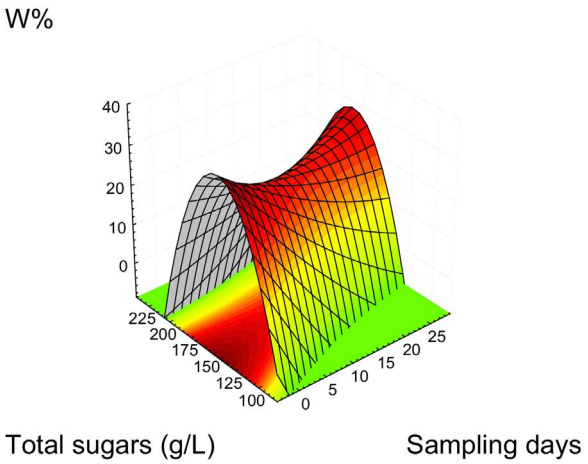

Fig. 1. Modeling of the distribution percentage in weight (W%) of Italia table grape berries with different sugar content (g/L) during ripening.

2.2. Chemicals

Ultrapure water was produced using Milli-Q equipment (Merck Millipore, Darmstadt, Germany). Protocatechuic acid, caftaric acid, *p*-coumaric acid, procyanidin B1, procyanidin B2, catechin, caffeic acid, epicatechin, ferulic acid, rutin hydrate, isoquercitrin, *t*-resveratrol, Folin-Ciocalteu reagent, formic acid, citric acid, tartaric acid, malic acid, glucose, fructose and methanol were purchased from Sigma–Aldrich (Milan, Italy).

2.3. Determination of technological ripeness

For each sample, two sets of 50 berries each were taken ($n = 2$) and manually crushed and centrifuged to obtain the respective juice. The juice was used for determining titratable acidity, organic acids and reducing sugars. Titratable acidity (TA) was determined as defined by International Organization of Vine and Wine (OIV, 2011) method and expressed in g/L tartaric acid. Sugars (SSC, as sum of glucose and fructose), citric acid, tartaric acid, and malic acid were determined by HPLC following the protocol described by Giordano et al. (2009), and the contents were expressed in g/L. SSC/TA ratio was calculated as the ratio between the sugar content and titratable acidity values, both expressed in g/L (OIV, 2008).

2.4. Extraction and determination of phenolic compounds from berry skin and pulp

For each sample, three sets of ten berries each ($n = 3$) were taken, weighed, and peeled using a laboratory spatula (Di Stefano and Cravero, 1991). The pulp was collected in a flask containing 100 mg of $Na_2S_2O_5$ to avoid oxidation, diluted 9:1 (w/w) with H_2SO_4 5 mol/L to avoid tartaric precipitation, homogenized using a Ultra-Turrax T10 (IKA Labortechnik, Staufen, Germany) at 6000 rpm for 1 min, and centrifuged in a PK 131 centrifuge (ALC International, Milan, Italy) for 15 min at 3000 × *g* (Rolle et al., 2013, 2015). The resulting solution was used for pulp analysis. The skins were carefully cleaned from pulp residuals and immediately immersed in 25 mL hydro-alcoholic buffer solution prepared with 12% (v/v) ethanol, 5 g/L tartaric acid, 2 g/L $Na_2S_2O_5$, and adjusted to pH 3.2 with NaOH 1 mol/L. The skins were