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Influence of Berry Ripening Stages over Phenolics and Volatile Compounds in Aged Aglianico Wine

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Abstract: The harvest time of grapes is a major determinant of berry composition and of the wine quality, and it is usually established through empirical testing of main biochemical parameters of the berry. In this work, we studied how the ripening stage of Aglianico grapes modulates key secondary metabolites of wines, phenolics and volatile compounds. Specifically, we analyzed and compared four berry ripening stages corresponding to total soluble solids of 18, 20, 22, and 25 °Brix and related aged wines. Wine color intensity, anthocyanins level and total *trans*-resveratrol (free + glycosidic form) increased with grape maturity degree. Wines obtained from late-harvested grapes significantly differed from the others for a higher content of aliphatic alcohols, esters, acetates, α-terpineol and benzyl alcohol. The content of glycosidic terpene compounds, such as nerol, geraniol and α-terpineol, was higher in wines obtained with grapes harvested at 25 °Brix compared to the earlier harvests. Our work indicated that the maturity of the grape is a determining factor in phenolic and volatile compounds of red Aglianico wines. Moreover, extending grape ripening to a sugar concentration higher than 22 °Brix improves the biochemical profile of aged wine in terms of aroma compounds and of phytochemicals with known health-related benefits.

Keywords: *trans*-resveratrol; esters; terpenols; glycosidic precursors; harvest time; *Vitis vinifera*

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1. Introduction

Wine quality largely depends on identifying the optimal maturity of the grapes at harvest. During ripening, berry weight, sugars, pH, and acidity are traditionally monitored to choose the best moment for harvest. These parameters are often measured to empirically define the technological maturity of the grapes. However, for some red varieties, harvesting at technological maturity does not guarantee the production of balanced wines, because important characteristics of red wines depend also on polyphenols and volatiles, and these compounds are usually not monitored during ripening. For instance, grape phenolics are responsible for color, astringency, bitterness, and aging behavior of red wines. Although their bioavailability is still questioned [1,2], the interest of the scientific community towards phenolics, in particular *trans*-resveratrol and quercetin, has increased because they are accountable for several health-related effects correlated to wine intake [3]. Moreover, several odor active compounds, belonging to the chemical classes of monoterpens, norisoprenoids, C6 alcohols, and shikimate derivatives, which are present in the volatile fraction of grapes, play a decisive role in the aroma of wine. Most odor compounds as monoterpenes are present both as free volatiles and non-volatile, glycosidically bound forms and represent a potential reservoir of flavor [4,5].

Grape ripening is an important physiological process that influences the composition of the wine, as it is important for the development of its sensory properties. Due to their notable oenological and biological importance, numerous authors have investigated the changes during grape ripening of phenolics [6–10] as well as free and glycosylated bound volatiles [11,12]. The ripening process is also characterized by other important aspects influencing the ability of each class of chemical compounds to be released from grape to must during vinification. They include seed lignification for phenolics, the enzymatic release from non-volatile precursors for volatiles, and, generally, the gradual breakdown of the cellular structure of the skins. Therefore, investigations on the effect of the grape composition at harvest on wine quality should include an understanding of the ability of phenolics and volatiles to be extracted from the solid part of the grape to must during vinification.

During aging, polyphenolic and volatile compounds of red wines undergo numerous transformations. Anthocyanins, the grape polyphenols responsible for color of red wine, are involved in numerous reactions with other wine components, as well as tannins, flavanols, acetaldehyde, vinyl phenol and pyruvic acid, with the consequent development of new pigments and a yellow-orange hue [13–15]. The involvement of tannins in the polymerization reaction with anthocyanins and flavanols and in reactions with proteins and polysaccharides often causes a decrease in wine astringency and bitterness [16]. Changes in the content of aroma substances during wine aging include: the oxidation, isomerization and cyclization reactions of monoterpens to compounds that have higher odor thresholds [17]; the acid and enzyme-catalyzed hydrolysis of glycosidic aroma precursors of grape [18]; and the decrease in acetates and ethyl esters of fatty acids, resulting in an overall decrease in fruity notes [19]. Several studies have aimed at understanding the effect of grape maturity on volatile compounds in grapes and wine [20–29]. For instance, a positive influence of the degree of grape ripening on wine color and flavanol and anthocyanins content of 18 months aged red wines has been reported [30]. Papers detailing the influence of grape maturity on the content of free and glycosidically bound *trans*-resveratrol as well as on free and bound volatiles of red wine are relatively scarce. To our knowledge, no study has reported the influence of grape maturity degree on the content of free and glycosidically bound *trans*-resveratrol as well as on free and bound volatile compounds in Aglianico red wine. *Vitis vinifera* cv. "Aglianico" is one of the most prestigious southern Italian native grapes used to produce aged wine in agreement with related Appellation of Controlled and Guaranteed Origin (DOCG) and Appellation of Controlled Origin (DOC) regulation.

In the present work, we studied chromatic characteristics, anthocyanins, tannins, catechin, epicatechin, quercetin, *trans*-resveratrol, *trans*-polydatin content and free and bound volatiles of aged wines obtained with grapes harvested at four stages according to the soluble sugar content of the berries.

2. Materials and Methods

2.1. Plant material, Location, and Treatments

The grape production was carried out in a commercial grapevine vineyard (380 m a.s.l.) located in Foglianise (Benevento, Campania region, Italy) within the Taburno area, one of the major Italian viticultural areas for wine production. Vines were 8-year old *V. vinifera* L. cv. "Aglianico" plants grafted onto 1103P and trained to a spur-pruned permanent cordon. Vines were spaced 2.20 m × 1.30 m (3497 vines/ha) and rows had a north–south orientation. The trials compared four stages of berry ripening (four harvest times) corresponding to total soluble solids (TSS) in the berries of 18, 20, 22, and 25 °Brix (hereafter these treatments will be indicated as S18, S20, S22, and S25, respectively). For each treatment, the harvest date was determined by monitoring TSS accumulation in the berries every five days starting from veraison on three samples (replicates) of 50 berries (a total of 150 berries per treatment). When the target TSS values defined for each treatment were reached, an additional three samples (each made of 250 berries) were collected and used for berry

composition analyses. In addition, on the same dates, a sample of 100 kg of grapes was harvested and used for vinification.

2.2. Vinification

Vinification was carried out using 100 kg of grapes. Grapes were destemmed and crushed and the must was treated with $K_2S_2O_5$ (60 mg/kg of grapes). Fermentation was carried out at 26 °C using a *S. cerevisiae* D254 active dry yeast inoculum (Lallemand Italy, Castel d'Azzano, Italy) and the cap was immersed twice a day for 10 days. The must was then pressed (at about 8 bar), and 65 L of finished wine was obtained. Upon completion of alcoholic fermentation (residual sugars < 2 g/L), wines were racked with 8 g/hL of $K_2S_2O_5$, bottled and stored for 24 months at 10 °C. Two repetitions per vinification were carried out. All wines were analyzed two years after winemaking.

Physicochemical analysis of grapes. TSS, titratable acidity and pH were measured according to the Official European Method (1990). Berries of each sample were analyzed for phenolic potential (total anthocyanins), potential anthocyanins (A pH 1), extractable anthocyanins (A pH 3.2), extractability and tannins of skins and seeds, according to Glories [31].

2.3. Main Wine Characteristics and Spectrophotometric Analysis

Ethanol, sugar, pH, dry extract, titratable acidity, volatile acidity, total and free SO_2, optical densities (OD) and total polyphenols (Folin-Ciocalteau Index) were measured according to the Official European Methods (1990). Color intensity, hue, percentage of free anthocyanins on the total amount of anthocyanins (dAL %) and percentage of anthocyanins combined with tannins and not bleachable by SO_2 on the total amount of anthocyanins (dTaT %) were evaluated according to the method described by Glories [32]. When the absorbance values were higher than 0.9 Abs units, a dilution with a hydroalcoholic buffer solution (12% *v*/*v* of ethanol in water) at pH 3.3 (obtained by using tartaric acid and sodium hydroxide) was used, in order to be in the range of validity of the Lambert–Beer law. Total anthocyanins and tannins were determined by spectrophotometric methods on the berry extracts and directly on wines [31].

2.4. Determination of Trans-Resveratrol, Trans-Polydatin, Catechin, Epicatechin and Quercetin

The analysis was performed using an HPLC apparatus (Shimadzu Italy, Milan, Italy), consisting of an SCL-10AVP system controller, two LC-10ADVP pumps, a SPD-M 10 AVP detector, an injection system full Rheodyne model 7725 (Rheodyne, Cotati, CA, USA) equipped with a 20 µL loop. Separation and quantification of catechin, epicatechin, *trans*-resveratrol and quercetin were carried out by HPLC, as previously described [33]. The glucosidic form of *trans*-resveratrol was detected following 24 h of enzymatic hydrolysis with a glycosidase rich enzyme preparation in wine, at pH 4.5 and at a temperature of 45 °C. For each sample of wine, analysis was carried out in triplicate.

2.5. Extraction and Analysis of Free and Bound Aroma Compounds

C18 reversed-phase solid-phase extraction (SPE) was adopted for the extraction of free and glycosidically bound aroma compounds from wines according to the method earlier described [34]. A sample of 50 mL was diluted (1:1 *v*/*v*) with water after the addition of 2-octanol as internal standard (250 µL 2-octanol at 200 mg/L in methanol) loaded onto 1-g C18 cartridges (Phenomenex, Torrance, CA, USA). Free and bound volatiles were eluted with dichloromethane and methanol, respectively. The dichloromethane fraction was collected in a separating funnel, was dried over Na_2SO_4 and concentrated first in a Kuderna–Danish concentrator (Supelco, Bellefonte, PA, USA) and then under a stream of pure N_2 for gas-chromatographic analysis. The methanol fraction was concentrated to dryness under vacuum at 35 °C, and redissolved in 5 mL of citrate phosphate buffer (pH = 5.0) containing a glycosidase rich enzyme preparation (80 mg). After 16 h of incubation at 40 °C, 2-octanol

was added, and the mixture was extracted with dichloromethane for gas chromatographic analyses. All extractions were carried out in triplicate.

A 1.2 µL aliquot of each concentrated wine extract was injected in splitless mode into a Hewlett-Packard 5890 series II gas chromatograph equipped with a split/splitless injector (Hewlett-Packard, Avondale, PA, USA) and with a flame ionization detector. The column used was a DBWax from J&W Scientific (Folsom, CA, USA), 30 m length × 0.32 mm with 0.5 film thickness. The temperature program was the following: 40 °C for 5 min, 5 °C/min rate to 220 °C, 10 min at maximum temperature. The carrier gas was He flowing at 37 cm/s. Both detector and injector temperatures were maintained at 250 °C. The identity of the volatile compounds was determined through the comparison of their chromatographic retention properties with those of pure references. Comparison of mass spectra stored in the NIST database with those obtained for each compound was performed by GC/MS and consisted of a 6890 series Agilent Technologies gas chromatograph and 5973 Network series mass selective detector (Agilent Technologies) fitted with a 4 electronic impact source. Electron impact mass spectra were recorded with ion-source energy of 70 eV. Quantitative data were obtained by interpolation of relative areas versus the internal standard.

2.6. Chemicals

All chromatographic solvents were HPLC ultra-gradient grade and were purchased from Merck (Darmstadt, Germany). *trans*-Resveratrol and quercetin standards were purchased from Sigma-Aldrich (Milan, Italy), (+)-catechin and (−)-epicatechin standards were purchased from Fluka (Milan, Italy). Because (−)-catechin has recently been found in grape extracts when analyzed with a chiral column [35], the results of the analysis were reported as catechin and epicatechin.

2.7. Statistical Analysis

Analysis of variance and Tukey's test were used to assess the significance of the differences between means. Data elaboration was carried out using XLSTAT version 2014.5.03 (Addinsoft Corp., Paris, France). A correlogram representing the Pearson correlation coefficient (n = 12) matrix between grape and wine compounds and chromatic characteristics was built in RStudio (RStudio, Boston, MA, USA) with corrplot package.

3. Results and Discussion

Table 1 shows the anthocyanin and tannins content of grapes harvested at the four different ripening stages, S18, S20, S22, and S25. The tendency observed for total and potential anthocyanins confirms the known trend of these pigments during ripening: a quick increase until a maximum (S20) followed by stabilization or decrease in the over-ripe grape (S25). After prolonging the on-vine berry maturation (S20 to S25), anthocyanin content in the grapes decreased, but these pigments became progressively easier to extract, as suggested by the trends of extractable anthocyanins and of extractability values. A similar result was previously reported and it is considered to be the results of a decrease in cell turgor pressure causing the breakdown of cell walls and the release of anthocyanins from vacuoles [36]. Tannins in berry skins did not significantly vary during ripening, while their level in the seeds declined considerably (Table 1) as also previously reported [8,9].

Alcohol percentage, pH, and dry extract of the wines increased with the maturation stage of the grapes from which it was made. Conversely, total acidity gradually decreased (Table 2). Data reported for wines confirm the soluble solids and acid trends occurring during grape ripening [37,38].

Table 1. Mean values (±standard deviation) of skin and seed tannins, total anthocyanins, potential anthocyanins (A pH 1), extractable anthocyanins (A pH 3.2), and anthocyanin extractability measured in Aglianico grapes harvested at four ripening stages, corresponding to 18 °Brix (S18), 20 °Brix (S20), 22 °Brix (S22) and 25 °Brix (S25).

Ripening Stage	Skin Tannins (g/L of Extract)	Seed Tannins (g/L extract)	Total Anthocyanins (mg/L of Extract)	A pH 1	A pH 3.2	Anthocyanin Extractability (%)
S18	1.19 ± 0.56	2.59 ± 0.92 a	620 ± 9 b	468 ± 6 a	216 ± 2 b	53.9 ± 4.5 a
S20	2.11 ± 0.28	1.57 ± 0.10 ab	742 ± 18 a	431 ± 8 c	237 ± 4 a	45.0 ± 0.2 b
S22	1.77 ± 0.96	0.81 ± 0.49 b	499 ± 4 c	399 ± 4 d	179 ± 3 c	50.0 ± 1.4 a
S25	2.69 ± 0.38	0.76 ± 0.47 b	487 ± 15 c	456 ± 2 b	205 ± 9 b	55.0 ± 1.7 a
Significance	n.s.	*	***	***	**	**

Within each column, means followed by different letters are significantly different according to the Tukey test ($p < 0.05$); n.s., *, **, *** correspond to not significant, and significant at $p \leq 0.05$, 0.01, and 0.001, respectively.

Table 2. Mean value (±standard deviation) of ethanol, sugar, total acidity, pH volatile acidity, free SO_2, total SO_2, and dry extract in wines obtained with Aglianico grapes harvested at four ripening stages, corresponding to 18 °Brix (S18), 20 °Brix (S20), 22 °Brix (S22) and 25 °Brix (S25).

Ripening Stage	Ethanol (*v/v* %)	Sugar (g/L)	Total Acidity (g/L)	pH	Volatile Acidity (g/L)	Free SO_2 (mg/L)	Total SO_2 (mg/L)	Dry Extract (g/L)
S18	9.0 ± 0.5 d	1.1 ± 0.8	7.2 ± 0.4 a	3.07 ± 0.11 c	0.39 ± 0.27	13.4 ± 3.9	134.0 ± 11.8	22.7 ± 1.1 b
S20	11.1 ± 0.4 c	1.1 ± 1.0	5.7 ± 0.4 b	3.28 ± 0.15 bc	0.57 ± 0.10	14.1 ± 6.7	102.4 ± 12.8	20.9 ± 0.9 b
S22	11.9 ± 0.3 b	1.6 ± 0.3	5.4 ± 0.6 bc	3.34 ± 0.16 b	0.64 ± 0.13	19.2 ± 6.1	110.1 ± 16.1	21.6 ± 1.4 b
S25	14.5 ± 0.6 a	1.8 ± 0.9	4.6 ± 0.6 c	3.63 ± 0.10 a	0.86 ± 0.28	19.8 ± 4.7	107.5 ± 10.1	28.9 ± 0.7 a
Significance	***	n.s.	**	**	n.s.	n.s.	n.s.	***

Within each column, means followed by different letters are significantly different according to the Tukey test ($p < 0.05$); n.s., **, *** correspond to not significant, and significant at $p \leq 0.01$ and 0.001, respectively.

Total polyphenols did not differ between experimental wines, while S22 and S25 wines were characterized by a higher content of anthocyanins than the other treatments (Table 3). These data are not in agreement with the trend of total and potential anthocyanins and of their extractability reported in Table 1. This result may arise from factors affecting the extractability of these pigments during maceration, such as the presence of copigments [39], and the numerous reactions stabilizing the anthocyanins and occurring during aging [40]. Tannins were significantly less in S25 wines compared to the other treatments. This could be due to a predominant effect of seed tannins, but also phenomena determining their precipitation should be considered. Since in both seeds and skins there is some evidence of oxidative processes causing high polymerization of tannins with ripening [6,7], it is possible that an easier precipitation of these high polymerized phenolics occurred during vinification of over-ripe grapes.

Table 3. Mean value (±standard deviation) of total phenolics, total anthocyanins, and tannins in wines obtained with Aglianico grapes harvested at four ripening stages, corresponding to 18 °Brix (S18), 20 °Brix (S20), 22 °Brix (S22) and 25 °Brix (S25).

Ripening Stage	Total Phenolics (Folin-Ciocalteau Index)	Total Anthocyanins (mg/L of Malvidin-3-Monoglucoside)	Tannins (g/L)
S18	69.9 ± 2.3	47.4 ± 2.5 c	2.4 ± 03 a
S20	78.8 ± 6.9	70.1 ± 0.9 b	2.4 ± 0.2 a
S22	72.5 ± 4.3	114.8 ± 5.6 a	2.4 ± 0.1 a
S25	69.0 ± 3.5	125.1 ± 11.7 a	2.0 ± 0.1 b
Significance	n.s.	***	**

Within each column, means followed by different letters on the column are significantly different according to the Tukey test ($p < 0.05$); n.s., **, *** correspond to not significant, and significant at $p \leq 0.01$ and 0.001, respectively.

Values of optical density at 420, 520 and 620 nm and the colorant intensity of wine progressively increased with the degree of grape maturation (Table 4). These results may be explained by considering the higher content of anthocyanins as well as the new pigments derived from the reaction of anthocyanins with other compounds stabilizing flavylium

form of anthocyanins [40], and also the occurrence of the co-pigmentation [41] due to an elevated cofactor/pigment ratio in wines obtained from grapes at a higher ripening degree. It is also well known that wine color depends on ethanol content and pH. Nevertheless, our results disagree with the earlier findings showing a lowering in the magnitude of the hypercromic shift of several wine pigments at the increase of pH and ethanol content of the medium [39]. A higher colorant intensity was detected in that wines less acidic and more alcoholic, suggesting that the effect of pH and ethanol is negligible compared to the anthocyanin and new pigments content in these wines. Concerning the color parameters O.D. 420 nm, O.D. 520 nm and O.D. 620 nm, Pérez-Magarino and Gonzáles-San José [30] reported that aging accentuated the "harvest data effect" owing to the higher values for percentage blue (O.D. 620 nm) in aged wines made from the ripest grapes. The results of our study appear to support these findings, as the contribution of O.D. 620 nm to colorant intensity significantly increased to 12.3% in S25 wines. The shift of the dominant wavelength towards blue is probably correlated with the presence of pigments resulting from the reaction between anthocyanin-pyruvic acid adducts and vinyl flavanols [42]. An important contribution to color is also due to numerous stable pigments deriving from the reaction of native anthocyanins with colorless phenolic compounds because of the action of ethanal [43]. This high reactive aldehyde has a double origin: from yeasts during alcoholic fermentation and from chemical oxidation of wines during aging. In S22 and S25 wines, more sugar was fermented and, consequently, more acetaldehyde was produced [44]. In addition, the higher pH favors the oxidation reactions in wines. It is, therefore, possible that more stable ethyl-bridged pigments were formed in these wines, accounting for the higher values of color intensity and O.D. detected in S22 and S25 wines.

Table 4. Mean value (±standard deviation) of optical densities (O.D. 420 nm, O.D. 520 nm and O.D. 620 nm) colorant intensity, and color hue of wines obtained with Aglianico grapes harvested at four ripening stages, corresponding to 18 °Brix (S18), 20 °Brix (S20), 22 °Brix (S22) and 25 °Brix (S25).

Ripening Stage	O.D. 420 nm	O.D. 520 nm	O.D. 620 nm	Colorant Intensity	Color Hue
S18	1.9 ± 0.05 d	2.01 ± 0.05 c	0.45 ± 0.02 d	4.37 ± 0.12 c	0.94 ± 0.06
S20	2.45 ± 0.04 c	2.91 ± 0.07 b	0.68 ± 0.01 c	6.18 ± 0.12 b	0.84 ± 0.01
S22	3.08 ± 0.04 b	3.59 ± 0.10 a	0.91 ± 0.02 b	7.76 ± 0.16 a	0.86 ± 0.01
S25	3.31 ± 0.07 a	3.70 ± 0.10 a	1.01 ± 0.01 a	8.19 ± 0.19 a	0.89 ± 0.01
Significance	***	***	***	***	n.s.

Within each column, means followed by different letters are significantly different according to the Tukey test ($p < 0.05$); n.s., *** correspond to not significant, and significant at $p \leq 0.001$, respectively.

The content of total *trans*-resveratrol was directly correlated to the grape ripening stage (Table 5). These results are not due to an increase in resveratrol concentration during maturation, because its biosynthesis generally tends to decrease at this developmental stage [45]. However, it is well known that the extraction of *trans*-resveratrol from skins is enhanced by the alcoholic content of the medium. This behavior is less pronounced for the glycosylated form due to its higher hydrophilic character [46]. Thus, both the high level of ethanol produced during maceration and the gradual softening of cell walls during grape ripening may account for values of total *trans*-resveratrol more than three times higher in S25 than in S18 wines.

Table 5. Mean value (±standard deviation) of antioxidant phenolic compounds of wines obtained with Aglianico grapes harvested at four ripening stages, corresponding to 18 °Brix (S18), 20 °Brix (S20), 22 °Brix (S22) and 25 °Brix (S25). n.d.: not determined.

Ripening Stage	Catechin (mg/L)	Epicatechin (mg/L)	*trans*- Polidatin (mg/L)	*trans*- Resveratrol (mg/L)	Quercetin (mg/L)
S18	77.0 ± 2.3 a	48.1 ± 0.2 a	0.7 ± 0.3 b	0.5 ± 0.2 c	6.9 ± 1.1 a
S20	72.7 ± 2.8 a	39.6 ± 0.7 b	0.5 ± 0.6 ab	1.8 ± 0.3 b	7.8 ± 1.9 a
S22	55.7 ± 0.7 b	26.1 ± 0.8 c	2.4 ± 0.7 a	1.0 ± 0.2 c	5.4 ± 0.8 ab
S25	72.3 ± 4.2 a	49.4 ± 0.9 a	n.d.	3.5 ± 0.4 a	3.8 ± 1.8 b
Significance	***	***		***	*

Within each column, means followed by different letters are significantly different according to the Tukey test ($p < 0.05$); *, *** correspond to not significant, and significant at $p \leq 0.05$ and 0.001, respectively.

The level of catechin and epicatechin decreased from the S18 to the S22 wine. Contrasting results are reported in the literature regarding the trend followed by flavan-3-ols during ripening. Kennedy et al. [6] detected a dramatic decrease in flavan-3-ol monomers in Cabernet Sauvignon seeds during grape ripening; whereas, in a more recent study, a definite trend for seeds and skins flavanols of the same grape variety was not detected [47]. Concerning the condition of maceration, it has been reported that the extraction of flavan-3-ols from seeds and skins increases with ethanol [48]. Moreover, the contribution of skins to the flavanol composition of wine is assumed to be prevailing because they are more available for extraction [49]. Therefore, the higher values found in S25 wines may be due to both the advanced senescence of skin cells and the higher level of ethanol of solution. The lower amount of catechin and epicatechin detected in S22 wines compared to S25 wines could be due to the greater involvement of these flavan-3-ols in condensation reactions with anthocyanins and acetaldehyde, as these reactions can be favored at lower pH (3.34 in S22 wine with respect to 3.63 in S25 wine) [50]. However, taking into account the high involvement of these compounds in condensation reactions giving more stable pigments during wine aging [13], it is possible to hypothesize that the higher flavan-3-ols content of Aglianico wines obtained from over-ripened grapes may be responsible for its greater O.D. 620 nm.

A correlation analysis was carried out to highlight the possible relationships between the phenolic parameters of the grape and the main phenolic composition and chromatic characteristics of aged wines (Figure 1). A negative significant correlation was detected for total phenolics and A pH 1 indicating that the evaluation of total and extractable anthocyanins are not useful for predicting the color and anthocyanin content of aged red wine. For skin tannins, after two years of aging, a significant positive correlation with color intensity and O.D 420 nm and O.D. 620 nm was detected instead. This result could be related to the greater extractability of skin tannins and to the role that non-pigmented native phenolics have on all these reactions that stabilize wine color over time [40]. Jensen et al. [51] showed that it is possible to predict the color quality of fresh wines from grape measurements. Pérez-Magariño and González-San José [30] found a correlation between individual native phenolics of Cabernet Sauvignon and Tinto Fino grapes and wines; in our study a positive correlation was detected only between wine tannins and total anthocyanins of grape. This result underlines that, after two years of aging, the whole phenolic composition of wines should be considered for a possible correlation with grape anthocyanins because the reactions of native pigments in the formation of high molecular weight structure involving tannins and stabilizing color over time became dominant.

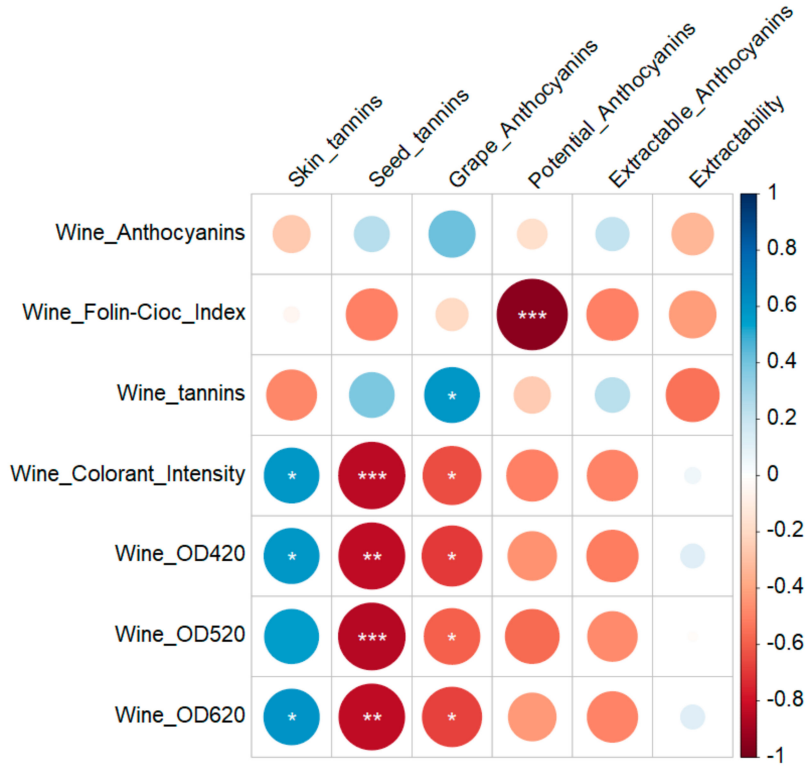

Figure 1. Correlogram representing the Pearson correlation between grape and wine compounds and chromatic characteristics. Asterisks indicate the significance of the Pearson correlation coefficient (*, **, *** correspond to $p \leq 0.05$, 0.01, and 0.001, respectively). Colors indicate different values of the correlation coefficient according to the scale bar reported on the right. The size of the circle is proportional to the correlation coefficient.

A total of 35 volatile compounds were quantified in Aglianico wines (Table 6). The S25 sample showed a significantly higher content of alcohols (1-butanol, 1-pentanol, 3-methyl-1-pentanol, 1-hexanol, (E)-3-hexen-1-ol, (Z)-3-hexen-1-ol, (E)-2-hexen-1-ol, benzyl alcohol, α-terpineol and 7-hydroxy-3,7-dimethyl-1-ol), esters (ethyl butanoate, ethyl hexanoate, ethyl lactate, ethyl octanoate, diethyl succinate), acetates (3-methylbutyl acetate, 2-phenylethyl acetate), thiols (3-methylthio-1-propanol) and amides (N-3-methylbutyl acetamide). Hexanol, (E)-3-hexen-1-ol, (Z)-3-hexen-1-ol, (E)-2-hexen-1-ol and other 1-alkanols are grape constituents and are related to fatty acid metabolism [52,53]. C_6 alcohols are produced during grape ripening from C_{18} fatty acids through the lipoxygenase pathway and the activity of the alcohol dehydrogenase. In contrast, 1-alkanols are obtained from homolytic cleavage of fatty acids when grapes are crushed under oxidative conditions. Our results are in agreement with those reported by Bindon et al. [22] on Cabernet Sauvignon wine. Benzyl alcohol, a derivative of the phenylpropanoid pool in plants [54], showed a higher content in S25 wines. Both a higher concentration and an elevated extraction from the pomace of overripe grape may account for the higher amounts detected.

The level of α-terpineol was almost four times higher in S25 than S18. In an aged wine, this compound may arise from a chemical modification of other more odorous terpenoids [17] and the hydrolysis of non-volatile glycosylated precursors [18]. The higher content detected in S25 wine seems to confirm earlier studies showing that terpenols increase with ripening [11].

Most of the identified esters, responsible for fruity odorous notes, were higher in S25 wine. It is known that the synthesis of esters by yeasts is enhanced when the rate of fermentation decreases [55]. Therefore, the consumption of the reducing sugars during fermentation of experimental musts is also reported to explain the observed behavior (Figure 2).

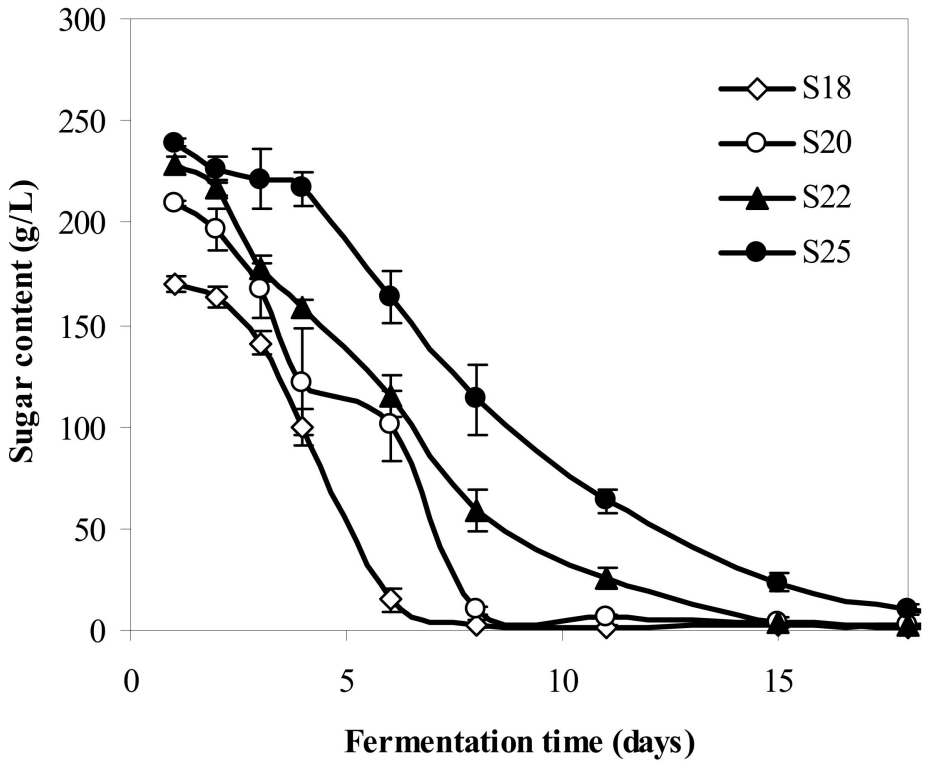

Figure 2. Sugar content during the fermentation of Aglianico grapes harvested at four ripening stages, corresponding to 18 °Brix (S18), 20 °Brix (S20), 22 °Brix (S22) and 25 °Brix (S25).

The fermentation rate was negatively correlated with the grape ripening degree, owing to the rise in the sugar content and to the decrease in the content of yeast's assimilable nitrogen during the last stages of grapes development. As expected, higher amounts of esters are detected in wines obtained through a slower fermentation. Among esters, the amount of 3-methylbutyl acetate, an important wine odorous compound responsible for banana notes, was higher in S25 compared to S18 wines. Similar results have been reported in two studies on the fermentation of Chardonnay juices and Cabernet Sauvignon wine [22,56]. It may be ascribed to a higher activity of alcohols acetyltransferases (AAT) of yeasts in slower fermentation batches. However, the higher values of esters and acetates in S25 wines are likely due also to the higher pH of wines obtained from ripest grapes, which is expected to reduce their hydrolysis during aging. The higher level of esters and acetates in S25 wines could be responsible for an improvement in their fruity notes.

Conversely, ethyl malate is found at the highest level in S18 wines. This ester originates from the reaction of esterification of malic acid by ethanol and the high amounts detected in S18 wine could be explained considering the higher level of malic acid present in the unripe grape (as suggested by the values of total acidity, Table 1).

Concerning the glycosidically bound volatile composition, 21 volatile compounds were identified (Table 7). Glycosidic volatile compounds were present at small concentrations as expected considering that two-year aged wines were analyzed. In some cases, there was an opposite trend in the concentration levels making it difficult to understand a correlation with the grape maturation degree, e.g., some terpene compounds and benzyl alcohol. Numerous factors involved in glycoside decline during fermentation and aging such as pH [57], adsorption by yeast cells and specific hydrolysis of bound aglycons [18].

Table 6. Mean value (±standard deviation) of level of free volatile compounds (μg/L) detected in the wines obtained with Aglianico grapes harvested at four ripening stages, corresponding to 18 °Brix (S18), 20 °Brix (S20), 22 °Brix (S22) and 25 °Brix (S25). n.d.: not detected.

Compounds	Descriptor [1]	S18	S20	S22	S25	Sig.
Alcohols						
2-methyl-1-propanol	wine-like	122.4 ± 15.0	100.3 ± 16.6	104,2 ± 4.4	134.0 ± 17.0	n.s.
1-butanol	medicinal	14.9 ± 3.9 b	16.7 ± 1.6 b	16.1 ± 2.3 b	54.0 ± 10.5 a	***
3+2-methyl-1-butanol	grass	63958 ± 388	53146 ± 633	54892 ± 612	51385 ± 277	n.s.
1-pentanol	mild green	14.1 ± 0.5 b	10.7 ± 0.8 b	9.1 ± 0.7 b	35.3 ± 2.9 a	***
4-methyl-1-pentanol	wine-like	57.4 ± 1.2 c	81.2 ± 4.8 b	96.3 ± 4.5 a	93.3 ± 6.5 ab	***
2-heptanol	herbaceous	n.d.	n.d.	n.d.	19.2 ± 0.5	-
3-methyl-1-pentanol	wine-like, green	93.2 ± 2.5 d	172.5 ± 10.9 c	245.5 ± 18.0 b	292.6 ± 23.3 a	***
1-hexanol	grass, herbaceous	2515 ± 52 c	1842 ± 82 b	1758 ± 67 b	3501 ± 25 a	***
(E)-3-hexen-1-ol	grass, herbaceous	49.4 ± 0.2 a	21.6 ± 0.9 c	17.7 ± 1.2 c	41.7 ± 3.5 b	***
(Z)-3-hexen-1-ol	grass, herbaceous	48.9 ± 1.3 a	25.1 ± 1.9 b	24.4 ± 4.2 b	28.1 ± 4.5 b	***
(E)-2-hexen-1-ol	grass, herbaceous	5.8 ± 0.1 c	12.8 ± 1.3 b	6.3 ± 0.9 c	22.3 ± 3.8 a	***
1-heptanol	apple, fruit	46.0 ± 4.0	41.1 ± 9.9	34.3 ± 1.4	103.2 ± 10.5	n.s.
1-octanol	waxy, citrus	16.8 ± 0.8	23.8 ± 2.1	29.7 ± 0.5	58.7 ± 2.8	n.s.
α-terpineol	sweet, floral	5.9 ± 0.8 c	10.5 ± 1.7 b	11.8 ± 0.3 b	21.7 ± 1.6 a	***
benzyl alcohol	toasty, sweet	21.0 ± 1.5 b	58.3 ± 1.1 b	20.0 ± 2.0 b	99.7 ± 15.3 a	**
2-phenylethanol	rose	38881 ± 3270	40490 ± 4181	41614 ± 2659	35852 ± 4345	n.s.
7-hydroxy-3,7-dimethyl-1-ol		25.5 ± 6.8 bc	29.0 ± 0.1 b	15.8 ± 0.6 c	45.3 ± 6.9 a	*
Esters						
ethyl butanoate	kiwi, fruity	45.7 ± 3.8 b	38.6 ± 1.8 b	38.4 ± 4.1 b	173.1 ± 13.2 a	***
ethyl 2-methylbutanoate	red fruity	72.2 ± 8.5	93.4 ± 0.8	82.4 ± 10.0	76.7 ± 3.7	n.s.
ethyl 3-methylbutanoate	exotic fruit	99.7 ± 3.7 ab	112.1 ± 0.4 a	101.8 ± 11.1 ab	88.3 ± 6.3 b	**
3-methylbutyl acetate	banana	80.2 ± 1.9 c	205.9 ± 2.9 b	184.6 ± 17.5 b	441.2 ± 29.5 a	***
ethyl hexanoate	apple	150 ± 4 b	108 ± 3 b	113 ± 7 b	275 ± 22 a	***
ethyl lactate	butter-scotch	8.6 ± 0.3 c	50.6 ± 8.0 bc	77.0 ± 8.1 ab	117.9 ± 22.6 a	**
ethyl octanoate	pineapple	148 ± 3 ab	111 ± 9 b	114 ± 5 b	174 ± 20 a	***
ethyl decanoate	floral, brandy	6.4 ± 0.1 b	7.7 ± 1.5 b	7.7 ± 0.2 b	39.9 ± 4.0 a	***
diethyl succinate	pleasant	5944 ± 64 c	10058 ± 650 b	11059 ± 675 b	14731 ± 1317 a	***
2-phenylethyl acetate	rose	20.4 ± 0.6 c	56.3 ± 1.6 b	55.0 ± 2.6 b	97.6 ± 16.8 a	***
diethyl malate	fruity	1466 ± 92 a	126 ± 20 b	83 ± 7 b	58 ± 6 b	***
Acids						
acetic acid	vinegar	33.0 ± 1.0 a	23.6 ± 1.6 b	21.0 ± 0.4 b	31.1 ± 3.6 a	**
3+2-methylbutanoic acid	cheese	153 ± 12	141 ± 18	141 ± 19	114 ± 25	n.s.
hexanoic acid	cheesy, rancid	897 ± 15 a	440 ± 55 c	408 ± 11 c	755 ± 22 b	***
octanoic acid	cheese, oily	1200 ± 239	891 ± 86	680 ± 93	992 ± 132	*
decanoic acid	fatty, rancid	99.7 ± 14.9	106.1 ± 18.0	148.0 ± 12.6	181.2 ± 36.3	n.s.
Other						
3-methylthio-1-propanol	potato, garlic	19.5 ± 0.6 ab	11.5 ± 3.1 b	14.5 ± 2.1 b	36.0 ± 6.9 a	***
N-3-methylbutyl acetamide		7.7 ± 0.5 b	19.0 ± 1.1 b	7.6 ± 0.7 b	398.8 ± 61.2 a	***

[1] Descriptors from: Genovese et al. [58]; Genovese et al. [4]; Flavors and Fragrances, Aldrich International Edition, 2011; Within each row, means followed by different letters on the column are significantly different according to the Tukey test ($p < 0.05$); n.s., *, **, *** correspond to not significant, and significant at $p \leq 0.05$, 0.01, and 0.001, respectively.

Table 7. Mean value (±standard deviation) of the level of glycosidic bound compounds (μg/L) of the wines obtained with Aglianico grapes harvested at four ripening stages, corresponding to 18 °Brix (S18), 20 °Brix (S20), 22 °Brix (S22) and 25 °Brix (S25). n.d.: not detected.

Compounds	Descriptor [1]	S18	S20	S22	S25	Sig.
Alcohols						
3-methyl-1-butanol	grass	144 ± 40	80 ± 21	112 ± 11	91 ± 26	n.s.
1-pentanol	mild green	5.1 ± 0.8	4.3 ± 1.4	6.2 ± 0.9	5.2 ± 1.2	n.s.
2-heptanol	herbaceous	7.8 ± 1.7	6.7 ± 1.4	7.6 ± 0.4	6.7 ± 1.1	n.s.
1-hexanol	grass, herbaceous	72.7 ± 18.1	37.7 ± 1.0	75.9 ± 7.0	75.8 ± 14.8	n.s.
(Z)-3-hexen-1-ol	grass, herbaceous	10.1 ± 2.1 a	6.3 ± 1.8 b	8.5 ± 1.2 b	4.8 ± 1.3 c	*
1-heptanol	apple, fruit	12.0 ± 1.5	10.9 ± 1.0	12.0 ± 0.2	11.9 ± 1.2	n.s.
(Z)-5-octen-2-ol		2.3 ± 0.6	2.1 ± 0.4	2.4 ± 0.3	2.3 ± 0.4	n.s.
1-octanol	waxy, citrus	3.6 ± 0.7	2.8 ± 0.6	3.2 ± 0.4	4.1 ± 0.4	n.s.
benzyl alcohol	toasty, sweet	246 ± 44 a	123 ± 20 b	157 ± 22 b	137 ± 25 b	**
2-phenylethanol	rose	163 ± 21 a	89 ± 15 b	121 ± 20 b	102 ± 13 a	*

Table 7. *Cont.*

Compounds	Descriptor [1]	S18	S20	S22	S25	Sig.
Terpene compounds						
α-terpineol	sweet, floral	2.2 ± 0.1 c	4.4 ± 0.1 b	8.8 ± 0.1 b	13.4 ± 2.3 a	**
epoxylinalool (I)		41.0 ± 7.5	30.6 ± 5.9	37.7 ± 6.6	28.4 ± 3.8	n.s.
epoxylinalool (II)		14.2 ± 4.0 a	6.3 ± 1.9 c	11.5 ± 0.2 ab	10.0 ± 1.4 bc	*
nerol	orange flowers	n.d.	n.d.	n.d.	10.0 ± 0.4	-
geraniol	orange flowers	n.d.	n.d.	n.d.	8.2 ± 0.2	-
exo-2-hydroxycineol		5.1 ± 0.5	2.5 ± 0.7	4.5 ± 0.9	4.0 ± 0.1	n.s.
trans-linalool oxide		78.9 ± 15.7 a	54.1 ± 14.6 ab	78.3 ± 9.0 a	48.3 ± 7.7 b	*
cis-linalool oxide		51.4 ± 10.1 a	33.7 ± 9.1 ab	52.9 ± 5.9 a	33.7 ± 4.1 b	*
Aldehydes and ketones						
furfural	sweet, woody, almond	1.9 ± 0.3	2.9 ± 0.4	2.9 ± 0.2	3.0 ± 0.8	n.s.
benzaldehyde	bitter almond	18.8 ± 3.7	18.0 ± 4.8	14.1 ± 2.2	16.6 ± 4.8	n.s.
5-methylfurfural	spice, bitter almond	3.1 ± 0.6	3.2 ± 0.7	4.1 ± 0.8	4.7 ± 0.7	n.s.

[1] Descriptors from: Genovese et al. [58]; Genovese et al. [4]; Flavors and Fragrances, Aldrich International Edition, 2011; within each row, means followed by different letters on the column are significantly different according to the Tukey test ($p < 0.05$); n.s., *, ** correspond to not significant, and significant at $p \leq 0.05$ and 0.01, respectively.

4. Conclusions

This study demonstrated that the choice of the ripening stage when harvesting the grapes is a crucial decision that will be reflected in the phenolic and aromatic composition of Aglianico wines after 20 months of aging in bottles. Aglianico grapes produce wines with more biologically active phenolic compounds (e.g., total *trans*-resveratrol), more stable color (e.g., anthocyanins) and richer in aroma compounds (free and bound) when grapes are harvested at a soluble solids content of 25 °Brix. Our work is a helpful tool to support the decisions of viticulturists and oenologists to modulate the biochemical profile and potentially, the health qualities of aged Aglianico red wines. Our results highlight that taste panel studies will be needed to define the sensory properties (color, taste, mouthfeel) of the chemically different wines that can be obtained by vinification at different maturation stages.

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