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# Key norisoprenoid compounds in wines from early-harvested grapes in view of climate change

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ABSTRACT

In view of climate change, the scheduling of an early harvest may be an agronomic option to limit wine alcohol, provided that a satisfactory content of secondary metabolites can be ensured in grapes. To better understand the link between grape ripening, seasonal trend and wine aroma, the aromatic expression of Barbera and Pinot Noir wines produced with early harvested grapes was assessed. Attention was focused on C13 norisoprenoids during both alcoholic fermentation and after three months of storage. At the end of fermentation, the highest β-damascenone content was detected in wines obtained from less ripe grapes, the content subsequently increased significantly after three months of storage; however, the levels of β-ionone decreased significantly during the same period. The reduction of wine alcohol as a result of harvesting earlier, especially for Barbera, was associated with optimal aromatic levels as well as good technological parameters.

## 1. Introduction

Global warming and related climate change, mainly linked to anthropogenic factors, are phenomena that currently represent a significant world issue. The consequences of these changes involve agriculture and have considerable repercussions both from a social and economic point of view (Barros et al., 2014). Among the agricultural sector, viticulture is highly susceptible to these changes mainly due to its interaction with the environment, soil, and human choices. Climate change may influence the well-known and well-established variety–environment combination, thus many other aspects could be affected, such as cultivar distribution, timing of phenological phases, vine productivity and pathology (Palliotti et al 2014; Sacchelli, Fabbrizzi, & Menghini, 2016).

Numerous studies have highlighted that over the last few decades there has been an advance of the phenological phases (Webb et al., 2012; Webb, Whetton, & Barlow, 2007), in particular flowering and veraison, compared with what was considered 'normal' for a specific cultivar and area (van Leeuwen & Darriet, 2016). The increase in average temperatures of summer months, as a major consequence of climate change, as well as the different distribution of rainfall during the ripening phase, lead to a higher concentration of sugar and to a general change of the acidic profile of grapes, due to reduced malic acid content. Microbiologically, the consequent increase in must pH can facilitate bacterial contamination of wine, whereas the high sugar content may induce stuck fermentations or high production of unwanted by-products, such as acetic acid and glycerol (De Orduna, 2010).

Furthermore, in several viticulture areas, ripening occurs during the warmest part of the season, when both colour and aroma profile can be adversely affected (Asproudi, Petrozziello, Cavalletto, & Guidoni, 2016; Mori, Goto-Yamamoto, Kitayama, & Hashizume, 2007). At high temperatures, vine metabolism is inhibited, leading to a lower accumulation of polyphenols and a lack of synchrony among the timing of the sugar/acid balance and polyphenolic optimum, especially under Mediterranean conditions (Mori et al 2007; Tomasi et al., 2011).

The excessive alcohol content of wines, resulting from exceptionally sugary grapes, has become an unwelcome feature for consumers. Nowadays, consumers gravitate to drinks with a moderate level of alcohol, such as fresh and fruity wines, as a result of both health concerns and the changing taste of consumers (Caballero & Segura, 2017). From a sensorial point of view, wine with a high alcohol content has numerous organoleptic consequences including a decrease in freshness and a change in the perception of the aromatic bouquet. In fact, ethanol may enhance the perception of sweetness and bitterness while reducing that of saltiness and sourness. Moreover, ethanol influences the headspace partitioning of aromatic compounds (Robinson et al., 2009), decreasing their volatility (Le Berre, Atanasova, Langlois, Etiévant, &

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Thomas-Danguin, 2007). Thus, climate-change related variations of grape ripeness can also cause modification of the aromatic perception of wines, directly, with the formation of compounds characterized by overripe fruit notes, the reduction of vegetal, fresh and flowery notes (Pons et al., 2017), or indirectly, through the sensitive modification of their aromatic profile, due to the increase in alcohol content.

One of the major current challenges in oenology and viticulture is how to mitigate and respond to the effects of climate change (Mozell & Thach, 2014), in order to preserve the specific and distinctive olfactory and gustatory notes that link wines to their territory of origin. In this regard, the early harvest of grapes to limit wine alcohol levels may be an alternative to the use of subtractive cellar technologies, which may cause compositional changes, compromising the aromatic quality of the product. Previous studies have doubted that, from an aromatic point of view, wines produced with early harvested grapes could be endowed with a high acidity and an excessive content of C6 compounds to which vegetal notes are attributed (Kalua & Boss, 2010). Nevertheless, the high sugar content of the grapes recorded during the last vintages has renewed interest in early harvesting, especially in the warmest areas, where early harvested grapes can provide an optimal balance between the different qualitative components of the berry, especially volatile and polyphenol concentrations and profiles.

To the authors' knowledge, few investigations on key aroma compounds, such as norisoprenoids and their content in wines produced from sequential grape harvests, have been reported and only some research has linked technological and aromatic maturity of the grapes to the aroma of finished wines. Norisoprenoids derive from carotenoid degradation through both non-specific and enzymatic mechanisms, involving carotenoid cleavage dioxygenases (CCDs) whose expression is strictly correlated to climatic and agronomic parameters (Chen et al., 2017). The most interesting norisoprenoids from an aromatic point of view are megastigmane, notably β-ionone and α-ionone with typical violet notes, and β-damascenone, characterized by notes of quince and flowers (Mendes-Pinto, 2009). β-damascenone is a key aroma-active compound found in many foods and beverages. It has a complex aroma, reminiscent of honey, tropical fruit, quince and apple, and its perception depends upon the matrix and concentration (Pineau, Barbe, Van Leeuwen, & Dubourdieu, 2007). Some researchers have suggested that β-damascenone also has an indirect impact on wine aroma by enhancing the fruity notes of ethyl esters (Escudero, Campo, Fariña, Cacho, & Ferreira, 2007).

The authors' previous research has shown that in wines obtained from grapes with high total acidity, the concentration of β-damascenone was higher than that of wines produced with grapes harvested when fully ripe (Petrozziello, 2012). Thus, more information is needed to define the optimum harvest time, coupling together strategies able to enhance the wine aroma and meet the demand for wines with both reduced alcohol content and balanced organoleptic properties. To this purpose, the effect of different grape ripening levels on the aroma of wines produced under the same fermentation conditions was investigated, comparing two non-floral varieties, Pinot Noir and Barbera grown in the same vineyard.

Pinot Noir is a grape cultivar that is spread worldwide, mostly in cold viticultural regions. When young, wines made from Pinot Noir tend to have red-fruit aromas, such as cherries, raspberries and strawberries, and overall, the characteristics of Pinot Noir wine vary significantly with grape maturity (Fang & Qian, 2005, 2006; Miranda-Lopez, Libbey, Watson, & Mc Daniel, 1992). Barbera is an Italian cultivar producing berries with high titratable acidity. Traditionally, some viticulturists used to delay harvest if the seasonal climatic conditions were favourable, to increase sugar levels to balance Barbera wine acidity. From an aromatic point of view, previous studies have pointed out that Barbera grapes were characterized by significant amounts of volatiles, including terpenes and β-ionone (Carlomagno et al., 2012).

In this work, the main technological parameters of Pinot Noir and Barbera grapes harvested at three different ripening stages (−15 d, −7 d and 0 d, indicating the days before full ripeness) were assessed, together with important key aromas of musts and wines. Attention was focused on β-damascenone, β-ionone and α-ionone which were quantified by stable isotope dilution assay (SIDA) and HS-SPME-GCMS quantification, whereas the most important fermentative aromatic compounds were extracted and quantified by solid phase extraction gas chromatography coupled with mass spectrometry (SPE/GC–MS).

## 2. Materials and methods

### 2.1. Vineyard site

Grape samples of Pinot Noir and Barbera were collected at the DISAFA (*Università degli Studi di Torino*) experimental vineyard located in Grugliasco (45°03′N, 7°35′E; Piedmont, Italy), in 2015. Vine density was 4400 vines/ha (0.90 m × 2.50 m), vines were vertical shoot positioned (VSP) and trained to the Guyot pruning system. The vineyard is located at 293 m above s.l. in a plain area and vines were planted in 2008; Pinot Noir plants were grafted onto 1103P, while Barbera plants onto SO4. The vineyard was organized into randomized blocks of 10 plants each. Three blocks for each variety were used as biological replicates (named: A, B and C). Starting from bud-burst, the main phenological phases of the plant were observed (flowering, veraison and ripening).

### 2.2. Grape sampling

The first sampling of Pinot Noir was carried out at veraison (50% coloured berries) and grapes were then sampled again on the 13th (21 days after veraison, DAF), the 19th (27 DAF) and the 25th (33 DAF) of August 2015. Barbera was first sampled at veraison and then sequentially on the 25th (29 DAF) and 31st (35 DAF) of August and on the 7th September 2015 (42 DAF). Approximately 30 clusters for each biological replicate (A, B and C) were harvested manually at each sampling date (veraison and 3 ripening levels). For each replicate, 500 berries were sampled for the analysis of the main physico-chemical parameters namely, berry weight, pH, titratable acidity (TA) and total soluble solids (TSS). The remaining berries were prepared to obtain grape extracts for polyphenol, anthocyanin and total flavonoid measurements; two further 50 g replicates of grapes were stored in the dark at −80 °C for carotenoid compound assessment.

### 2.3. Microvinifications

Vinification trials at laboratory scale were carried out in triplicate for each maturation point for a total of 9 fermentations per variety. Grapes (approximately 2 kg per replica) were manually destemmed, crushed and placed into 3 L Erlenmeyer flasks. The inoculum ($5 \times 10^6$ cells $g^{-1}$) was *Saccharomyces cerevisiae* yeast strain ISE 167, belonging to the CREA-VE culture collection, after preventive growth in YPG (Yeast Peptone Glucose) medium. Fermentations were performed at 25 °C, and two punchings per day were carried out to simulate a standard red wine vinification. Fermentations were followed by daily monitoring of the flask weight loss, indirectly calculating the consumed sugar. Sampling was carried out at crushing (day 0), 50% of fermented sugars (approximately day 3 for all trials) and at the end of fermentation (day 8). pH, AT, TSS and polyphenolic index measurements were assessed at crushing, at the half-way stage and at the end of fermentation. The final alcohol content was determined for each wine.

The measurement of TSS, total acidity and pH of grape musts, as well as the analysis of reducing sugars by HPLC at the end of alcoholic fermentation, density, total dry extract and ethanol in wines was carried out according to official EC methods (Commission Regulation, 1990). The evolution of norisoprenoid compounds was thoroughly investigated during fermentation; namely the determination of α-ionone, β-ionone and β-damascenone was carried out at crushing, at mid-