



# Article Screening of the Volatile Composition and Olfactory Properties of Aglianico and Primitivo, Two Southern Italian Red Wines

Elisabetta Pittari 🔍, Luigi Moio and Paola Piombino \*🔘

Division of Vine and Wine Sciences, Department of Agricultural Sciences, University of Naples Federico II, Viale Italia, 83100 Avellino, Italy

\* Correspondence: paola.piombino@unina.it; Tel.: +39-081-25-32-621

Abstract: Gas-chromatography/mass-spectrometry and sensory descriptive analyses were applied to provide new data on volatile and olfactory properties of Aglianico and Primitivo (Zinfandel), Italian red wines of growing interest. The relationships between data sets were investigated by multivariate statistical analyses: Principal Component and Hierarchical Clustering Analyses (PCA, HCA). A total of 35% of the volatiles varied significantly (ANOVA) between the two wines, mostly showing higher amounts in the Aglianico samples. Multivariate analyses showed intra-varietal similarity and inter-varietal diversity in terms of aromatic characteristics. PCA indicated that Aglianico wines were mainly related to the main fermentative alcohols, with a sensory impact, and to terpenols, suggesting a potential discriminating power at a compositional level. Primitivo wines formed two groups, one of which correlated to the floral aroma vector linked to beta-phenethyl acetate and beta-ionone. These findings may be valuable for updating the information on these wines and for future research to improve and obtain more targeted production and communication approaches.

Keywords: wine; aroma; GC/MS; descriptive sensory assessment; multivariate analysis; PCA; HCA



Citation: Pittari, E.; Moio, L.; Piombino, P. Screening of the Volatile Composition and Olfactory Properties of Aglianico and Primitivo, Two Southern Italian Red Wines. *Appl. Sci.* 2023, *13*, 2165. https:// doi.org/10.3390/app13042165

Academic Editor: Ioannis G. Roussis

Received: 12 December 2022 Revised: 2 February 2023 Accepted: 5 February 2023 Published: 8 February 2023



**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/).

# 1. Introduction

The Italian wine industry is renowned for its high level of diversification, which represents a richness in terms of biodiversity and potential market value. On average, 50 million hL of wine are produced annually [1], and there are nearly 600 grapevine varieties listed in the Registro Nazionale delle Varietà di Vite [2]. In this regard, Aglianico and Primitivo are two of the most important non-aromatic red grape varieties in Southern Italy, from which high-quality wines can be produced. Nearly the entire 10,000 hectares of Aglianico that are grown worldwide are cultivated in Southern Italy. Indeed, with around 10,000 hectares representing 1.46% of the whole Italian grapevine area and 3.32% of all Italian red grapes [3], it is particularly grown in the Campania and Basilicata regions. The Aglianico grape variety is used to produce Taurasi wine (Campania-DOCG), as well as for other important premium red wines (i.e., Irpinia Aglianico-DOC; Aglianico del Vulture-DOC). Being a late-ripening grape variety [2,4–6], its cultivation has assumed great importance in late years, since late-ripening varieties are the ones that should respond best to the current climate change issue [7]. In the case of Primitivo, it is one of the typical non-aromatic red grape varieties mainly cultivated in the Puglia region (16,321 hectares) [3]. In Italy, it represents 2.39% of the total Italian grapevine area and 5.44% of all Italian red grapes [3]. As reported in the OIV Focus [3], this red grape variety is also extremely important for the US market, as it is the second most widely cultivated red wine grape in California (18,850 hectares), under the name of Zinfandel [8,9].

At the beginning of the 21st century, a rising propagation trend (a parameter evaluating the market interest in cultivars) was observed for many Italian grapevine varieties [10]. In the specific cases of Aglianico and Primitivo, the annual nursery production of graftings grew from 200,000 to 1,000,000 and from 100,000 to 1,000,000, respectively. Thanks to this growth, research interest in these two grape varieties has increased and several studies have been conducted from both a viticultural and an oenological point of view, in some cases investigating their chemical and sensory properties. Differences have been found in terms of basic chemical parameters, phenolic composition, colour characteristics, proteins, and polysaccharides content [11–14], and also in terms of sensory properties (i.e., astringency) [15], sometimes applying a chemical-sensory approach, as performed by Piombino et al. [16] and Pittari et al. [17].

Important research has also been carried out with the aim of studying the aromatic composition of wines produced from these two grape varieties [18,19]. Genovese et al. [18] observed that Aglianico wines were characterised by the major fermentation compounds (i.e., esters, fatty acids, and 2-phenylethanol), together with  $\beta$ -damascenone,  $\beta$ -ionone, and linalool, while Primitivo wines were richer in furaneol, methoxypyrazine,  $\gamma$ -nonalactone, and acetaldehyde. More recently, investigating the occurrence of different monoterpenoids and norisoprenoids in 10 monovarietal Italian red wines, some authors observed a higher content of linear monoterpene alcohols (i.e., linalool and geraniol) in Aglianico and Primitivo wines [19]. However, apart from the study by Genovese et al. [18], there are no works where chemical and sensory approaches have been combined analysing these same wines. Nevertheless, knowing exclusively the volatile components and sensory characteristics of a given wine is not enough to fully understand its flavour. In fact, one important aspect of flavour research is the exploration of relationships between sensory and instrumental data [20], as previously explored by other researchers [21–26].

Thus, the objective of this work is to provide new data on these two wines of growing interest, both in terms of volatile and sensory properties, applying GC/MS and sensory descriptive analyses. Moreover, using multivariate statistical analyses, Principal Component Analysis (PCA) and Hierarchical Clustering Analysis (HCA), relationships between data sets were investigated.

#### 2. Materials and Methods

#### 2.1. Wine Samples

Thirteen commercial red wines, six Aglianico and seven Primitivo samples (2016 vintage), 100% mono-varietal, were produced on a commercial scale in wineries that were among the most representative in each typical area of production (the Campania and Puglia regions, respectively), using their standard production techniques with commercial selected yeasts (ZYMAFLORE<sup>®</sup> F15, Laffort, Bordeaux, France). All wines were fermented in stainless-steel vats and sampled before malolactic fermentation and oak barrel ageing. All samples were stored at a controlled cellar temperature ( $12 \pm 2$  °C) until analyses.

## 2.2. Volatile Organic Compounds (VOCs) Analysis

VOCs analysis was carried out as previously reported [27] and recently applied by De Filippis et al. [28] and Bianchi et al. [29] on both white and red wines.

VOCs extraction was carried out by Liquid–Liquid Extraction (LLE). Briefly, 100 mL of each sample was added to 5 mL of  $CH_2Cl_2$  as a solvent and 250 µL of an alcoholic solution of 2-octanol as an internal standard (258 ppm/ethanol) (Sigma Aldrich, St. Louis, MO, USA). The mixture was magnetically stirred for 1 h at room temperature ( $21 \pm 1$  °C). The resulting emulsion was transferred to a separating funnel with an emery top and kept at 4 °C for 12 h to help the two phases separate more easily. Finally, the obtained organic aromatic extract was recovered, dehydrated using Na<sub>2</sub>SO<sub>4</sub>, and then kept at -20 °C until GC/MS analysis.

For High Resolution Gas-Chromatography/Mass-Spectrometry (HRGC/MS) analysis, chromatographic conditions and the identification procedure were the same as that already reported in Piombino et al. [30]. One  $\mu$ L of organic extract was injected in splitless mode, while the injection port of a GC/MS-QP2010 quadrupole mass spectrometer (Shimadzu, Shimadzu corp., Kyoto, Japan) was maintained at 250 °C. The GC/MS was equipped with a DB-WAX UI column (60 m, 0.25 mm i.d., 0.25  $\mu$ m film thickness, J&W Scientific Inc., Folsom,

CA 95360, USA). The carrier gas was helium (1.3 mL/min) and the temperature program used was the following: 40 °C for 5 min, raised up to 220 °C at a rate of 2 °C/min, and held for 20 min at the maximum temperature. Electron impact mass spectra were recorded with ion source energy of 70 eV, while the temperature was kept at 230 °C. The peak areas were measured using a GC/MS solution program Shimadzu version 2.30 (Shimadzu corp., Kyoto, Japan). The compounds content (semiquantitative) was estimated as a ratio of each compound's response (peak area) to that of the internal standard and reported in mg/L. The VOCs were identified by comparing their retention times with those of pure reference standards under the same chromatographic conditions, as well as by the comparison of experimental mass spectra with those found in the NIST library. When the pure chemical standard was not available, the detected substances were given the designation "tentative" (t).

#### 2.3. Sensory Analysis

Panel: The jury was composed of 14 judges (7 females and 7 males, aged between 21 and 50 years) recruited among students and researchers of the Department of Agricultural Sciences, Division of Vine and Wine Sciences, University of Naples Federico II. They were all expert wine tasters with previous experience in performing sensory tests on wine. They were recruited based on their interest and availability. The recruited subjects were then selected on the basis of their ability in recognizing odour stimuli. The subjects who achieved at least 80% of correct identifications underwent a training phase aimed at memorizing, recognizing, and rating odour stimuli in wine. All data were collected anonymously. All procedures were conducted in accordance with the ethical standards of the institutional and/or national research committee and with the 1964 Helsinki declaration and its later amendments or comparable ethical standards. Participation was on a voluntary basis, and prior to the experiments tasters were required to sign an informed consent form disclosing the type of research, voluntary participation, and agreement to taste/smell reference solutions and wines.

Panel training: judges' training with olfactory stimuli using a numerical category scale (anchored at 1 = very weak, 2 = weak, 3 = medium, 4 = strong, 5 = very strong, with half values allowed) was performed according to the procedures recently published by Pittari et al. [17].

Olfactory sensory assessment: the selected and trained panel analysed a sub-set of 8 samples (4 Aglianico and 4 Primitivo wines) by descriptive sensory assessment. The other 5 wines were not included in the sensory analysis because of their limited available volume.

During olfactory sensory assessment, the judges were asked to rate the ten olfactory descriptors considered in the training phase (fruity, dehydrated fruit, dried fruit, floral, vegetal, spicy, toasted, woody, earthy, and alcoholic), using the same numerical category scale. The analyses were performed in duplicate, in two separated sessions. In each of the two sessions, all judges analysed the 8 wine samples focusing on their olfactory characteristics. Panellists were asked to smell each wine samples, to recognize the perceived odour descriptors and to rate their intensity. During the sensory assessment, for each sample 30 mL of wine was served in INAO tasting glasses coded with three digits and presented in a randomized order, to minimize order and carryover effects. Wines were served at room temperature ( $21 \pm 1$  °C) and evaluated in individual booths [31].

# 2.4. Data Processing

VOCs chemical data were treated by an analysis of variance ANOVA (Tukey; p < 0.05, p < 0.01) to test significant differences among wines, and by a Principal Component Analysis (PCA) to study the relationships between wines and volatile compounds.

Regarding sensory variables, for each individual olfactory descriptor the quantitative score was attributed, considering the geometric mean of frequency and mean intensity (mean sensory modified frequency (MF)), as described by Dravnieks [32] and recently applied by Piombino et al. [17]: MF = (F × I)1/2, where F is the frequency of citation

expressed as a proportion of the maximum frequency of citation (i.e., total number of judges) and I is the mean intensity expressed as a proportion of the maximum rate.

Relationships between wines, olfactory sensory variables and volatile compounds were investigated by a Hierarchical Clustering Analysis (HCA) (Ward algorithm, Euclidean distance).

ANOVA and PCA analyses were computed using XLStat 2012.6.02 (Addinsoft Corp., Paris, France). The clustered heat map was generated using MetaboAnalyst 5.0 platform (https://www.metaboanalyst.ca, accessed on 8 September 2022).

## 3. Results and Discussion

The LLE GC/MS analysis of wines allowed the identification of forty-eight common compounds belonging to different groups of volatiles (Table 1): ethyl esters/acetates, alcohols (higher and C6 alcohols), acids, terpenols, lactones, and other miscellaneous compounds. In Table 1, the mean relative amount (mg/L), the standard deviation and the results of the ANOVA (Tukey; p < 0.05, p < 0.01) for each compound in the two wine types are reported.

**Table 1.** VOCs detected and semi-quantified (mg/L are calculated as a ratio of each compound's response to the response of the internal standard) by LLE/GC-MS in both Aglianico and Primitivo wines. Standard deviation (SD) and significance (one-way ANOVA) are reported.

RT	Compounds (mg/L)	$\frac{ \  \   Aglianico}{Mean \pm SD}$	Primitivo	- Significance
			$\mathbf{Mean} \pm \mathbf{SD}$	
	Ethyl esters/Acetates			
12.193	Ethyl isobutyrate	$0.174 \pm 0.005$	$0.129 \pm 0.007$	ns
15.407	Ethyl butanoate	$0.152\pm0.015$	$0.163 \pm 0.007$	ns
16.312	Ethyl 2-methyl butanoate	$0.021\pm0.002$	$0.014 \pm 0.001$	ns
17.228	Ethyl 3-methyl butanoate (Ethyl isovalerate)	$0.041\pm0.002$	$0.027\pm0.001$	ns
20.470	Isoamyl acetate	$0.320\pm0.019$	$0.328 \pm 0.012$	ns
27.838	Ethyl hexanoate	$0.204\pm0.010$ a	$0.132\pm0.003\mathrm{b}$	***
30.034	Ethyl pyruvate	$0.038 \pm 0.005$	$0.062\pm0.002$	ns
35.215	Ethyl lactate	$5.089 \pm 0.185$	$4.630\pm0.109$	ns
41.258	Ethyl octanoate	$0.177 \pm 0.009$ a	$0.130\pm0.004\mathrm{b}$	**
48.139	Ethyl 2-hydroxyhexanoate	$0.105 \pm 0.010$ a	$0.070\pm0.008\mathrm{b}$	**
49.734	Isoamyl lactate	$0.188 \pm 0.006$	$0.079\pm0.002$	ns
53.817	Ethyl decanoate	$0.030\pm0.002$	$0.031\pm0.001$	ns
56.100	Diethyl succinate	$6.038 \pm 0.233$	$6.881 \pm 0.183$	ns
63.788	beta-Phenethyl acetate	$0.036\pm0.003$	$0.049 \pm 0.004$	ns
90.749	Ethyl hydrogen succinate	$6.466 \pm 0.650$	$6.442 \pm 0.069$	ns
	Subtotal	19.079	19.167	ns
	%	27.32	35.54	
	Alcohols			
18.565	Isobutyl alcohol	$1.986 \pm 0.198$ a	$1.311\pm0.053\mathrm{b}$	***
21.891	1-Butanol	$0.032\pm0.003$	$0.041\pm0.002$	ns
26.486	2 + 3-Methyl-1-butanol	$29.521 \pm 1.942$	$18.213\pm0.403$	ns
33.411	4-Methyl-1-pentanol	$0.022 \pm 0.001$ a	$0.014\pm0.000\mathrm{b}$	**
34.256	3-Methyl-1-pentanol	$0.029 \pm 0.002$ a	$0.012\pm0.000\mathrm{b}$	**
36.004	1-Hexanol	$0.670 \pm 0.017$ a	$0.428\pm0.008\mathrm{b}$	***
36.668	trans-3-Hexen-1-ol	$0.018 \pm 0.001$ a	$0.013\pm0.001~\mathrm{b}$	**
38.026	cis-3-Hexen-1-ol	$0.013\pm0.000~\mathrm{a}$	$0.007\pm0.000~\mathrm{b}$	**
42.307	1-Octen-3-ol	$0.005\pm0.000~\mathrm{b}$	$0.007 \pm 0.000$ a	***
42.696	1-Heptanol	$0.047\pm0.002$	$0.032\pm0.001$	ns
49.106	1-Octanol	$0.016 \pm 0.000$ a	$0.012\pm0.000\mathrm{b}$	**
67.050	Benzyl alcohol	$0.041 \pm 0.002$	$0.133\pm0.003$	ns
69.018	Phenylethyl alcohol	$15.214 \pm 1.262$	$11.828\pm0.365$	ns
	Subtotal	47.612 a	32.050 b	***
	%	68.17	59.42	

#### Table 1. Cont.

DT	Compounds (mg/L)	Aglianico	Primitivo	<b>C</b> ::C
KI		$\mathbf{Mean} \pm \mathbf{SD}$	$\mathbf{Mean} \pm \mathbf{SD}$	- Significance
	Acids			
42.017	Acetic acid	$0.410\pm0.041$	$0.557\pm0.013$	ns
49.478	Isobutyric acid	$0.033\pm0.002$	$0.031\pm0.001$	ns
55.545	Isovaleric acid	$0.142\pm0.007~\mathrm{a}$	$0.095\pm0.003\mathrm{b}$	**
65.296	Hexanoic acid	$0.411\pm0.021~\mathrm{a}$	$0.255\pm0.009b$	**
71.543	2-Hexenoic acid	$0.009\pm0.001$	$0.008 \pm 0.001$	ns
76.180	Octanoic Acid	$0.953\pm0.035~\mathrm{a}$	$0.615\pm0.014b$	***
86.053	Decanoic acid	$0.166 \pm 0.008$	$0.186\pm0.006$	ns
	Subtotal	2.124	1.747	ns
	%	3.04	3.24	
	Terpenols			
48.367	beta-Linalool <sup>t</sup>	$0.005\pm0.001$	$0.004 \pm 0.000$	ns
57.312	alpha-Terpineol	$0.016\pm0.001$	$0.011\pm0.001$	ns
61.168	beta-Citronellol <sup>t</sup>	$0.003\pm0.000~\mathrm{a}$	$0.001\pm0.000\mathrm{b}$	***
	Subtotal	0.024 a	0.016 b	**
	%	0.03	0.03	
	Lactones			
53.092	gamma-Butyrolactone	$0.794 \pm 0.031$	$0.721 \pm 0.026$	ns
71.200	(E)-Whiskeylactone	$0.021\pm0.000$	$0.025\pm0.000$	ns
74.714	gamma-Nonalactone <sup>t</sup>	$0.041\pm0.002$	$0.053 \pm 0.001$	ns
	Subtotal	0.855	0.799	ns
	%	1.22	1.48	
	Miscellaneous			
31.094	Acetoin	$0.142 \pm 0.005$	$0.150\pm0.006$	ns
42.856	Furfural	$0.031\pm0.002$	$0.050\pm0.002$	ns
46.626	Benzaldehyde	$0.045 \pm 0.002$ a	$0.019\pm0.001\mathrm{b}$	***
58 397	3-(Methylthio)-1-propanol	$0.087 \pm 0.007$	$0.072 \pm 0.002$	ne
30.377	(Methionol)	0.007 ± 0.007	$0.072 \pm 0.002$	115
70.622	beta-Ionone	$0.005\pm0.001$	$0.007\pm0.001$	ns
	Unknown furanone			
	compound			
84.193	(tentative of identification:	$0.475\pm0.022~\mathrm{b}$	$0.675 \pm 0.020$ a	**
	5-Hydroxyme-			
	thyldihydrofuran-2-one) <sup>t</sup>			
85.718	Syringol <sup>t</sup>	$0.007\pm0.003$	$0.009\pm0.001$	ns
	Subtotal	0.149	0.160	ns
	%	0.21	0.30	
	Total	69.843	53.938	
	%	100	100	

Values with different letters refer to significant differences tested by ANOVA followed by multiple comparison Tukey HSD post hoc test (\*\* p < 0.05; \*\*\* p < 0.01); ns: non-significant difference; t: tentative of identification.

The most abundant classes are represented by esters, alcohols, and acids, fermentative wine VOCs linked to microbial activity [33–35]. Thirteen ethyl esters and two acetates were identified, accounting for 27% and 35% of the total volatiles detected in both Aglianico and Primitivo wines, respectively. Among them, three compounds showed significant differences between the two wine types, with a trend to higher values in Aglianico wines compared to Primitivo: ethyl hexanoate (p < 0.01), ethyl octanoate and ethyl 2-hydroxyhexanoate (p < 0.05).

The 68% (Aglianico) and 59% (Primitivo) of the total detected volatile fraction was represented by alcohols. Within this chemical class, higher alcohols represented the majority, both in terms of number of identified volatiles and detected amount. In particular, the two compounds 2+3-methyl-1-butanol and phenylethyl alcohol accounted for almost the totality of this class of compounds. Significant differences between the two types of wines were observed for alcohol compounds, with Aglianico wine samples generally displaying

greater values. In fact, out of the thirteen identified alcohols, eight compounds showed significant differences, with only 1-octen-3-ol exhibiting a higher value in Primitivo wine.

The group of acids was also relatively large, including acetic, isobutyric, isovaleric, hexanoic, 2-hexenoic, octanoic, and decanoic acids. Among the identified acids, isovaleric, hexanoic (p < 0.05), and octanoic (p < 0.01) acids showed significant differences between the two wine types, with higher values in Aglianico wines compared to Primitivo.

Despite the possibility of the observed differences being linked to several parameters, ranging from grape features to winemaking practices (e.g., YAN and other yeast nutrients, suspended solids, temperature, etc.), the findings seem in line with data reported by Genovese et al. [18]. In fact, the authors showed that Aglianico wines, compared to Primitivo, were characterized by a higher amount of the major fermentation compounds (i.e., esters, fatty acids and phenylethyl alcohol).

In addition to these major compounds, mostly related to fermentation conditions and nutrient availability, other minor classes such as terpenols, lactones, and other miscellaneous compounds showed some significant differences for specific VOCs. Terpenols, which are grape aromas, included three identified compounds: beta-linalool, alpha-terpineol, and beta-citronellol. Beta-citronellol showed a significant difference with a higher trend (p < 0.01) in Aglianico wine, while for beta-linalool and alpha-terpineol no significant differences were found. Three lactones were detected: gamma-butyrolactone, (E)-whiskeylactone, and gamma-nonalactone, showing no significant differences between the two types of wines. However, a trend for a higher amount of gamma-nonalactone and (E)-whiskeylactone in Primitivo wine samples was observed, in line with Genovese et al. [18], which observed a higher concentration of gamma-nonalactone in Primitivo wines compared to Aglianico. Finally, regarding miscellaneous compounds, seven compounds were identified in the two wine types, with benzaldehyde and an unknown furanone compound showing significant differences between the two varieties. While benzaldehyde displayed a significantly higher amount in Aglianico wines (p < 0.01), the unknown furanone compound showed a greater amount in Primitivo wine samples (p < 0.05). Regarding this latter compound, it was tentatively identified as 5-hydroxymethyldihydrofuran-2-one, which was previously detected in Madeira wines [36,37].

Results suggest a potential discriminability between Aglianico and Primitivo wines based on their VOCs profiles, as shown by the Principal Component Analysis (Figure 1).

The PCA was performed to study the relationships between the thirteen wine samples (observations) and the volatile composition (variables). Moreover, a Hierarchical Clustering Analysis (HCA) (Ward algorithm, Euclidean distance) was conducted on a subset of eight samples (four Aglianico and four Primitivo wines) to investigate the relationships between the entire set of data (wines, volatile compounds, and sensory attributes) (Figure 2).

Figure 1 shows the biplot where wines and volatiles are plotted on the first two components, representing 50.21% of the total variance (PC1: 30.83% and PC2: 19.39%). Looking at Figure 1a, it can be observed that, while the first component (PC1) separates the two types of wines, the second component (PC2) would seem to describe the heterogeneity within Primitivo wines into two groups: PRI001, PRI002, PRI003, and PRI004; PRI005, PRI006 and PRI007. All Aglianico wines are mostly correlated to fermentative alcohols such as phenylethyl-, isobutylalcohols, and 2+3-methyl-1-butanol, and even to the varietal terpenols beta-citronellol, alphaterpineol and beta-linalool (Figure 1b), all compounds reported as impacting wine aromas because they are key players of the alcoholic-solvent and flowery aroma vectors, respectively [38,39]. The first group of Primitivo wines (PRI001, PRI002, PRI003, and PRI004) seems to be related to gamma-butyrolactone, (E)-whiskeylactone, and gamma-nonalactone, together with syringol, furfural (Figure 1b), and a pool of VOCs responsible for woody, spicy, liquorice, toasty, smoky, cocoa, coconut, leather, and vanilla nuances [40]. The second group, formed by PRI005, PRI006, and PRI007 shows correlations with beta-phenethyl acetate and isoamyl acetate, decanoic acid, and, to a lesser extent, beta-ionone and 1-butanol. Among these compounds, both beta-phenethyl acetate and beta-ionone are relevant VOCs for the floral aroma vector in wine, as well as isoamyl acetate for the fruity one [38,39].



**Figure 1.** Principal component analysis (PCA) plots of (**a**) wines—observations (six Aglianico: AGL; seven Primitivo: PRI) and (**b**) volatile compounds—variables.





The clustered heatmap computed on both VOCs and sensory quantitative data measured on a subset of eight samples (Figure 2) confirms the discriminability of Aglianico and Primitivo wines that were correctly clustered according to the grape variety. This confirms the intra-varietal similarity and the inter-varietal diversity of the two wine types.

The clustering between VOCs and sensory data shows correlations not easy to interpret; however, some remarks seem to be of interest. Indeed, even if significant differences between the two wine types were not found in terms of terpenols levels (Table 1), the heatmap shows that beta-citronellol, alpha-terpineol and beta-linalool are positively correlated with Aglianico wines while negatively correlated with Primitivo ones, suggesting that they might serve as molecular markers of varietal origin to distinguish between these two single-varietal wines. In a recent study conducted on a larger sample-set and by applying a headspace VOCs isolation technique, Slaghenaufi et al. [19] determined the terpenoids composition in some Italian red wines including Aglianico and Primitivo. In this study, beta-citronellol, alpha-terpineol and beta-linalool were detected among other terpenoids, but no evidence of their potential discriminating power between the two wine types was found. From a sensory point of view, Aglianico wines do not strongly correlate with floral notes, a descriptor associable to terpenols. This could be due to the higher level of higher alcohols in Aglianico wines (Table 1), as such as 2+3-methyl-1-butanol and isobutyl alcohol [41], which are aroma suppressors of some powerful aroma compounds [42,43]. In Figure 2, these two alcohols were clustered together with phenylethyl alcohol and the "alcoholic" descriptor, in line with the concept of "alcoholic-solvent aroma vector" recently developed ([39], and references therein). As hypothesized above for Aglianico wines, the "alcoholic" sensory variable shows a positive correlation with three out of four Aglianico samples.

On the other hand, 75% of Primitivo wines included in the HCA show positive correlations with the floral descriptors and, even if negatively correlated with the three detected terpenols, good correlations with other compounds associated with the floral aroma vector are highlighted, namely beta-phenethyl acetate and beta-ionone [38,39].

In recent years, many works have investigated the effects of the interactions between volatiles. Many authors observed the capacity of some VOCs to enhance or mask the perception of other odorants present in the matrix, and the related olfactory attributes [23–26,44–47]. It is, nowadays, clear that the olfactory profile of a given wine cannot be explained exclusively by the presence of volatile compounds related to a specific note, but also by the synergistic effect of different volatiles and/or by the presence of other VOCs negatively affecting its perception [23,48]. Therefore, the correlations found between volatile compounds and sensory descriptors and their relationships with the specific wine samples investigated in the present work need to be further investigated.

#### 4. Conclusions

Overall, this work represents a screening of the aroma features of wines produced from two important red grape varieties grown in Southern Italy, Aglianico and Primitivo, both in terms of volatile profile and sensory properties, applying gas-chromatography/massspectrometry and sensory descriptive analysis.

Despite the samples being commercial wines and, therefore, produced according to different protocols, the Aglianico and Primitivo samples investigated in this study were discriminable based on semiquantitative data describing differences in their VOCs profiles, and on olfactory features. ANOVA showed a significant effect of the "cultivar" on the volatile composition, with 35% of the detected common volatiles varying significantly between the two mono-varietal wines, mostly showing a trend towards higher amounts in Aglianico samples. The application of a semiquantitative method is a limit of the results reported in this work and, therefore, further quantitative studies are necessary to confirm the observed trends, which, however, are in line with some previous findings [18,19].

Multivariate statistical analyses showed that wines belonging to the same grape variety were discriminable from each other, revealing an intra-varietal similarity and an intervarietal diversity based on both VOCs composition and odour descriptors. PCA shows that Aglianico wines formed a compact cluster, mainly related to a pool of VOCs linked to the main fermentative alcohols and to terpenols, with the former group of volatiles showing a sensory impact and the latter one a potential discriminating power at a compositional level. Primitivo wines formed two groups, one of which correlated to the floral aroma vector linked to beta-phenethyl acetate and beta-ionone.

Since the growing relevance of Aglianico and Primitivo grapes and wine in Italy and elsewhere, these findings could be useful as new data improving the information currently available on these wines and could be helpful for future studies to improve and obtain more targeted production and communication approaches.

**Author Contributions:** Conceptualization, E.P., L.M. and P.P.; methodology, E.P. and P.P.; formal analysis, E.P.; investigation, E.P.; resources, L.M. and P.P.; data curation, E.P. and P.P.; writing—original draft preparation, E.P. and P.P.; writing—review and editing, E.P., L.M. and P.P.; supervision, L.M. and P.P.; project administration, P.P. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Informed Consent Statement: Informed consent was obtained from all subjects involved in the study.

Acknowledgments: The authors acknowledge the wineries that provided wines for the present work.

Conflicts of Interest: The authors declare no conflict of interest.

# References

- 1. OIV. 2019 Statistical Report on World Vitiviniculture. 2019. Available online: https://www.oiv.int/public/medias/6782/oiv-20 19-statistical-report-on-world-vitiviniculture.pdf (accessed on 16 September 2022).
- Registro Nazionale delle Varietà di Vite. Updated on May 2022. Available online: http://catalogoviti.politicheagricole.it/catalogo. php (accessed on 16 September 2022).
- OIV. Focus OIV 2017—Distribution of the World's Grapevine Varieties. 2017. Available online: http://www.oiv.int/public/ medias/5336/infographie-focus-oiv-2017-new.pdf (accessed on 16 September 2022).
- Biafore, A.; Vitti, A.; Gioia, D.; Rendina, N.; Silletti, M.F.; Camele, I.; Lardo, E.; Nuzzaci, M.; Nuzzo, V. Preliminary investigations on bioactive molecules concentration in 'Aglianico' grape berries. *Acta Hortic.* 2017, 1188, 299–306. [CrossRef]
- Caccavello, G.; Giaccone, M.; Scognamiglio, P.; Mataffo, A.; Teobaldelli, M.; Basile, B. Vegetative, Yield, and Berry Quality Response of Aglianico to Shoot-Trimming Applied at Three Stages of Berry Ripening. *Am. J. Enol. Vitic.* 2019, 70, 351–359. [CrossRef]
- 6. Tarricone, L.; Faccia, M.; Masi, G.; Gambacorta, G. The Impact of Early Basal Leaf Removal at Different Sides of the Canopy on Aglianico Grape Quality. *Agriculture* **2020**, *10*, 630. [CrossRef]
- 7. van Leeuwen, C.; Darriet, P. The Impact of Climate Change on Viticulture and Wine Quality. J. Wine Econ. 2016, 11, 150–167.
- Maletić, E.; Pejić, I.; Kontić, J.K.; Piljia, J.; Dangl, G.; Vokurka, A.; Lacombe, T.; Mirosević, N.; Meredith, C. Zinfandel, Dobricic, and Plavac mali: The genetic relationship among three cultivars of the Dalmatian coast of Croatia. *Am. J. Enol. Vitic.* 2004, 55, 174–180. [CrossRef]
- 9. Fidelibus, M.V.; Christensen, L.P.; Katayama, D.G.; Verdenal, P.T. Performance of Zinfandel and Primitivo grapevine selections in the central San Joaquin Valley, California. *Am. J. Enol. Vitic.* **2005**, *56*, 254–286.
- 10. Mannini, F. Italian indigenous grapevine cultivars: Guarantee of genetic biodiversity and economic resource. *Acta Hortic.* 2004, 652, 87–95. [CrossRef]
- 11. Parpinello, G.P.; Ricci, A.; Arapitsas, P.; Curioni, A.; Moio, L.; Río Segade, S.; Ugliano, M.; Versari, A. Multivariate characterisation of Italian monovarietal red wines using MIR spectroscopy. *OENO One* **2019**, *53*, 2558. [CrossRef]
- Arapitsas, P.; Ugliano, M.; Marangon, M.; Piombino, P.; Rolle, L.; Gerbi, V.; Versari, A.; Mattivi, F. Use of untargeted liquid chromatography-mass spectrometry metabolome to discriminate Italian monovarietal red wines, produced in their different terroirs. J. Agric. Food. Chem. 2020, 68, 13353–13366. [CrossRef]
- Giacosa, S.; Parpinello, G.P.; Río Segade, S.; Ricci, A.; Paissoni, M.A.; Curioni, A.; Marangon, M.; Mattivi, F.; Arapitsas, P.; Moio, L.; et al. Diversity of Italian Red Wines: A Study by Enological Parameters, Color, and Phenolic Indices. *Food Res. Int.* 2021, 143, 110277. [CrossRef]
- 14. Marangon, M.; De Iseppi, A.; Gerbi, V.; Mattivi, F.; Moio, L.; Piombino, P.; Parpinello, G.P.; Rolle, L.; Slaghenaufi, D.; Versari, A.; et al. The macromolecular diversity of Italian monovarietal red wines. *OENO One* **2022**, *56*, 81–90. [CrossRef]
- 15. Trani, A.; Verrastro, V.; Punzi, R.; Faccia, M.; Gambacorta, G. Phenols, Volatiles and Sensory Properties of Primitivo Wines from the "Gioia Del Colle" PDO Area. S. Afr. J. Enol. Vitic. 2016, 37, 139–148. [CrossRef]
- 16. Piombino, P.; Pittari, E.; Curioni, A.; Giacosa, S.; Mattivi, F.; Parpinello, G.P.; Rolle, L.; Ugliano, M.; Moio, L. Preliminary sensory characterization of the diverse astringency of monovarietal Italian red wines and correlation of sub-qualities with chemical parameters. *Aust. J. Grape Wine Res.* **2020**, *26*, 233–246. [CrossRef]
- 17. Pittari, E.; Moio, L.; Arapitsas, P.; Curioni, A.; Gerbi, V.; Parpinello, G.P.; Ugliano, M.; Piombino, P. Exploring olfactory-Oral Cross-Modal interactions through sensory and chemical characteristics of Italian red wines. *Foods* **2020**, *9*, 1530. [CrossRef]
- 18. Genovese, A.; Lisanti, M.T.; Gambuti, A.; Piombino, P.; Moio, L. Relationship between sensory perception and aroma compounds of monovarietal red wines. *Acta Hortic.* **2007**, *754*, 549–556. [CrossRef]
- 19. Slaghenaufi, D.; Vanzo, L.; Luzzini, G.; Arapitsas, P.; Marangon, M.; Curioni, A.; Mattivi, F.; Piombino, P.; Moio, L.; Versari, A.; et al. Monoterpenoids and norisoprenoids in Italian red wines. *OENO One* **2022**, *56*, 185–193. [CrossRef]
- 20. Noble, A.C.; Ebeler, S.E. Use of multivariate statistics in understanding wine flavor. Food Rev Int 2002, 18, 1–20. [CrossRef]
- 21. Rapp, A. Natural flavours of wine: Correlation between instrumental analysis and sensory perception. J. Agric. Food Chem. 1990, 337, 777–785.
- 22. Francis, I.L.; Newton, J.L. Determining wine aroma from compositional data. Aust. J. Grape Wine Res. 2005, 11, 114–126. [CrossRef]
- 23. Vilanova, M.; Genisheva, Z.; Masa, A.; Oliveira, J.M. Correlation between volatile composition and sensory properties in Spanish Albariño wines. *Microchem. J.* 2010, *95*, 240–246. [CrossRef]
- González Álvarez, M.; González-Barreiro, C.; Cancho-Grande, B.; Simal-Gándara, J. Relationships between Godello white wine sensory properties and its aromatic fingerprinting obtained by GC-MS. *Food Chem.* 2011, 129, 890–898. [CrossRef]
- 25. Vilanova, M.; Campo, E.; Escudero, A.; Graña, M.; Masa, A.; Cacho, J. Volatile composition and sensory properties of Vitis vinifera red cultivars from NW Spain. *Anal. Chim. Acta* 2021, 720, 104–111. [CrossRef] [PubMed]

- Vilanova, M.; Escudero, A.; Graña, M.; Cacho, J. Volatile composition and sensory properties of NorthWest Spain white wines. Food Res. Int. 2013, 54, 562–568. [CrossRef]
- Priser, C.; Etievant, P.X.; Nicklaus, S.; Brun, O. Representative champagne wine extracts for gas chromatography olfactometry analysis. J. Agric. Food Chem. 1997, 45, 3511–3514.
- De Filippis, F.; Aponte, M.; Piombino, P.; Lisanti, M.T.; Moio, L.; Ercolini, D.; Blaiotta, G. Influence of microbial communities on the chemical and sensory features of Falanghina sweet passito wines. *Food Res. Int.* 2019, 120, 740–747. [CrossRef]
- Bianchi, A.; Santini, G.; Piombino, P.; Pittari, E.; Sanmartin, C.; Moio, L.; Modesti, M.; Bellincontro, A.; Mencarelli, F. Nitrogen maceration of wine grape: An alternative and sustainable technique to carbonic maceration. *Food Chem.* 2022, 404, 134138. [CrossRef]
- Piombino, P.; Genovese, A.; Gambuti, A.; Lamorte, S.A.; Lisanti, M.T.; Moio, L. Effects of off-vine bunches shading and cryomaceration on free and glycosylated flavours of Malvasia delle Lipari wine. *Int. J. Food Sci. Technol.* 2010, 45, 234–244. [CrossRef]
- 31. *ISO. 8589;* Sensory Analysis-General Guidance for the Design of Test Rooms. International Organization for Standardization: Geneva, Switzerland, 2007.
- 32. Dravnieks, A. Odor quality: Semantically generated multidimensional profiles are stable. Sciences 1982, 218, 799–801.
- 33. Bartowsky, E.J. Oenococcus oeni and malolactic fermentation moving into the molecular arena. *Aust. J. Grape Wine Res.* 2005, 11, 174–187. [CrossRef]
- 34. Belda, I.; Ruiz, J.; Alastruey-Izquierdo, A.; Navascués, E.; Marquina, D.; Santos, A. Unraveling the enzymatic basis of wine "flavorome": A phylo-functional study of wine related yeast species. *Front. Microbiol.* **2016**, *7*, 12. [CrossRef]
- Ruiz, J.; Kiene, F.; Belda, I.; Fracassetti, D.; Marquina, D.; Navascués, E.; Calderón, F.; Benito, A.; Rauhut, D.; Santos, A.; et al. Effects on varietal aromas during wine making: A review of the impact of varietal aromas on the flavor of wine. *Appl. Microbiol. Biotechnol* 2019, 103, 7425–7450. [CrossRef] [PubMed]
- 36. Perestrelo, R.; Barros, A.S.; Câmara, J.S.; Rocha, S.M. In-depth search focused on furans, lactones, volatile phenols, and acetals as potential age markers of Madeira wines by comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry combined with solid phase microextraction. J. Agric. Food Chem. 2011, 59, 3186–3204. [CrossRef]
- Perestrelo, R.; Silva, C.; Gonçalves, C.; Castillo, M.; Câmara, J.S. An Approach of the Madeira Wine Chemistry. *Beverages* 2020, 6, 12. [CrossRef]
- Denat, M.; Pérez, D.; Heras, J.M.; Sáenz-Navajas, M.P.; Ferreira, V. Impact of two yeast strains on Tempranillo red wine aroma profiles throughout accelerated ageing. OENO One 2021, 55, 181–195. [CrossRef]
- 39. Ferreira, V.; de la Fuente-Blanco, A.; Sáenz-Navajas, M.P. Wine aroma vectors and sensory attributes. In *Managing Wine Quality*, 2nd ed.; Reynolds, A.G., Ed.; Woodhead Publishing: Cambridge, UK, 2022; Volume 1.
- 40. Grützmann-Arcari, S.G.; Caliari, V.; Sganzerla, M.; Godoy, H.T. Volatile composition of Merlot red wine and its contribution to the aroma: Optimization and validation of analytical method. *Talanta* **2017**, *174*, 752–766. [CrossRef]
- 41. Escudero, A.; Gogorza, B.; Melus, M.A.; Ortin, N.; Cacho, J.; Ferreira, V. Characterization of the aroma of a wine from Maccabeo. Key role played by compounds with low odor activity values. *J. Agric. Food Chem.* **2004**, *52*, 3516–3524. [CrossRef]
- 42. de la Fuente-Blanco, A.; Sáenz-Navajas, M.P.; Ferreira, V. On the effects of higher alcohols on red wine aroma. *Food Chem.* 2016, 210, 107–114. [CrossRef]
- 43. de la Fuente-Blanco, A.; Sáenz-Navajas, M.P.; Ferreira, V. Levels of higher alcohols inducing aroma changes and modulating experts' preferences in wine model solutions. *Aust. J. Grape Wine Res.* 2017, 23, 162–169. [CrossRef]
- 44. Atanasova, B.; Thomas-Danguin, T.; Chabanet, C.; Langlois, D.; Nicklaus, S.; Etiévant, P. Perceptual Interactions in Odour Mixtures: Odour Quality in Binary Mixtures of Woody and Fruity Wine Odorants. *Chem. Senses* **2005**, *30*, 209–217. [CrossRef]
- Lytra, G.; Tempere, S.; de Revel, G.; Barbe, J.C. Impact of Perceptive Interactions on Red Wine Fruity Aroma. J. Agric. Food Chem. 2021, 60, 12260–12269. [CrossRef] [PubMed]
- 46. Cameleyre, M.; Lytra, G.; Tempere, S.; Barbe, J.C. Olfactory Impact of Higher Alcohols on Red Wine Fruity Ester Aroma Expression in Model Solution. *J. Agric. Food Chem.* **2015**, *63*, 9777–9788. [CrossRef] [PubMed]
- 47. Ferreira, V.; Sáenz-Navajas, M.P.; Campo, E.; Herrero, P.; de la Fuente, A.; Fernández-Zurbano, P. Sensory interactions between six common aroma vectors explain four main red wine aroma nuances. *Food Chem.* **2016**, *199*, 447–456. [CrossRef] [PubMed]
- 48. Aznar, M.; López, R.J.; Cacho, F.; Ferreira, V. Prediction of aged red wine aroma properties from aroma chemical composition. Partial least squares regression models. J. Agric. Food Chem. 2003, 51, 2700–2707. [CrossRef] [PubMed]

**Disclaimer/Publisher's Note:** The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.