

Article

Aromatic Profiles and Vineyard Location: Uncovering Malvasija Dubrovačka Wines

Domagoj Ivan Žeravica ^{1,†}, Ivana Tomaz ^{2,3,*}, Darko Preiner ^{2,3}, Iva Šikuten ^{2,3}, Domagoj Stupić ², Ana Jeromel ² and Edi Maletić ^{2,3}

¹ Department of Mediterranean Plants, University of Dubrovnik, Marka Marojice 4, 20000 Dubrovnik, Croatia; domagoj-ivan.zeravica@unidu.hr

² Department of Viticulture and Enology, Faculty of Agriculture, University of Zagreb, Svetošimunska 25, 10000 Zagreb, Croatia; dpreiner@agr.hr (D.P.); isikuten@agr.hr (I.Š.); dstupic@agr.hr (D.S.); amajdak@agr.hr (A.J.); emaletic@agr.hr (E.M.)

³ Centre of Excellence for Biodiversity and Molecular Plant Breeding, Faculty of Agriculture, University of Zagreb, 10000 Zagreb, Croatia

* Correspondence: itomaz@agr.hr

† PhD Thesis from Faculty of Agriculture, University of Zagreb, Svetošimunska 25, 10000 Zagreb, Croatia.

Abstract: The quality and sensory characteristics of wines are influenced by several factors, including grape variety, local climate, soil conditions, viticultural practices, and vintage. This study investigates the volatile organic compounds (VOCs) in Malvasija Dubrovačka wines, which include various chemical groups such as terpenes, esters, alcohols, acids, and C13-norisoprenoids. The aim was to investigate how vineyard location and vintage influence the VOC profiles of these wines in two consecutive vintages. Using gas chromatography–mass spectrometry, 54 individual VOCs were identified and quantified. The results showed remarkable differences in the composition of VOCs, especially C13-norisoprenoids, terpenes, and acids, between the two vintages and the studied locations. Principal component analysis showed a significant influence of vineyard location on the composition of Malvasija Dubrovačka wines, a result that was reinforced by conventional descriptive analysis (CDA) of sensory testing.



Academic Editors: Elisabeth Koussissi and Maria Kyrleou

Received: 28 March 2025

Revised: 27 May 2025

Accepted: 5 June 2025

Published: 9 June 2025

Citation: Žeravica, D.I.; Tomaz, I.; Preiner, D.; Šikuten, I.; Stupić, D.; Jeromel, A.; Maletić, E. Aromatic Profiles and Vineyard Location: Uncovering Malvasija Dubrovačka Wines. *Beverages* **2025**, *11*, 87. <https://doi.org/10.3390/beverages11030087>

Copyright: © 2025 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/>).

Keywords: volatile aroma compounds; vineyard location; sensory analysis; Malvasija Dubrovačka

1. Introduction

Volatile organic compounds (VOCs) play a crucial role in defining the aromatic and sensory characteristics of white wines. So, their study is therefore crucial for understanding the quality potential of certain grape varieties [1–3]. To date, more than 1000 VOCs have been identified in wine. Based on their chemical structure, these compounds can be classified into several groups, including thiols, terpenes, methoxypyrazines, norisoprenoids, C6 alcohols, and aldehydes, with concentrations ranging from several mg/L to a few ng/L [3,4]. Desirable wine aromas are the result of a complex interaction between these compounds. While the overall composition of volatiles is generally similar for most grape varieties, the distinct aromatic profiles of individual grape varieties are determined by differences in the relative proportions of these VOCs [1,4]. The importance of the composition and content of VOCs for wine quality has led to increased scientific interest in identifying the key molecules responsible for aroma perception, contributing to a deeper understanding of the chemical and sensory complexity of wine [1,5].

VOCs are synthesized in grapevines through different biosynthetic pathways specific to each group of substances. Their initial composition and content are characteristic of the grape variety and are further modified during the fermentation process and wine maturation. These biosynthetic pathways are very complex and are influenced by various abiotic factors, such as sunlight exposure, soil, cover crops, and defoliation. Despite advances in analytical techniques, it remains challenging to distinguish the influence of individual factors [6].

Malvasija Dubrovačka is an old grape variety grown in the Dubrovnik region and has been well known for centuries for its unique aroma. The earliest mention of its name dates back to 1383, and numerous documents from the Dubrovnik Republic underline the importance of this wine in diplomacy [7]. Malvasija Dubrovačka belongs to the group of Mediterranean Malvasias, a genetically and morphologically heterogeneous group of varieties that share the name Malvasia but do not have uniform morphological characteristics [8]. Analysis of simple sequence repeat markers has shown that this variety is cultivated in Croatia, Italy, Spain, and Portugal, and has many synonyms such as Greco di Gerace, Malvasia de Lanzarote, Malvasia delle Lipari, Malvasia di Sardegna, Malvasia di Bosa etc. [8,9]. However, a comparison of allele frequency has shown that none of the countries where it is cultivated (Croatia, Greece, Italy, Spain, Portugal) can be clearly identified as the country of origin of Malvasija Dubrovačka [9]. Although its aroma once led to the assumption that it is genetically related to the Muscat varieties, genetic analyses have proven that Moscato Bianco (Muscat à Petits Grains) and Muscat of Alexandria (Zibibbo) do not have a parent–progeny relationship with this variety. Previous scientific studies [10,11] on the Malvasia Dubrovačka variety have mostly focused on the ampelographic description and SSR (simple sequence repeat) markers and investigated its origin and/or relationship with other varieties, while only a few studies have investigated its aromatic profile. According to Jeromel et al. [12], the addition of enzymes can positively influence the aromatic profile of Malvasia Dubrovačka wines, although the detected terpenes content below 1 mg/L defines the variety as non-Muscat. Moreover, the application of stabulation and fermentation with different yeast strains has shown significant impact on the aromatic profile of the wine [13].

According to the International Organisation of Vine and Wine (OIV), the vitivinicultural term “terroir” is a concept that refers to an area in which a collective knowledge of the interactions between the identifiable physical and biological environment and applied vitivinicultural practices develops, providing distinctive characteristics to the products originating from that area. The term encompasses specific soil characteristics, topography, climate, landscape, and biodiversity features. Recently, the concept of terroir has become increasingly important for producers and researchers seeking to improve the quality and diversity of wines by emphasizing the interplay between regional climate, soil structure, and grape variety [14].

The aim of this study was to determine the influence of location and vintage on the composition and concentration of VOCs responsible for the characteristic aroma of this variety. Additionally, the compounds that contribute most to the aroma were identified by comparing their concentrations with the odor detection threshold (ODT) and relative odor contributions (ROCs).

2. Materials and Methods

2.1. Vineyard Location

The grapes used for vinification in this study came from two vineyards located in the region of Dalmatia (Croatia), Central and South Dalmatia sub-region, Gruda village (Konavle). Konavle is a small geographical area, but its configuration (Konavosko polje and the surrounding hills with slopes) creates multiple micro-locations with significant

influences on the accumulation of VOCs in grapes and wine. The two examined locations, Grude-K and Grude-B are about 2 km apart, but their microclimatic differences are remarkable (Figure 1).

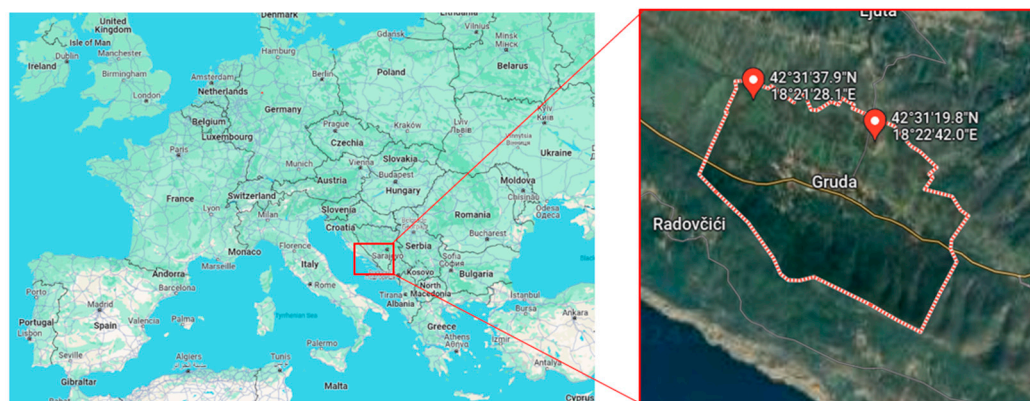


Figure 1. Location of two vineyards in Gruda (Konavle region) in Croatia.

The Grude-K vineyard is located 48 m above sea level, coordinates $42^{\circ}31.642' \text{ N}$, $018^{\circ}21.485' \text{ E}$, in Konavosko polje, and is exposed to higher humidity due to the surrounding hills and its location in a basin area. The soil type at this location is anthropogenic soil with an alluvial–colluvial layer over flysch. It was planted in 2001 on Kober 5BB rootstock and has a row spacing of 120 cm and an inter-row spacing of 280 cm. The Grude-B vineyard is located 65 m above sea level, coordinates $42^{\circ}31.327' \text{ N}$, $018^{\circ}22.712' \text{ E}$, on a gentle slope and is exposed to air currents. The vineyard is planted on pure flysch. Malvasija Dubrovačka, planted in 2004 on Ruggeri 140 rootstock, has a row spacing of 100 cm and a distance between rows of 260 cm. According to Mihelčić et al. [15] vineyards on flysch terrace soils consist of up to 90% coarse material and therefore contain less organic matter than the dense and largely skeleton-free loamy alluvial soils of the flat vineyards. These two extreme groups of vineyards in the same vine-growing region differ considerably in terms of morphology and soil profile characteristics, as well as microclimatic conditions and relief. So, the diversity of vineyards is reflected, among other things, in the quality of the grapes.

In 2020 and 2021, there were similar temperature and precipitation patterns at these locations. In 2020, the monthly average temperatures in the summer months ranged from 21.9°C in June to a peak of 26.9°C in August. In 2021, the temperature ranged from 24.3°C in June to 26.6°C in August. Although the total annual precipitation was lower in 2020 than in 2021, the precipitation from June to September was significantly higher in 2020, which was mainly due to the increased precipitation in September.

2.2. Experiment

This experiment was carried out in 2020 and 2021 at the Grude-B and Grude-K locations. The grapes were harvested from three primary plots located in different parts of the vineyards, with each plot containing 10 vines. The harvest took place when the grapes had reached full technological ripeness, as defined by the BBCH scale (BBCH 89—when sugar accumulation stops and acidity decreases simultaneously, without considering changes due to dehydration).

2.3. Winemaking Process

The wines were produced from healthy grapes of *Vitis vinifera* L. Malvasija Dubrovačka, from the 2020 and 2021 vintages. The grapes were destemmed, crushed, and pressed, and the must obtained was clarified for 24 h. All variants were treated with 5 mg/L of potas-

sium metabisulphite (AEB SPA Brescia, Italy). The clarified musts were inoculated with 3 mg/L of rehydrated dry yeast *Saccharomyces cerevisiae* (Lalvin EC-1118®, Lallemand Inc., Montreal, QC, Canada). The addition of 10 mg/L of yeast additive (Fermaid E®, Lallemand Inc., Montreal, QC, Canada) took place on the second and fifth day of fermentation. In all variants, fermentation started 24 h after inoculation and lasted between 7–10 days. During this period, the fermentation kinetics monitored via sugar degradation showed no significant differences. The finished wines were bottled in 750 mL glass bottles with screw caps and transported to the laboratory of the Department of Viticulture and Enology, Faculty of Agriculture, University of Zagreb for chemical and sensory analysis.

2.4. Physicochemical Profiling of Wine

The basic wine parameters such as alcohol content (% *v/v*), pH, total acidity, and volatile acidity were determined according to the standardized protocols of the International Organisation of Vine and Wine (OIV) [16].

2.5. Identification and Quantification of Volatile Compounds

The analysis of volatile compounds in the wine samples was performed using SPME-Arrow-GC/MS (gas chromatography–mass spectrometry) [17]. The SPME-Arrow extraction was performed using an RSH Triplus autosampler (Thermo Fisher Scientific Inc., Brookfield, WI, USA). A total of 5 mL of sample and 2.00 g were NaCl added to 20 mL headspace screw-top vials sealed with PTFE/silicone septum-containing caps. The sorption conditions were as follows. The sample was incubated at 60 °C for 20 min and the SPME-Arrow fiber DVB/CWR/PDMS (120 µm × 20 mm; Thermo Fisher Scientific Inc., Brookfield, WI, USA) was exposed for 49 min. The fiber was then inserted into the GC injector port, operated in splitless mode, and was desorbed at 250 °C for 7 min.

Sample analysis was performed using on a TRACE 1300 Gas Chromatographer coupled to an ISQ 7000 TriPlus quadrupole mass spectrometer (Thermo Fisher Scientific Inc., Waltham, MA, USA) equipped with a TG-WAXMS A capillary column (60 m × 0.25 mm × 0.25 µm film thickness; Thermo Fisher Scientific, Waltham, MA, USA). The volatile compounds injected into the inlet were delivered to the column in splitless mode and helium was used as a carrier gas at a constant flow rate of 1 mL/min. The oven temperature program was as follows. An initial temperature of 40 °C was maintained for 5 min, after which the temperature was increased by 2 °C/min to 210 °C and held for 10 min. The MS spectra were recorded in the electron impact ionization mode (EI) at an ionization energy of 70 eV. Mass spectrometry was performed in full scan mode in the range of 30–300 *m/z*. The data obtained were processed using the Chromeleon Data System (Thermo Fisher Scientific Inc., Waltham, MA, USA).

2.6. Organic Acids Analysis

Organic acids, including tartaric, malic, and citric acids, were analyzed using high-performance liquid chromatography (HPLC) on an Agilent 1050 system (Palo Alto, CA, USA). Prior to analysis, samples were filtered through 0.45 µm PTFE membrane filters. Identification and quantification were performed at a wavelength of 210 nm using an Aminex HPX-87H column (BioRad, Hercules, CA, USA).

2.7. Odor Activity Values and Relative Odor Contributions Determinations

Each volatile compound can contribute uniquely to the overall aroma of wine. Their impact can be evaluated with two indicators: the odor activity value (OAV) and the relative odor contribution (ROC). These metrics serve as markers for evaluating the role of individual compounds in the aroma profile of a sample. The OAV is determined by dividing the compound's concentration (*c*) by its odor detection threshold (ODT) as reported in

the literature [18]. Compounds with an OAV ≥ 1 are considered to have a direct effect on aroma and are typically identified as key odor-active components [19]. Meanwhile, compounds with OAV less than 1 can increase the complexity of wine aroma and enhance the perception of other volatiles through synergistic interactions [20]. The ROC of each compound is calculated as the proportion of its OAV relative to the sum of the OAVs of all compounds in a given wine [21].

2.8. Sensory Analysis

Sensory evaluation of wines from the 2020 and 2021 vintages was carried out by a panel of ten expert tasters (four women and six men), all members of the Committee for Organoleptic Evaluation of Wine and Fruit Wines, appointed by the Ministry of Agriculture of the Republic of Croatia. The evaluations took place in the Laboratory for Sensory Analysis of Agricultural and Food Products, University of Zagreb Faculty of Agriculture, under standardized conditions in individual tasting booths in accordance with ISO 8589:2010.

Conventional descriptive analysis (CDA) was carried out six months after the completion of alcoholic fermentation. Malvasija Dubrovačka wine samples (20 mL) were served at 10 °C in standardized ISO 3591:1977 wine tasting glasses, covered with watch-glasses to minimize aroma loss. A blind tasting was conducted using coded samples in three randomized replicates. Sensory evaluation focused on six primary aroma descriptors (fruity, floral, nutty, herbal, dried fruit, and vegetal) and five key taste attributes (acidity, bitterness, fullness, harmony, and aftertaste), and an overall impression rating was included. Each attribute was rated on a paper-based scale from 0 (not perceptible) to 5 (strongly perceptible). The differences between the samples were visualized using spiderweb (radar) plots.

2.9. Statistical Analysis

A two-way analysis of variance (ANOVA) was performed to assess the statistical significance of location, vintage, and their interaction on all measured parameters. When significant differences were found, Duncan's multiple range test was applied for mean comparison at a 95% confidence level ($p \leq 0.05$). Principal component analysis (PCA) was performed to assess the overall variability of the wine aroma profiles between the two locations and vintages. The scores and loadings of the first two principal components were used to create scatter plots, illustrating the multivariate differences between samples. Additionally, partial least squares regression (PLSR) was used to investigate potential correlations between wine samples, sensory attributes, and key volatile compounds. This technique effectively models the relationship between chemical data (X variables) and sensory data (Y variables). All statistical analyses were performed with XLSTAT software (version 2020.3.1, Addinsoft, New York, NY, USA).

3. Results and Discussion

3.1. Physicochemical Composition

The results describing the physicochemical characteristics of Malvasija Dubrovačka wines from the two study locations, as presented in Table 1, indicate that the main differences lie in the composition of organic acids and ash concentration. Vineyards situated at higher altitudes tend to ripen later in the cooler months and thus offer greater potential for producing high-quality grapes characterized by higher acidity and lower alcohol levels. This may increase the significance of vineyard location with regard to future warmer temperatures [22]. The results obtained are consistent with this; in both years, the wines from the higher altitude Grude-B location had significantly higher concentrations of tartaric, malic, and citric acids. Furthermore, research dealing with the quality of Merlot wine produced in terraced and non-terraced vineyards in the Vipava Valley, Slovenia [15] reported

higher values for alcohol content, total dry extract and titratable acidity in the wines from the terraces, while no differences in ash content or pH were found between wines from non-terraced and terraced vineyards. Also according to Nguyen et al. [23] wines from different soil types have different aromas, taste, and mouthfeel. Thus, in the present case, different soil types between locations could therefore be the reason for the differences in ash content and the higher concentrations in the wines from the Grude-B location, in both investigated years.

Table 1. Physicochemical properties of Malvasija Dubrovačka wines from two locations and production years.

Compounds	2020		2021		<i>p</i> -Values		
	Grude-K	Grude-B	Grude-K	Grude-B	Location	Vintage	Location × Vintage
Alcohol (% <i>v/v</i>)	14.10 ± 0.09	13.10 ± 0.05	11.90 ± 0.06	12.70 ± 0.1	0.034	0.021	0.130
Dry extract (g/L)	19.6 ± 0.2	21.2 ± 0.3	19.8 ± 0.1	19.1 ± 0.1	0.052	0.008	0.024
Reducing sugars (g/L)	2.5 ± 0.1 a	1.1 ± 0.1 b	5.4 ± 0.2 a	1.7 ± 0.1 b	0.005	0.020	0.002
Total acidity * (g/L)	8.3 ± 0.1	8.5 ± 0.1	9.0 ± 0.2	9.1 ± 0.1	0.490	0.023	0.055
Volatile acidity ** (g/L)	0.32 ± 0.03	0.30 ± 0.05	0.40 ± 0.06	0.44 ± 0.05	0.002	0.001	0.396
pH	2.86 ± 0.01	2.88 ± 0.02	2.99 ± 0.02	2.90 ± 0.01	0.643	0.340	0.549
Ash (g/L)	1.27 ± 0.03 b	1.62 ± 0.05 a	1.16 ± 0.03 b	1.39 ± 0.04 a	0.001	0.009	0.001
Tartaric acid (g/L)	5.46 ± 0.09 b	6.34 ± 0.1 a	5.05 ± 0.11 b	6.11 ± 0.08 a	0.002	0.068	0.001
Malic acid (g/L)	0.46 ± 0.05 b	1.51 ± 0.03 a	0.38 ± 0.06 b	0.82 ± 0.03 a	<0.0001	<0.0001	<0.0001
Citric acid (g/L)	0.13 ± 0.01	0.32 ± 0.02	0.15 ± 0.01	0.31 ± 0.02	<0.0001	0.020	0.440

* Tartaric acid and ** acetic acid equivalents. Concentrations expressed as mean values (*n* = 3). Regarding location × vintage, means with different letters in the same row differ significantly (*p* ≤ 0.05).

The results presented in Table 1 confirm the clear influence of the vineyard locations studied and indicate that wines produced from grapes grown in the higher altitude vineyard generally had higher concentrations of ash and individual organic acids, while the alcohol content was slightly lower, as found in the work by Gutiérrez-Gamboa et al. [24].

3.2. Aromatic Profile of Malvasija Dubrovačka Wines

In Table 2a,b, fifty-four volatile compounds are presented belonging to several chemical classes including terpenes, C13-norisoprenoids, esters, fatty acids, alcohols, and other compounds, showing a significant influence of the growing location and vintage on the aromatic profiles of Malvasija Dubrovačka wines. Depending on their influence on the aromatic profile, the detected volatile compounds have been divided into Table 2a (those with an OAV < 1) and Table 2b (those with an OAV > 0.5). Overall, the most frequently occurring chemical groups, regardless of location and vintage, were alcohols, followed by acids and esters.

Table 2. (a) Concentrations of individual volatile compounds in Malvasija Dubrovačka wines from two locations and vintages. (b) Concentrations of individual volatile compounds with OAV > 0.5 in Malvasija Dubrovačka wines from two locations and vintages.

a							
Compounds (µg/L)	2020 Year		2021 Year		p-Values		
	Grude-B	Grude-K	Grude-B	Grude-K	Location	Vintage	Location × Vintage
3-Methylbutanoic acid	719.91 ± 21.60 a	585.26 ± 17.56 c	732.27 ± 21.97 a	668.84 ± 20.07 b	<0.0001	0.004	0.016
Dodecanoic acid	43.22 ± 1.30 c	146.29 ± 4.39 a	42.52 ± 1.28 c	102.36 ± 3.07 b	<0.0001	<0.0001	<0.0001
Nonanoic acid	30.00 ± 0.90 c	67.11 ± 2.01 a	30.28 ± 0.91 c	49.20 ± 1.48 b	<0.0001	<0.0001	<0.0001
2-Methyl-propanoic acid	395.02 ± 11.85 b	412.89 ± 12.39 ab	353.78 ± 10.61 c	420.03 ± 12.60 a	0.000	0.038	0.008
Acids							
1-Butanol	300.86 ± 9.03 b	0.00	326.87 ± 9.81 a	0.00	<0.0001	0.010	0.010
1-Octanol	25.33 ± 0.76 c	27.59 ± 0.83 b	28.56 ± 0.86 b	32.33 ± 0.97 a	0.000	<0.0001	0.166
4-Methyl-1-pentanol	398.79 ± 11.96 a	281.85 ± 8.46 b	172.69 ± 5.18 c	134.05 ± 4.02 d	<0.0001	<0.0001	<0.0001
1-Propanol	402.17 ± 12.07 a	197.74 ± 5.93 c	328.67 ± 9.84 b	126.71 ± 3.80 d	<0.0001	<0.0001	0.809
3-Ethoxy-1-propanol	2273.40 ± 68.20 c	3074.19 ± 92.23 b	1609.20 ± 42.28 d	3385.05 ± 101.55 a	<0.0001	0.005	<0.0001
2,3-Butanediol	299.58 ± 8.99 c	371.80 ± 11.15 b	401.17 ± 12.04 a	421.37 ± 12.64 a	0.000	<0.0001	0.004
(E) + (Z)-3-Hexen-1-ol	527.53 ± 15.83 c	1046.14 ± 31.38 a	436.59 ± 13.10 d	995.46 ± 29.86 b	<0.0001	0.001	0.184
3-Methylpentan-1-ol	4773.41 ± 143.20 a	1586.00 ± 47.58 c	3959.81 ± 118.79 b	1320.79 ± 39.62 d	<0.0001	<0.0001	0.001
Isobutanol	510.80 ± 15.32 b	417.09 ± 12.51 c	330.52 ± 9.92 d	613.11 ± 18.39 a	<0.0001	0.371	<0.0001
Alcohols							
TPB	11.19 ± 0.34 bc	13.91 ± 0.42 a	10.73 ± 0.32 c	11.66 ± 0.35 b	<0.0001	0.000	0.003
Vitispirane A	28.65 ± 0.86 b	16.59 ± 0.50 c	33.17 ± 1.00 a	12.04 ± 0.36 d	<0.0001	0.974	<0.0001
Vitispirane B	15.53 ± 0.47 b	13.61 ± 0.41 c	10.90 ± 0.32 c	18.81 ± 0.56 a	<0.0001	0.303	<0.0001
C13							
3-Hexen-1-ol acetate	95.08 ± 2.85	96.17 ± 2.89	94.36 ± 2.83	95.36 ± 2.86	0.543	0.657	0.979
3-Methylbutyl decanoate	88.79 ± 2.66 b	96.78 ± 2.90 a	90.37 ± 2.71 b	100.15 ± 3.00 a	0.001	0.167	0.600
Diethyl butanedionate	333.24 ± 10.00 b	413.57 ± 12.41 a	412.98 ± 12.39 a	425.95 ± 12.78 a	0.000	0.000	0.001
Ethyl dodecanoate	8.17 ± 0.25 b	0.00	9.45 ± 0.28 a	0.00	<0.0001	0.000	0.000
Ethyl 2-hydroxypropanoate	71.82 ± 2.15 a	63.26 ± 1.90 b	69.49 ± 2.08 a	43.11 ± 1.29 c	<0.0001	<0.0001	<0.0001
Ethyl 4-hydroxybutanoate	70.68 ± 2.12 b	50.14 ± 1.50 d	84.13 ± 2.52 a	62.48 ± 1.87 c	<0.0001	<0.0001	0.649
Ethyl 9-decenoate	128.02 ± 3.84	127.62 ± 3.83	128.05 ± 3.84	127.04 ± 3.81	0.757	0.905	0.892
Ethyl 9-hexadecenoate	13.67 ± 0.41 b	0.00	14.49 ± 0.43 a	0.00	<0.0001	0.045	0.045
Ethyl hydrogen succinate	130.27 ± 3.91 d	354.29 ± 10.63 a	197.66 ± 5.93 b	159.86 ± 4.80 c	<0.0001	<0.0001	<0.0001
3-Methylbutyl octanoate	33.92 ± 1.02 c	62.85 ± 1.89 b	60.28 ± 1.81 b	80.69 ± 2.42 a	0.040	<0.0001	0.902
Esters							
α-Terpinen	165.34 ± 4.96 a	88.95 ± 2.67 b	160.08 ± 4.80 a	85.70 ± 2.57 b	0.000	0.022	0.612
Guaiazulene	5.35 ± 0.16 c	6.07 ± 0.18 a	5.12 ± 0.15 c	5.75 ± 0.17 b	<0.0001	<0.0001	<0.0001
α-Bisabolene	7.94 ± 0.24 a	0.00	6.30 ± 0.19 b	0.00	<0.0001	<0.0001	<0.0001
β-Farnesene	17.28 ± 0.52 a	0.00	13.55 ± 0.41 b	0.00	<0.0001	0.127	0.015
D-Limonene	53.46 ± 1.60 b	90.47 ± 2.21 a	47.35 ± 1.42 c	92.21 ± 2.77 a	<0.0001	<0.0001	0.311

Table 2. Cont.

a																		
Compounds (μg/L)		2020 Year				2021 Year				p-Values								
	Grude-B		Grude-K		Grude-B		Grude-K		Location		Vintage		Location × Vintage					
3-Carene	66.64 ± 2.00 c		133.32 ± 4.00 a		50.04 ± 1.50 d		120.44 ± 3.61 b		<0.0001		<0.0001		<0.0001					
Isocaryophyllene	12.39 ± 0.37 a		0.00		10.34 ± 0.31 b		0.00		<0.0001		<0.0001		<0.0001					
Menthol	8.68 ± 0.26 a		0.00		7.15 ± 0.21 b		0.00		<0.0001		<0.0001		0.141					
(E)-Linalool oxide (furanoid)	96.24 ± 2.89 d		121.81 ± 3.65 c		274.41 ± 8.23 b		312.57 ± 9.38 a		<0.0001		<0.0001		0.836					
α-Terpineol	36.95 ± 1.11 b		11.57 ± 0.35 d		45.05 ± 1.35 a		19.43 ± 0.58 c		<0.0001		<0.0001		0.012					
Terpenes																		
3-(Methylthio)-1-propanol	3.90 ± 0.12 c		5.19 ± 0.16 b		4.99 ± 0.15 b		6.46 ± 0.19 a		<0.0001		0.000		0.000					
4-Vinylguaicol	29.53 ± 0.89 a		0.00		25.56 ± 0.77 b		0.00		<0.0001		<0.0001		0.436					
Acetoin	6.92 ± 0.21 a		3.87 ± 0.12 c		6.18 ± 0.19 b		2.99 ± 0.09 d		<0.0001		0.004		0.016					
b																		
Compounds (μg/L)		ODT (μg/L)		Grude-B 20		Grude-K 20		Grude-B 21		Grude-K 21		p-Values						
Acids				OAV	ROC %	OAV	ROC %	OAV	ROC %	OAV	ROC %	Location	Vintage	Vintage × Location				
Butanoic acid	400		rancid, cheese	510.7 ± 15.32 b	1.28	0.30	434.19 ± 13.03 c	1.09	0.30	612.82 ± 18.38 a	1.53	0.24	359.46 ± 10.78 d	0.90	0.16	<0.0001	0.145	<0.0001
Decanoic acid	1000		rancid, waxy	4258.02 ± 127.74 b	4.26	1.01	6250.85 ± 127.74 a	6.25	1.71	4136.70 ± 124.10 b	4.14	0.65	6461.93 ± 193.86 a	6.46	1.13	<0.0001	0.643	0.113
Hexanoic acid	420		cheese, oily	8118.13 ± 243.54 c	19.33	4.60	14,257.49 ± 427.72 a	33.95	9.28	7903.98 ± 237.12 c	18.82	2.97	11,562.44 ± 346.87 b	27.53	4.83	<0.0001	<0.0001	0.000
Octanoic acid	500		rancid, oily	6895.78 ± 206.87 c	13.79	3.28	13,531.00 ± 405.93 a	27.06	7.40	6980.43 ± 209.41 c	13.96	2.20	9765.85 ± 292.98 b	19.53	3.43	<0.0001	<0.0001	<0.0001
Σ				19,782.69 ± 306.87 c		9.20	34,473.55 ± 405.93 a		18.68	19,633.93 ± 299.41 c		6.06	28,149.68 ± 332.98 b		9.55	<0.0001	0.000	0.000
Alcohols																		
Isoamyl alcohol	30,000		alcohol, nail polish	35,487.88 ± 1064.64 a	1.18	0.28	34,790.53 ± 1043.72 a	1.16	0.32	32,724.77 ± 981.74 b	1.09	0.17	31,433.65 ± 343.01 b	1.05	0.18	0.126	0.001	0.624
1-Decanol	5000		pear, waxy, violet	3776.98 ± 113.31 a	0.76	0.18	2496.05 ± 74.88 c	0.50	0.14	3303.83 ± 99.12 b	0.66	0.10	2045.19 ± 61.36 d	0.51	0.07	<0.0001	<0.0001	0.835
1-Hexanol	2500		grass just cut	2401.90 ± 72.06 a	0.96	0.23	2471.16 ± 74.14 a	0.99	0.27	2188.98 ± 65.67 b	0.88	0.14	2122.25 ± 63.67 b	0.85	0.15	0.975	0.000	0.126
Phenylethyl alcohol	14,000		floral, rose, honey	18,188.69 ± 545.66 c	1.30	0.31	21,074.32 ± 623.23 b	1.51	0.41	19,064.90 ± 571.95 c	1.36	0.21	22,615.35 ± 678.46 a	1.62	0.28	<0.0001	0.009	0.372
Σ				59,855.45 ± 1064.69 a		1.00	60,832.08 ± 943.75 a		1.13	57,282.49 ± 989.24 a		0.63	58,216.45 ± 746.01 a		0.69	0.624	0.016	0.435
C13																		
β-Damascenone	0.05		sweet, fruity, floral, honey	8.22 ± 0.25 b	164.38	39.14	3.85 ± 0.12 d	77.08	21.06	9.98 ± 0.30 a	199.64	31.48	5.69 ± 0.17 c	113.86	19.98	<0.0001	<0.0001	0.772
TDN	2		petrol, kerosene	15.18 ± 0.46 a	7.59	1.81	18.38 ± 0.55 a	9.19	2.51	15.71 ± 0.47 a	7.85	1.24	17.43 ± 0.52 a	8.71	1.53	<0.0001	0.483	0.033
Σ				23.40 ± 0.96 a		40.94	18.38 ± 0.55 b		23.58	25.69 ± 0.97 a		32.72	23.12 ± 0.32 a		21.51	0.006	0.385	0.065

Table 2. Cont.

b																	
Compounds (μg/L)	ODT (μg/L)		Grude-B 20			Grude-K 20			Grude-B 21			Grude-K 21			p-Values		
Acids			OAV	ROC %		OAV	ROC %		OAV	ROC %		OAV	ROC %	Location	Vintage	Vintage × Location	
Esters																	
Isoamyl acetate	30	banana	1475.34 ± 44.26 b	49.18	11.71	1012.44 ± 30.37 c	33.75	9.22	2319.11 ± 69.57 a	77.30	12.19	2326.09 ± 69.78 a	77.54	13.60	0.000	<0.0001	<0.0001
2-Phenylethyl acetate	250	rose, honey, tobacco	1199.93 ± 36.00 b	4.80	1.14	1419.12 ± 42.57 a	5.68	1.55	1005.44 ± 30.16 c	4.02	0.63	1134.63 ± 34.04 b	4.54	0.80	<0.0001	<0.0001	0.062
Ethyl decanoate	200	floral, grape, fruity	314.83 ± 9.44 a	1.57	0.37	305.08 ± 9.15 a	1.53	0.42	328.74 ± 9.86 a	1.64	0.26	307.35 ± 8.24 a	1.54	0.27	0.021	0.175	0.316
Ethyl hexanoate	14	fruity, green, apple, banana	2011.89 ± 60.36 c	143.71	34.22	2287.15 ± 68.61 b	163.37	44.64	4136.23 ± 124.09 a	295.45	46.59	4228.78 ± 126.86 a	302.06	52.99	0.013	<0.0001	0.151
Ethyl octanoate	580	sweet, floral, fruity, pear	1478.98 ± 44.37 b	2.55	0.61	1502.65 ± 45.08 b	2.59	0.71	1487.09 ± 44.61 b	2.56	0.40	1662.79 ± 49.88 a	2.87	0.50	0.006	0.013	0.021
Σ			6480.96 ± 49.27 b		48.05	6526.46 ± 55.18 b		56.54	9276.61 ± 41.33 a		60.08	9659.63 ± 54.78 a		68.17	0.040	<0.0001	0.902
Terpenes																	
Citronellol	40	rose	25.34 ± 0.76 a	0.63	0.15	0.00			25.34 ± 0.76 a	0.63	0.16	0.00			<0.0001	0.995	0.995
Hotrienol	110	fresh, floral, fruity	78.10 ± 2.34 b	0.71	0.17	14.55 ± 0.44 d	0.13	0.04	94.51 ± 2.84 a	0.86	0.14	40.74 ± 1.22 c	0.37	0.08	<0.0001	<0.0001	0.002
Linalool	25	citrus, floral, sweet	24.92 ± 0.75 a	1.00	0.24	0.00			17.57 ± 0.53 b	0.70	0.17	0.00			<0.0001	<0.0001	<0.0001
Σ			128.35 ± 5.75 a		0.56	14.55 ± 0.44 d		0.04	137.42 ± 1.73 b		0.47	40.74 ± 1.22 c		0.08	<0.0001	<0.0001	0.012

Concentrations expressed as mean values (n = 3). Regarding the interaction of location × vintage, mean values with different letters in the same row differ significantly ($p \leq 0.05$).

In the Malvasija Dubrovačka wine samples, eight volatile organic acids were detected, including four (hexanoic, octanoic, decanoic, butanoic acid) with potential influence on the sensory profiles of the wines (Table 2b). It is well known that C6–C10 fatty acids play a crucial role in wine aroma profiling, being the precursors to the corresponding ethyl esters [25]. The most representative fatty acid, similar to the data published by Šikuten et al. [26], was hexanoic acid, followed by octanoic and decanoic acids, aligning with the findings reported by Lukic et al. [27]. Significantly higher total concentrations of the above-mentioned acids were detected in wines from the Grude-K location, regardless of the year. A similar trend was also noted among other acids (Table 2a), again with the highest concentrations in Grude-K wines. The results from the two-way ANOVA (Table 2a) indicate strong effects of location, vintage, and their interaction on the concentrations of fatty acids in Malvasija Dubrovačka wines. Notably, butanoic and decanoic acids were more strongly affected by location than by vintage. The low concentration of nonanoic acid detected in Malvasija Dubrovačka wines emerged as a potentially typical feature of Muscat yellow wines [27]. Furthermore, Gambetta et al. [28] reported elevated concentrations of butanoic acid in wines with pronounced fruity aromas. Additionally, that research identified decanoic acid as one of the eight key volatile compounds that contribute to the unique profile of Chardonnay wines. In Malvasija Dubrovačka wines, butanoic acid levels were higher in samples from the Grude-B location, whereas decanoic acid concentrations were significantly lower.

Alcohols primarily develop during the initial stages of vinification, from unsaturated fatty acids undergoing enzymatic degradation, or they are released from glycosidic precursors. These compounds contribute to the aroma of wine, often imparting green and herbal notes [25]. Higher alcohols, when present at concentrations below 300 mg/L, can enhance the complexity of wine [29], which was the case for all the analyzed Malvasija Dubrovačka wines. Among the volatile compounds, alcohols represented the most abundant group, with isoamyl alcohol and phenylethyl alcohol detected at the highest concentrations (Table 2b). The study by Šikuten et al. [26] demonstrated that in 50 varieties from Spain, France, Portugal, Italy, and Croatia, (*E*)-2-hexen-1-ol and 1-hexanol were the most prevalent alcohols. Oliveira et al. [30] reported that these higher alcohols contributed to the differentiation of monovarietal wines. According to these studies, the content and ratio between (*E*)-3-hexenol, its isomer (*Z*)-3-hexenol, and 1-hexanol can be used as key markers to determine significant variations among varietal wines. Their concentrations are influenced by various factors, including winemaking techniques, vintage, and vineyard location. Most of the compounds identified in this study were significantly affected by both location and vintage, as well as their interaction (Table 2a,b). However, there were exceptions. For example, 1-hexanol concentration was significantly influenced by vintage but not by location—a finding that contrasts with the conclusions of Oliveira et al. [30]. In contrast, (*E*)+(Z)-3-hexen-1-ol levels were strongly location-dependent, with significantly higher concentrations found in wines from Grude-K. Of the 13 alcohols identified, four had OAV values greater than 0.5. In this study, 1-octanol was detected at the lowest concentrations, while 1-butanol was observed only in wines from the Grude-B location. Although total alcohol concentrations did not differ significantly between samples (Table 2b), vintage appeared to have a stronger influence on isoamyl alcohol, while phenylethyl alcohol levels were more closely related to vineyard location.

Although numerous norisoprenoids have been detected in grapes, only a limited number contribute significantly to wine aroma [31]. These compounds are typically found at low concentrations in wine, but due to their extremely low thresholds for odor detection, they play pivotal roles in the aromatic profiles of varieties such as Chardonnay, Chenin Blanc, Semillon, Sauvignon Blanc, Cabernet Sauvignon, Syrah, Merlot, Pinot Noir, Ries-

ling, and Montepulciano [1,32,33]. In Malvasija Dubrovačka wines, five norisoprenoid compounds were detected, with vitispirane A and B the most abundant, followed by TDN (1,1,6-trimethyl-1,2-dihydronaphthalene) and TPB (4-(2,3,6-trimethylphenyl)buta-1,3-diene). TDN is a characteristic compound of Riesling wines, in which concentrations up to 200 µg/L can be reached. Very little research on the content of TDN in varieties other than Riesling has been conducted, but small amounts of TDN have been identified in juices and wines of other cultivars, suggesting that Riesling has higher concentrations of TDN precursors. TDN concentrations have been found to correlate positively with vitispirane, although it is possible that TDN can be reduced to the latter compound by yeast during fermentation [34]. According to Marais et al. [35], environmental factors such as sun exposure, shading, and ripeness level can influence the levels of volatile C13 norisoprenoids, with significant increases observed in sun-exposed and riper grapes. Accordingly, the location of grape growing can have a marked influence, which is consistent with our data showing higher concentrations of total norisoprenoids, as well as vitispirane A (Table 2a,b), in Grude-B wines. Among five native Croatian varieties analyzed in the work by Lukic et al. [25], the highest concentration of β -damascenone (3.52 µg/L) was detected in Istrian Malvasia, while Škrlet, Kraljevina, Pošip, and Maraština had significantly lower concentrations. In contrast, the concentrations of β -damascenone in Malvasija Dubrovačka wines were much higher, with a strong influence of location, aligning with the results observed by Oliveira et al. [36], indicating that vineyards placed on high-elevation terraces with higher humidity levels promoted the accumulation of carotenoids that degraded during the grape-ripening period to form odor-active C13-norisoprenoids. However, Falcão et al. [37] found no correlation between altitude (and associated temperature changes) and the concentrations of α -ionone, β -ionone, and β -damascenone, suggesting that other factors may also be at play.

The composition and content of fermentation-derived aromatic compounds are primarily influenced by fermentation conditions. However, the composition of grapes also plays an important role. Studies have shown that volatile compounds formed during fermentation can be highly effective in differentiating wines, especially for neutral grape varieties, sometimes even exceeding the monoterpene concentrations [25]. This is particularly evident for C6–C10 fatty acids and their corresponding ethyl esters, which, unlike acetates, are more influenced by precursor availability, grape variety, and vineyard conditions than by yeast activity [38]. Ethyl hexanoate and ethyl octanoate were the most abundant fatty acid esters in the Malvasija Dubrovačka wine, while ethyl decanoate was recorded at a significantly lower concentration. The results of this study are consistent with the findings of Antalick et al. [39], who reported a similar ester composition in 183 French wines and that this trend was consistent in different types of wine, including dry white wines. Among the 15 recorded esters in Malvasija Dubrovačka wines, five of them (Table 2b) were present in concentrations above the odor threshold, contributing to the fruity and floral aromas of Malvasija Dubrovačka wine. Their total concentration was strongly influenced by the year of their vintage, while wines from the Grude-K location stood out in terms of their individual fatty acids ester concentrations (Table 2b).

Terpenoids, particularly monoterpenes, are key volatile compounds that contribute to the floral and citrus aromas characteristic of both grapes and wines [31,40]. Terpene biosynthesis is influenced by environmental, viticultural, and genetic factors. Previous research has demonstrated their significance in differentiating white grape varieties [40]. Among the 13 individual terpene compounds quantified in Malvasija Dubrovačka, three of them had concentrations above the odor detection threshold and have a significant influence on the wine's aromatic profile (Table 2b). Marked differences were also noted between grape growing locations, highlighting wine from the Grude-B location as having a significantly higher presence of citronellol, hotrienol, and linalool compounds. In con-

trast, citronellol and linalool were not present in the Grude-K wines at all. Similarly, 2021 wines had significantly higher total terpene concentrations than 2020 (Table 2b), suggesting that vintage conditions (temperature, sunlight, and precipitation) also influenced the accumulation of terpenes. According to Savoi et al. [41], long-lasting water deficit conditions, particularly in vineyards on slopes with low water-holding capacity, can increase the concentrations of some volatile thiols and terpenes responsible for tropical, floral, and sweet/sugary aromas. A negative effect of higher temperatures on linalool and geraniol concentrations was also reported in the work by Duchêne et al. [42]. A more pronounced water deficit as well as a lower water-holding capacity at the Grude-B location, combined with temperature differences, may be the reason why the Malvasija Dubrovačka wines from Grude-B had significantly higher terpene concentrations. Although Malvasija Dubrovačka is often associated with a Muscat-like aroma [8], and the aromatic profile of wine is linked to monoterpenes [43], only linalool had an OAV > 1. It is widely acknowledged that a wine's aroma is not the result of any single dominant compound but the result of the synergistic action of many [44]. Thus, the specific aroma of Malvasija Dubrovačka cannot be attributed to any group of compounds or a single compound. Among all the terpenes, the most abundant in Malvasija Dubrovačka wine were (*E*)-linalool oxide (furanoid) and α -terpinene. Based on the recorded values of free monoterpenes, wines of both vintages and locations had total monoterpene concentrations below 1 mg/L, thus classifying Malvasija Dubrovačka as a neutral variety [43].

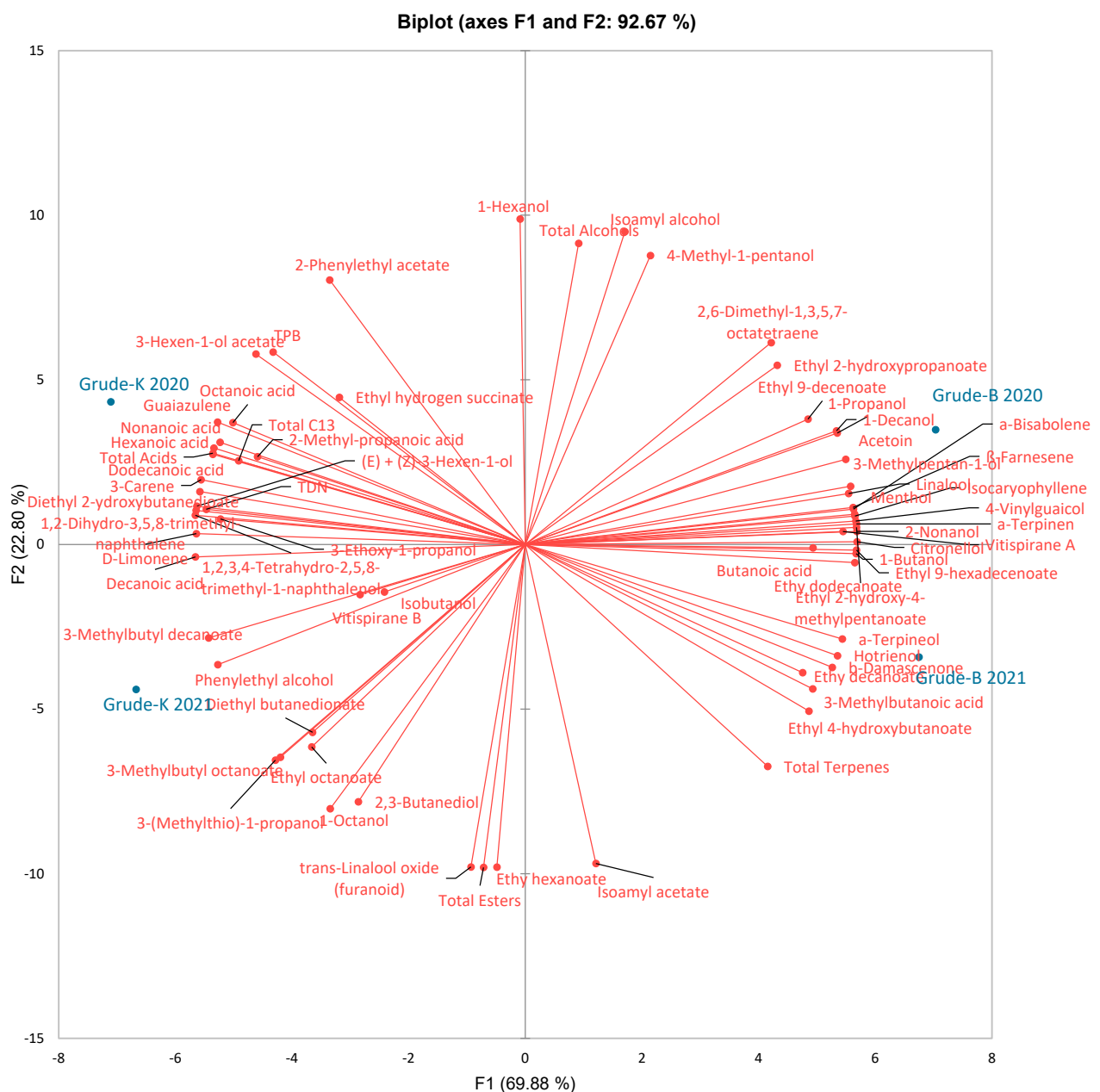
3.3. Odour Active Values (OAV) and Relative Odour Contribution (ROC)

To evaluate the influence of individual volatile compounds on the overall aroma of Malvasija Dubrovačka wines, the OAV values and the ROC indexes were calculated as presented in Table 2b. The overall aroma of these Malvasija Dubrovačka wines was significantly influenced by a relatively small group of volatile compounds—only 18 out of 54 identified volatiles exceeded the odor activity value (OAV) threshold (>0.5), indicating that these were the main contributors to the sensory profile of the wines. Among these, the most abundant were esters, especially ethyl hexanoate and isoamyl acetate, contributing fruity, banana, and green apple notes followed by fatty acids and alcohols that contributed to the background complexity and added waxy, cheesy and floral notes, C13-norisoprenoids like β -damascenone that added floral, fruity, and honey-like aromas, and terpenes that contributed to floral notes in general. In the analyzed wines, the highest OAV was for β -damascenone, and there were marked differences in ROC between the Grude-B and Grude-K wines. Among individual esters, the one with the highest OAV values was ethyl hexanoate, followed by isoamyl acetate, with a more pronounced influence on the Grude-K wines. The total C13-norisoprenoids and total esters ROC contributions in Grude-B wines were 88.99% in 2020 and 92.80% in 2021, while in Grude-K wines, their contributions were 80.12% in 2020 and 89.68% in 2021. β -damascenone demonstrated significant differences in ROC values between the Grude-B and Grude-K wines, suggesting sensitivity to the vineyard location and the environmental conditions. Total ROC values for C13-norisoprenoids and esters were higher in Grude-B wines, especially those from 2021, strongly suggesting that these compound groups are key markers of vineyard location for Malvasija Dubrovačka. Overall, the aroma of Malvasija Dubrovačka wines can be described as fruity, floral, and fresh, shaped by the specific volatile profile dominated by esters and norisoprenoids.

3.4. Principal Component Analysis

Principal component analysis (PCA) based on 63 volatile organic compounds of Malvasija Dubrovačka wine samples obtained from two different vintage years (2020, 2021) and two

Figure 2. Biplot representing the differences in VOC profiles of Malvasija Dubrovačka wines produced from grapes grown at two locations (Grude-B, Grude-K) in the two study years, based on PCA and related vector diagram of VOC compounds contributing to this differentiation.



The distribution of compounds around the F1 axis suggests a greater influence of location on the composition and content of VOCs than the influence of the vintage year. A positive correlation was observed between total C13-norisoprenoids and total acids, while a negative correlation was observed between total alcohols and total esters, total acids and total terpenes, and total C13-norisoprenoids and total terpenes. Total alcohols were significantly associated with the Grude-B 2020 samples, total terpenes with the Grude-B 2021 samples, total esters with Grude-K the 2021 samples, and total C13-norisoprenoids and acids with the Grude-K 2020 samples. This suggests that the mentioned compounds prevailed in these individual wines, making a difference to their chemical composition.

3.5. Sensory Analysis and Partial Least Square Regression of Malvasija Dubrovačka Wines

Figure 3 represents the results of the sensory analysis of wines from two vintages. In both years, the sensory panel evaluated the wines from the two locations in a similar manner. Wine from Grude-K location in both years was evaluated as fruitier and more vegetal, which may relate to stronger ROC of esters and alcohols, while that from the Grude-B location was more floral and nutty, which is likely to have been due to higher C13-norisoprenoid and terpene values. In the 2020 vintage, the wine from the Grude-K location was more harmonious and had a longer aftertaste, whereas in the 2021 vintage, these attributes were assigned to the Grude-B wine. However, the overall impression of the wines of both vintages was similar.

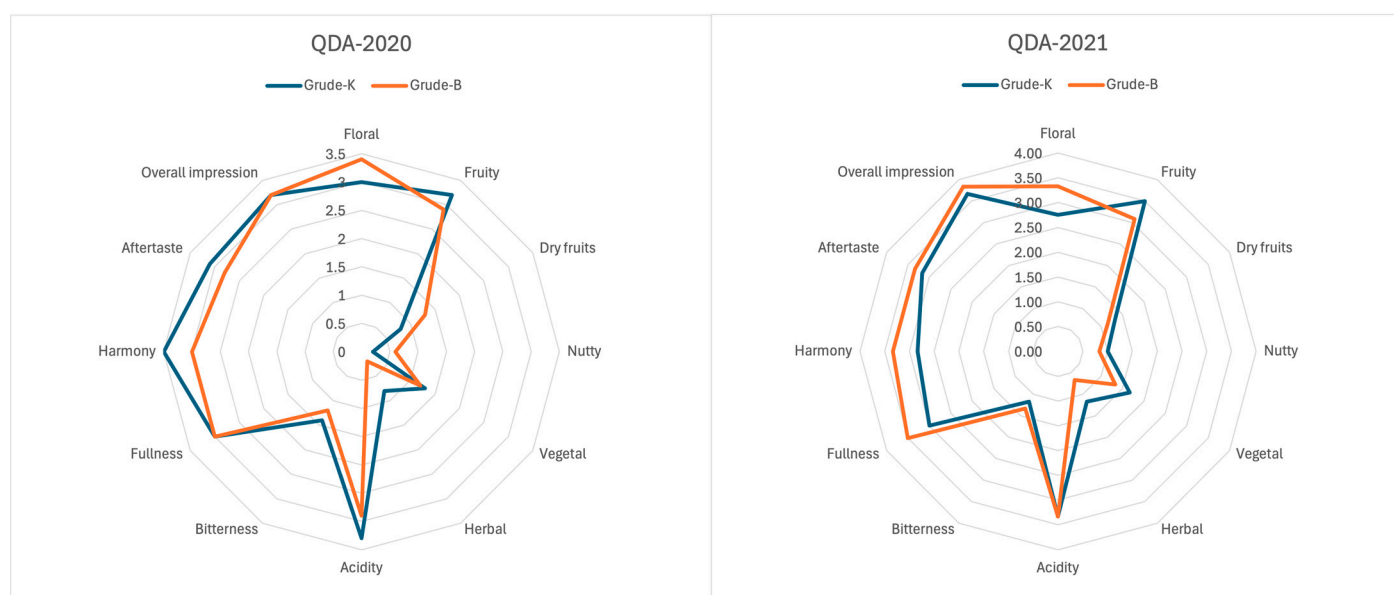


Figure 3. Conventional descriptive analysis (CDA) results for Malvasija Dubrovačka wines.

PLS is a powerful technique for modelling relationships between chemical analysis data (X variables) and sensory data (Y variables). Among the VOCs, all compounds were initially included. However, to obtain the optimal number of variables for the model, VIP (variable importance in projection) scores were used, eliminating variables whose VIP score was less than 0.8. This resulted in 39 variables that were used in the model. The sensory data used were obtained from the conventional descriptive analysis. In the PLS model, only data concerning aromas and flavors were included in the model, since these attributes relate to the chemical data, i.e., the VOC concentrations. In total, five attributes were included in the final PLS model, namely, floral, fruity, nutty, vegetal, and herbal. The model's quality is presented in Figure 4. The model exhibited strong predictive performance, as indicated by the cumulative Q^2 value, especially after adding Component 2. The proportion of

variance in the response variables (R^2Y cum) reflected a very good model fit and a high degree of explained variability in the sensory data. Furthermore, the explanatory power for the predictor variables (R^2X cum) suggested that the model efficiently captured the multivariate structure of the chemical data.

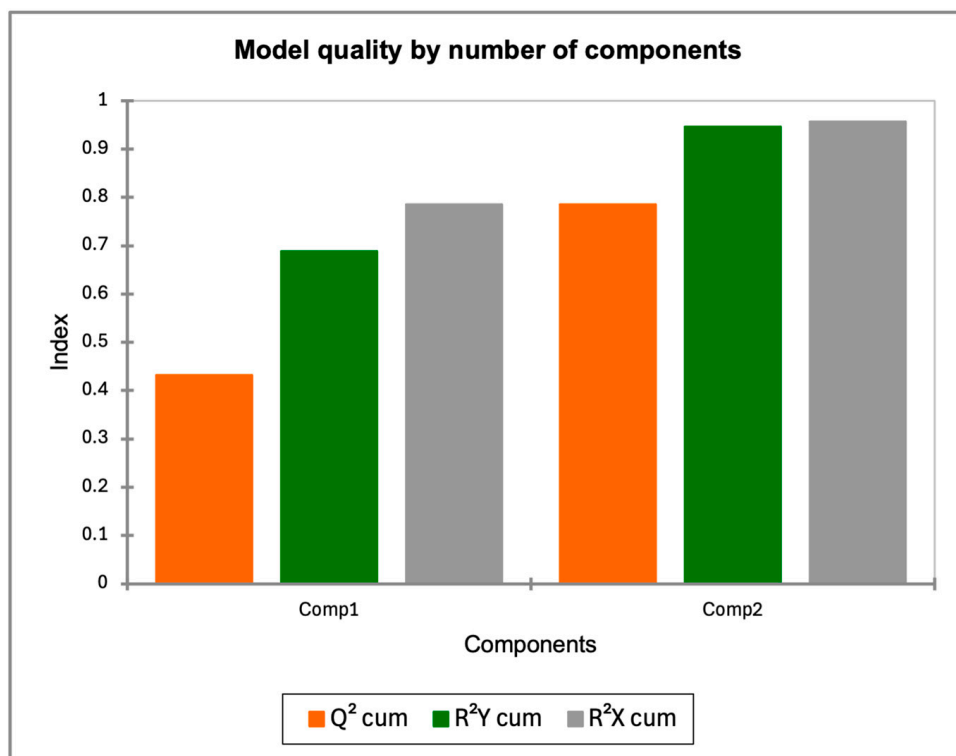


Figure 4. Quality of fit of partial least squares (PLS) model.

Figure 5 presents the results of the PLS analysis. The sensory descriptors fruity, herbal, and vegetal are in the third quadrant, in the negative region of the t_1 axis, aligning closely with the compounds 1-octanol, 2,3-butanediol, 3-(methylthio)-1-propanol, ethyl octanoate, and diethyl butanedioate. Most of these compounds are alcohols, which can impart green and vegetal aromas [25], while esters contribute to fruity aromas in wines, particularly in the Grude-K wine from the 2021 vintage. The floral attribute is located opposite, in the first quadrant, and is closely associated with monoterpenes such as linalool, citronellol, and menthol. This suggests that the floral attributes perceived in the wine samples were driven by the presence of these terpene compounds. The wines associated with floral perception included both vintages from the Grude-B location. The nutty attribute is also located in the third quadrant near the t_1 axis and appears to be moderately associated with trans-linalool oxide (furanoid) and ethyl hexanoate. The Grude-K 2020 wine sample was characterized by the presence of dodecanoic acid, TDN, and 3-carene. The PLS model gave insight into the role of specific volatile organic compounds in the shaping of the sensory character of the wine.

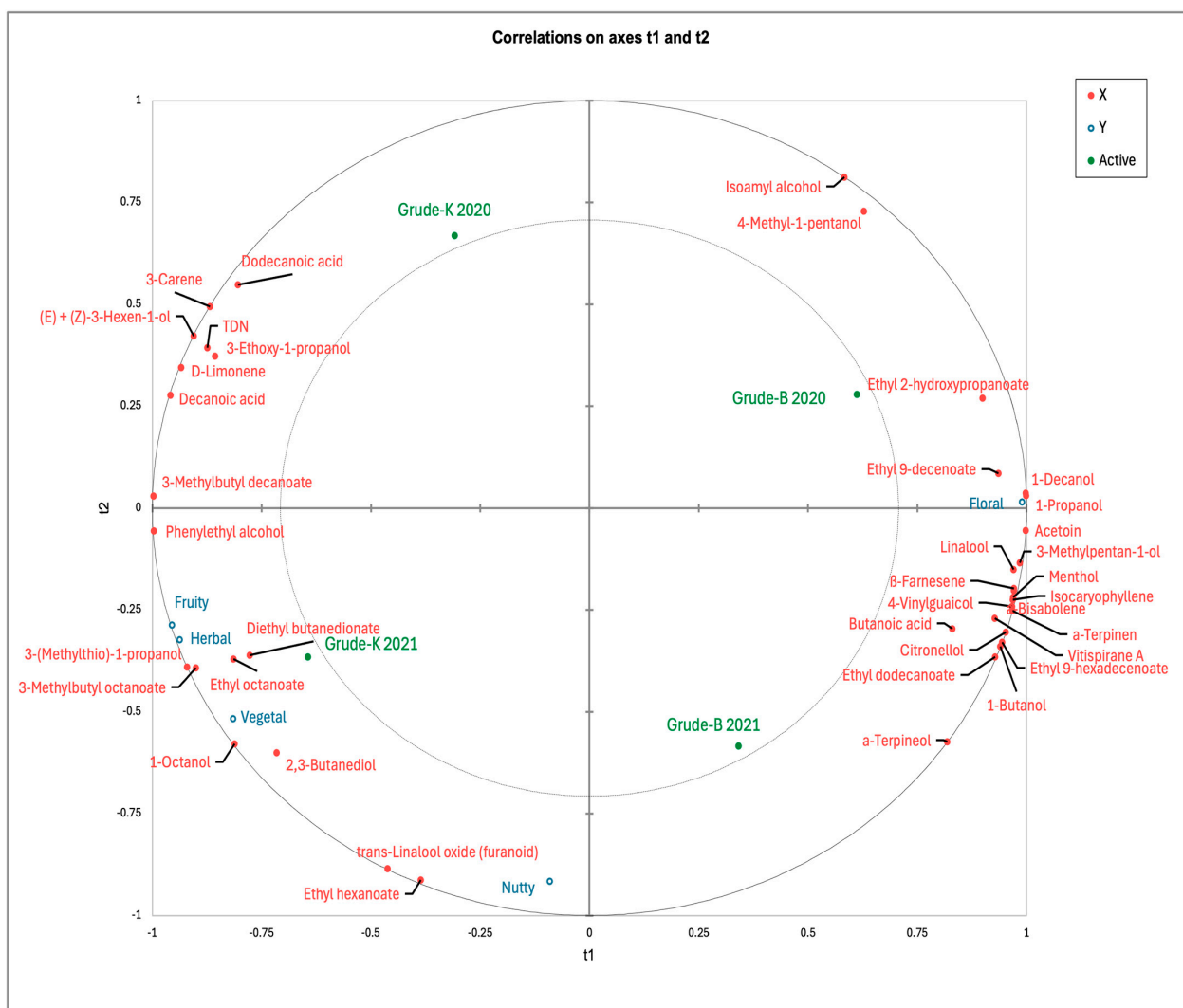


Figure 5. The PLS loading plot with wines presented in green, chemical data in red, and sensory attributes in blue.

4. Conclusions

This study demonstrates the significant influence of growing location and vintage year on the volatile organic compound profile of Malvasija Dubrovačka wines from the Konavle region in Croatia. A total of 54 VOCs were identified and quantified, showing clear distinctions between wines produced in two different locations and in two consecutive vintages (2020 and 2021). The results confirm that location had a stronger influence than the vintage on the overall VOC composition. The Grude-K wines showed the highest total fatty acid values, including hexanoic, octanoic, and decanoic acids, while the Grude-B wines were richer in terpenes—particularly α -terpinene, citronellol, hotrienol, and linalool—suggesting that location-specific factors significantly impacted the development of these aromatic compounds. (E)-linalool oxide (furanoid) was the most abundant terpene at both locations. A total of 18 VOCs had an ODT > 0.5, indicating their direct influence on the aroma profile of this wine. Statistical analysis (ANOVA and principal component analysis) demonstrated a clear differentiation between wines, with the formation of four distinct clusters corresponding to specific vineyard location and vintage interactions. Although most of the VOC groups had significant differences depending on location and year, the alcohol content remained stable.

The findings of this study highlight the crucial role of the vineyard location for the aroma and quality of the wine. Furthermore, long-term monitoring of climatic influences on VOC profiles could offer valuable information on the future evolution of Malvasija Dubrovačka wines under changing environmental conditions.

Author Contributions: Conceptualization, I.T. and E.M.; methodology, A.J.; formal analysis, D.I.Ž. and I.Š.; investigation, D.I.Ž. and D.S.; data curation, I.Š. and D.P.; writing—original draft preparation, D.I.Ž. and I.Š.; writing—review and editing, A.J. and D.P.; supervision, I.T. and E.M. All authors have read and agreed to the published version of the manuscript.

Funding: Dubrovnik-Neretva County, the City of Dubrovnik, and the Municipality of Konavle “Improvement of Grape and Wine Production of the Malvasija Dubrovačka Bijela Variety—Phase I (2020–2025)”. Research and Development of Plant Genetic Resources for Sustainable Agriculture, Center of Excellence for Biodiversity and Molecular Plant Breeding (CoE CroP-Bio-Div), Zagreb, Croatia (PK.1.1.10).

Data Availability Statement: The original contributions presented in this study are included in the article. Further inquiries can be directed to the corresponding author.

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

References

- Gonzalez-Barreiro, C.; Rial-Otero, R.; Cancho-Grande, B.; Simal-Gandara, J. Wine Aroma Compounds in Grapes: A Critical Review. *Crit. Rev. Food Sci. Nutr.* **2013**, *55*, 202–218. [CrossRef] [PubMed]
- Zhu, F.; Du, B.; Li, J.; Zhu, F.; Du, B.; Li, J. Aroma Compounds in Wine. In *Grape and Wine Biotechnology*; IntechOpen: London, UK, 2016; ISBN 978-953-51-2693-5.
- Cataldo, E.; Salvi, L.; Paoli, F.; Fucile, M.; Mattii, G.B. Effect of Agronomic Techniques on Aroma Composition of White Grapevines: A Review. *Agronomy* **2021**, *11*, 2027. [CrossRef]
- Polášková, P.; Herszage, J.; Ebeler, S.E. Wine Flavor: Chemistry in a Glass. *Chem. Soc. Rev.* **2008**, *37*, 2478–2489. [CrossRef]
- Ferreira, V.; Lopez, R. The Actual and Potential Aroma of Winemaking Grapes. *Biomolecules* **2019**, *9*, 818. [CrossRef] [PubMed]
- Šikuten, I.; Štambuk, P.; Andabaka, Ž.; Tomaz, I.; Marković, Z.; Stupić, D.; Maletić, E.; Kontić, J.K.; Preiner, D. Grapevine as a Rich Source of Polyphenolic Compounds. *Molecules* **2020**, *25*, 5604. [CrossRef]
- Orešković, I. *Malvasija—Glasovito VINO još iz Doba Dubrovačke Republike*; Vinarska poljoprivredna zadruga Malvasija dubrovačka bijela: Pridvorje, Croatia; Alfa—2 d.o.o.: Dubrovnik, Croatia, 2010; ISBN 978-953-56445-0-7.
- Lacombe, T.; Boursiquot, J.M.; Laucou, V.; Dechesne, F.; Varès, D.; This, P. Relationships and Genetic Diversity within the Accessions Related to Malvasia Held in the Domaine de Vassal Grape Germplasm Repository. *Am. J. Enol. Vitic.* **2007**, *58*, 124–131. [CrossRef]
- Crespan, M.; Cabello, F.; Giannietto, S.; Ibáñez, J.; Karoglan Kontić, J.; Maletic, E.; Pejić, I.; Rodríguez-Torres, I.; Antonacci, D. Malvasia Delle Lipari, Malvasia Di Sardegna, Greco Di Gerace, Malvasia de Sitges and Malvasia Dubrovačka—Synonyms of an Old and Famous Grape Cultivar. *Vitis Geilweilerhof* **2006**, *45*, 69–73.
- Maletić, E.; Pejić, I.; Karoglan Kontić, J.; Zdunić, D.; Preiner, D.; Šimon, S.; Andabaka, Ž.; Žulj Mihaljević, M.; Bubola, M.; Marković, Z.; et al. Ampelographic and Genetic Characterization of Croatian Grapevine Varieties. *VITIS—J. Grapevine Res.* **2015**, *54*, 93–98. [CrossRef]
- Zdunić, G.; Preece, J.; Dangl, G.; Pitcher, A.; Mucalo, A.; Maletic, E.; Pejić, I. Genetic Characterization of Grapevine Cultivars Collected throughout the Dalmatian Region. *Am. J. Enol. Vitic.* **2013**, *64*, 285–290. [CrossRef]
- Jeromel, A.; Jagatić Korenika, A.-M.; Tuščić, V.; Tomaz, I.; Maletić, E. The Effect of Enzyme Treatment on the Aroma Profile of Malvasija Dubrovačka Wine. In Proceedings of the VII Međunarodni Simpozij, Malvazije Mediterana, Dubrovnik, Croatia, 27–29 September 2023.
- Cirimotić, I.-A. Utjecaj Stabulacije na Sastav i Senzorna Svojstva Vina “Malvasija Dubrovačka”. Master’s Thesis, Department of Viticulture and Enology, Faculty of Agriculture, University of Zagreb, Zagreb, Croatia, 2024.
- Uzkuç, N.M.Ç.; Uzkuç, H.; Kavdır, Y.; Hamzaoglu, F.; Toklucu, A.K. Soil-Driven Terroir: Impacts on *Vitis vinifera* L. Cv. Karasakiz Wine Quality and Phenolic Composition. *J. Food Compos. Anal.* **2025**, *142*, 107444. [CrossRef]
- Mihelčič, A.; Lisjak, K.; Vanzo, A.; Sivilotti, P.; Čule, M.; Vrščaj, B. Different Soil Types and Relief Influence the Quality of Merlot Grapes in a Relatively Small Area in the Vipava Valley (Slovenia) in Relation to the Vine Water Status IVES. Available online: <https://ives-openscience.eu/12740/> (accessed on 25 March 2025).

16. OIV. *Compendium of International Methods of Wine and Must Analysis*; International Organization of Vine and Wine: Paris, France, 2021; Volume 1, ISBN 978-2-85038-033-4. Available online: https://scholar.google.com/scholar_lookup?title=Compendium+of+International+Methods+of+Wine+and+Must+Analysis&author=OIV&publication_year=2021 (accessed on 12 March 2025).
17. Tomaz, I.; Šikuten, I.; Tuščić, V.; Rendulić, N.; Preiner, D.; Buljević, N.; Korenika, A.-M.J.; Jeromel, A. Optimisation of SPME Arrow GC/MS Method for Determination of Wine Volatile Organic Compounds. *OENO One* **2024**, *58*. [\[CrossRef\]](#)
18. Falqué, E.; Fernández, E.; Dubourdieu, D. Differentiation of White Wines by Their Aromatic Index. *Talanta* **2001**, *54*, 271–281. [\[CrossRef\]](#) [\[PubMed\]](#)
19. Allen, M.S.; Lacey, M.J.; Boyd, S. Determination of Methoxypyrazines in Red Wines by Stable Isotope Dilution Gas Chromatography–Mass Spectrometry. *J. Agric. Food Chem.* **1994**, *42*, 1734–1738. [\[CrossRef\]](#)
20. Francis, I.L.; Newton, J.L. Determining Wine Aroma from Compositional Data. *Aust. J. Grape Wine Res.* **2005**, *11*, 114–126. [\[CrossRef\]](#)
21. Ohloff, G. *The Fashion of Odors and Their Chemical Perspectives: Scent and Fragrances*; Springer: Berlin/Heidelberg, Germany, 1994.
22. Mansour, G.; Ghanem, C.; Mercenaro, L.; Nassif, N.; Hassoun, G.; Caro, A.D. Effects of Altitude on the Chemical Composition of Grapes and Wine: A Review. *OENO One* **2022**, *56*, 227–239. [\[CrossRef\]](#)
23. Nguyen, T.H.; Zimmermann, D.; Müller, J.; Durner, D. Soil Types as Extrinsic Cues Differentially Shape Sensory Perception of German Riesling Wine. *OENO One* **2024**, *58*. [\[CrossRef\]](#)
24. Gutiérrez-Gamboa, G.; Zheng, W.; Martínez de Toda, F. Strategies in Vineyard Establishment to Face Global Warming in Viticulture: A Mini Review. *J. Sci. Food Agric.* **2021**, *101*, 1261–1269. [\[CrossRef\]](#)
25. Lukić, I.; Carlin, S.; Vrhovsek, U. Comprehensive 2D Gas Chromatography with TOF-MS Detection Confirms the Matchless Discriminatory Power of Monoterpenes and Provides In-Depth Volatile Profile Information for Highly Efficient White Wine Varietal Differentiation. *Foods* **2020**, *9*, 1787. [\[CrossRef\]](#)
26. Šikuten, I.; Štambuk, P.; Tomaz, I.; Marchal, C.; Kontić, J.K.; Lacombe, T.; Maletić, E.; Preiner, D. Discrimination of Genetic and Geographical Groups of Grape Varieties (*Vitis vinifera* L.) Based on Their Volatile Organic Compounds. *Front. Plant Sci.* **2022**, *13*, 942148. [\[CrossRef\]](#)
27. Lukic, I.; Horvat, I. Differentiation of Commercial PDO Wines Produced in Istria (Croatia) According to Variety and Harvest Year Based on HS-SPME-GC/MS Volatile Aroma Compound Profi Ling. *Food Technol. Biotechnol.* **2017**, *55*, 95–108. [\[CrossRef\]](#)
28. Gambetta, J.; Bastian, S.; Cozzolino, D.; Jeffery, D. Factors Influencing the Aroma Composition of Chardonnay Wines. *J. Agric. Food Chem.* **2014**, *62*, 6512–6534. [\[CrossRef\]](#) [\[PubMed\]](#)
29. Korenika, A.M.J.; Preiner, D.; Tomaz, I.; Jeromel, A. Volatile Profile Characterization of Croatian Commercial Sparkling Wines. *Molecules* **2020**, *25*, 4349. [\[CrossRef\]](#) [\[PubMed\]](#)
30. Oliveira, J.; Faria, M.; Sá, F.; Barros, F.; Araújo, I. C6-Alcohols as Varietal Markers for Assessment of Wine Origin. *Anal. Chim. Acta* **2006**, *563*, 300–309. [\[CrossRef\]](#)
31. Dunlevy, J.; Kalua, C.; Keyzers, R.; Boss, P.K. The Production of Flavour & Aroma Compounds in Grape Berries. In *Grapevine Molecular Physiology and Biotechnology*, 2nd ed.; Springer: Berlin/Heidelberg, Germany, 2009; pp. 293–340. ISBN 978-90-481-2304-9.
32. Mendes-Pinto, M.M. Carotenoid Breakdown Products the—Norisoprenoids—In Wine Aroma. *Arch. Biochem. Biophys.* **2009**, *483*, 236–245. [\[CrossRef\]](#) [\[PubMed\]](#)
33. 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: This Article Is Published in Cooperation with Macrowine 2021, 23–30 June 2021. *OENO One* **2022**, *56*, 185–193. [\[CrossRef\]](#)
34. Lin, J.; Massonnet, M.; Cantu, D. The Genetic Basis of Grape and Wine Aroma. *Hortic. Res.* **2019**, *6*, 81. [\[CrossRef\]](#)
35. Marais, J.; van Wyk, C.J.; Rapp, A. Effect of Sunlight and Shade on Norisoprenoid Levels in Maturing Weisser Riesling and Chenin Blanc Grapes and Weisser Riesling Wines. *S. Afr. J. Enol. Vitic.* **1992**, *13*, 23–32. [\[CrossRef\]](#)
36. Oliveira, C.; Ferreira, A.C.; Costa, P.; Guerra, J.; Guedes De Pinho, P. Effect of Some Viticultural Parameters on the Grape Carotenoid Profile. *J. Agric. Food Chem.* **2004**, *52*, 4178–4184. [\[CrossRef\]](#)
37. Falcão, L.D.; de Revel, G.; Perello, M.C.; Moutsiou, A.; Zanús, M.C.; Bordignon-Luiz, M.T. A Survey of Seasonal Temperatures and Vineyard Altitude Influences on 2-Methoxy-3-Isobutylpyrazine, C13-Norisoprenoids, and the Sensory Profile of Brazilian Cabernet Sauvignon Wines. *J. Agric. Food Chem.* **2007**, *55*, 3605–3612. [\[CrossRef\]](#)
38. Louw, L.; Tredoux, A.G.J.; van Rensburg, P.; Kidd, M.; Naes, T.; Nieuwoudt, H.H. Fermentation-Derived Aroma Compounds in Varietal Young Wines from South Africa. *S. Afr. J. Enol. Vitic.* **2010**, *31*, 213–225. [\[CrossRef\]](#)
39. Antalick, G.; Perello, M.-C.; Revel, G. de Esters in Wines: New Insight through the Establishment of a Database of French Wines. *Am. J. Enol. Vitic.* **2014**, *65*, 293–304. [\[CrossRef\]](#)
40. Luo, J.; Brothie, J.; Pang, M.; Marriott, P.J.; Howell, K.; Zhang, P. Free Terpene Evolution during the Berry Maturation of Five *Vitis vinifera* L. Cultivars. *Food Chem.* **2019**, *299*, 125101. [\[CrossRef\]](#)
41. Savoi, S.; Herrera, J.C.; Carlin, S.; Lotti, C.; Bucchetti, B.; Peterlunger, E.; Castellarin, S.D.; Mattivi, F. From Grape Berries to Wines: Drought Impacts on Key Secondary Metabolites. *OENO One* **2020**, *54*, 569–582. [\[CrossRef\]](#)

42. Duchêne, E.; Butterlin, G.; Claudel, P.; Jaegli, N. Consequences of Elevated Temperatures During Ripening on the Biosynthesis of Monoterpenols in Grape Berries. In Proceedings of the Climwine2016, Bordeaux, France, 10–13 April 2016.
43. Mateo, J.J.; Jiménez, M. Monoterpenes in Grape Juice and Wines. *J. Chromatogr. A* **2000**, *881*, 557–567. [[CrossRef](#)]
44. Šikuten, I.; Anić, M.; Štambuk, P.; Tomaz, I.; Stupić, D.; Andabaka, Ž.; Marković, Z.; Karoglan Kontić, J.; Maletić, E.; Karoglan, M.; et al. *Biosynthesis and Profiling of Grape Volatile Compounds*; Jordao, A.M.S.T., Ed.; Nova Science Publishers: New York, NY, USA, 2020; pp. 271–320. ISBN 978-1-5361-8308-5.

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.