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Analysis of Volatile Aroma Compounds and Sensory Characteristics Contributing to Regional Style of Red Wines from Hexi Corridor Based on Sixteen Grape Varieties/Clones

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Abstract: Hexi Corridor is an excellent region for high-quality wines in China, but the characteristic and style of red wine from this region is unclear. To elucidate the regional style of red wines from Hexi Corridor, the aroma properties of red wines made from 16 different varieties/clones of grapes were comprehensively analyzed using HS-SPME-GC-MS, sensory evaluation, odor activity value method, and partial least squares regression analyses. We identified 52 aroma compounds and found that floral and black berry provided a good reference for shaping red wine style and selecting related varieties in Hexi Corridor region. Ethyl caproate, (Z)-3-hexen-1-ol, ethyl 9-decenoate, and hexyl alcohol, which were the characteristic aroma substances of Hexi Corridor red wines, had positive effects on the floral aroma of Merlot, Cabernet Sauvignon, Pinot Noir, and Malbec wines. Hexyl alcohol and (Z)-3-hexen-1-ol also contributed to the black berry and spice aromas, while isobutyl acetate opposed the expression of these aromas of Malbec and Cabernet Franc wines. These results showed that the sensory characteristics of floral and black berry are of vital significance in shaping the red wine style of Hexi Corridor, among which ethyl caproate, (Z)-3-hexen-1-ol, ethyl 9-decenoate, and hexyl alcohol are important contributors.

Keywords: red wine; characteristic aroma; volatile compounds; Hexi Corridor region; odor activity value

Citation: Zang, X.; Du, Q.; Qu, R.; Ye, D.; Lu, Y.; Liu, Y. Analysis of Volatile Aroma Compounds and Sensory Characteristics Contributing to Regional Style of Red Wines from Hexi Corridor Based on Sixteen Grape Varieties/Clones. *Fermentation* **2022**, *8*, 501. https://doi.org/10.3390/fermentation8100501

Academic Editor: Ye Liu

Received: 31 August 2022
Accepted: 28 September 2022
Published: 30 September 2022

1. Introduction

The Gansu Hexi Corridor region is located in northwestern China, at latitudes of 36–40° N and altitudes of 1500–2000 m. It has the most suitable combination of water, soil, light, and heat resources for the production of wine grapes, as well as a profound cultural heritage and long history of winemaking [1]. This region is one of the high-quality wine producing areas in China. Hexi Corridor is windy and experiences little rainfall, with annual precipitation and evaporation of approximately 110.5 and 2646.4 mm, respectively [2]. The production regions from which the grapes used in this study were sourced are dominated by sierozem soils. Local cloudiness is scarce and the annual sunshine duration can be as long as 3297 h. The abundance of local light resources is conducive to the accumulation of material for crops. A previous study showed that the rapid accumulation of sugar and highly soluble solids and the sparse occurrence of pests and diseases in the region facilitate the production of high-quality wine grapes [3].

The unique style and typicality of wine are influenced by the geographical location of the vineyard, local climate and soil, grape variety, planting method, fertility management, the winemaking process, aging environment, and other "terroir" factors [4]. Style plays an extremely important role in the grape and wine industry, influencing consumer preferences [5]. The aroma characteristic of wine, influenced by the terroir, is the main component of its style and is one of the most important factors that determine the quality of the wine, as organic acids, phenolics, and other flavor substances constitute the taste profile of the wine [6]. Therefore, an investigation of the prominent aromatic characteristics of a wine is important for understanding the distinctive style of its region of origin. Recently, many studies have been conducted on the regional aroma characteristics of wines. Because those wines were made from the same grape variety, the wines from various regions were presented with unique regional chemical matrices and aromatic attributes [7,8]. Likewise, Vidal icewines from Canada and China had different characteristic sensory attributes, which were associated with acetates and alcohols and ethyls and terpenes, respectively [9]. Specifically, the sensory profiles of icewines from China were characterized by nut and honey aromas, while those from Canada had more caramel and rose aromas. Apart from Vidal icewines, the aromatic characteristics of Cabernet Sauvignon and Merlot wines from several regions in China have also been reported [10,11].

Currently, research on Hexi Corridor wines is focused on tracing their geographical origins and detecting the substances in the wines that affect food safety, such as biogenic amines and fungal toxins [3,12]. Nonetheless, limited studies have been conducted on wine aroma. Thus, insufficient information on regional features of Hexi Corridor wines hindered shaping and development of local wine styles. To address this issue, 16 typical grape varieties/clones from Hexi Corridor, China were chosen to produce dry red wines with the indigenous commercial wine yeast, CECA. The resultant wines were characterized for aroma typicality of Hexi Corridor wines via analyzing their volatile and sensory profile. Subsequently, partial least squares regression (PLSR) analysis was conducted to identify the outstanding aroma characteristics and the corresponding volatile compounds. This study provides substantial insights into the regional characteristics of dry red wines sourced from Hexi Corridor, which can contribute to the diverse expression of aroma characteristics in wines from high-quality wine regions in China.

2. Materials and Methods

2.1. Grape Materials

In this study, 16 different clones of 5 main red wine grape varieties from Hexi Corridor were used. Grapes were harvested in 2017 from Minqin (38°43′ N, 103°26′ E), Gansu, China; the standard enological parameters are listed in Table 1.

Table 1. Standard enological parameters of grape berries.

Variety	Clone	Abbreviate	Reducing Sugars (g/L)	Titratable Acidity (g Tartaric Acid/L)	pH
Merlot	343	ML	257.38	7.02	3.60
	VCR1		230.20	6.27	3.91
	VCR9		210.30	7.34	3.70
Pinot Noir	375	PN	235.70	6.75	3.71
	VCR18		226.40	7.53	3.80
	792		246.30	6.95	3.81
	VCR10		231.30	5.79	3.60
Cabernet Franc	215	CF	268.20	4.25	3.79
	678		235.30	5.02	3.70
	396		233.50	6.57	3.51
	15		229.40	7.33	3.61
Cabernet Sauvignon	169	CS	248.90	7.72	3.60
	170		222.70	7.72	3.60
	VCR11		238.70	8.87	3.50
Malbec	598	MB	245.70	8.87	3.71
	VCR6		228.00	8.50	3.60

2.2. Yeast Strains

The wine was fermented using CECA, an indigenous *S. cerevisiae* strain isolated by our team from Ningxia, China. The dried yeast powder is produced and commercialized by Angel Yeast Co., Ltd. (Yichang, China).

2.3. Chemical Reagents

Chromatographically pure chemical standards (≥97%) were purchased from Sigma-Aldrich Co., Ltd. (Beijing, China) and included 1-hexanol, isobutanol, 1-butanol, isoamyl alcohol, 1-octanol, linalool, 1-decanol, benzyl alcohol, phenylethanol, isobutyric acid, hexanoic acid, octanoic acid, ethyl acetate, isoamyl acetate, ethyl butanoate, ethyl caproate, ethyl octanoate, ethyl caprate, diethyl succinate, ethyl laurate, and β-damascenone.

2.4. Winemaking Process

Grapes were destemmed and crushed, and 50 mg/L SO_2 was added. The fermentations were conducted in 10 L glass jars containing 7.5 L grape must with skin. Pectinase (Lallzyme EX) purchased from Lallemand Co., Ltd. (Montreal, Canada), was added to the must. The amount of dried yeast used was 200 mg/L. The dried CECA yeast powder was dissolved in 10 times its weight in distilled water and activated in a 38 °C water bath for 20 min. Then, the grape juice to be fermented was added to the above yeast solution in batches, so that the yeast can adapt to the fermentation environment in advance. The final volume of grape juice and yeast liquid was equal. When the temperature difference between the yeast solution and the must to be inoculated was less than 10 °C, the yeast solution was added to the must. During fermentation, the temperature was kept at 22–26 °C, and the temperature and specific gravity were measured every 12 h. After fermentation, the must was filtered using gauze, supplemented with SO_2 to 50 mg/L, and clarified naturally at 10 °C, followed by bottling and storage at 10–15 °C. Each treatment was conducted in triplicate.

2.5. Volatile Compound Analysis

The volatility of the samples was analyzed by headspace solid-phase microextraction (HS-SPME) coupled with gas chromatography-mass spectrometry (GC-MS), following a method described by Lan et al., 2019 [13]. The sample pre-treatment procedure was as follows: 5 mL of the sample was added to a 20-mL vial, and 2 g of NaCl and 10 µL of 4-methyl-2-pentanol (internal standard, 2.004 g/L) were added simultaneously and the vial was sealed. The sample was then agitated at 250 rpm for 30 min and maintained at 40 °C through a heated platform. Pretreated 2 cm 50/30-µm divinylbenzene/Carboxen/polydimethylsiloxane (DVB/CAR/PDMS) SPME fiber (Supelco, Bellefonte, PA, USA) inserted into the headspace for extraction for 30 min. Thereafter, an injection system PAL RSI 85 (CTC Analytics AG, Zwingen, Switzerland) was used to automatically inject the sample at an inlet temperature of 250 °C followed by the resolution of the sample for 8 min.

A 7890B-5975B GC-MS coupler (Agilent, Santa Clara, CA, USA) equipped with an HP-INNOWAX capillary column (60 m × 0.25 mm, 0.25 µm) was used. The operating conditions for the GC-MS analyses were as follows: The column temperature was held at 50 °C for 1 min. Subsequently, the temperature was increased to 220 °C at a rate of 3 °C/min and the solution was kept under this condition for 5 min. The carrier gas was high-purity helium with a flow rate of 1 mL/min. During the solid-phase microextraction, splitless injection of the analyte was performed. MS was conducted at an interface temperature of 280 °C, and the temperature of the ion source was 230 °C. Electron ionization (EI) was employed as the ionization method and the ion energy was 70 eV. The mass scan range was m/z 29–350, and the running time was 62.67 min. Three independent replicates were performed for each sample.

Qualitative analysis of the aromatic substances in the wine samples was performed using MS in fullion scan mode, based on the chromatographic retention times and MS information of existing standards, NIST14. L standard library comparison results, retention index based on n-alkanes (C7–C24) (Supelco, Bellefonte, PA, USA) and references to relevant literature. The quantification was based on standard compounds, and the semi-quantification of aromatic substances in the absence of specimens was based on the principle of similar chemical structures and similar carbon atomic number.

2.6. Sensory Evaluation

Sensory evaluation of the aroma characteristics of the wines was performed according to the method described by Tao et al., 2010 [14]. The tasting group consisted of 15 judges majoring in enology. The tasting panel was trained in wine sniffing twice a week for 60–90 min. Each wine sample was sniffed at least for 5–7 s and while shaking for 8–10 s. Five descriptors from the given odor profile were selected and scored on a 5-point scale. Quantification of the sensory assessment was performed using the combined index of intensity and frequency of occurrence of aroma (MF), and the calculation formula 1 used is as follows:

$$MF\% = \sqrt{F(\%)I(\%)} \quad (1)$$

where F (%) represents the frequency of the aroma descriptors used, and I (%) is the aroma intensity.

2.7. Identification of Characteristic Aroma

The odor activity value (OAV) of an aroma compound equals its concentration divided by its threshold concentration in water. Published threshold values were used for the calculations [14]. Compounds with OAVs ≥ 1 are considered potential contributors to the odor characteristics of the samples [15].

Partial least squares regression (PLSR) models for single sensory attributes and volatile aroma components were developed for the wine samples corresponding to each grape variety. The uncertainty analysis was performed based on cross-validation to identify volatile aroma substances that contributed significantly to the sensory characteristics. The MF (%) values of each sensory characteristic are denoted as Y, and the fermentation aroma components which OAV > 0.1 are collected as X.

2.8. Data Processing

Analysis of variance (ANOVA) was performed using the IBM SPSS Statistics 25 (SPSS Inc., Chicago, IL, USA) software, principal component analysis (PCA), and PLSR analysis were performed using the Unscrambler X software (CAMO Software AS, Oslo, Norway), and all variables were standardized (1/standard deviation). The comparison and visualization of the MF (%) values of different types of sensory characteristics were performed using the "vioplot" function in the "ggplot2" version 3.3.5. Data are expressed as mean ± standard deviation (SD).

3. Results and Discussion

3.1. Volatile Component Analysis

The volatile aroma substances of the wines were detected using HS-SPME-GC-MS. As shown in Table S1, 52 volatile substances were detected in the test samples. These substances included esters, higher alcohols, volatile fatty acids, C6 compounds, carbonyl compounds, terpenoids, and isoprenoids. The total aroma content measured for each wine sample ranged from 174.58 to 290.26 mg/L. Among the samples, wines made from Merlot 343 grapes had the highest total contents of aroma components. It is also significantly higher than the aroma content of Merlot wines from some areas of Ningxia and Hebei in China [10]. However, those made from the four Pinot Noir clones had relatively low total contents of aroma components, which were 60–76% of those in the Merlot 343 wines (Table S1).

Depending on the source, volatile aroma substances can be classified into varietal and fermentation aromas. The varietal aroma originated from grape berries, including C6 compounds, terpenoids, and norisoprenoids. The fermentation aromas originated from the fermentation process, and the corresponding compounds included higher alcohols, esters, fatty acids, and carbonyl compounds [1]. As shown in Figure 1, the total varietal aroma contents of the wine samples from the four Pinot Noir clones were higher and significantly different from those of the wine samples obtained from the other grape varieties. This result is similar to that of Pinot Noir wines from the Central Otago region of New Zealand [16]. However, the wines produced from the Cabernet Franc clones contained significantly lower proportions of varietal components, which were 27.8–47.8% of those of the Pinot Noir wine samples. The Cabernet Franc wines from the Hebei region of China presented similar results in terms of varietal aromas [17]. The 16 wine samples differed slightly in fermentation aroma contents. In general, the wines from the Merlot and Pinot Noir clones exhibited higher and lower levels of total fermentation aroma content, respectively, and the Pinot Noir VCR 9 sample from the latter group had the lowest.

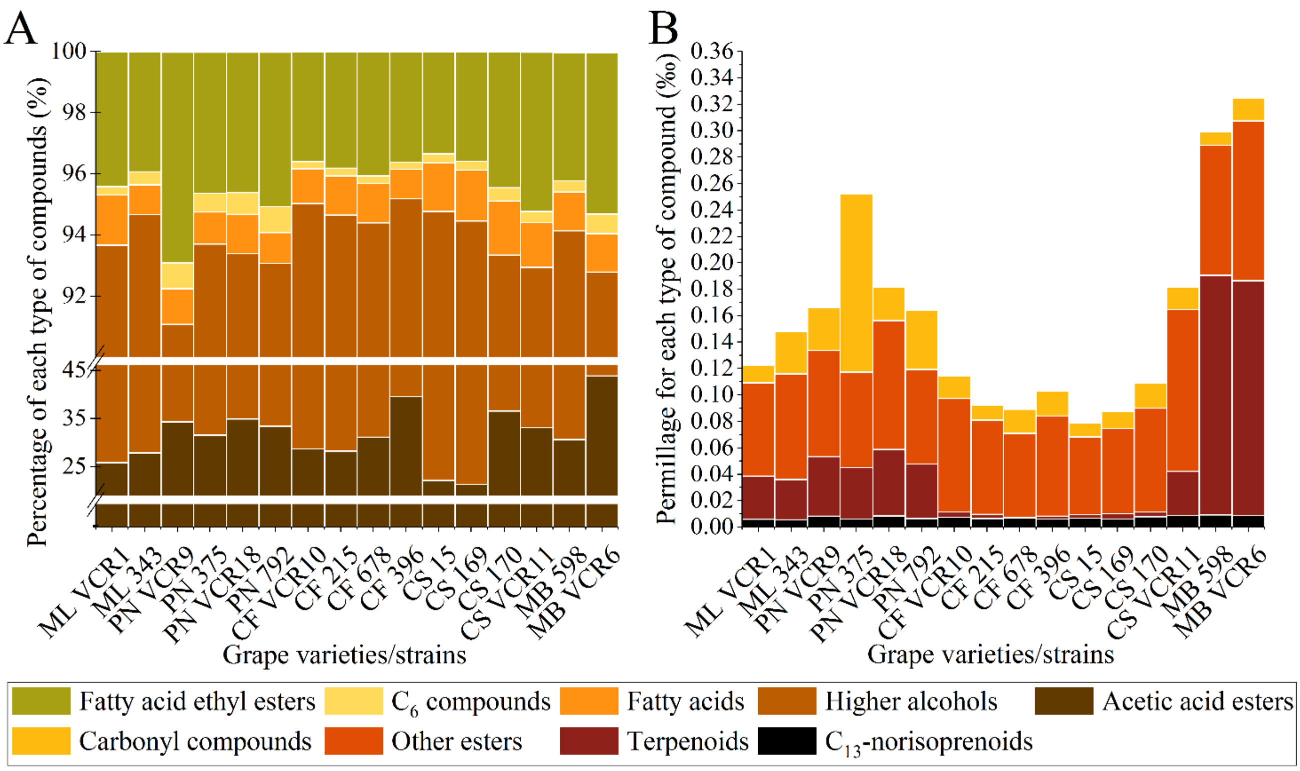

Figure 1. Proportions of various aroma substances in wine samples. (**A**) Percentage share of each type of aroma having high content. (**B**) Percentage of thousand points for some of the lower content aromas.

3.2. OAV-Based Characteristic Aroma Analysis

A total of eight varietal aroma components were detected in the wine samples, including four terpenoids, three C6 compounds, and one C_{13}-norisoprenoid (Figure S1 and Table S1). Among these, β-damascenone had an OAV > 1 and a potentially large contribution to the floral aroma of the wine samples. Substances with OAV > 0.1 included hexanol, (Z)-3-hexen-1-ol, and geraniol, which influence the aroma of the wines through their interaction with each other (Table S2).

As shown in Table S1, among the wines prepared from the five grape varieties in this study, Malbec wines had the most abundant varietal aroma components, while Cabernet Franc and Cabernet Sauvignon, each with only five aroma components, with the lowest abundance of varietal aroma components. In terms of the contents of each type of aroma, Pinot Noir had a significantly higher content of C6 compounds than the other varieties and exhibited a stronger herbaceous vegetal flavor [18]. The contents of terpenoids in the Malbec wine samples from both clones were significantly higher (5–10 times) than those in the other wine samples. As shown in Figure S1, in terms of terpenoid content, the Malbec wine samples were outliers because there were no significant differences in terpenoid content between the other varieties. Terpenoids impart floral and fruity aromas to wine [19]. Notably, citronellyl butyrate, and nerol were exclusively detected in the Malbec wine samples. In addition, the geraniol content of Malbec was significantly higher than other varieties. The OAV of geraniol exceeded 0.1, which imparted a rose aroma to the wine samples [20]. There was a significant difference in geraniol content between the two clones of this variety, with Malbec 598 having a geraniol content that was 1.5 times higher than that of Malbec VCR6. However, geraniol was not detected in the Cabernet Franc and Cabernet Sauvignon wine samples. β-Damascenone, a C_{13}-norisoprenoids compound, mainly imparts sweet and floral aromas to the wine [21]. Despite being present in minute quantities, β-damascenone, with a low threshold of 0.05 μg/L, is the largest contributor to the overall aromatic composition.

There were 19 detected fermentation aroma components with OAV > 0.1, among which ethyl acetate, ethyl butyrate, isoamyl acetate, ethyl caproate, ethyl caprylate, ethyl decanoate, ethyl 9-decenoate, isobutanol, isoamyl alcohol, and isovaleric acid had an OAV > 1 (Table S2). All the fermentation aroma components with an OAV > 0.1 were subjected to PCA. The loadings of fermentation aroma components on the first two main components and the distribution of the samples are shown in Figure 2.

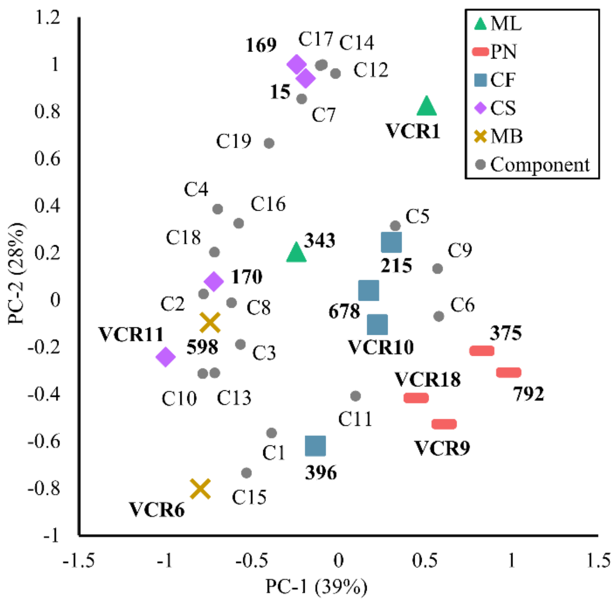

Figure 2. Loadings of fermented and varietal aroma compounds and the distribution of the wine samples in the first two PCs. C1: ethyl acetate; C2: isobutyl acetate; C3: ethyl butyrate; C4: isoamyl acetate; C5: isobutanol; C6: 1-butanol; C7: isoamyl alcohol; C8: ethyl caproate; C9: ethyl lactate; C10: ethyl octanoate; C11: decanal; C12: isobutyric acid; C13: ethyl decanoate; C14: isovaleric acid; C15: ethyl 9-decenoate; C16: hexyl alcohol; C17: 2-phenylethanol; C18: octanoic acid; C19: decanoic acid.

PC1 and PC2 accounted for 39% and 28%, respectively, of the overall variance. Most of the fermentation aroma components and the three grape clones, viz. Cabernet Sauvignon 170, Cabernet Sauvignon VCR11, and Malbec 598, were distributed at the negative end of PC1. Fatty acids, fatty acid ethyl esters, acetates, most of the higher alcohols, isobutyric acid, Cabernet Sauvignon 15, and Cabernet Sauvignon 169 were distributed in the positive end of PC2. The wine samples from the four Pinot Noir clones were distributed in the fourth quadrant, surrounded principally by 1-butanol and decanal. The other three Cabernet Franc clones, except Cabernet Franc 396, were distributed at the positive end of PC1, close to isobutanol, ethyl lactate, 1-butanol, and decanal. Cabernet Franc 396 was distributed at the negative end of PC2, surrounded by ethyl acetate, ethyl 9-decenoate, and decanal. Merlot VCR1 was distributed in the first quadrant with only isobutanol distributed around it, while Merlot 343 was distributed in the second quadrant, close to most of the fermentation aroma components. Malbec VCR6 was distributed in the fourth quadrant, surrounded by most of the fatty acid ethyl ester components.

The analysis showed that Cabernet Sauvignon 170, Cabernet Sauvignon VCR11, and Malbec 598 had high contents of high-quality fermentation aroma components, mainly including fatty acids, fatty acid ethyl esters, and acetate, which accounted for the high-quality fruit flavors in the wines. The compositions and contents of the fermentation aromas of the wines from the four Pinot Noir clones were similar. Although the compounds responsible for the fermentation aromas of the wine samples from different clones of other varieties were similar, their contents varied widely. Among the four Cabernet Franc clones, Cabernet Franc 396 produced wines with higher levels of ethyl acetate, ethyl 9-decenoate, and decanal, which impart floral, cream, and cheese aromas [22]. The other three clones led to similar distributions of wine samples with higher levels of isobutanol, ethyl lactate, and 1-butanol, which provide aromas of pineapple, honey, butter, and caramel [23]. Among the different clones, Cabernet Sauvignon was found to be more dispersed. The distance between Cabernet Sauvignon 15 and Cabernet Sauvignon 169 was short, and the contents of isoamyl alcohol, isobutanol, isovaleric acid, and phenylethanol were higher; they produce aromas reminiscent of rose, bread, fermentation, grains, and sweet fruits [24]. Cabernet Sauvignon 170 had higher levels of isobutyl acetate, isoamyl acetate, ethyl caproate, capric acid, and caprylic acid, producing more sweet fruit, candied fruit, banana, and oil aromas [25]. Cabernet Sauvignon VCR11 had higher levels of ethyl caprylate and ethyl caprate, adding pleasant fruit flavors. The wine samples from the two Merlot clones were farther apart, with Merlot 343 having a higher content of isoamyl alcohol and more prominent fermented and grainy flavors, while Merlot VCR1 had a higher content of ethyl lactate and more creamy and buttery flavors. Malbec VCR6, which was rich in tropical fruit flavors, had higher contents of ethyl acetate and ethyl 9-decenoate. Malbec 598 had higher levels of isobutyl acetate and ethyl caprate, which resulted in banana, candied fruit, and coconut aromas. In summary, fermentation aromas contributed more to the sensory flavor of the wine samples than varietal aromas. Therefore, more volatiles belonging to the class of fermentation aromas were selected during the analysis using the PLSR model.

3.3. PLSR-Based Characteristic Aroma Analysis

The sensory evaluation results of the tasting panel were quantified by the MF (%) values (Table S3). From the overall level of MF (%) values, we found there were significant differences in black berry, floral, and green sensory characteristics, while there was no obvious divergence in spice and red berry sensory characteristics of the wine samples among various varieties and clones (Figure 3 and Table S3). The Merlot, Cabernet Franc VCR10, and Pinot Noir (except Pinot Noir 792) varieties had significantly lower sensory characteristics of black berries than the other wine samples, and the overall aroma reflected relatively weak characteristics of ripe fruit. Merlot VCR1, Pinot Noir 375, Cabernet Franc 215, Cabernet Sauvignon 170, and two clones of Malbec had significant floral characteristics, and the floral characteristics of the wine samples from different clones were different. The green flavor is closely dependent on the maturity of varieties and we found that there was a large difference in green flavor among different clones of the same variety. However, there was no green in Malbec VCR6, which can be used to create a mature wine style. Noteworthily, the diversity of the characteristics of black berry and floral suggested that the adaptability between the terroir and varieties/clones in Hexi Corridor made an important contribution to the formation of these two flavors. That is to say, those two characteristics can provide a good reference for the shaping of wine style and the selection of related varieties in this region. We further performed the PLSR analysis of the volatile components and the corresponding sensory attributes of the wine samples to identify the key compounds contributing to the formation of those sensory characteristics.

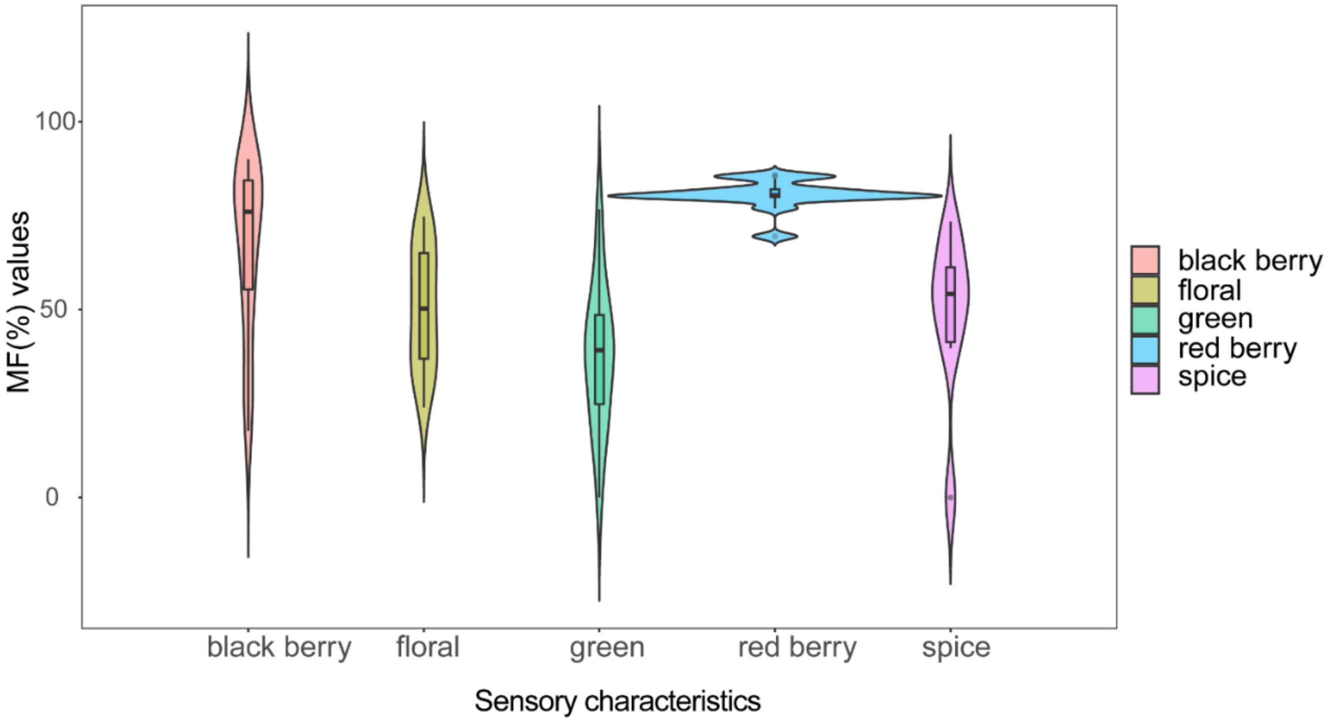

Figure 3. Violin plot showing the MF (%) values of sensory characteristics of the wine samples among various varieties and clones.

PLSR analysis was performed on the sensory characteristic attributes and the corresponding compounds in the wine samples. The regression results for the floral aromas with Merlot, Cabernet Sauvignon, Pinot Noir, and Malbec were satisfactory. The PLSR models of single sensory attributes of grape varieties with volatile aroma substances showed that floral aromas were positively correlated with ethyl caproate, ethyl 9-decenoate, hexanol, and (Z)-3-hexen-1-ol (Figure 4). As shown in Table S4, the correlation coefficients of ethyl caproate with the Merlot, Cabernet Sauvignon, and Pinot Noir samples were 0.061, 0.069, and 0.089, respectively; the correlation coefficients of ethyl 9-decenoate with the Merlot, Cabernet Sauvignon, and Malbec samples were 0.06, 0.038, and 0.056, respectively; the correlation coefficients of hexanol with the Merlot, Cabernet Sauvignon, and Malbec samples were 0.062, 0.116, and 0.056, respectively; and the correlation coefficients of (Z)-3-hexen-1-ol with the Merlot, Cabernet Sauvignon, and Malbec samples were 0.067, 0.121, and 0.057, respectively.

Ethyl caproate, which is formed as a byproduct during the synthesis of long-chain fatty acids by yeast, presents aromas of apple, raw green banana, and pineapple, as well as floral aromas reported in Moscatel vine-shoots [26]. Ethyl caproate has been found to be a prominent volatile component of Cabernet Sauvignon, Cabernet Gernischt, Cabernet Franc and Chardonnay wines from parts of Hexi Corridor region. Ethyl caproate is an important volatile component of Marselan wines and is considered to be one of the compounds that distinguish wine regions [27,28]. It is also an aroma commonly found in top-fermented beers [29]. In addition, ethyl caproate, an aroma component specific to Chinese strong-flavor baijiu, is one of the core components that determine the quality of baijiu [30]; therefore, it is possible that ethyl caproate is one of the main aroma compounds found in fermented spirits.

Ethyl 9-decenoate has a pleasant floral aroma [22]. It is less reported but detected at higher levels in white wines [31]. This compound aids distinction between icewines and late harvest wines from the same wineries, grape varieties, and vintages in Canada and the Czech Republic [32]. Fruit wines, such as mulberry and strawberry wines, have been reported to contain this ester, which contributes to the floral aromas of these wines [33].

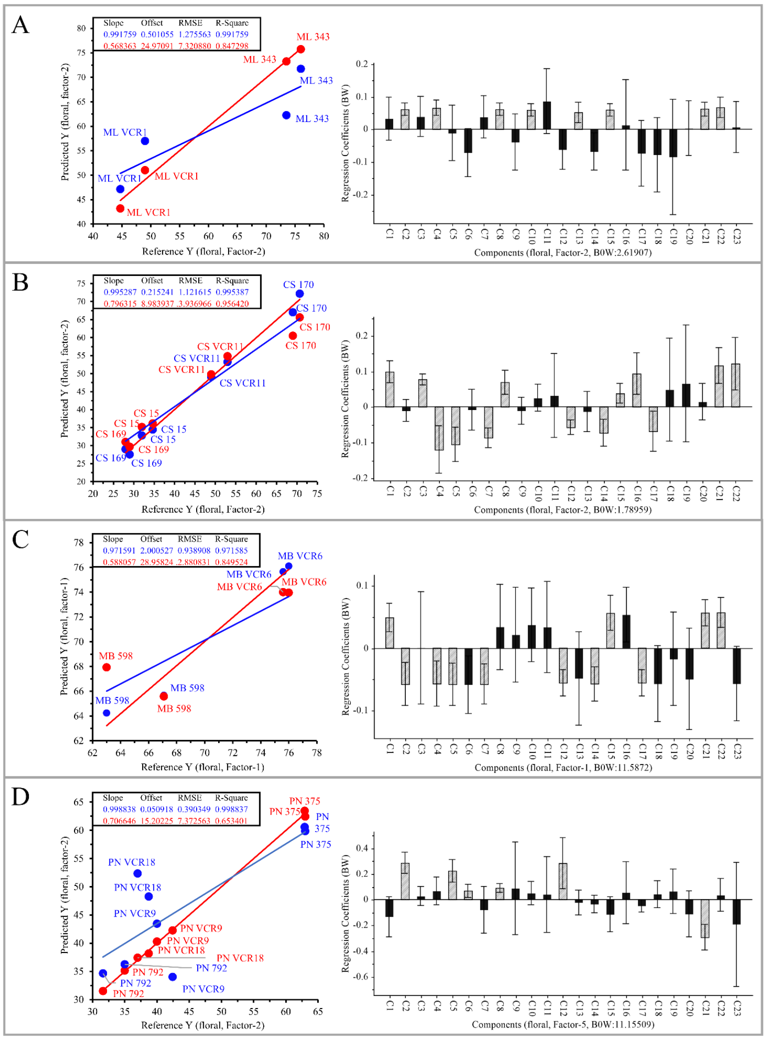

Figure 4. The PLSR analysis of floral sensory and volatile compounds, standardized and estimated regression coefficients from the PLSR model showed a significant correlation between volatile compounds and floral sensory odor attributes in Merlot (**A**), Cabernet Sauvignon (**B**), Malbec (**C**), and Pinot Noir (**D**) wine samples. Bar with slash indicates a significant effect ($p < 0.05$).

Hexanol imparts botanical-type aromas, commonly described as green/herbaceous, and freshly cut grass, but has also been reported to provide floral aromas [36]. Hexanol is associated with nut and honey aromas in Vidal icewines [9]. This compound has also been reported to be the key aroma component in peach. Aroma analysis of flat peach juice using PLSR showed that (Z)-3-hexen-1-ol provided a floral aroma, which is consistent with the results obtained from this study [37].

The black berry properties of the Malbec and Cabernet Franc wine samples were analyzed, as shown in Figure 5A,B. The volatile compounds that correlated positively and negatively with the black berry aroma were (Z)-3-hexen-1-ol and isobutyl acetate, respectively. The corresponding correlation coefficients were 0.059 and −0.058 for Malbec, and 0.126 and −0.165 for Cabernet Franc (Table S4). Isobutyl acetate contributed 'stone fruit' aromas to the natural fermentation of Chardonnay and banana aromas to the aligoté wines of Burgundy [38,39]. It was found to impart fruit aromas to beers, thus improving the flavor and aroma harmony and making the beer more pleasant [40]. In conclusion, the aroma of isobutyl acetate is biased towards bananas and drupes and opposes the expression of black berry aroma.

As shown in Figure 5C, ethyl 9-decenoate, hexyl alcohol, and (Z)-3-hexen-1-ol were positively correlated with spice aroma in Malbec, with correlation coefficients of 0.057, 0.059, and 0.059, respectively (Table S4). Combining the previous analyses for the floral (Figure 4C) and black berry aromas (Figure 5A) of Malbec, the results of the PLSR analysis for Malbec were found to be more consistent, and ethyl 9-decenoate, hexyl alcohol, and (Z)-3-hexen-1-ol were found to correlate positively with floral, black berry, and spice aroma characteristics, respectively.

The PLSR presented some characteristic volatile compounds that were useful in discerning the sensory origin of red wine samples between Hexi Corridor and other wine regions. In addition, identification of the most important wine aroma compounds and their contribution to wine aroma has potential to assist wine producers to brew and blend wines and establish region style, and guide researchers to better understand the mechanisms governing transformation of precursor compounds into contributors to the aroma of finished wines.

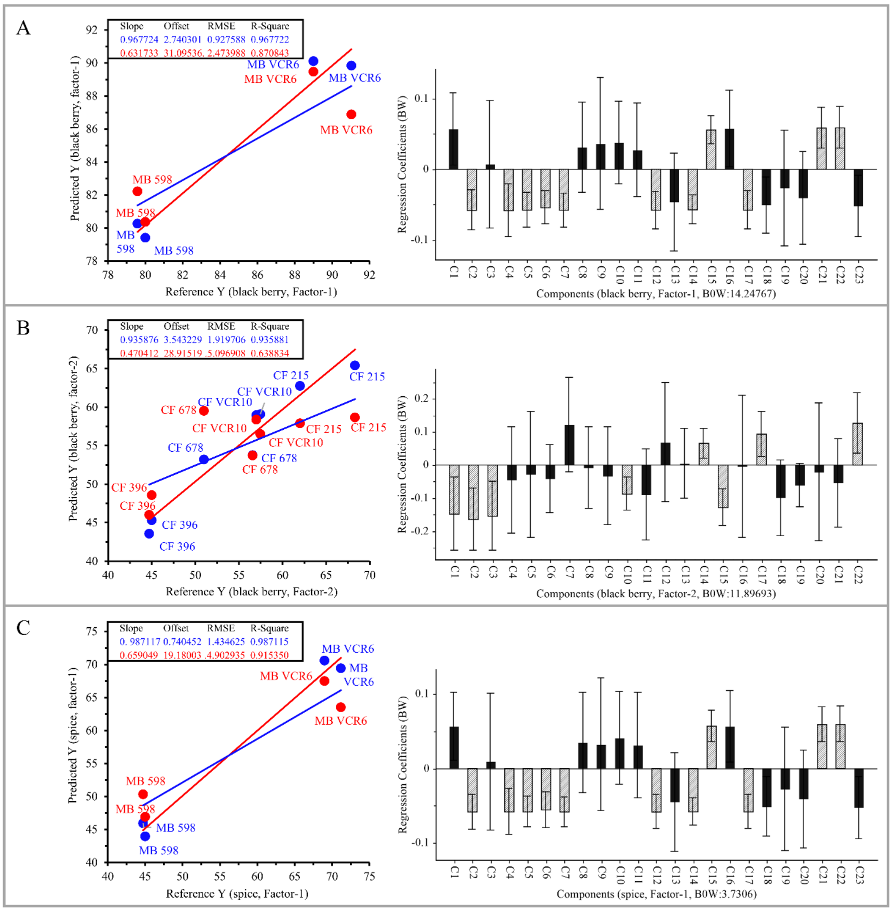

Figure 5. PLSR analysis of black berry sensory attributes of Malbec (A) and Cabernet Franc (**B**) and spice sensory attributes of Malbec (**C**) with volatile compounds. Normalized and estimated regression coefficients from the PLSR model showed significant correlations between volatile compounds and black berry and spice sensory aroma attributes in these wine samples. Bar with slash indicates a significant effect ($p < 0.05$).

4. Conclusions

In this study, typical aroma characteristics and the corresponding volatile compounds of Hexi Corridor wines were analyzed. Ethyl caproate had a positive effect on the floral sensory characteristics of Merlot, Cabernet Sauvignon, and Pinot Noir wine samples; (Z)-3-hexen-1-ol, ethyl 9-decenoate, and hexyl alcohol had a positive correlation with the floral sensory characteristics of Malbec, Merlot, and Cabernet Sauvignon wine samples. (Z)-3-Hexen-1-ol had a positive effect on the sensory characteristics of black berries in Malbec and Cabernet Franc and the sensory attribute "spice" in Malbec. Isobutyl acetate had an aroma bias toward banana and drupe, and opposed the expression of black berry aroma in Malbec and Cabernet Franc. The sensory characteristics of floral and black berry are of great significance in shaping the red wine style of Hexi Corridor. Ethyl caproate, (Z)-3-hexen-1-ol, ethyl 9-decenoate, and hexyl alcohol are the characteristic volatile compounds of dry red wines from Hexi Corridor.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/fermentation8100501/s1, Figure S1: Contents of varietal aroma compounds in wine samples made from different grape varieties/clones; Table S1: Content of aroma volatile compounds in wine samples from the Hexi Corridor; Table S2: The OAV values of aroma volatile compounds in Hexi Corridor wine samples; Table S3: MF% of aromatic characteristics of wines made from 16 varieties/clones; Table S4: The correlation coefficients of PLSR between wine volatiles and sensory odor descriptors.

Author Contributions: Conceptualization, D.Y.; Data curation, X.Z., Q.D. and R.Q.; Funding acquisition, Y.L. (Yanlin Liu); Methodology, X.Z. and Q.D.; Project administration, Y.L. (Yanlin Liu); Resources, Y.L. (Yao Lu); Software, R.Q.; Supervision, Y.L. (Yao Lu); Validation, D.Y.; Writing—original draft, X.Z. and R.Q.; Writing—review and editing, Q.D. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the Joint Funds of the National Natural Science Key Foundation of China (U21A20269), Ningxia Hui Autonomous Region Key R&D Project (2020BCF01003), China Agriculture Research System (CARS-29-jg-03), Natural Science Basic Research Program of Shaanxi (2022JM-129), and Chinese Universities Scientific Fund (2452021023).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

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

References

1. Zhang, B.; Wang, X.-Q.; Yang, B.; Li, N.-N.; Niu, J.-M.; Shi, X.; Han, S.-Y. Copigmentation evidence of phenolic compound: The effect of caffeic and rosmarinic acids addition on the chromatic quality and phenolic composition of Cabernet Sauvignon red wine from the Hexi Corridor region (China). *J. Food Compos. Anal.* **2021**, *102*, 104037. [CrossRef]
2. Jiang, X.J.; Liu, W.; Chen, C.; Liu, J.; Yuan, Z.-Q.; Jin, B.C.; Yu, X.Y. Effects of three morphometric features of roots on soil water flow behavior in three sites in China. *Geoderma* **2018**, *320*, 161–171. [CrossRef]
3. Han, S.Y.; Hao, L.L.; Shi, X.; Niu, J.M.; Zhang, B. Development and application of a new QuEChERS method in UHPLC-QqQ-MS/MS to detect seven biogenic amines in Chinese wines. *Foods* **2019**, *8*, 552. [CrossRef]
4. Bokulich, N.A.; Thorngate, J.H.; Richardson, P.M.; Mills, D.A. Microbial biogeography of wine grapes is conditioned by cultivar, vintage, and climate. *Proc. Natl. Acad. Sci. USA* **2013**, *111*, E139–E148. [CrossRef] [PubMed]
5. Urvieta, R.; Buscema, F.; Bottini, R.; Coste, B.; Fontana, A. Phenolic and sensory profiles discriminate geographical indications for Malbec wines from different regions of Mendoza; Argentina. *Food Chem.* **2018**, *265*, 120–127. [CrossRef]
6. González-Barreiro, C.; Rial-Otero, R.; Cancho-Grande, B.; Simal-Gándara, J. Wine aroma compounds in grapes: A critical review. *Crit. Rev. Food Sci.* **2015**, *55*, 202–218. [CrossRef]
7. Dall'Asta, C.; Cirlini, M.; Morini, E.; Galaverna, G. Brand-dependent volatile fingerprinting of Italian wines from Valpolicella. *J. Chromatogr. A* **2011**, *1218*, 7557–7565. [CrossRef]
8. Longo, R.; Carew, A.; Sawyer, S.; Kemp, B.; Kerslake, F. A review on the aroma composition of *Vitis vinifera* L. Pinot noir wines: Origins and influencing factors. *Crit. Rev. Food Sci.* **2021**, *61*, 1589–1604. [CrossRef]
9. Huang, L.; Ma, Y.; Tian, X.; Li, J.-M.; Li, L.-X.; Tang, K.; Xu, Y. Chemosensory characteristics of regional Vidal icewines from China and Canada. *Food Chem.* **2018**, *261*, 66–74. [CrossRef]
10. Jiang, B.; Xi, Z.; Luo, M.; Zhang, Z. Comparison on aroma compounds in Cabernet Sauvignon and Merlot wines from four wine grape-growing regions in China. *Food Res. Int.* **2013**, *51*, 482–489. [CrossRef]
11. Tao, Y.; Zhang, L. Intensity prediction of typical aroma characters of cabernet sauvignon wine in Changli County (China). *LWT* **2010**, *43*, 1550–1556. [CrossRef]
12. Su, Y.-Y.; Gao, J.; Zhao, Y.-F.; Wen, H.-S.; Zhang, J.-J.; Zhang, A.; Yuan, C.-L. Geographical Origin Classification of Chinese Wines Based on Carbon and Oxygen Stable Isotopes and Elemental Profiles. *J. Food Prot.* **2020**, *83*, 1323–1334. [CrossRef]

13. Lan, Y.-B.; Xiang, X.-F.; Qian, X.; Wang, J.-M.; Ling, M.-Q.; Zhu, B.-Q.; Liu, T.; Sun, L.-B.; Shi, Y.; Reynolds, A.G.; et al. Characterization and differentiation of key odor-active compounds of 'Beibinghong' icewine and dry wine by gas chromatography-olfactometry and aroma reconstitution. *Food Chem.* **2019**, *287*, 186–196. [CrossRef] [PubMed]
14. Tao, Y.-S.; Liu, Y.-Q.; Li, H. Sensory characters of Cabernet Sauvignon dry red wine from Changli County (China). *Food Chem.* **2009**, *114*, 565–569. [CrossRef]
15. Nicolotti, L.; Mall, V.; Schieberle, P. Characterization of Key Aroma Compounds in a Commercial Rum and an Australian Red Wine by Means of a New Sensomics-Based Expert System (SEBES)—An Approach To Use Artificial Intelligence in Determining Food Odor Codes. *J. Agric. Food Chem.* **2019**, *67*, 4011–4022. [CrossRef]
16. Schueuermann, C.; Khakimov, B.; Engelsen, S.B.; Bremer, P.; Silcock, P. GC-MS Metabolite Profiling of Extreme Southern Pinot noir Wines: Effects of Vintage, Barrel Maturation, and Fermentation Dominate over Vineyard Site and Clone Selection. *J. Agric. Food Chem.* **2016**, *64*, 2342–2351. [CrossRef]
17. Zhang, M.; Xu, Q.; Duan, C.; Qu, W.; Wu, Y. Comparative Study of Aromatic Compounds in Young Red Wines from Cabernet Sauvignon, Cabernet Franc, and Cabernet Gernischet Varieties in China. *J. Food Sci.* **2007**, *72*, C248–C252. [CrossRef] [PubMed]
18. Capone, D.; Barker, A.; Pearson, W.; Francis, I. Influence of inclusion of grapevine leaves, rachis and peduncles during fermentation on the flavour and volatile composition of Vitis vinifera cv. Shiraz wine. *Aust. J. Grape Wine R.* **2021**, *27*, 348–359. [CrossRef]
19. Black, C.; Parker, M.; Siebert, T.E.; Capone, D.L.; Francis, I. Terpenoids and their role in wine flavour: Recent advances. *Aust. J. Grape Wine Res.* **2015**, *21*, 582–600. [CrossRef]
20. Fariña, L.; Boido, E.; Carrau, F.; Versini, G.; Dellacassa, E. Terpene Compounds as Possible Precursors of 1,8-Cineole in Red Grapes and Wines. *J. Agric. Food Chem.* **2005**, *53*, 1633–1636. [CrossRef]
21. Pineau, B.; Barbe, J.C.; Van Leeuwen, C.; Dubourdieu, D. Which impact for β-damascenone on red wines aroma? *J. Agr. Food Chem.* **2007**, *55*, 4103–4108. [CrossRef]
22. Welke, J.E.; Zanus, M.; Lazzarotto, M.; Zini, C.A. Quantitative analysis of headspace volatile compounds using comprehensive two-dimensional gas chromatography and their contribution to the aroma of Chardonnay wine. *Food Res. Int.* **2014**, *59*, 85–99. [CrossRef]
23. Ubeda, C.; Kania-Zelada, I.; del Barrio-Galán, R.; Medel-Marabolí, M.; Gil, M.; Peña-Neira, Á. Study of the changes in volatile compounds, aroma and sensory attributes during the production process of sparkling wine by traditional method. *Food Res. Int.* **2019**, *119*, 554–563. [CrossRef]
24. de Lerma, N.L.; Peinado, R.A.; Puig-Pujol, A.; Mauricio, J.C.G.; Moreno, J.; Garcia-Martinez, T. Influence of two yeast strains in free, bioimmobilized or immobilized with alginate forms on the aromatic profile of long aged sparkling wines. *Food Chem.* **2018**, *250*, 22–29. [CrossRef]
25. Tristezza, M.; di Feo, L.; Tufariello, M.; Grieco, F.; Capozzi, V.; Spano, G.; Mita, G. Simultaneous inoculation of yeasts and lactic acid bacteria: Effects on fermentation dynamics and chemical composition of Negroamaro wine. *LWT* **2016**, *66*, 406–412. [CrossRef]
26. Sánchez-Gómez, R.; Zalacain, A.; Pardo, F.; Alonso, G.; Salinas, M. Moscatel vine-shoot extracts as a grapevine biostimulant to enhance wine quality. *Food Res. Int.* **2017**, *98*, 40–49. [CrossRef]
27. Lu, Y.; Sun, F.; Wang, W.; Liu, Y.; Wang, J.; Sun, J.; Mu, J.; Gao, Z. Effects of spontaneous fermentation on the microorganisms diversity and volatile compounds during 'Marselan' from grape to wine. *LWT* **2020**, *134*, 110193. [CrossRef]
28. Fabani, M.; Ravera, M.J.; Wunderlin, D.A. Markers of typical red wine varieties from the Valley of Tulum (San Juan-Argentina) based on VOCs profile and chemometrics. *Food Chem.* **2013**, *141*, 1055–1062. [CrossRef]
29. Pires, E.J.; Teixeira, J.A.; Brányik, T.; Vicente, A.A. Yeast: The soul of beer's aroma—A review of flavour-active esters and higher alcohols produced by the brewing yeast. *Appl. Microbiol. Biotechnol.* **2014**, *98*, 1937–1949. [CrossRef]
30. Wang, Q.; Liu, K.; Liu, L.; Zheng, J.; Chen, T.; Chen, F.; Li, P.; Zhang, M.; Shen, X. Correlation analysis between aroma components and microbial communities in Wuliangye-flavor raw liquor based on HS-SPME/LLME-GC–MS and PLFA. *Food Res. Int.* **2020**, *140*, 109995. [CrossRef]
31. Rodrigues, F.; Caldeira, M.; Câmara, J. Development of a dynamic headspace solid-phase microextraction procedure coupled to GC–qMSD for evaluation the chemical profile in alcoholic beverages. *Anal. Chim. Acta* **2008**, *609*, 82–104. [CrossRef]
32. Setkova, L.; Risticevic, S.; Pawliszyn, J. Rapid headspace solid-phase microextraction-gas chromatographic–time-of-flight mass spectrometric method for qualitative profiling of ice wine volatile fraction: II: Classification of Canadian and Czech ice wines using statistical evaluation of the data. *J. Chromatogr. A* **2007**, *1147*, 224–240. [CrossRef]
33. Kafkas, E.; Cabaroglu, T.; Selli, S.; Bozdoğan, A.; Kürkçüoğlu, M.; Paydaş, S.; Başer, K.H.C. Identification of volatile aroma compounds of strawberry wine using solid-phase microextraction techniques coupled with gas chromatography–mass spectrometry. *Flavour Frag. J.* **2006**, *21*, 68–71. [CrossRef]
34. Matsui, K. Green leaf volatiles: Hydroperoxide lyase pathway of oxylipin metabolism. *Curr. Opin. Plant Biol.* **2006**, *9*, 274–280. [CrossRef]
35. Hatanaka, A. The biogeneration of green odour by green leaves. *Phytochemistry* **1993**, *34*, 1201–1218. [CrossRef]
36. Genovese, A.; Yang, N.; Linforth, R.; Sacchi, R.; Fisk, I. The role of phenolic compounds on olive oil aroma release. *Food Res. Int.* **2018**, *112*, 319–327. [CrossRef]

37. Tian, H.; Wang, P.; Zhan, P.; Yan, H.; Zhou, W.; Zhang, F. Effects of β-glucosidase on the aroma characteristics of flat peach juice as assessed by descriptive sensory analysis and gas chromatography and compared by partial least squares regression. *LWT* **2017**, *82*, 113–120. [CrossRef]
38. Puertas, B.; Jimenez-Hierro, M.; Cantos-Villar, E.; Marrufo-Curtido, A.; Carbú, M.; Cuevas, F.; Moreno-Rojas, J.; González-Rodríguez, V.; Cantoral, J.; Ruiz-Moreno, M. The influence of yeast on chemical composition and sensory properties of dry white wines. *Food Chem.* **2018**, *253*, 227–235. [CrossRef]
39. Darsonval, M.; Alexandre, H.; Grandvalet, C. Genetically engineered Oenococcus oeni strains to highlight the impact of estA2 and estA7 esterase genes on wine ester profile. *Food Microbiol.* **2016**, *60*, 21–28. [CrossRef]
40. Dack, R.E.; Black, G.W.; Koutsidis, G.; Usher, S.J. The effect of Maillard reaction products and yeast strain on the synthesis of key higher alcohols and esters in beer fermentations. *Food Chem.* **2017**, *232*, 595–601. [CrossRef]