

Varietal volatile patterns in young and model-aged white wines: a case study on eighteen monovarietal Italian wine types

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ABSTRACT

During aging, wines undergo substantial compositional transformation through complex reactions impacting wine volatile composition. Most white wines are obtained from aromatically neutral grape varieties, although aging might induce chemical changes of potential relevance for viticulture and enology. This study investigated aging-induced changes in varietal volatile compounds across 18 monovarietal white wine types from nine Italian regions, namely Albana, Cortese, Arneis, Erbaluce, Falanghina, Fiano, Garganega, Gewürztraminer, Greco di Tufo, Lugana, Müller-Thurgau, Nosiola, Pallagrello bianco, Pinot grigio, Ribolla gialla, Verdicchio, Vermentino, and Vernaccia. Results provided for the first time clear chemical clues about the existence of distinct aging patterns for each wine type. Aging treatment enhanced classification complexity while simultaneously reducing intra-varietal diversity. Certain wines developed characteristic patterns and markers during aging. In particular, compounds such as methyl salicylate, cineole isomers, dimethyl sulfide (DMS) and methanethiol were primarily associated with specific varietal types. These findings provide insights for optimizing viticultural and wine-making strategies to manage varietal typicality during aging.

1. Introduction

In the context of wine production, a period of months or years normally exists between completion of the main fermentation step and the moment of wine consumption. This period, commonly referred to as aging, includes production steps that take place in the winery and that are aimed at stabilizing the wine and developing specific sensory qualities (e.g. aging in contact with yeast lees and/or oxygen and/or wood) as well as the time that the wine spends in the bottle, which might vary from weeks to years (Ma et al., 2022; Ugliano, 2013). From a chemical perspective, wine is a constantly evolving matter in which various chemical reactions can take place during aging, involving significant

changes in wine composition and sensory properties. Among these, the generation of novel aroma compounds from different precursors and the degradation of existing ones are central to aroma evolution during aging (Daniel et al., 2009; Ferreira & Lopez, 2019; Loscos et al., 2008; Luzzini et al., 2022; Picard et al., 2017; Slaghenaufi & Ugliano, 2018; Williams et al., 2025).

In the current global market, consumers increasingly seek products with a sense of typicality reflecting a connection between organoleptic characteristics, compositional features, and their geographical or varietal origin (Fernández-Ferrín et al., 2019; Guy, 2011; Parr et al., 2020; Cross et al., 2011). The variety employed for winemaking is one central element of wine typicality; both in terms of its impact on wine

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composition and sensory characteristics as well as for the unique relationship between grape variety and place of origin of the wine (Celik et al., 2015; Robinson et al., 2014; Sabon et al., 2002; Slaghenaufi, Peruch, et al., 2021; Slaghenaufi, Vanzo, et al., 2022). In the context of white wine, the relationship between grape variety and wine perceived characteristics is mostly associated with volatile composition, with the occurrence of individual aroma compounds or groups thereof (Carlin, Piergiovanni, et al., 2022; Ferreira & Lopez, 2019). However, while in terpenic or thiolic varieties such as Muscat and Gewürztraminer or Sauvignon blanc, young wines usually exhibit aroma characteristics typical of the grape of origin, for the majority of the other varieties, often referred to as 'neutral', this is less obvious. Varietal volatile compounds with aroma impact occur indeed in relatively low concentrations in young wines from neutral varieties, although with aging they can be generated through different chemical reactions, eventually contributing to perceived aroma (Baiano et al., 2017; Carlin, Lotti, et al., 2022; Samaniego Solis et al., 2024; Slaghenaufi & Ugliano, 2018). In particular, the acidic environment significantly influences the evolution of wine aroma composition, driving a range of chemical reactions including hydrolysis of non-volatile glycosidic precursors, chemical rearrangements of certain volatile compounds derived from grapes or fermentation (Arapitsas et al., 2024; Maicas & Mateo, 2005; Skouroumounis & Sefton, 2000; Winterhalter, 1991; Yang et al., 2022), and degradation of sulfur-containing amino acids derivatives. Potent aroma-active norisoprenoids, terpenes, benzenoids, and sulfur compounds arise from these reactions (Fariña et al., 2005; Ferreira et al., 2014; Mendes-Pinto, 2009; Samaniego Solis et al., 2024; Segurel et al., 2005; Slaghenaufi & Ugliano, 2018; Yang et al., 2022). While many aspects of these aroma-relevant reactions have been studied, a systematic investigation aiming at profiling aroma development patterns linked to wine varietal origin has not been carried out. Evidence suggests, however, that certain varieties are characterized by specific patterns of aroma development during aging, for example, in the case of the Riesling aging-related norisoprenoid TDN (Tarasov et al., 2020; Winterhalter, 1991). Other studies have shown that the pool of grape volatile compounds released from glycosidic precursors upon aging contributes to sensorially detectable aroma differences (Alegre et al., 2020; Francis et al., 1992). However, the question arises as to whether, across several wines of the same variety/appellation, it is possible to identify distinctive varietal aging-related volatile patterns, and which are the main chemical markers of such patterns.

Italy owns one of the largest ampelographic heritages worldwide, with over 644 different varieties (Italian Catalogue of Grapevine Varieties—Catalogo Nazionale Delle Varietà Di Vite. Available Online: <http://Catalogoviti.Politicheagricole.It/Catalogo.php> (Accessed on 26 January 2025), 2025). Among these, many white grapes are employed for the production of dry still white wines, often with one single variety largely dominating the final blend. Some of these wines are consumed young, while others are considered suitable for either bottle aging, cask aging, or both. Nevertheless, for many of these wines, the volatile patterns related to varietal volatile composition are still unknown for both young and aged wines, preventing the development of specific viticultural, winemaking, and aging protocols.

This study aimed to investigate varietal volatile patterns in young and model-aged wines of 18 monovarietal Italian white wine types, namely Nosiola, Vermentino, Müller-Thurgau, Greco di Tufo, Garganega, Lugana, Erbaluce di Caluso, Pinot Grigio, Cortese, Arneis, Albana, Pallagrello, Falanghina, Fiano, Ribolla Gialla, Vernaccia, Gewürztraminer, and Verdicchio. For each category, six distinct samples were analysed, and the concentrations of volatile sulfur compounds, terpenes, norisoprenoids, and benzenoids were quantified.

2. Materials and methods

2.1. Wines

One hundred eight monovarietal white wines (vintage 2019) from 18 Italian grape cultivars collected in 9 Italian regions were employed in this study (Supplementary 1). For each variety, 6 different commercial wines produced without malolactic fermentation and wood aging were collected, for a total of 108 wine samples: Albana (Emilia-Romagna, ALB) (cv. Albana bianca accession number 224; VIVC, 2025); Cortese (Piemonte, CRT) (cv. Cortese, accession number 2856; VIVC, 2025); Arneis (Piemonte, ARN) (cv. Arneis, accession number 626; VIVC, 2025); Erbaluce (Piemonte, ERB) (cv. Erbaluce, accession number 3925; VIVC, 2025); Falanghina (Campania, FAL) (cv. Falanghina Beneventana, accession number 24584; VIVC, 2025); Fiano (Campania, FIA) (cv. Fiano, accession number 4124; VIVC, 2025); Garganega (Veneto, GAR) (cv. Garganega, accession number 4419; VIVC, 2025); Gewürztraminer (Trentino Alto Adige, GWR) (cv. Gewürztraminer, accession number 12609; VIVC, 2025); Greco di Tufo (Campania, GRE) (cv. Greco bianco di Tufo, accession number 4970; VIVC, 2025); Lugana (Veneto, LUG) (cv. Verdicchio bianco, accession number 12963; VIVC, 2025); Müller-Thurgau (Trentino Alto Adige, MLR) (cv. Mueller Thurgau weiss, accession number 8141; VIVC, 2025); Nosiola (Trentino Alto Adige, NSL) (cv. Nosiola, accession number 8606; VIVC, 2025); Pallagrello Bianco (Campania, PAL) (cv. Guarnaccia, accession number 5097; VIVC, 2025); Pinot grigio (Friuli Venezia Giulia /Veneto, PG) (cv. Pinot gris, accession number 9275; VIVC, 2025); Ribolla Gialla (Friuli Venezia Giulia, RIB) (cv. Ribolla gialla, accession number 10054; VIVC, 2025); Verdicchio (Marche, VRD) (cv. Verdicchio bianco, accession number 12963; VIVC, 2025); Vermentino (Sardegna, VRM) (cv. Vermentino, accession number 12989; VIVC, 2025); Vernaccia (Toscana, VRN) (cv. Vernaccia di San Gimignano, accession number 12998; VIVC, 2025).

Wines were sourced directly from producers in the period of May–June 2020 and were kept at 14 °C until they were used for the experimental work, which took place in October 2020.

2.2. Model aging protocol

Wines were submitted to a model aging treatment previously described (Slaghenaufi et al., 2019; Slaghenaufi & Ugliano, 2018) with minor differences. Wine bottles were opened in a polyethylene glove box under nitrogen, free SO₂ levels were determined and adjusted to 30 ± 3 mg/L by addition of potassium metabisulfite. Sixty mL of each wine were then placed in glass vials with polypropylene screw caps and butyl/Teflon septa. Vials were kept under vacuum in thermally-sealed oxygen barrier plastic bags at either 10 °C (Control), and 60 °C (T60) (± 0.2 °C) for 30 days, after which analysis of volatile compounds was carried out. All samples were produced in duplicate.

2.3. Determination of volatile compounds

Volatile compounds determined in the present study are reported in Supplementary 2 with the relevant identification and quantification parameters, while methods are described in the following sections.

2.3.1. Volatile sulfur compounds (VSCs)

Volatile sulfur compounds (VSCs) were analysed by solid phase microextraction coupled with gas chromatography–mass spectrometry (SPME–GC–MS), as described by Slaghenaufi et al. (Slaghenaufi, Luzzini, et al., 2021). In order to limit volatilization, wine samples were kept at 4 °C for 24 h before analysis. Samples were prepared by adding 100 µL of DMS-d₆ internal standard (2 mg/L of hexadeuterodimethyl sulfide in ethanol) to 10 mL of wine placed in a 20 mL glass vial together with 3 g NaCl. Samples were then kept at 4 °C until SPME extraction. Prior to SPME, samples were equilibrated for 1 min at 40 °C, then a 1 cm 65 µm. polydimethylsiloxane-divinylbenzene fibre (PDMS/DVB) (Supelco,

Bellafonte, PA, USA) was exposed to the sample headspace for 30 min. Compounds were desorbed in the injector port at 270 °C for 2 min in splitless mode. GC–MS analyses were performed on an HP 7890 A (Agilent Technologies, Santa Clara, CA, USA) gas chromatograph coupled to a 5977B quadrupole mass spectrometer equipped with a Gerstel MPS3 auto sampler (Müllheim/Ruhr, Germany). Separation was performed using a DB-WAX UI capillary column (30 m × 0.25 mm, 0.25 µm film thickness, Agilent Technologies) and helium (6.0 grade) as the carrier gas at a 1.2 mL/min constant flow rate. The GC oven was programmed as follows: started at 35 °C for 5 min, increased to 90 °C at 5 °C/min, and then increased to 260 °C at 15 °C/min and maintained for 2 min. The mass spectrometer was equipped with an electron impact ionization source (EI) (70 eV). The transfer line, the source, and the quadrupole temperature were set at 200 °C, 230 °C, and 150 °C, respectively. Mass spectra were acquired in SIM mode. Samples were analysed in random order. A calibration curve was prepared for each analyte using pure commercial standards of each single compound, with seven concentration points and three replicate solutions per point in white wines. A volume of 100 µL of DMS-d6 (2 mg/L in ethanol) was added to each calibration solution, which was then subjected to SPME extraction and GC–MS analysis, as described for the samples. Calibration curves were obtained using Chemstation B.04.03 software (Agilent Technologies, Inc., Santa Clara, CA, USA) by linear regression, plotting the response ratio (analyte peak area divided by internal standard peak area) against the concentration ratio (added analyte concentration divided by internal standard concentration).

2.3.2. Terpenoids, norisoprenoids, and methyl salicylate

Terpenes, norisoprenoids, and methyl salicylate (MeSA) were analysed using SPME extraction coupled with GC–MS analysis, as described by Slaghenaufi et al. (Slaghenaufi, Vanzo, et al., 2022). Five millilitres of wine were placed into a 20 mL glass vial together with 5 mL of water, 3 g of NaCl, and 5 µL of the internal standard 2-octanol (4.2 mg/L in ethanol). Samples were equilibrated for 1 min at 40 °C, and then SPME extraction was performed by exposing a 1 cm 50/30 µm divinylbenzene-carboxen-polydimethylsiloxane (DVB/CAR/PDMS) fibre (Supelco, Bellafonte, PA, USA) to the sample headspace for 60 min. Injection was performed in splitless mode by desorbing the SPME fibre into the injection port of an HP 7890 A (Agilent Technologies) gas chromatograph coupled to a 5977B quadrupole mass spectrometer, equipped with a Gerstel MPS3 auto sampler (Müllheim/Ruhr, Germany). Separation was performed using a DB-WAX UI capillary column (30 m × 0.25 mm, 0.25 µm film thickness, Agilent Technologies). Helium (6.0 grade) was used as a carrier gas at a constant flow rate of 1.2 mL/min. The GC oven temperature was initially set at 40 °C for 3 min, then raised to 230 °C at 4 °C/min and maintained for 20 min. The mass spectrometer was operated in electron ionization (EI) mode at 70 eV with the ion source temperature at 230 °C and the quadrupole temperature at 150 °C. Mass spectra were acquired in synchronous Scan (m/z 40–200) and SIM mode. Samples were analysed in random order.

A calibration curve was prepared for each analyte using seven concentration points and three replicate solutions per point in white wines. A volume of 100 µL of 2-Octanol (0.42 mg/L in ethanol) was added to each calibration solution, which was then subjected to SPME extraction and GC–MS analysis, as described for the samples. Calibration curves were obtained using Chemstation B.04.03 software (Agilent Technologies, Inc., Santa Clara, CA, USA) by linear regression, plotting the response ratio (analyte peak area divided by internal standard peak area) against the concentration ratio (added analyte concentration divided by internal standard concentration).

2.3.3. Analysis of methyl salicylate glycosides

Methyl salicylate glycosides were analysed with the method described by Carlin et al. (Carlin, Masuero, et al., 2019) for UHPLC-MS/MS Ion Trap. Wine samples were filtered at 0.22 µm after bottle opening and injected. The separation was performed at 40 °C in reverse phase

with an Exion LC system provided by AB Sciex LLC (Framingham; MA; USA) using an Acquity UPLC® BEH HSS-T3 (1.8 µm; 2.1 mm × 50 mm) precolumn coupled to an Acquity UPLC® C18 HSS-T3 (1.8 µm; 2.1 mm × 150 mm) column from Waters Corporation (Milford; MA; USA). The mobile phase consisted of water (A) and methanol (B); both acidified at 0.1% v/v with formic acid. Elution was performed at 0.28 mL/min with the following multistep linear gradient: 0–1 min; 100% A isocratic; 1–3 min; 100–90% A; 3–18 min; 90–60% A; 18–21 min; 60–0% A; 21–25.5 min; 0% A isocratic; 25.5–25.6 min; 0–100% A; 25.6–28 min 100% isocratic. The electrospray ionization (ESI) was performed using an AB Sciex LLC QTRAP 6500+ system (Framingham; MA; USA) operating with the same optimal setting described in detail by Carlin, Masuero, et al. (2019) and Carlin, Vrhovsek, et al. (2019). The best-performing transitions were selected to be used as the quantifier (Q) and qualifier (q). The m/z 337.09 was used for quantification purposes.

2.4. Enological parameters

Total and volatile acidity, primary amino nitrogen (PAN), and ammonia were determined using a Dionysos multiparametric analyser (Sinatch, Grottazzolina, Italy). For each parameter, a specific kit (Sinatch, Grottazzolina, Italy) was used. Ethanol (%) was determined with a Lyza 5000 FT-IR analyser (Anton Paar, Graz, Austria). The pH was evaluated with a Crison Basic 20+ pH meter (Barcelona, Spain).

2.5. Statistical analyses

Mann-Whitney test ($\alpha = 0.05$), Kruskal-Wallis test ($\alpha = 0.05$), t -test ($\alpha = 0.05$), Correlation analysis (Spearman, $\alpha = 0.05$) Hierarchical Cluster Analysis (HCA), and Heatmap were performed with XLSTAT 2017 (Addinsoft SARL, Paris, France).

3. Results

Base enological parameters of the wines are given in Table 1. Volatile compounds of Control and T60 wines are reported in Tables 1 and 2, while differences according to Kruskal-Wallis multiple pairwise comparison (Dunn, $\alpha = 0.05$) are reported in Supplementary 3 and 4. A total of 34 compounds were quantified, including 7 sulfur compounds, 7 norisoprenoids, 19 terpenoids, and methyl salicylate. To have an overview of the whole data set, heatmaps with HCA (Ward's method) of wine samples were created. (Figs. 1 and 2).

In Control wines (Fig. 1) HCA showed the existence of 5 clusters (C), two of which (C1 and C2) included the vast majority of the samples (45 each), with the remaining C3, C4, and C5 including 8, 7, and 3 wines, respectively. Clusters were formed by different wine types, and in most cases, all samples of the same wine type belonged to the same cluster. For example, ALB, ARN, FIA, PAL, VRN, and NSL were all grouped in C1, while CRT, ERB, FAL, PG, RIB, LUG and VRD were grouped in C2. In terms of volatile compounds defining each cluster, different profiles were present within both C1 and C2, highlighting the presence of several sub-clusters with specific volatile patterns. For example, C1 contained four main sub-clusters characterized by increased concentrations of either vitispiranes and β -damascenone, DES and DMTS, DMS and DMDS, or combinations thereof. Likewise, in C2 six sub-clusters were observed in association with increased content of either TDN, TPB, and methanethiol, 1,4-cineole alone or in combination with either terpinen-4-ol, methyl salicylate or nerolidol, or rose oxides and certain cyclic terpenes. A major differentiation of C2 was the reduced content of the VSCs DES, DEDS, DMTS. As for the other clusters, C3 was clearly associated with increased concentrations of VSCs while C4 exhibited generally high concentrations of several VSCs but also of norisoprenoids, linalool, geraniol, and 1,8-cineole. Finally, C5, which included three GWR, was characterized by a high concentration of all the terpene compounds measured. Overall, the varietal distribution within these clusters was not univocal, and in several cases they contained samples of different types.

Table 1
Enological parameters and volatile compounds concentrations (µg/L) of Control wines.

	Albana			Arneis			Cortese			Erbaluce			Falanghina			Fiano		
	mean	min	max	mean	min	max	mean	min	max	mean	min	max	mean	min	max	mean	min	max
<i>Enological parameters</i>																		
Ethanol (%)	13.73	12.76	14.82	13.43	12.73	14.49	12.66	12.02	13.39	12.48	11.80	13.22	13.46	12.98	14.50	13.53	12.84	14.34
pH	3.33	3.16	3.67	3.23	3.12	3.32	3.22	3.07	3.32	3.25	3.06	3.60	3.47	3.30	3.66	3.24	3.12	3.46
Total acidity (g/LI)	6.04	4.83	7.37	5.26	4.32	5.88	5.37	4.89	6.29	6.38	5.13	8.46	6.24	4.75	6.95	5.98	5.55	6.38
Volatile acidity (g/L)	0.41	0.27	0.62	0.33	0.26	0.47	0.31	0.22	0.46	0.35	0.11	0.50	0.36	0.28	0.41	0.39	0.27	0.75
PAN (mg/L)	35.2	13.0	61.0	30.8	16.0	43.0	31.6	15.1	58.4	28.3	14.4	56.2	38.3	20.8	55.1	10.3	0.0	27.0
Ammonia (mg/L)	0.0	0.0	0.0	14.5	4.0	30.0	13.5	3.1	47.8	7.7	0.7	24.4	23.4	7.5	86.5	13.0	6.0	31.0
<i>VOCs</i>																		
Carbon disulfide	3.49	3.05	4.34	7.77	4.47	10.91	3.09	2.93	3.53	3.50	3.15	4.73	3.62	2.76	4.74	7.27	5.23	9.68
Methanthiol	2.48	2.06	3.39	2.69	1.48	3.71	8.95	5.35	12.20	3.32	2.54	3.95	3.70	2.92	4.78	2.66	1.94	3.48
DMS	5.93	3.65	7.08	3.46	2.68	4.26	10.11	6.01	13.95	3.73	2.86	4.45	4.25	3.28	5.94	5.45	4.93	5.88
Diethyl sulfide DES	0.35	0.23	0.58	0.54	0.40	0.88	0.12	0.09	0.18	0.18	0.04	0.40	0.24	0.07	0.43	0.56	0.28	1.11
Dimethyl disulfide DMDS	0.21	0.13	0.28	0.64	0.53	0.75	0.00	0.00	0.00	0.00	0.00	0.06	0.06	0.00	0.13	0.68	0.61	0.76
Diethyl disulfide DEDS	0.31	0.17	0.43	1.21	0.82	1.55	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.45	1.17	1.70
Dimethyl trisulfide DMTS	0.10	0.05	0.15	0.44	0.33	0.55	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.55	0.42	0.63
Nerolidol 2	0.00	0.00	0.00	0.00	0.00	0.00	0.13	0.00	0.33	0.13	0.00	0.49	0.17	0.00	0.49	0.00	0.00	0.00
Geraniol	0.00	0.00	0.00	0.70	0.00	1.21	3.18	2.01	3.65	2.05	0.00	5.25	1.06	0.00	2.14	0.52	0.06	0.93
α-Phellandrene	0.07	0.00	0.23	0.00	0.00	0.00	0.04	0.00	0.12	0.05	0.00	0.14	0.19	0.00	0.41	0.05	0.00	0.10
α-Terpinen	0.35	0.07	0.74	0.13	0.09	0.16	0.21	0.00	0.52	0.47	0.00	2.28	1.00	0.50	1.72	0.38	0.25	0.63
4-Carene	0.00	0.00	0.04	0.00	0.00	0.00	0.00	0.00	0.04	0.00	0.00	0.06	0.00	0.00	0.05	0.00	0.00	0.00
β-Myrcene	1.86	0.17	6.28	0.11	0.08	0.15	4.98	3.52	6.87	3.47	2.03	4.52	14.48	1.55	25.41	0.50	0.00	1.48
Limonene	3.63	1.10	8.31	0.43	0.32	0.64	2.52	1.03	4.45	0.80	0.33	2.03	5.73	2.18	11.59	0.97	0.00	1.67
1,4-Cineole	0.11	0.00	0.58	0.31	0.00	0.68	0.54	0.20	0.84	1.25	0.78	2.84	1.49	1.06	1.77	1.06	0.27	3.13
1,8-Cineole	0.30	0.00	0.87	0.38	0.00	2.18	0.56	0.25	1.46	1.01	0.00	5.52	0.38	0.27	0.56	1.02	0.19	2.41
p-Cymene	0.50	0.10	1.08	0.42	0.23	0.62	0.40	0.20	0.56	1.16	0.24	3.93	1.17	0.60	2.08	0.53	0.00	0.92
Terpinolene	1.52	0.24	3.79	0.14	0.09	0.17	1.22	0.49	2.42	0.55	0.16	1.63	3.56	1.46	6.75	0.62	0.00	1.20
cis-Linalool oxide	3.95	2.05	7.28	2.25	0.00	4.54	5.19	2.87	8.19	1.92	0.26	5.18	2.64	1.32	3.99	2.65	0.25	3.89
Linalool	2.42	0.16	8.65	2.05	1.42	3.03	6.49	1.51	14.98	2.20	0.62	4.02	18.48	5.35	36.66	10.60	0.10	23.68
Terpinen-4-ol	0.24	0.00	0.36	1.08	0.79	1.70	0.49	0.28	0.77	1.66	0.54	4.49	1.46	0.73	3.25	1.26	0.00	1.76
α-Terpineol	2.28	0.44	5.54	1.61	1.21	2.02	7.53	3.05	12.49	2.39	0.71	4.78	6.98	3.65	9.90	7.13	0.00	11.52
β-Citronellol	0.26	0.00	1.58	0.84	0.00	5.02	1.05	0.00	3.58	0.96	0.52	1.64	2.36	0.99	4.28	0.67	0.00	3.25
Nerol	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
trans Rose oxide	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
cis Rose Oxide	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
β-Damascenone	0.10	0.04	0.18	0.42	0.19	0.67	0.15	0.10	0.30	0.17	0.10	0.33	0.56	0.13	1.11	0.39	0.00	1.12
Vitispirane 1	0.56	0.33	0.97	3.87	1.85	6.65	1.31	1.05	1.60	0.92	0.53	1.46	3.26	1.51	6.60	1.57	0.18	2.51
Vitispirane 2	0.37	0.22	0.53	3.34	1.73	5.71	0.75	0.58	0.88	0.69	0.21	2.05	2.37	1.29	4.46	0.80	0.18	1.47
TPB	0.09	0.04	0.18	0.19	0.08	0.33	0.17	0.14	0.21	0.13	0.08	0.20	0.14	0.10	0.23	0.00	0.00	0.06
TDN	1.03	0.54	1.56	2.27	1.03	3.71	6.44	3.07	11.66	2.35	1.79	3.73	3.51	1.80	6.07	2.38	0.00	3.92
α-Ionone	0.00	0.00	0.00	0.07	0.00	0.19	0.05	0.00	0.13	0.00	0.00	0.00	0.00	0.00	0.04	0.04	0.00	0.08
β-Ionone	0.00	0.00	0.05	0.00	0.00	0.08	0.52	0.48	0.56	0.36	0.22	0.48	0.15	0.05	0.49	0.05	0.00	0.11
Methyl salicylate	0.69	0.32	1.11	1.21	0.55	2.50	0.69	0.30	1.01	3.28	2.10	7.77	1.49	0.63	2.66	1.32	0.32	2.68
<i>Garganega</i>																		
	mean	min	max	mean	min	max	mean	min	max	mean	min	max	mean	min	max	mean	min	max
<i>Enological parameters</i>																		
Ethanol (%)	12.47	11.87	13.05	13.38	12.54	14.30	12.88	12.23	13.76	12.32	11.88	12.78	12.18	10.86	13.33	13.42	12.58	14.27
pH	3.21	3.11	3.31	3.29	3.10	3.41	3.24	3.06	3.39	3.19	3.05	3.27	3.17	3.10	3.40	3.34	3.14	3.53
Total acidity (g/LI)	5.50	4.93	6.02	6.24	5.57	7.32	5.90	4.96	6.68	5.78	5.22	6.48	6.03	4.64	7.36	5.66	4.80	6.37
Volatile acidity (g/L)	0.29	0.16	0.44	0.38	0.25	0.58	0.33	0.21	0.45	0.31	0.24	0.43	0.33	0.28	0.46	0.35	0.25	0.46
PAN (mg/L)	49.5	15.4	82.7	35.0	19.0	73.0	92.3	55.5	135.8	39.5	5.0	71.0	59.8	28.0	143.0	29.8	16.0	46.0
Ammonia (mg/L)	14.8	3.0	32.4	45.5	15.0	113.0	46.6	1.3	117.8	11.0	0.0	22.7	6.0	2.2	13.8	16.8	8.0	39.0

(continued on next page)

Table 1 (continued)

	Albana			Arneis			Cortese			Erbaluce			Falanghina			Fiano		
	mean	min	max	mean	min	max	mean	min	max	mean	min	max	mean	min	max	mean	min	max
VOCs																		
Carbon disulfide	2.96	2.88	3.14	34.20	11.97	48.89	3.05	2.83	3.43	26.72	14.74	46.32	15.22	7.93	26.29	8.24	6.45	10.21
Methanthiol	1.15	0.52	2.38	1.91	0.83	4.31	2.71	1.66	5.82	11.57	5.11	21.16	3.70	2.09	5.47	2.96	2.13	4.25
DMS	7.76	3.00	16.60	26.24	8.12	35.74	3.79	2.23	6.54	15.96	5.19	26.73	7.71	5.09	9.76	4.95	3.47	5.88
Diethyl sulfide DES	0.31	0.00	0.88	1.51	1.19	1.69	0.08	0.06	0.16	1.37	0.88	1.64	0.68	0.58	0.76	0.70	0.56	0.89
Dimethyl disulfide DMDS	0.00	0.00	0.07	2.49	2.21	2.83	0.00	0.00	0.06	1.36	0.28	2.52	0.60	0.44	0.79	0.52	0.49	0.58
Diethyl disulfide DEDS	0.00	0.00	0.00	1.14	0.92	1.35	0.00	0.00	0.00	0.52	0.00	1.10	0.24	0.19	0.31	0.65	0.59	0.79
Dimethyl trisulfide DMTS	0.00	0.00	0.00	0.13	0.06	0.28	0.00	0.00	0.00	0.07	0.00	0.14	0.00	0.00	0.00	0.21	0.18	0.26
Nerolidol 2	0.13	0.00	0.45	0.00	0.00	0.09	0.16	0.00	0.43	0.11	0.00	0.26	0.36	0.07	1.52	0.51	0.00	1.24
Geraniol	2.19	0.00	4.48	0.63	0.18	0.94	2.47	1.87	3.98	2.01	0.56	4.38	2.23	0.28	7.61	2.12	0.90	4.84
α -Phellandrene	0.13	0.00	0.75	0.07	0.00	0.14	0.25	0.00	1.34	0.06	0.00	0.11	0.10	0.00	0.22	0.00	0.00	0.05
α -Terpinen	0.08	0.04	0.16	0.36	0.22	0.63	0.40	0.20	0.65	0.32	0.07	0.63	0.12	0.08	0.20	0.19	0.09	0.25
4-Carene	0.00	0.00	0.00	0.00	0.00	0.06	0.00	0.00	0.00	0.06	0.00	0.12	0.00	0.00	0.08	0.00	0.00	0.04
β -Myrcene	2.17	0.54	3.21	3.05	1.72	4.47	2.75	0.49	4.27	3.91	2.17	4.85	1.85	1.15	3.82	0.52	0.12	0.82
Limonene	0.45	0.17	1.01	2.48	1.38	4.86	0.47	0.35	0.59	3.48	1.64	5.81	0.96	0.35	1.51	2.20	0.72	4.86
1,4-Cineole	0.52	0.28	0.72	0.25	0.00	0.40	1.22	0.93	1.52	0.39	0.16	0.79	0.15	0.00	0.27	0.18	0.00	0.30
1,8-Cineole	0.17	0.00	0.65	0.25	0.00	0.45	0.13	0.07	0.27	0.37	0.25	0.56	0.12	0.06	0.25	0.79	0.00	4.34
p-Cymene	0.43	0.22	0.73	0.69	0.40	1.14	1.35	0.54	2.53	0.55	0.23	0.88	0.28	0.11	0.62	0.42	0.12	0.80
Terpinolene	0.21	0.10	0.46	1.29	0.75	2.34	0.33	0.27	0.43	2.38	0.83	3.36	0.42	0.15	0.95	0.46	0.19	0.78
cis-Linalool oxide	2.07	0.88	3.83	2.48	1.17	3.08	2.12	1.50	3.05	5.49	2.16	12.56	3.46	0.84	10.94	3.11	2.24	3.82
Linalool	2.63	0.46	6.77	2.15	0.79	4.35	2.10	0.52	4.60	12.72	2.43	32.91	15.01	6.45	47.43	8.52	1.17	17.53
Terpinen-4-ol	0.88	0.26	1.93	0.20	0.16	0.28	1.66	0.82	2.54	0.81	0.10	1.82	0.87	0.42	1.71	1.06	0.58	1.64
α -Terpineol	2.35	1.03	5.36	0.66	0.39	0.99	2.15	1.37	3.16	13.16	0.71	32.53	4.62	1.84	8.68	4.93	2.78	8.38
β Citronellol	1.12	0.00	2.43	1.25	0.61	2.13	0.71	0.00	1.54	1.77	0.76	3.61	2.22	0.86	4.43	1.73	0.00	4.57
Nerol	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
trans Rose oxide	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
cis Rose Oxide	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
β -Damascenone	0.33	0.13	0.55	0.23	0.11	0.46	0.31	0.25	0.39	0.28	0.11	0.45	0.48	0.06	1.68	0.48	0.27	0.72
Vitispirane 1	2.93	1.25	4.72	0.96	0.48	1.41	1.63	0.88	3.03	2.24	1.00	4.17	2.17	1.08	4.99	3.20	1.15	4.72
Vitispirane 2	1.50	0.70	2.27	0.48	0.36	0.73	0.94	0.49	1.70	1.77	0.66	3.26	1.44	0.57	3.08	1.71	0.41	2.34
TPB	0.10	0.05	0.13	0.17	0.11	0.26	0.17	0.09	0.44	0.20	0.13	0.24	0.05	0.00	0.08	0.07	0.05	0.10
TDN	5.69	1.71	13.40	2.87	1.34	3.88	4.94	1.33	17.44	3.65	2.82	4.77	2.78	0.36	10.56	2.52	1.23	4.64
α -Ionone	0.09	0.00	0.23	0.00	0.00	0.00	0.00	0.00	0.05	0.04	0.00	0.20	0.00	0.00	0.00	0.14	0.00	0.27
β -Ionone	0.47	0.32	0.60	0.27	0.12	0.42	0.38	0.23	0.49	0.33	0.20	0.59	0.19	0.16	0.25	0.18	0.06	0.31
Methyl salicylate	1.84	1.29	2.72	0.45	0.29	0.87	10.09	2.68	22.34	0.52	0.27	0.89	0.59	0.10	2.75	0.77	0.26	2.46
Pinot Grigio			Ribolla Gialla			Vernaccia			Verdicchio			Vermentino			Gewurtztraminer			
	mean	min	max	mean	min	max	mean	min	max	mean	min	max	mean	min	max	mean	min	max
Enological parameters																		
Ethanol (%)	12.55	11.91	13.13	12.75	12.19	13.50	12.85	12.36	13.49	5.63	0.43	13.76	13.76	12.27	15.41	14.81	13.98	15.67
pH	3.37	3.29	3.48	3.31	3.14	3.50	3.37	3.27	3.51	3.40	3.28	3.70	3.43	3.27	3.80	3.65	3.61	3.77
Total acidity (g/L)	5.44	5.02	6.26	5.62	4.80	6.67	5.60	4.76	6.43	5.01	0.44	13.48	5.38	4.73	6.48	4.89	4.11	6.53
Volatile acidity (g/L)	0.25	0.22	0.30	0.32	0.24	0.56	0.31	0.24	0.42	5.47	0.45	13.07	0.28	0.12	0.40	0.42	0.33	0.56
PAN (mg/L)	105.4	66.7	140.8	47.9	24.6	63.7	35.5	19.0	59.0	72.0	32.1	113.6	59.3	27.0	128.0	74.4	47.5	102.5
Ammonia (mg/L)	40.3	14.1	80.1	12.4	5.8	37.6	15.3	8.0	30.0	36.7	0.8	93.6	47.5	0.0	119.9	27.0	12.7	48.0
VOCs																		
Carbon disulfide	3.55	3.18	4.17	2.93	2.86	3.08	8.30	6.54	9.55	5.34	4.49	6.40	14.39	8.96	23.08	6.55	4.72	9.39
Methanthiol	5.02	2.38	7.99	2.20	1.58	2.71	2.65	2.20	3.05	3.24	2.41	4.16	7.56	1.87	15.93	5.74	2.49	10.48
DMS	5.64	2.68	8.98	2.47	1.78	3.04	5.10	3.89	6.08	3.64	2.71	4.62	15.06	8.18	29.25	6.46	2.80	11.78
Diethyl sulfide DES	0.17	0.14	0.21	0.07	0.00	0.15	0.39	0.23	0.76	0.63	0.33	0.87	1.09	0.60	2.03	1.06	0.45	1.75
Dimethyl disulfide DMDS	0.06	0.05	0.08	0.00	0.00	0.00	0.38	0.33	0.46	0.14	0.06	0.24	0.52	0.13	1.02	0.36	0.13	0.51
Diethyl disulfide DEDS	0.00	0.00	0.00	0.00	0.00	0.00	0.70	0.49	0.94	0.00	0.00	0.00	0.00	0.00	0.00	0.07	0.00	0.09
Dimethyl trisulfide DMTS	0.00	0.00	0.00	0.00	0.00	0.00	0.25	0.23	0.30	0.00	0.00	0.05	0.11	0.00	0.32	0.11	0.00	0.18

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Table 1 (continued)

	Albana			Arneis			Cortese			Erbaluce			Falanghina			Fiano		
	mean	min	max	mean	min	max	mean	min	max	mean	min	max	mean	min	max	mean	min	max
Nerolidol 2	0.36	0.00	1.26	0.07	0.00	0.22	0.00	0.00	0.00	0.23	0.00	0.49	0.64	0.00	2.61	0.00	0.00	0.10
Geraniol	4.70	2.24	7.36	0.90	0.00	2.11	0.09	0.00	0.56	1.18	0.56	2.26	6.47	1.51	20.58	5.40	1.14	18.33
α -Phellandrene	0.00	0.00	0.10	0.07	0.00	0.15	0.08	0.00	0.18	0.00	0.00	0.13	0.05	0.00	0.17	1.32	0.33	3.44
α -Terpinen	0.04	0.00	0.15	0.36	0.22	0.48	0.18	0.12	0.43	0.17	0.00	1.02	0.15	0.05	0.44	6.93	1.71	18.13
4-Carene	0.00	0.00	0.00	0.00	0.00	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.10	0.00	0.44	0.34	0.00	1.43
β -Myrcene	3.74	3.09	5.17	10.60	3.13	15.02	1.61	0.37	6.23	13.46	11.00	15.27	5.42	0.89	17.25	62.59	26.18	124.85
Limonene	0.46	0.22	0.60	2.56	1.27	4.03	2.30	0.72	6.75	1.04	0.74	1.78	3.64	1.33	6.17	40.82	11.56	99.30
1,4-Cineole	0.65	0.28	0.89	1.57	1.34	1.70	0.00	0.00	0.00	1.45	1.07	1.86	0.73	0.00	1.35	1.16	1.01	1.24
1,8-Cineole	0.05	0.00	0.14	0.26	0.08	0.55	0.45	0.00	1.57	0.06	0.00	0.18	1.09	0.28	2.09	1.09	0.45	2.34
p-Cymene	0.41	0.23	0.62	0.78	0.52	0.97	0.30	0.08	0.90	1.13	0.78	2.14	0.89	0.38	2.03	7.75	4.47	14.56
Terpinolene	0.28	0.15	0.37	1.27	0.60	2.22	1.00	0.41	3.29	0.78	0.50	1.28	1.83	0.53	3.45	25.98	6.70	64.01
cis-Linalool oxide	1.69	0.64	3.30	3.07	1.40	6.36	1.98	0.46	4.20	0.83	0.00	2.68	7.09	3.13	11.30	8.16	3.30	19.78
Linalool	2.18	1.44	3.08	5.19	1.58	11.33	4.59	0.88	17.46	2.74	0.41	10.44	36.94	15.27	103.14	46.49	12.69	128.81
Terpinen-4-ol	0.43	0.19	0.69	0.38	0.25	0.65	0.23	0.13	0.41	1.11	0.69	1.55	3.41	2.46	6.00	0.54	0.20	1.22
α -Terpineol	1.44	0.75	2.16	2.25	1.01	4.35	1.65	0.56	4.98	1.83	0.97	4.64	21.47	8.97	32.99	7.33	1.27	18.62
β Citronellol	1.32	0.94	2.34	1.18	0.00	1.89	0.90	0.00	3.62	0.69	0.00	2.19	5.45	2.17	17.51	32.23	11.97	62.67
Nerol	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	7.69	0.92	19.08
trans Rose oxide	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	35.77	12.31	71.57
cis-Rose Oxide	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	5.10	1.69	10.67
β -Damascenone	0.16	0.09	0.22	0.26	0.16	0.53	0.10	0.00	0.19	0.17	0.09	0.42	0.39	0.17	0.79	0.22	0.08	0.45
Vitispirane 1	0.62	0.20	1.17	1.29	0.49	2.06	1.16	0.66	1.83	1.04	0.69	1.56	4.77	2.46	7.02	0.86	0.42	1.16
Vitispirane 2	0.32	0.16	0.57	0.67	0.26	0.99	1.11	0.64	1.65	0.65	0.44	0.84	1.85	1.02	2.84	0.65	0.39	0.90
TPB	0.14	0.09	0.20	0.16	0.12	0.23	0.08	0.04	0.12	0.12	0.07	0.19	0.07	0.04	0.10	0.11	0.06	0.15
TDN	3.53	1.00	7.18	3.73	1.30	5.67	1.82	1.12	3.07	2.83	1.18	4.75	10.00	4.16	14.51	1.67	0.83	2.75
α -Ionone	0.06	0.00	0.11	0.05	0.00	0.15	0.00	0.00	0.00	0.06	0.00	0.19	0.07	0.00	0.27	0.38	0.00	1.05
β -Ionone	0.45	0.31	0.67	0.08	0.05	0.13	0.00	0.00	0.00	0.14	0.09	0.30	0.35	0.18	0.57	0.16	0.05	0.29
Methyl salicylate	0.96	0.43	2.08	0.79	0.50	1.11	0.36	0.15	0.54	9.92	2.18	18.17	0.46	0.32	0.81	1.57	1.07	2.34

Table 2
Volatile compounds concentrations (µg/L) of T60 wines.

Varietà	Albana			Arneis			Cortese			Erbaluce			Falanghina			Fiano		
	mean	min	max	mean	min	max	mean	min	max	mean	min	max	mean	min	max	mean	min	max
VOCs																		
Carbon disulfide	33.98	13.61	44.26	103.14	72.66	140.90	17.85	13.90	24.34	37.09	22.88	49.89	83.44	53.56	140.85	103.86	54.31	155.87
Methanthiol	6.81	4.42	8.76	15.11	10.43	21.74	6.61	5.37	8.86	6.38	5.33	7.71	12.13	6.96	18.97	16.28	8.38	25.84
DMS	12.90	11.33	17.19	12.86	7.26	26.83	7.45	6.04	9.96	7.17	5.99	8.67	13.61	7.65	21.33	17.08	14.96	19.83
Diethyl sulfide DES	0.56	0.38	0.86	0.86	0.49	1.56	0.13	0.09	0.20	0.17	0.12	0.21	0.50	0.33	0.66	0.98	0.34	2.07
Dimethyl disulfide DMDS	0.51	0.38	0.69	2.66	2.17	4.47	0.04	0.00	0.08	0.07	0.06	0.09	0.96	0.20	2.34	1.80	1.22	2.31
Diethyl disulfide DEDS	0.59	0.43	0.76	3.18	2.31	4.13	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.91	1.70	2.23
Dimethyl trisulfide DMTS	0.28	0.20	0.37	1.71	1.30	2.48	0.00	0.00	0.00	0.00	0.00	0.00	0.40	0.00	1.28	1.14	0.74	1.56
Nerolidol 2	0.00	0.00	0.00	0.04	0.00	0.26	0.00	0.00	0.00	0.00	0.00	0.04	0.00	0.00	0.00	0.00	0.00	0.00
Geraniol	0.00	0.00	0.00	0.98	0.00	2.27	0.00	0.00	0.10	0.75	0.00	1.42	1.15	0.00	3.74	0.87	0.00	2.01
α-Phellandrene	0.00	0.00	0.00	0.00	0.00	0.00	0.05	0.00	0.30	0.00	0.00	0.06	0.00	0.00	0.00	0.08	0.00	0.44
α-Terpinen	0.20	0.06	0.48	0.19	0.11	0.31	0.30	0.12	0.60	1.12	0.31	1.78	1.19	0.51	2.78	0.51	0.32	0.71
4-Carene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.04	0.00	0.05	0.04	0.00	0.07	0.00	0.00	0.04
β-Myrcene	0.39	0.08	0.97	0.05	0.00	0.14	1.08	0.80	1.41	2.76	2.74	2.78	11.40	0.76	18.38	0.00	0.00	0.06
Limonene	0.82	0.45	1.43	0.34	0.25	0.45	0.52	0.24	1.12	0.60	0.33	1.00	2.24	0.86	3.82	0.53	0.34	0.78
1,4-Cineole	0.92	0.26	2.73	0.92	0.60	1.34	0.83	0.61	1.19	3.71	1.73	7.56	1.94	0.00	2.74	1.41	0.00	2.59
1,8-Cineole	0.92	0.26	2.20	0.71	0.23	2.12	1.10	0.45	1.90	1.07	0.58	1.81	1.21	0.52	1.75	1.26	0.62	2.27
p-Cymene	0.56	0.32	1.00	1.90	1.15	3.25	0.57	0.35	0.86	4.64	2.28	8.17	2.25	0.84	4.65	1.25	0.53	1.95
Terpinolene	0.44	0.13	1.03	0.17	0.12	0.23	0.45	0.19	1.00	0.69	0.30	1.20	1.97	0.60	3.74	0.40	0.17	0.70
cis-Linalool oxide	14.93	6.62	31.85	7.16	4.06	11.00	15.18	8.47	26.75	5.96	0.72	16.98	11.71	3.70	23.65	22.83	9.11	36.20
Linalool	0.25	0.00	0.56	0.41	0.22	0.82	0.21	0.00	0.53	0.06	0.00	0.15	0.78	0.00	1.54	0.24	0.00	0.85
Terpinen-4-ol	0.14	0.00	0.42	0.34	0.21	0.59	0.30	0.20	0.50	1.20	0.53	2.24	1.20	0.22	2.25	1.60	1.20	2.84
α-Terpineol	1.08	0.37	2.29	0.95	0.72	1.30	1.58	0.59	3.90	3.22	1.37	5.84	6.66	1.00	14.59	7.57	5.13	16.08
β Citronellol	1.36	0.00	3.94	0.37	0.00	2.21	0.15	0.00	0.47	0.00	0.00	0.00	0.15	0.00	0.92	0.34	0.00	2.01
Nerol	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
trans Rose oxide	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
cis-Rose Oxide	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
β-Damascenone	0.18	0.12	0.28	0.46	0.25	0.55	0.22	0.13	0.28	0.37	0.34	0.42	0.44	0.11	0.59	1.15	0.70	1.72
Vitispirane 1	1.52	1.25	2.16	7.45	3.33	13.03	2.29	0.72	2.94	3.53	1.62	5.63	31.70	4.80	102.96	4.20	2.43	5.64
Vitispirane 2	0.82	0.71	1.03	3.94	1.33	6.18	1.11	0.24	1.70	1.78	0.73	3.25	19.36	2.25	73.22	2.23	1.20	3.48
TPB	0.32	0.16	0.57	0.72	0.36	1.02	0.49	0.40	0.57	0.64	0.63	0.64	1.13	0.16	2.45	0.45	0.31	0.58
TDN	18.80	12.67	34.55	30.49	24.59	40.77	54.92	26.66	105.88	43.12	33.67	53.25	171.01	18.28	419.98	31.20	24.32	40.10
α-Ionone	0.08	0.04	0.21	0.10	0.00	0.18	0.00	0.00	0.05	0.05	0.00	0.09	0.18	0.00	0.62	0.27	0.14	0.41
β-Ionone	0.00	0.00	0.00	0.00	0.00	0.07	0.09	0.00	0.13	0.34	0.27	0.42	0.12	0.00	0.31	0.00	0.00	0.00
Methyl salicylate	1.75	0.99	2.69	1.64	0.81	2.77	1.90	0.99	3.75	10.62	7.35	18.34	1.54	0.94	2.72	3.99	2.58	5.54

Garganega	Greco			Lugana			Muller Thurgau			Nosiola			Pallagrello					
	mean	min	max	mean	min	max	mean	min	max	mean	min	max	mean	min	max			
VOCs																		
Carbon disulfide	15.52	13.01	21.89	535.74	493.53	637.40	24.03	16.18	39.92	332.52	204.56	534.27	157.62	88.67	263.81	94.05	62.40	114.02
Methanthiol	3.60	0.81	6.68	1.96	0.91	4.07	7.62	6.19	10.35	20.48	12.70	28.85	18.68	10.12	32.50	11.54	6.88	17.42
DMS	7.77	5.96	10.57	67.01	56.31	74.65	8.52	6.34	11.64	30.80	20.11	37.64	39.91	22.65	61.78	9.18	6.15	11.17
Diethyl sulfide DES	0.09	0.05	0.15	2.05	1.78	2.58	0.20	0.10	0.32	1.72	1.46	2.38	0.91	0.68	1.40	0.94	0.54	1.59
Dimethyl disulfide DMDS	0.05	0.00	0.13	3.56	3.21	3.85	0.08	0.07	0.10	2.85	0.84	5.85	1.31	0.88	1.90	1.34	0.87	2.33
Diethyl disulfide DEDS	0.00	0.00	0.00	1.43	1.33	1.52	0.00	0.00	0.00	0.66	0.04	1.30	0.33	0.24	0.49	0.98	0.79	1.16
Dimethyl trisulfide DMTS	0.00	0.00	0.04	0.30	0.17	0.40	0.00	0.00	0.00	0.14	0.04	0.29	0.15	0.05	0.42	0.53	0.31	0.99
Nerolidol 2	0.00	0.00	0.06	0.00	0.00	0.00	0.15	0.00	0.45	0.04	0.00	0.25	0.00	0.00	0.00	0.06	0.00	0.34
Geraniol	0.89	0.00	3.74	0.58	0.36	1.10	0.80	0.00	1.43	0.74	0.37	1.10	1.60	0.93	2.15	0.08	0.00	0.47
α-Phellandrene	0.00	0.00	0.00	0.09	0.00	0.28	0.00	0.00	0.04	0.15	0.04	0.40	0.05	0.00	0.08	0.00	0.00	0.04
α-Terpinen	0.12	0.00	0.32	0.30	0.00	0.55	0.55	0.28	0.71	0.14	0.00	0.31	0.19	0.00	0.86	0.17	0.00	0.30
4-Carene	0.00	0.00	0.00	0.15	0.07	0.25	0.00	0.00	0.05	0.36	0.00	0.85	0.34	0.00	0.72	0.00	0.00	0.04
β-Myrcene	1.13	0.00	2.88	1.53	0.76	2.13	2.15	0.23	3.42	2.13	1.30	2.90	0.95	0.38	1.70	0.09	0.00	0.31

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Table 2 (continued)

Varietà	Albana			Arneis			Cortese			Erbaluce			Falanghina			Fiano		
	mean	min	max	mean	min	max	mean	min	max	mean	min	max	mean	min	max	mean	min	max
Limonene	0.20	0.05	0.43	1.20	0.57	1.80	0.40	0.30	0.55	1.28	0.46	1.66	0.48	0.19	0.91	0.45	0.00	0.96
1,4-Cineole	0.72	0.11	1.11	0.61	0.33	0.88	2.55	1.68	3.37	0.89	0.53	1.17	0.57	0.24	0.91	0.98	0.28	1.42
1,8-Cineole	0.31	0.19	0.57	0.45	0.26	0.62	0.54	0.26	0.69	1.30	0.86	1.95	0.61	0.23	0.93	1.23	0.47	3.83
p-Cymene	0.54	0.18	0.91	0.92	0.53	1.29	3.78	2.50	5.19	1.37	0.76	2.77	0.71	0.23	1.24	0.66	0.31	0.97
Terpinolene	0.13	0.05	0.34	0.91	0.45	1.39	0.41	0.31	0.64	1.37	0.45	3.29	0.38	0.24	0.61	0.23	0.07	0.40
cis-Linalool oxide	9.42	5.08	18.44	8.88	7.20	12.55	7.73	3.81	15.30	25.20	9.83	49.14	23.13	8.88	35.11	16.05	9.26	21.46
Linalool	0.52	0.00	0.99	0.10	0.00	0.30	0.05	0.00	0.29	0.23	0.00	1.30	1.06	0.74	1.83	0.00	0.00	0.07
Terpinen-4-ol	0.60	0.30	1.04	0.14	0.07	0.21	1.25	0.35	3.07	0.70	0.17	1.55	0.73	0.30	1.00	0.30	0.09	0.49
α -Terpineol	1.51	0.90	2.38	0.46	0.26	0.71	2.89	1.00	6.82	2.87	0.40	8.09	4.30	2.40	6.54	0.87	0.18	2.06
β Citronellol	0.32	0.00	0.95	0.46	0.00	0.78	0.59	0.00	2.39	0.29	0.00	0.54	0.72	0.00	1.28	0.00	0.00	0.00
Nerol	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
trans Rose oxide	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
cis-Rose Oxide	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
β -Damascenone	0.47	0.34	0.66	0.34	0.26	0.38	0.51	0.30	0.70	0.39	0.26	0.59	0.56	0.23	0.97	0.51	0.33	0.69
Vitispirane 1	3.97	1.77	7.35	5.18	3.00	7.81	3.58	2.36	4.91	6.45	2.66	16.00	7.65	1.98	14.06	5.05	1.63	7.44
Vitispirane 2	2.31	0.98	4.40	2.49	1.67	3.50	2.06	1.00	3.08	3.03	1.06	8.11	3.94	0.93	7.53	2.94	0.79	4.99
TPB	0.43	0.34	0.57	1.01	0.69	1.40	0.51	0.40	0.61	1.00	0.56	1.45	0.78	0.24	1.41	0.44	0.24	0.58
TDN	42.57	15.88	87.56	71.66	37.66	105.11	32.94	18.45	50.00	55.63	36.99	92.58	52.23	16.88	92.75	30.00	17.88	40.19
α -Ionone	0.06	0.00	0.11	0.00	0.00	0.04	0.04	0.00	0.05	0.04	0.00	0.06	0.16	0.04	0.29	0.25	0.15	0.48
β -Ionone	0.34	0.16	0.52	0.15	0.10	0.19	0.34	0.28	0.39	0.23	0.16	0.34	0.20	0.10	0.35	0.11	0.07	0.13
Methyl salicylate	4.77	3.22	6.19	1.01	0.64	1.80	20.51	11.07	31.86	0.73	0.47	1.04	0.77	0.53	1.20	2.02	0.74	5.74
VOCs	Pinot Grigio			Ribolla Gialla			Vernaccia			Verdicchio			Vermentino			Gewurtztraminer		
	mean	min	max	mean	min	max	mean	min	max	mean	min	max	mean	min	max	mean	min	max
Carbon disulfide	45.51	25.79	59.89	15.77	12.62	20.69	72.22	60.77	83.74	38.84	24.98	57.69	283.89	137.46	681.56	59.81	32.88	78.89
Methanthiol	12.38	7.70	16.51	5.61	4.45	6.53	8.14	5.24	9.97	7.57	6.12	9.76	20.17	6.76	48.40	5.84	4.62	8.67
DMS	16.14	8.65	23.87	5.92	4.25	7.34	11.86	7.14	17.53	8.31	6.56	10.97	35.13	8.17	60.84	6.65	5.19	9.74
Diethyl sulfide DES	0.34	0.17	0.59	0.23	0.07	0.83	0.44	0.35	0.52	0.74	0.28	1.11	1.64	0.66	4.39	0.76	0.39	1.19
Dimethyl disulfide DMSD	0.47	0.28	0.76	0.00	0.00	0.04	1.27	0.64	2.15	1.37	0.18	2.35	1.49	0.43	3.15	0.56	0.26	1.03
Diethyl disulfide DEDS	0.00	0.00	0.00	0.00	0.00	0.00	0.68	0.41	0.88	0.05	0.00	0.08	0.58	0.00	3.00	0.00	0.00	0.04
Dimethyl trisulfide DMTS	0.14	0.04	0.22	0.00	0.00	0.00	0.76	0.58	0.99	0.47	0.06	1.04	0.04	0.00	0.08	0.17	0.08	0.25
Nerolidol 2	0.04	0.00	0.24	0.04	0.00	0.21	0.00	0.00	0.08	0.12	0.00	0.34	0.07	0.00	0.39	0.00	0.00	0.08
Geraniol	0.09	0.00	0.55	0.00	0.00	0.00	0.08	0.00	0.20	0.00	0.00	0.15	1.64	0.63	2.35	10.33	0.00	53.13
α -Phellandrene	0.00	0.00	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.32	0.00	1.11	0.95	0.33	2.02
α -Terpinen	0.21	0.05	0.38	0.59	0.37	0.77	0.15	0.00	0.32	1.03	0.65	1.63	0.09	0.04	0.18	5.96	2.55	11.44
4-Carene	0.00	0.00	0.00	0.00	0.00	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.44	0.23	0.66	0.27	0.04	0.63
β -Myrcene	2.58	0.31	3.25	8.42	6.01	9.79	0.00	0.00	0.07	8.24	4.59	10.66	3.18	0.51	5.69	25.47	7.41	66.30
Limonene	0.40	0.12	0.56	1.55	0.99	2.31	0.56	0.39	0.78	1.53	0.87	3.03	2.41	1.04	5.28	39.04	12.73	66.14
1,4-Cineole	1.22	0.60	1.92	2.05	1.67	2.44	0.20	0.00	0.51	2.58	2.03	3.14	2.37	1.69	3.10	2.92	2.09	4.17
1,8-Cineole	0.47	0.25	0.74	0.83	0.45	1.02	1.07	0.72	1.61	0.56	0.39	0.95	2.29	0.84	7.60	4.01	2.11	6.36
p-Cymene	1.51	0.27	2.47	2.03	1.33	2.88	0.52	0.20	0.87	6.05	4.58	9.76	5.80	4.08	8.69	6.87	3.20	11.43
Terpinolene	0.27	0.14	0.41	1.12	0.66	1.66	0.12	0.06	0.23	1.23	0.76	2.35	5.42	2.63	12.26	25.20	8.52	43.34
cis-Linalool oxide	10.04	5.68	13.84	15.16	10.66	25.78	5.12	1.83	6.80	2.94	1.44	5.17	17.49	7.53	35.68	58.27	41.58	93.36
Linalool	0.00	0.00	0.00	0.58	0.00	1.32	0.22	0.00	0.51	0.00	0.00	0.00	5.62	1.23	23.84	10.69	2.46	26.28
Terpinen-4-ol	0.24	0.16	0.34	0.24	0.15	0.37	0.12	0.00	0.52	0.34	0.12	0.73	2.74	1.57	6.61	2.51	1.35	4.50
α -Terpineol	1.04	0.66	1.41	1.15	0.62	2.05	0.88	0.34	1.15	0.66	0.18	1.50	15.63	5.68	27.19	24.96	9.45	48.68
β Citronellol	0.06	0.00	0.37	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.88	0.92	7.99	15.30	2.54	30.77
Nerol	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	13.91	3.48	20.11
trans Rose oxide	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	32.28	5.22	63.50
cis-Rose Oxide	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3.94	1.62	7.12
β -Damascenone	0.41	0.33	0.47	0.53	0.42	0.66	0.33	0.16	0.60	0.19	0.07	0.32	0.74	0.28	1.51	0.43	0.32	0.67
Vitispirane 1	2.03	0.93	3.56	5.82	2.28	8.40	7.63	3.29	13.43	2.67	0.88	4.18	18.66	10.35	26.98	6.64	3.17	11.09

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Table 2 (continued)

Varietà	Albana			Arneis			Cortese			Erbaluce			Falanghina			Fiano		
	mean	min	max	mean	min	max	mean	min	max	mean	min	max	mean	min	max	mean	min	max
Vitispirane 2	0.97	0.27	1.90	2.74	0.97	4.72	6.05	3.37	9.21	1.33	0.40	2.29	8.37	4.68	12.64	4.52	2.13	7.03
TPB	0.91	0.77	1.11	1.36	0.84	1.78	0.26	0.16	0.39	0.46	0.31	0.53	0.47	0.25	0.78	0.82	0.55	1.17
TDN	44.49	15.50	73.60	57.13	20.89	76.97	55.61	24.61	94.71	36.71	13.13	57.35	161.25	108.40	210.00	18.09	9.59	26.27
α -ionone	0.05	0.04	0.08	0.00	0.00	0.04	0.07	0.00	0.11	0.00	0.00	0.00	0.11	0.04	0.22	0.07	0.00	0.16
β -ionone	0.51	0.38	0.62	0.10	0.07	0.12	0.00	0.00	0.00	0.16	0.09	0.22	0.47	0.25	0.77	0.21	0.11	0.30
Methyl salicylate	1.63	0.53	3.65	1.81	0.82	3.08	0.68	0.44	0.79	21.94	13.26	30.64	0.98	0.50	2.88	1.43	1.04	1.69

In the case of T60 wines, HCA showed the existence of 8 clusters with a different sample distribution. 44 wines formed the largest cluster (C1), whereas the C2, C3, and C4 were of similar size, with 17, 18, and 17 wines, respectively. Finally, C5, C6, C7, and C8 were formed by 2, 9, 3, and 1 samples, respectively (Fig. 2). Similar to Control, HCA clusters were formed of different wine types, and again, in the majority of cases, all samples of the same type belonged to the same cluster. C1 included samples of ALB, CRT, GAR, RIB, PAL, PG, and VRN. C3 grouped LUG, ERB, and VRD wines, as well as C2 did ARN and FIA, while C6 grouped all GRE samples. Interestingly, for some of these wine types, Control samples had already low concentrations of volatile compounds, while others showed high levels of certain target compounds. For example, PAL, along with some ARN and GAR, showed high concentrations of β -damascenone and vitispirane isomers (Fig. 1). Similarly, CRT in Control showed high levels of TDN, TPB, and β -ionone. Typically, these compounds are not prone to losses during wine aging; on the contrary, they tend to accumulate. Indeed, PAL, ARN, and GAR did not show a decrease of these VOCs at T60 compared to the CO (Tables 1 and 2). Instead, other wine types showed a greater accumulation, reaching higher concentrations.

Concerning the other clusters, C2 showed high content of DEDS, DMTS, and megastigmane norisoprenoids, C3 was associated with increased content of methyl salicylate and the terpenes p-cymene and 1,4-cineole. C4 showed generally high concentrations of VSCs and norisoprenoids, while C5 was characterized by high levels of non-megastigmane norisoprenoids. C6 was also characterized by higher concentrations of VSCs. C7 and C8 showed very high levels of all terpenes.

4. Discussion

During aging, a complex network of chemical reactions induces significant changes in wine aroma composition. Leaving aside those that are related to oxidation (Ugliano, 2013); many of these reactions involve the release of volatile compounds from non-volatile glycosidic or amino acidic precursors (Ganss et al., 2011; Loscos et al., 2007, 2008; Stribny et al., 2015) or from copper complexes (Vela et al., 2017) while others are related to the transformation of existing volatiles into other compounds; potentially involving variations in their odor potency (Slaghenaufi & Ugliano, 2018). Many of these reactions have been described previously, and, although they are likely to occur in many if not all wines, they have been shown to be particularly relevant to certain wine varietal types. In the present study, we intended to address the question of whether, in a large set of white wine samples mostly from non-aromatic varieties, changes in volatile composition due to aging could be traced back to the varietal origin of the wine, or conversely, whether aging reduces the varietal diversity of young wines.

4.1. Influence of model aging on volatile profiles

A total of 25 compounds showed statistically significant differences due to model aging (Supplementary 5). Aged wines were in general characterized by increased concentrations of non-megastigmane norisoprenoids such as TDN and TPB, vitispirane, β -damascenone, linalool oxide, several cyclic and bicyclic terpenes, the benzenoid methyl salicylate, and several VSCs. Conversely, Control wines showed higher concentrations of norisoprenoids such as α - and β -ionone, and monoterpene alcohols such as linalool, geraniol, α -terpineol, and β -citronellol. Rose oxides were stable during aging.

We hypothesize that the observed changes are associated with i) acid-catalyzed hydrolysis of different precursors (including glycosidic ones) leading to the release of TDN, TPB, β -damascenone, monoterpene alcohols, and methyl salicylate (Winterhalter, 1991; Parker et al., 2018; Carlin, Masuero, et al., 2019; Carlin, Vrhovsek, et al., 2019; Skouroumounis & Sefton, 2000;); ii) acid-catalyzed cyclization and rearrangements of monoterpenes; leading to the formation of cineoles and

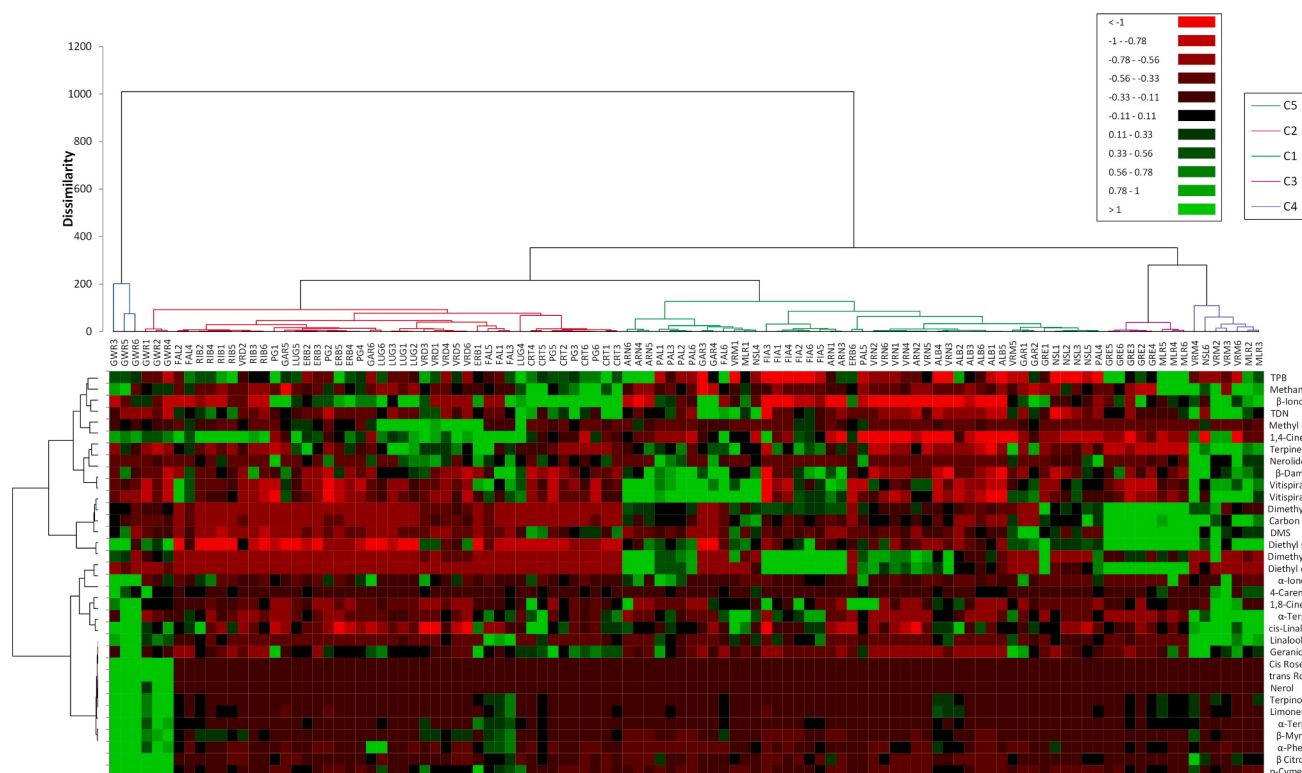


Fig. 1. Heat map and hierarchical cluster analysis of samples and VOCs of Control wines. Green denotes higher concentration, while red lower concentration. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

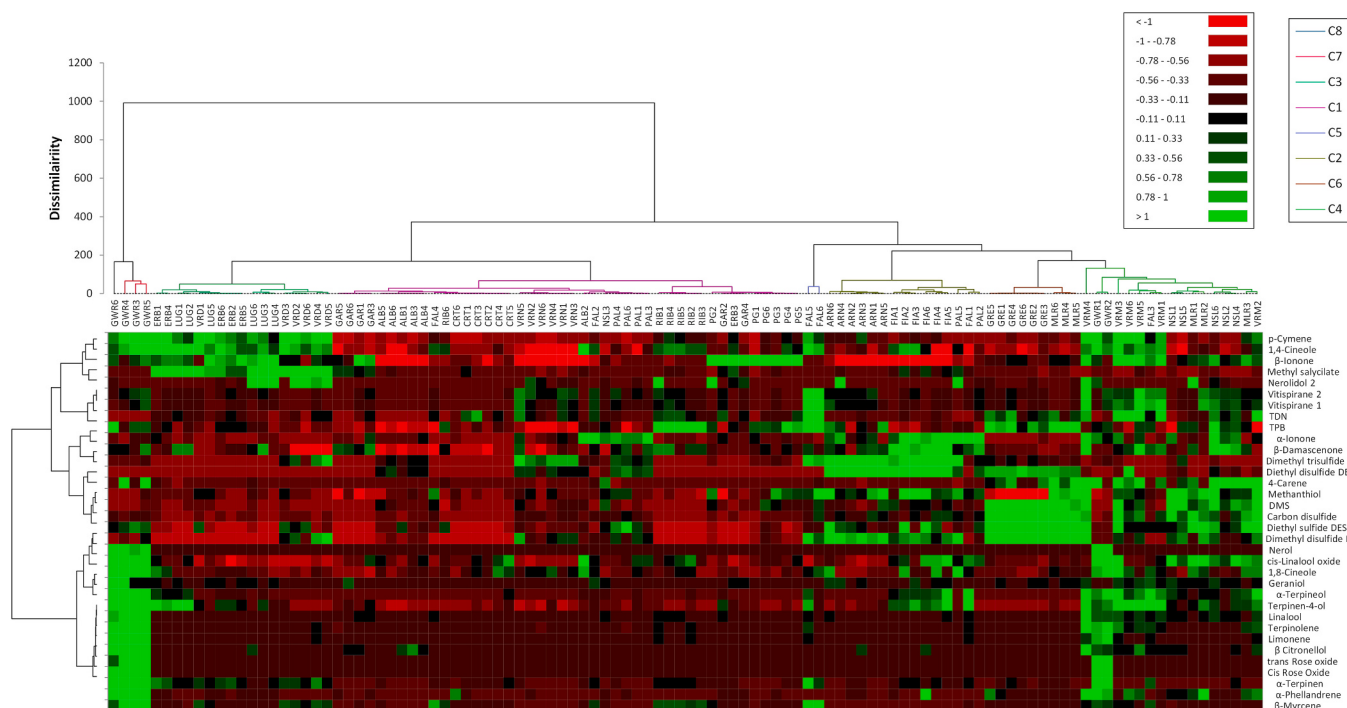


Fig. 2. Heat map and hierarchical cluster analysis of samples and VOCs of T60 wines. Green denotes higher concentration, while red denotes lower concentration. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

other cyclic terpenes (Luzzini et al., 2022; Slaghenauhi & Ugliano, 2018); iii) degradation of sulfur-containing amino acids (methionine and cysteine) and derivatives (e.g. *S*-methyl methionine) leading to the formation of different VSCs (Marchand et al., 2000; Segurel et al., 2004;

Ugliano et al., 2009; Ferreira et al., 2014; Franco-Luesma & Ferreira, 2016; Samaniego Solis et al., 2024;); iv) release of methanethiol (MeSH) from copper-bound forms (Sánchez-Gimeno et al., 2024).

Although to a general level these trends were observed in most of the

wines studied, the extent to which specific compounds were formed or degraded varied considerably depending on the wine. In the case of compounds arising from acid-catalyzed precursor hydrolysis, cyclization and rearrangements, the norisoprenoids TDN, TPB, and vitispirane were found to increase in all wines (Fig. 3a-c), with two samples of FAL reaching very high level of all these compounds, and in particular levels in the range of several hundreds of $\mu\text{g/L}$ for TDN. A varietal effect on the accumulation of these compounds could be observed. Indeed, some varieties that contained low amounts of these compounds in Control (e.g., RIB) showed significantly higher levels in T60. Conversely, varieties with moderate concentrations in Control (e.g. CRT) showed limited accumulation and low concentrations in T60. Although TDN is a well-known key aroma compound of aged Riesling, its occurrence in Italian white wines is less documented and the observation of high TDN potential in some FAL should be considered for the production of these wines. As for β -damascenone, the literature reports different patterns with concentration increasing or decreasing depending on the wine type and storage conditions (Cejudo-Bastante et al., 2013; Sefton et al., 2011; Silva Ferreira & Guedes De Pinho, 2004). In most of the wines studied herein, average concentrations tended to increase with aging, supporting that acid-labile precursors are generally present in white wines (Sefton et al., 2011). Accumulation of β -damascenone could also be due; at least in part; to SO_2 related reactions; as conditions supporting SO_2 consumption favour β -damascenone release (Daniel et al., 2004), which also applies to our T60 modality.

Terpenes showed variable patterns (Fig. 4), in agreement with the literature reporting a wide range of reactions promoted by wine acid environment (Fariña et al., 2005; Luzzini et al., 2022; Slaghenaufi & Ugliano, 2018; Yang et al., 2022). Cineoles showed distinct patterns depending on the wine type. Indeed, the ratio between the two isomers (1,4- and 1,8-cineole) showed high variability after aging (Supplementary 6). The literature reports that acid-catalyzed reactions of hydration/dehydration and cyclization lead to the formation of these compounds from the same pool of linear terpenes, in particular linalool, geraniol, and nerol (Fariña et al., 2005; Luzzini et al., 2022; Slaghenaufi & Ugliano, 2018). Significant correlations (p -value < 0.5) were observed between the sum of bicyclic terpenes (1,4 and 1,8-cineole) in T60 and linear terpenes ($p = 0.499$) as well as cyclic terpenes ($p = 0.50$) in Control. Regarding the two cineoles, they showed significant correlations with individual terpene precursors. 1,4-cineole showed the strongest correlations with terpinen-4-ol ($p = 0.577$), while 1,8-cineole correlated with α -terpineol ($p = 0.530$) and linalool ($p = 0.478$) (Supplementary 7). A significant correlation was also observed between the ratios of 1,4-cineole/1,8-cineole in T60 samples and terpinen-4-ol/ α -terpineol in Control (Supplementary 8), the latter being reported as two key precursors in their formation (Slaghenaufi & Ugliano, 2018). This observation suggests that although 1,4- and 1,8-cineole may theoretically be formed from the same precursors; the formation of one cineole over the other is preferential depending on the precursor. This observation is also in agreement with the global kinetic and thermodynamic modelling of the reactions of monoterpenoids occurring in wine (Arapitsas et al., 2024). In this case, wine types with higher levels of α -terpineol or linalool yielded higher amounts of 1,8-cineole, while wine types with higher levels of terpinen-4-ol produced greater amounts of 1,4-cineole.

MeSA content generally increased after aging, with ERB, LUG, and VRD accumulating up to $25 \mu\text{g/L}$ (Fig. 5a). While MeSA has been previously associated with the aging of LUG and VRD wines (Carlin, Vrhovsek, et al., 2019; Fracassetti et al., 2020; Slaghenaufi, Luzzini, et al., 2021; Slaghenaufi, Luzzini, et al., 2022; Slaghenaufi, Vanzo, et al., 2022), the observation of high MeSA levels in aged ERB wines has not been previously reported to our knowledge. Although MeSA release from glycosidic precursors is a key pathway, degradation and transesterification should also be considered (Cheng et al., 2021; Gutierrez et al., 2023; Slaghenaufi, Luzzini, et al., 2021; Slaghenaufi, Peruch, et al., 2021).

VSCs levels generally increased with aging, in particular in GRE, MLR, NSL, and VRM wines (Fig. 6). DMS and MeSH were typically the most abundant VSC at the end of the aging period, whereas DES, DEDS, DMDS, and DMTS attained much lower concentrations. The release of DMS during aging is a well-known phenomenon and primarily depends on the degradation of its precursor, *S*-methylmethionine and is greatly enhanced by the temperature, given that the hydrolytic release of DMS from *S*-methylmethionine has a high activation energy barrier, $EA = 186 \pm 12 \text{ kJ/mol}$ (Scheuren et al., 2014). Photo-oxidative degradation of methionine can also result in increased MeSH and DMDS concentrations (Carlin, Mattivi, et al., 2022; Fracassetti et al., 2019), although this should not occur in our samples as model aging was carried out in the dark.

4.2. Varietal aspects of wine classification before and after aging

Both in Control and aged wines, the HCA clusters (Figs. 1 and 2) did not correspond to a single wine type. However, the majority of the samples of the same type were grouped in the same cluster, with a few exceptions.

In Control, the HCA formed 5 clusters, while at T60 this number increased to 8. This suggests that, over time, chemical processes promoted greater differentiation among the sample set, resulting in a more complex clustering structure.

Interestingly, in Control (Fig. 1) few wine types formed homogeneous sub-clusters, while the majority appeared rather dispersed within the same group. For example, in C1, FIA, VRN, and ALB showed very low distance. In C2, on the other hand, a sub-cluster was observed for VRD and LUG. Conversely, some wine types were splitted across the clusters, such as GWR, MLR, and VRM. GWR and VRM are two wine types produced with aromatic and semi-aromatic grapes (Carlin, Lotti, et al., 2022; Skinkis et al., 2008). For this reason, it could be expected to obtain defined chemical profiles strongly characterized by terpenic markers. Interestingly, in T60 wines (Fig. 2), compared to Control, a greater number of sub-clusters comprising all samples of specific wine types were observed: ALB, CRT, VRN, PG, GAR, and RIB in C1; ARN and FIA in C2; VRD, ERB, and LUG in C3; and GRE in C6.

Seven wine types, including ALB, CRT, GAR, PAL, PG, RIB, and VRN, showed volatile chemical profiles lacking volatile markers, as already observed in Control. Therefore, they did not develop distinctive volatile compounds with aging and maintained relatively low levels of VOCs. However, it was interesting to observe that in Control (Fig. 1), these wine types were dispersed within the clusters they belonged to, with no homogeneous sub-clusters being observed, except for VRN, PAL, and ALB in C1. Conversely, in T60 wines (Fig. 2), it was possible to evidence that, within the clusters, many homogeneous sub-clusters were identified, including ALB, ARN, CRT, FIA, VRN, PG, GAR, and RIB in C1, and GRE in C6. Although no specific volatile markers were associated with this stronger classification, volatile chemical patterns were better defined overall, making wines of the same type more similar to each other. Only ARN showed quite high contents of MeSH, DEDS, and DMTS in T60, being clustered together with FIA (Figs. 2 and 6d). Although FIA was grouped in C1 in Control, it already showed a relatively high content of MeSH, DEDS, and DMTS, along with an intermediate level of norisoprenoids. In T60, besides showing a high content of certain VSCs and MeSH like ARN, FIA also showed high levels of megastigmane norisoprenoids such as α -ionone and β -damascenone. FIA was the only wine type that showed a significant increase in DEDS and DMTS, while the other types showed only minor differences, up to $1.72 \mu\text{g/L}$, which enhance the fruity aromas of wines (Pineau et al., 2007). Both ARN and FIA showed a significant increase in MeSH; from around $2.7 \mu\text{g/L}$ to $15.1 \mu\text{g/L}$ and $16.3 \mu\text{g/L}$; respectively; on average (Fig. 6d). In Burgundy Chardonnay; MeSH has been positively linked with perceived minerality (Rodrigues et al., 2017); however; it is also usually associated with *light struck* fault; as the result of the photocatalytic degradation of riboflavin (Carlin, Mattivi, et al., 2022; Grant-Preece et al., 2017). The

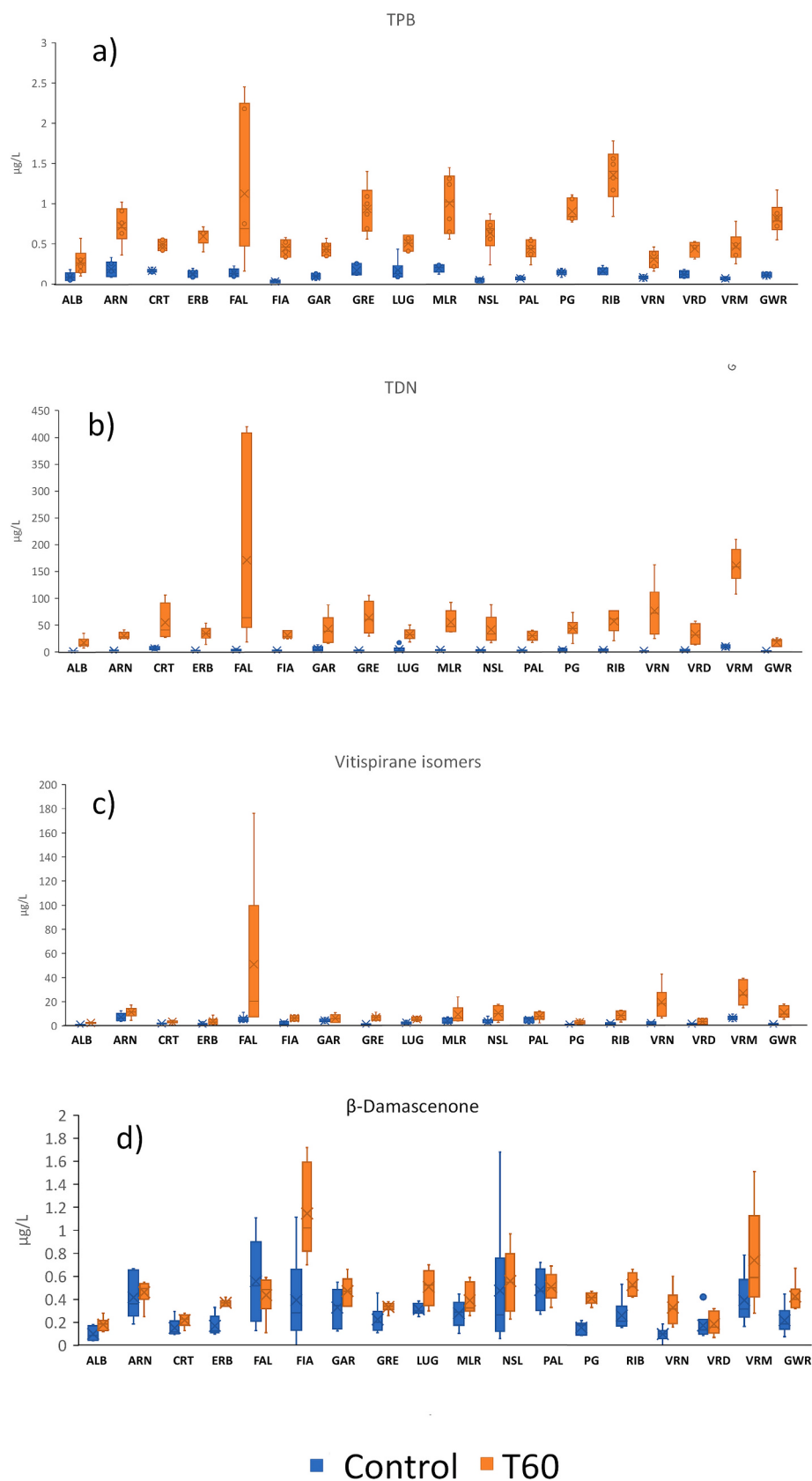


Fig. 3. Concentration of a) TPB, b) TDN, c) sum of vitispirane isomers and d) β -damascenone in different wine types in Control and T60+.

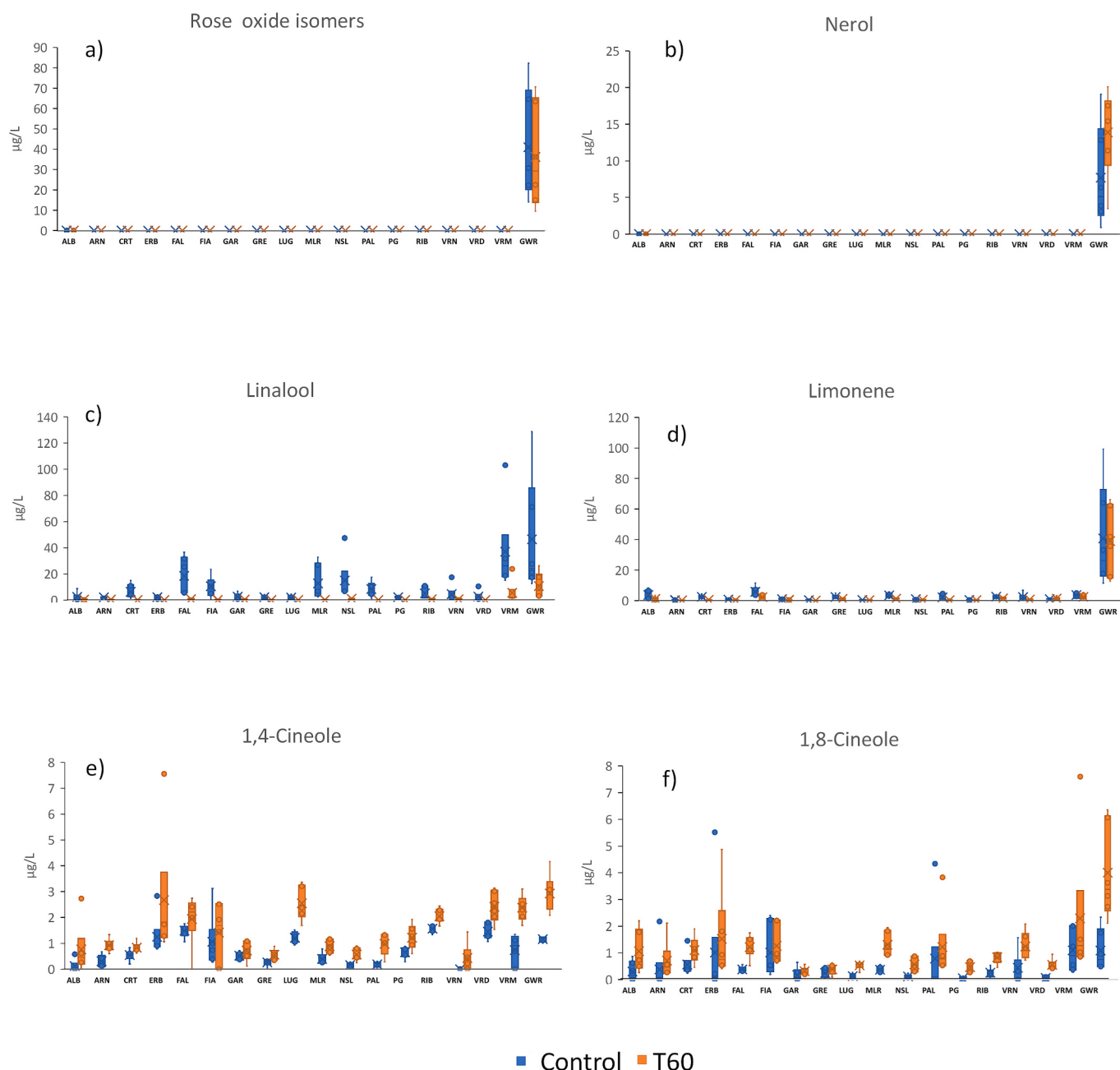


Fig. 4. Concentration of a) Rose oxide isomers, b) Nerol, c) Linalool, d) limonene, e) 1,4-cineole, and f) 1,8-cineole in Control and T60. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

concentrations observed herein for MeSH are of particular sensory relevance in light of the reported odor threshold of 5.7 $\mu\text{g/L}$ in white wines (Solomon et al., 2010).

ERB, LUG, and VRD were clustered together both in Control and T60. However, in Control, they were grouped with other wine types in C2, with most VRD and LUG samples being very similar to each other, while ERB samples were dispersed within the cluster. At T60, on the other hand, LUG, VRD, and ERB were grouped together without other wine types in C3, forming a very cohesive group. While LUG and VRD are primarily produced with the same grape variety (Trebiano di Lugana), ERB is a wine type produced from Erbaluce grape variety (Italian Catalogue of Grapevine Varieties—Catalogo Nazionale Delle Varietà Di Vite. Available Online: <http://Catalogoviti.Politicheagricole.It> (Accessed on 26 January 2025)., n.d.; Vantini et al., 2003). The classification of these three wine types at T60 was based on the high levels of

mainly MeSA and 1,4-cineole (Figs. 4e and 5a). In T60 LUG showed a mean content of MeSA of 21 $\mu\text{g/L}$; VRD of 22 $\mu\text{g/L}$; and ERB 11 $\mu\text{g/L}$. In Control; however, MeSA was found in high content in VRD and LUG (mean content of 10 $\mu\text{g/L}$); while ERB showed much lower levels (mean content of 3.3 $\mu\text{g/L}$). Free MeSA has been reported as a marker of VRD and LUG; while recently a high content of glycosidic precursors has been reported in LUG; VRD; and also ERB (Piergiorganni et al., 2023; Slaghenauft, Luzzini, et al., 2021; Slaghenauft, Peruch, et al., 2021). In a hypothetical scenario where in T60 MeSA is excluded from classification analysis by means of HCA, the absence of this molecule leads to the merging of C3 and C1 clusters and to a significant increase in the scattering of ERB, LUG, and VRD samples, even within the same wine type (Supplementary 9). Similarly, the ability to classify these three wine types strongly decreased in the absence of 1,4 cineole (Supplementary 9). Indeed, although 1,4-cineole cannot be considered a specific marker

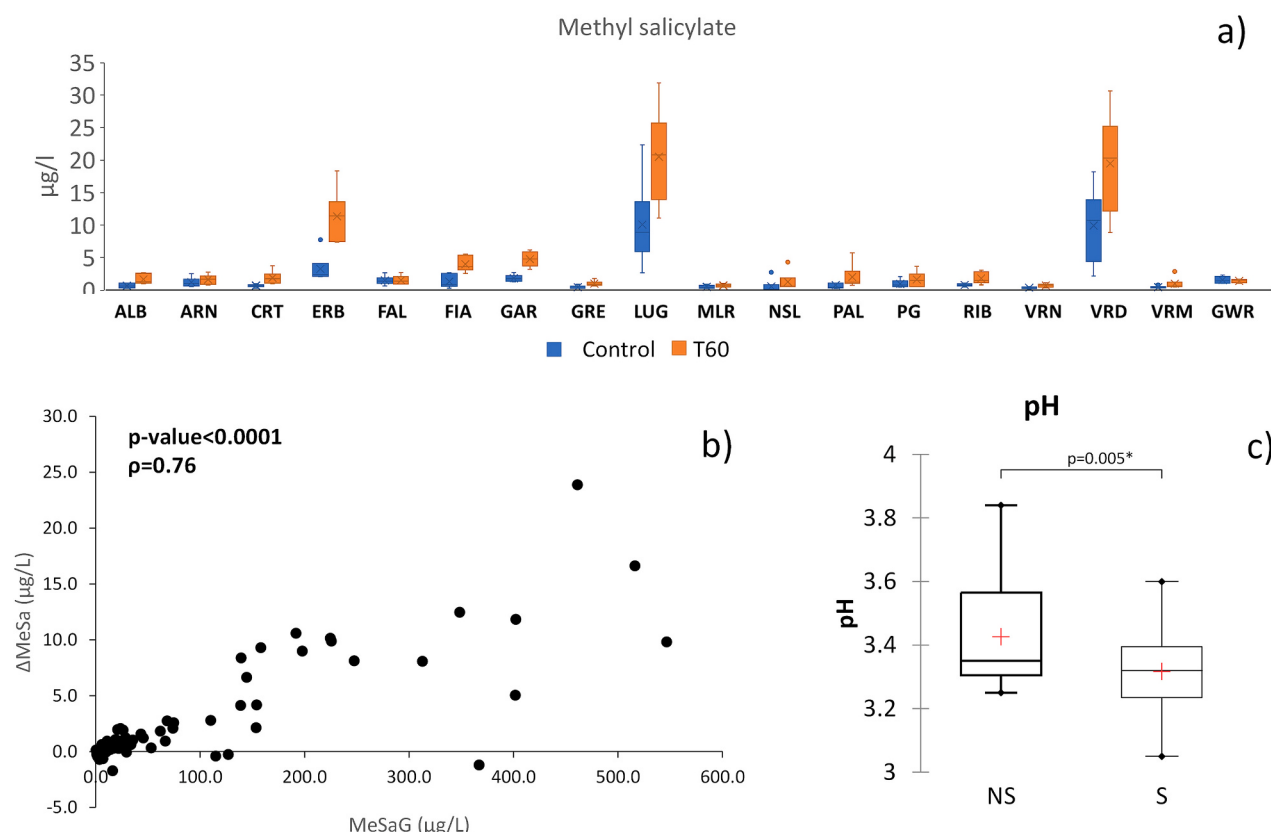


Fig. 5. a) Concentration of methyl salicylates in Control and T60 wines. b) Correlation between total MeSA glucoside and delta of free MeSA in T60, c) pH of wines with significant (S) and non-significant (NS) increase of free MeSA after aging.

for these wine types, they nevertheless showed very high levels, comparable to aromatic or semi-aromatic wine varieties such as GWR or VRM (3.7 µg/L in the case of ERB and 2.6 µg/L in the case of LUG and VRD) (Fig. 4e). Slaghenaufi, Luzzini, et al. (2021) and Slaghenaufi, Peruch, et al. (2021) already reported high concentrations of 1,4-cineole in both VRD and LUG. However, this is the first time it has been reported for ERB, and especially in comparison with such a wide range of Italian wine types.

Under accelerated aging, MeSA content generally increased, with ERB, LUG, and VRD accumulating up to 25 µg/L, although some samples showed no accumulation or even a slight decrease. This trend was not variety-specific, as nearly all varieties included samples with different trends. While MeSA release from glycosidic precursors is a key pathway, hydrolysis and transesterification should also be considered (Cheng et al., 2021; Gutierrez et al., 2023; Slaghenaufi, Luzzini, et al., 2021; Slaghenaufi, Peruch, et al., 2021). A positive correlation ($\rho = 0.76$) was observed between free MeSA increase after aging and MeSA glucoside content in Control wines (Fig. 5b). A role in MeSA accumulation was also observed for pH. Wines were divided into two groups, showing a significant increase of free MeSA (S) and not showing (NS) according to the *t*-test ($\alpha = 0.05$). NS wines showed higher pH (Kruskal-Wallis, $\alpha = 0.05$), suggesting that lower pH enhances MeSA release from precursors (Fig. 5c). In summary, MeSA accumulation during aging depends on precursor availability, degradation pathways, and pH-dependent release mechanisms. Although in the present study MeSA concentrations did not attain the reported sensorially-relevant concentrations of 38 µg/L (Slaghenaufi, Luzzini, et al., 2022; Slaghenaufi, Vanzo, et al., 2022), MeSA wine content is strongly impacted by vintage and grape geographical origin (Carlin, Masuero, et al., 2019; Carlin, Vrhovsek, et al., 2019), so in relevant varieties MeSA should still be considered a aging marker, potentially contributing to fresh balsamic attributes.

Regarding GRE and MLR 4–6, they were clustered together in both

Control and T60. This cluster was consistently characterized by high levels of VSCs (DMS, DES, and DMDS), despite metabolic differences in both treatments. MLR1–3 were instead clustered in another group. The MLR wines, therefore, showed two distinct volatile chemical patterns both in Control and T60 (Supplementary 10). Although all MLR wines showed a higher content of VSCs compared to the other varieties, MLR 1–3 displayed a lower content of VSCs compared to MLR 4–6, while simultaneously were richer in terpenes and norisoprenoids, similar to the wines belonging to C1 and C4 in Control and C4 in T60 (Figs. 1 and 2). These results therefore showed that while GRE, with aging, evolves towards aroma profiles characterized by sulfur compounds, MLR instead showed different styles that can be characterized either predominantly by VSCs or, conversely, by a quite high content of VSCs, terpenes or norisoprenoids. For Greco di Tufo, the literature does not report many studies characterizing its volatile chemical profile, and none of them reports the content of VSCs (Baiano et al., 2017; Carpentieri et al., 2019; Nasi et al., 2008). Among VSCs, DMS increase during aging is due to the degradation of *S*-methylmethionine, while MeSH, DMDS, and DMTS are released from precursors such methionine or in the case of MeSH also from complexes formed with copper (Clark et al., 2015; Ferreira et al., 2014; Franco-Luesma & Ferreira, 2016; Segurel et al., 2005).

FAL showed a different aging pattern. Indeed, while at Control it was mostly clustered in C2 (FAL1–5) and C1 (FAL6), after accelerated aging it showed different volatile patterns, being grouped into four distinct clusters (C1,C2,C4,C5). The main drivers of variability for this wine type, in particular at T60, were non-megastigmane norisoprenoids, namely vitispirane isomers, TPB, and TDN, which showed variations among the wines of up to 23-fold (Fig. 3). These compounds are associated with odors of camphor, kerosene, and tobacco (Daniel et al., 2009; Janusz et al., 2003; Slaghenaufi & Ugliano, 2018). Their origin is reported to be due to carotenoids degradation (Mendes-Pinto, 2009). In general, very different aging patterns were found within FAL; with

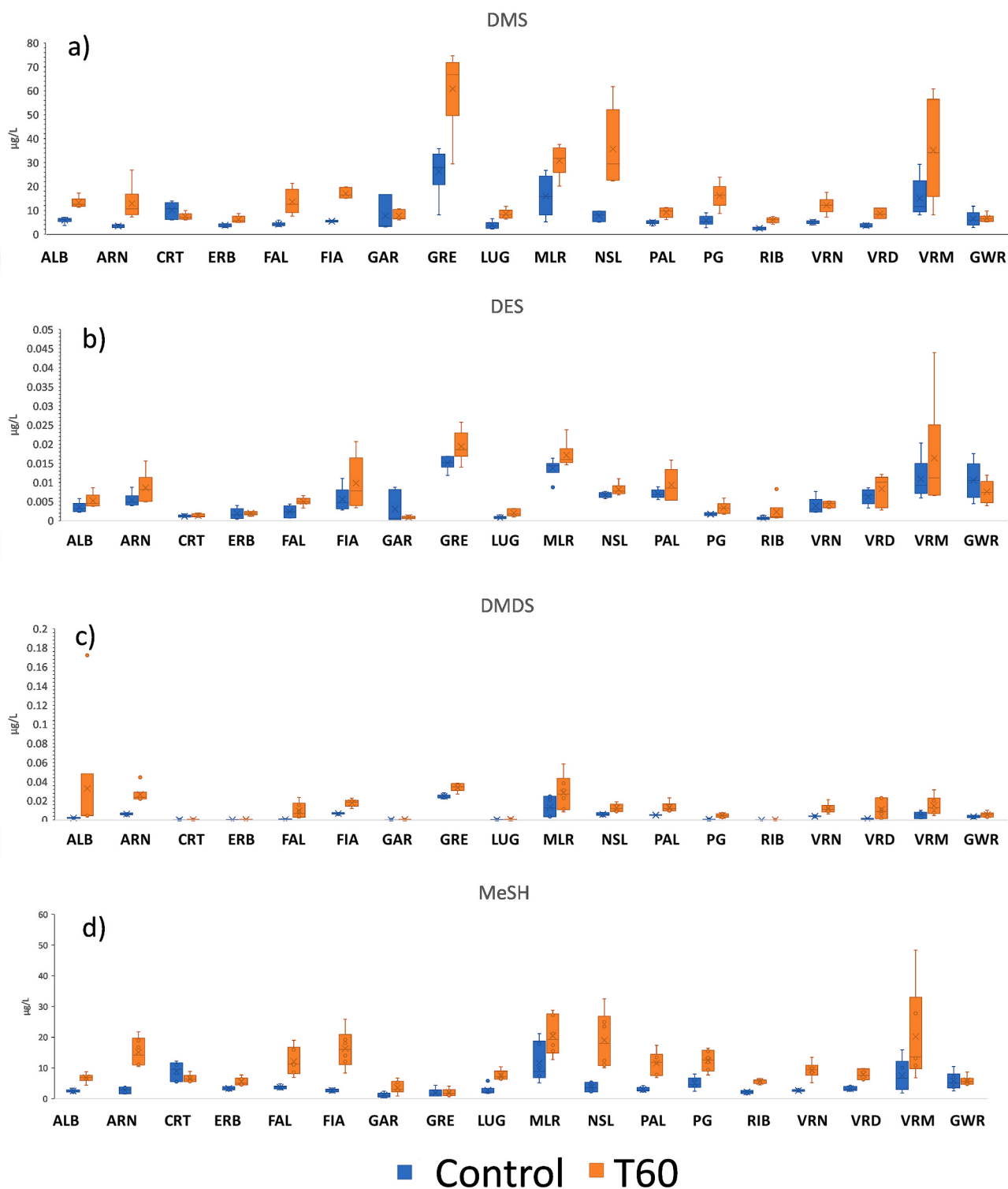


Fig. 6. Concentration of a) DMS, b) DES, c) DMDS and d) MeSH in Control and T60 wines.

either a high content of non-megastigmane norisoprenoids (FAL5 and FAL6); a rather neutral profile (FAL2 and FAL4); a quite high content of some VSCs (FAL1); or a relatively high content of all volatile compounds (FAL3); with the exception of some terpenes. Few studies have addressed the volatile chemical profile of Falanghina wine (Carpentieri et al., 2019; De Filippis et al., 2019; Moio, Ugliano, Gambuti, et al., 2004; Moio, Ugliano, Genovese, et al., 2004). However, to date, no study has reported the occurrence of such high content of non-megastigmane norisoprenoids after aging treatment.

Control samples of NSL and VRM showed different patterns, being grouped in two different clusters: NSL in C1 and VRM in C4, this last cluster being rather rich in terpenes and norisoprenoids (Fig. 1). After accelerated aging, the two varieties were found to be clustered together in C4, a cluster with quite high levels of almost all volatile compounds such as terpenes, norisoprenoids, volatile sulfur compounds, and MeSH (Fig. 2) compared to the others. While VRM showed a profile generally rich in volatile compounds already in Control samples, NSL did not. This difference in NSL patterns in Control and T60 could be due to a high

precursor content in Control. The literature does not provide information on the volatile profile of Nosiola. VRM showed high concentrations of some terpenes, such as linalool, terpinen-4-ol, α -terpineol, geraniol, 1,8-cineole, linalool oxide, and nerol, which were comparable to those found in GWR. In contrast, other terpenes, such as α -phellandrene, α -terpinen, β -myrcene, β -citronellol, rose oxide isomers, terpinolene, and limonene showed low concentrations, similar to those of the other wine types. Not only the total terpene content is known to be influenced by the grape varieties used, but also the patterns of individual terpenes (Black et al., 2015; López-Tamames et al., 1997; Slaghenaufi et al., 2019), in accordance with the results obtained from this study.

GWR was the only wine type produced from an aromatic variety (Guth, 1997; Skinkis et al., 2008), and in fact, was found to be rich in terpenes, being the only wine characterized by the presence of terpenoids such as rose oxide isomers and nerol, both in Control and T60 (Fig. 4). In Control, the wines were clustered into two groups: C5, which included GWR 3, 5, and 6, and C2, which included GWR 1, 2, and 4. However, the GWR wines in C2 were less similar to the other types in the same cluster and these three GWR formed a subcluster. C2 was a rather neutral cluster and the inclusion of wines produced from an aromatic variety such as Gewürztraminer was surprising, but it could depend on the fact that these three GWR, despite high content of the majority of terpenes, also showed rather low content of other terpenes such as geraniol, linalool, 1,8-cineole, α -terpineol, 4-carene, and linalool oxide. In T60, the samples were grouped into three clusters: two clusters (C7 and C8) consisting of 4 samples of GWR 3, 4, 5, and 6. GWR 1 and 2, on the other hand, were clustered into C4, a group that includes samples of VRM, NSL, and MLR. In general, although GWR showed the highest average terpene content, it also showed significant variability within the wine type, both in Control and T60. Terpenoids evolution is known to be influenced by pH and temperature, these factors have been much investigated in Gewürztraminer (Arapitsas et al., 2024). GWR showed significantly higher average pH value compared to the other varieties; between 3.61 and 3.77 (Table 1); which could have contributed to modulating the reaction speed and thus the occurrence and the patterns of certain terpenes; characteristic of GWR. Similar high values (3.80) were also observed in a single VRM wine (Table 1). Remarkable observations concern 1,4- and 1,8-cineole. According to the literature; formation of 1,8-cineole in GWT wines is significantly slower at 298 K than that of 1,4-cineole (about 90 times) but increases at higher temperatures more than the latter (Arapitsas et al., 2024). This was the case also in our study (Supplementary fig. 6). Compared to the content of other terpenoids; the differences between GWR and the other varieties were much smaller (Fig. 4). Additionally; many significant differences of cineoles among wine types were reported. Again; the high pH value of GWR may have contributed to a low yield of cineoles from the abundant pool of terpene precursors. 1,4- and 1,8-cineole potentially play an important sensory role during aging with their pleasant hay-like and balsamic aromas. Indeed; compared to the perception thresholds of the other cyclic and bicyclic terpenes; their thresholds are significantly lower; 0.63 $\mu\text{g/L}$ and 1.3 $\mu\text{g/L}$ (Antalick et al., 2015) respectively. Cineoles have been reported in high concentrations in some Italian wines; such as Durello; Lambrusco; Montepulciano; Raboso; Sangiovese; and Valpolicella (Luzzini et al., 2023; Luzzini, Bicego, Slaghenaufi and Ugliano, 2025; Slaghenaufi, Vanzo, et al., 2022). However, 1,4-cineole contributed more significantly than 1,8-cineole to the classification of wine types. If 1,4-cineole is removed, the number of clusters is reduced and at the same time the diversity among wines of the same type increases (supplementary 9). Conversely, the absence of 1,8-cineole showed much lower impact on wine classification (supplementary 9). This is because 1,4-cineole showed distinct aging patterns compared to 1,8-cineole and other terpenes (Fig. 4). Conversely, 1,8-cineole was clustered with many other terpenes to which it was correlated, meaning the impact of its absence could be “buffered” by the presence of other terpenes.

5. Conclusions

This study elucidates for the first time the chemical bases underlying the relationship between grape variety and white wine aroma aging, using a quantitatively-relevant dataset of 18 Italian monovarietal white wines, for a total of 108 wine samples. The results highlighted specific aging patterns for each wine type, underlining the role played by each class of volatile compounds. On one hand, aging to increase the complexity of classification by promoting a greater number of clusters. On the other hand, while it was possible to classify wines of the same type into the same group both before and after accelerated aging, the aging process enhanced type-driven volatile profile specificity.

For certain wine types aging was associated with characteristic markers. Verdicchio, Lugana, and Erbaluce showed high levels of methyl salicylate and 1,4-cineole. Greco was characterized by a high content of volatile sulfur compounds, DMS in particular. Vermentino and Nosiola showed generally high levels of almost all compounds. For other wine types aging affected several volatile compounds but in a more subtle way and with no specific marker. This was the case for Albana, Arneis, Cortese, Garganega, Pallagrello, Ribolla Gialla, Vernaccia, and Fiano, despite the latter showed a significantly higher content of β -damascenone compared to other wine types.

Some samples showed different aging patterns within the same wine type. This was the case for Falanghina, which showed different chemical patterns, including one very rich in non-megastigmane norisoprenoids such as TPB, TDN, and vitispirane isomers. Müller-Thurgau showed two distinct aging patterns: one similar to Greco, rich in sulfur compounds, and another similar to Vermentino and Nosiola, with high content of all studied compounds. Lastly, Gewürztraminer was generally found to be rich in terpenes but with significant variability. In fact, in some cases, the terpene content was lower than that of some non-aromatic wines.

Finally, the observation of a significant correlation between MeSA glycosylated precursor and MeSA formation during aging, and of a relationship between the content of bicyclic terpenes and the ratio of their precursor α -terpineol and terpinen-4-ol highlights the possibility to rationalize and to some extent predict wine aging patterns, which will ultimately support wine producers to develop tailored vineyard and/or winery techniques for optimal aroma aging.

Limitations of the study

Wine aging has timescales that are not compatible with research timeframe, so a model protocol was used for accelerated aging of wine. However, it is known that increased temperature can promote certain reactions more than others. This results in not perfect overlap between accelerated aging and aging in cellar conditions.

Compliance with ethics requirements

This study does not involve research on human participants or animals.

CRediT authorship contribution statement

Giovanni Luzzini: Writing – review & editing, Writing – original draft, Investigation, Formal analysis, Conceptualization. **Nicole Furlan:** Writing – original draft, Formal analysis. **Davide Slaghenaufi:** Formal analysis, Data curation. **Maurizio Piergiorgio:** Formal analysis. **Silvia Carlin:** Formal analysis, Data curation. **Fulvio Mattivi:** Funding acquisition, Conceptualization. **Susana Rfo Segade:** Conceptualization. **Simone Giacosa:** Conceptualization. **Paola Piombino:** Conceptualization. **Elisabetta Pittari:** Data curation. **Giuseppina Paola Parpinello:** Data curation, Conceptualization. **Arianna Ricci:** Data curation, Conceptualization. **Matteo Marangon:** Data curation, Conceptualization. **Christine Mayr Marangon:** Formal analysis, Conceptualization. **Maurizio Ugliano:** Writing – review & editing, Writing – original draft,

Funding acquisition, Data curation, Conceptualization.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.fochms.2026.100397>.

Data availability

The authors declare that the data supporting the findings of this study are available within the paper and its Supplementary Information files. Should any raw data files be needed in another format they are available from the corresponding author upon reasonable request.

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Glossary

DMS: Dimethyl sulfide
DMS: Dimethyl disulfide
DEDS: Diethyl disulfide

DMTS: Dimethyl trisulfide
HCA: Hierarchical Cluster Analysis
MeSA: Methyl salicylate
MeSH: Methanethiol
PAN: Primary amino nitrogen
PDO: Protected Designation of Origin

TDN: 1, 1, 6, –trimethyl-1,2-dihydronaphthalene
TPB: 4-(2,3,6-trimethylphenyl)buta-1,3-diene
PDMS: Polydimethylsiloxane
CAR: Carboxen
DVB: Divinylbenzene
VSCs: Volatile Sulfur Compounds