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Modulating the Formation of Meili Wine Aroma by Prefermentative Freezing Process

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ABSTRACT: The influence of a prefermentative freezing process on changes of aromatic characteristics and volatile compounds in Meili wines was studied to optimize freezing parameters and reveal the mathematical relationship between aromatic characteristics and volatile compounds. The wines obtained were characterized by sensory evaluation and stir bar sorptive extraction (SBSE) followed by a thermal desorption−gas chromatography−mass spectrometry analysis. A total of 28 aromatic descriptors from 6 categories of wine aroma terminology were identified by judging with high "modified frequency (MF%)". In addition, 19 varietal aroma compounds and 36 fermentation aroma compounds were quantitated, followed by the determination of odor activity values (OAVs). On the basis of the data obtained, principal component analysis (PCA) was used to find the relationship between characteristic aroma terms and different freezing conditions, and then partial least-squares regression (PLSR) was proposed to establish the mathematical relationship between the resulting terms and impact odorants. Natural thawing treatment on frozen must resulted in higher aroma quality with higher extraction of varietal aroma compounds. Lower frozen maceration temperature contributed to higher esters and organic acids. Impact aroma compounds were related to models for floral, sweet fruit, temperate fruit, and vegetal, whereas the model of rose and strawberry contained only varietal volatile compounds, and temperate fruit could be regressed by impact fermentation aroma compounds.

KEYWORDS: *Meili wine, aromatic characteristics, formation, volatile compounds, regression*

■ INTRODUCTION

Wine aroma is an important aspect of wine sensory quality, reflecting the styles and characteristics of wines. Volatile compounds influence the sensory characteristics of wines, particularly the aromatic characteristics. The profile of aromatic compounds in a wine depends on factors such as the grape variety, growing region, climatic conditions, agricultural practices, winemaking technology, and aging processes.

China lies to the west of the Pacific Ocean. More than half of the wine-producing districts of China have climates with abundant rain in the summer and autumn. Wine grapes cannot reach full maturity in most years. Therefore, the grapes cannot attain their optimal winemaking quality, lacking the aromatic characteristics and olfactometric traits of typical wines of the Mediterranean climate.

Winemaking techniques are used to express the strong points of grape varieties in wine. Different winemaking processes will decide the profile of chemical components in wine, and then they give different sensory styles and qualities. Recently, research on the influence of winemaking techniques on wine chemicals and quality has been published. Cold prefermentative maceration, also known as cold soaking, is one of these techniques, which has become very popular among winemakers over recent years. Prefermentative maceration is defined as the period of time from the filling of tanks with the crushed grapes to the beginning of the alcoholic fermentation. When it occurs at low temperature, it is called cold maceration.[1] In red wines, the target of cold prefermentative maceration is to enhance the extraction of soluble water compounds in the absence of ethanol. Because the cap has not been formed, the contact between the solid parts and the must is better.[2]

The effects of freezing treatments at the cellular level have been studied. The release of anthocyanins, tannins, and aroma precursors is enhanced,[3] providing a theoretical basis for frost treatment to improve the sensory quality of wine. Temperature and skin contact time are important factors to be considered in the prefermentative cold macerations. Parenti et al.[3] established that the lower the maceration temperature, the better the results obtained. Some research has suggested that a short maceration time could significantly enhance the sensory quality of wines from Muscat grapes and Merlot, Cabernet Sauvignon, and Pinot noir wines.[4,5] The combination of maceration and other treatments, such as freeze concentration and carbonic maceration, has a good effect on the quality of special varieties and wines under the special climatic conditions.[6,7] Freeze maceration treatments increased the amount of total aromatic components, especially terpenols and fatty acids.[4]

To reveal the effect of prefermentative freezing on Meili wine aroma, one important aspect in flavor research is the exploration of the existing relationships between sensory and instrumental data.[8−10] Several authors have suggested the use of multivariate strategies such as partial least-squares (PLS) regression to predict sensory descriptors from chemical composition in wine.[11−14]

Meili (*Vitis vinifera* L.), a new red grape cultivar, was released in 2010 by Northwest A&F University (Yangling, China). The cultivar was hybridized with European species (*V. vinifera* L.)

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including Merlot, Riesling, and Muscat by recurrent selection strategies. Contrary to its parents, this red grape cultivar is highly disease resistant and cold resistant. The red wine and rosé wine made from Meili are gorgeous and balanced, having a rose and elegant fruity flavor. Yangling is one county in Shaanxi province and is typical of the seasonal climate. Meili in Yangling is difficult to ripen enough to express its full winemaking characteristics. Álvarez et al.[15] reported that the effect of cold prefermentative maceration was more important when this technique was applied with less mature grapes. Therefore, in this work, a prefermentative freezing technique was designed to extract more aromatic compounds from Meili grapes grown in Yangling and then improve the aroma quality. The aim of the work was to find optimal parameters of the freezing process for Meili in Yangling and to reveal the mathematic correlations between aromatic characteristics and impact odorants of this variety.

■ MATERIALS AND METHODS

Grape Materials. About 650 kg of Meili (*V. vinifera* L.) grapes was collected from Cao Xinzhuang vineyard, Yangling, Shaanxi, in July 2010. Meili must had a titratable acidity of 8.5 g/L (expressed as tartaric acid) and reducing sugars of 160 g/L.

Winemaking Process. The primary vinification of the control wine was carried out in the following manner. Grapes were stemmed and crushed on a pocket grape destemmer−crusher. The must was treated with sulfur dioxide (about 50 mg/L) in stainless steel tanks (50 L capacity) for settling after about 24 h. Active dry yeast powder was used to start must fermentation. Fermentation was carried out at 25−30 °C. Sugar was added to increase the alcohol content to 11% (vol) during the vigorous fermentation period. The whole fermentation lasted for 7−8 days. After fermentation, the wine was racked, and sulfur dioxide (about 50 mg/L) was added. Then the wine was performed with the general stabilizing processes, which included fining with 1.0 g/L bentonite, cold treatment at −4 °C for 8 days, and enclosed racking. The wine was stored at 4 °C in stainless steel tanks prior to analysis. For the prefermentive freezing processes, grapes or the must was frozen after crushing. Berries were thawed to room temperature and then were stemmed and crushed. The following processes were the same as the control. If the must was frozen, it was inoculated with yeast after being thawed to room temperature. Then the following processes were the same.

The prefermentative freezing process was designed considering the following four influencing factors: freezing temperature (−20 and −10 °C), freezing time (4 and 6 h), grape state during freezing (must and berry), and thawing methods (microwave thawing and natural thawing). Each treatment was done in duplicate.

Sensory Analysis. The sensory analysis was performed as described by Tao et al.[16] A panel of tasters, consisting of 30 students, had been trained with a "Le Nez du Vin" aroma kit to conduct the wine sensory analysis. In the analysis of a balanced and completed block design, each panelist was told to describe the wine aroma profile using five or six terms of Le Nez du Vin. They scored the intensity of each term using a five-point scale. The data processed were a mixture of intensity and frequency of detection, which was calculated with the formula

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

where $F(\%)$ is the detection frequency of an aromatic attribute expressed as a percentage and $I(\%)$ is the average intensity expressed as a percentage of the maximum intensity.

Chemical and Reagents. All reagents used were of analytical grade. Absolute ethanol, tartaric acid, and sodium chloride were purchased from Xi'an Chemical Factory (Xi'an, China). Aromatic reference compounds were purchased from Sigma-Aldrich (Beijing sector, China).

Stir Bar Sorptive Extraction (SBSE) Sampling Conditions. Ten milliliters of wine sample was diluted with 10 mL of saturated salt water in a 20 mL vial, into which 20 μL of internal standard solution was added. A preconditioned stir bar (Twister) coated with polydimethylsiloxane (PDMS) phase (1 cm length, 0.5 mm thickness; Gerstel Inc., Baltimore, MD, USA) was used to extract volatile compounds. The stir bar was preconditioned with solvent (methanol/dichloromethane 1:1) according to the manufacturer's instruction, then dried with air, and conditioned for 30 min at 280 °C. The sample was extracted with the stir bar for 1 h at a speed of 1000 rpm. After extraction, the stir bar was rinsed with distilled water, dried with a tissue paper, and placed into a sample holder for GC-MS analysis. Each sample was extracted in triplicate.

Gas Chromatography−Mass Spectrometry (GC-MS) Analysis. GC-MS analyses were performed using an Agilent 6890 gas chromatograph with a 5973 mass selective detector (Agilent, Santa Clara, CA, USA). Samples were loaded into a thermal desorption unit (TDU) by a multipurpose autosampler (Gerstel). A cooled injection system (CIS4, Gerstel) was used in the GC-MS system. The TDU had an initial temperature of 25 °C. After the sample was loaded, the TDU was heated at a rate of 100 °C/min to a final temperature of 250 °C and held for 2 min. The TDU injection involved a splitless mode during thermal desorption, whereas the CIS4 was in a solvent vent mode with a venting flow of 50 mL/min for 4.7 min, at a venting pressure of 36.8 psi. After the solvent vent, the CIS4 was switched to splitless mode for 3.0 min, then changed to split mode with a venting flow of 50 mL/min. The initial temperature of the CIS4 was kept at −80 °C for 0.2 min, then ramped at a rate of 10 °C/s to a final temperature of 250 °C, and held for 10 min.

An RTX-1 column (60 m length, 0.25 mm i.d., 0.25 μm film thickness; Resteck Inc., Bellefonte, PA, USA) was used to separate the volatile compounds. The oven temperature was programmed at 40 °C for a 2 min hold, then to 210 °C at 3 °C/min, and to 270 °C at 5 °C/min with a 5 min hold. A constant helium column flow of 2.5 mL/min was used. A column splitter was used at the end of the column, 1 mL/min column flow was introduced to the MS, and the other 1.5 mL/min was vented out. The MS transfer line and ion source temperatures were 280 and 230 °C, respectively. Electron ionization mass spectrometric data from m/z 35 to 350 were collected using a scan rate of 5.27/s, with an ionization voltage of 70 eV.

Chemical Qualitation and Quantification. Volatile compounds were identified by comparing mass spectra with those in the Wiley 275.L Database (Agilent Technologies Inc.) and linear retention index (LRI) of authentic standards obtained from the laboratory using the same instrument.

The internal standard quantification method was used following the method published by Tao et al.[17] Thus, octan-3-ol was chosen as an internal standard (491.4 μg/L in wine and synthetic wine). The standard solutions were prepared by diluting the stock solution in synthetic wine to give a range of concentrations. The calibration curve for each target compound was built up by plotting the selected mass ion abundance ratio of the target compound with the internal standard against the concentration ratio. Quantitative data of the identified compounds were obtained by interpolation of the selected mass ion areas versus the internal standard area.

Statistical Analysis. A partial least-squares regression (PLSR) model was carried out using PLSR 1 with Unscrambler 9.7 (Camo, Trondheim, Norway). Principal component analysis (PCA) and other statistical analyses were performed using the SPSS statistical package version 19.0 for Windows (SPSS Inc., Chicago, IL, USA).

■ RESULTS AND DISCUSSION

Aromatic Characteristics. Sensory analysis involves detection and analysis by people, so it is inevitable that there are large subjective errors. To improve the accuracy and stability of sensory analysis, the results of sensory analysis must be quantified. More studies use the frequency of sensory vocabulary to indicate the intensity of aromatic characteristics,[18] but in earlier studies, aromatic characteristics given by

Table 1. MF% of Aromatic Characteristics of the Wine Samples[a]

no.	characteristic	CK	MP−20 °C/4 h	NP−20 °C/4 h	NF−10 °C/6 h	NP−10 °C/6 h	MP−10 °C/6 h	NP−10 °C/4 h	MP−10 °C/4 h
	tropical fruit	20.2	12.8	17.2	14.3	22.9	29.4	21.6	20.4
1	pineapple	20.2	17.8	13.8	17.8	22.9	28.7	25.8	0
2	banana	0	10.3	19.5	14.5	0	44.4	21.8	16.9
3	citrus	0	0	25.8	14.5	0	26	16.9	23.9
4	lemon	0	10.3	0	14.5	0	0	21.8	0
5	pomelo	0	0	9.8	10.3	0	18.3	0	0
	temperate fruit	26.4	28.7	29.9	25.2	34.3	21.2	22.8	24.7
1	apple	38.2	44.7	30.9	29	50.3	37	23.9	21.8
2	peach	17.8	0	30.9	17.8	37	17.8	16.9	27.6
3	pear	20.5	30.8	32.7	29	32.3	14.5	25.8	29.3
4	plum	0	10.3	27.6	0	17.8	10	21.8	9.8
5	cherry	29.2	29	27.6	25.1	34	26.8	25.8	35.2
	other fruits	14.5	10.3	19.5	20.5	15.4	26	16.9	25.8
1	melon	0	0	0	0	20.5	26	16.9	25.8
2	lichee	14.5	10.3	19.5	20.5	10.3	0	0	0
3	strawberry	16.7	17.8	32.7	10.3	27.1	24.5	23.9	25.8
	berry	16.0	17.7	32.7	23.4	18.7	26.0	23.7	26.4
2	red currant	0	25.1	35.5	37	0	26	19.5	25.8
3	black currant	15.3	10.3	29.8	22.9	10.3	27.4	27.6	27.6
	floral	16.4	11.7	23.9	14.2	18.7	12.2	15.7	16.8
1	osmanthus	0	0	0	0	0	18.3	0	0
2	violet	0	0	23.9	17.8	0	12.3	13.8	13.8
3	honeysuckle	0	0	0	0	14.5	10	0	19.5
4	jasmine	14.5	10.3	19.5	14.5	14.5	12.3	19.5	9.8
5	hawthorn	0	14.5	0	0	17.8	10	0	0
6	rose	18.2	10.3	38.5	10.3	32.4	10	13.8	23.9
7	clove	0	0	13.8	0	14.5	0	0	0
	vegetal	18.4	20.6	24.8	18.0	28.5	15.3	15.8	16.3
1	green	10.3	20.5	26.7	25.1	29	20.5	25.8	35.2
2	green grass	25.8	22.9	19.5	14.5	45.9	0	9.8	0
3	green pepper	19.1	14.5	28.9	14.5	25.1	0	13.8	16.9
4	tomato	0	0	23.9	0	20.5	10	13.8	9.8
5	cauliflower	0	17.8	0	0	25.1	0	0	9.8
6	green beans	0	27.1	0	0	25.1	0	0	9.8

[a] CK, control without any prefermentive freezing treatment; M, microwave thawing; N, natural thawing; P, frozen must; F, frozen fruit.

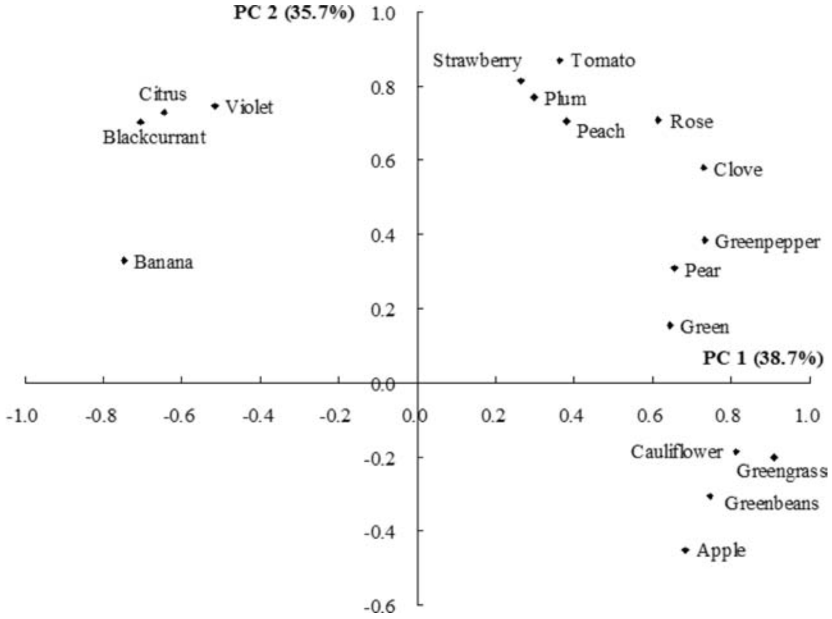

Figure 1. Loadings of aromatic characteristics in the first two PCs.

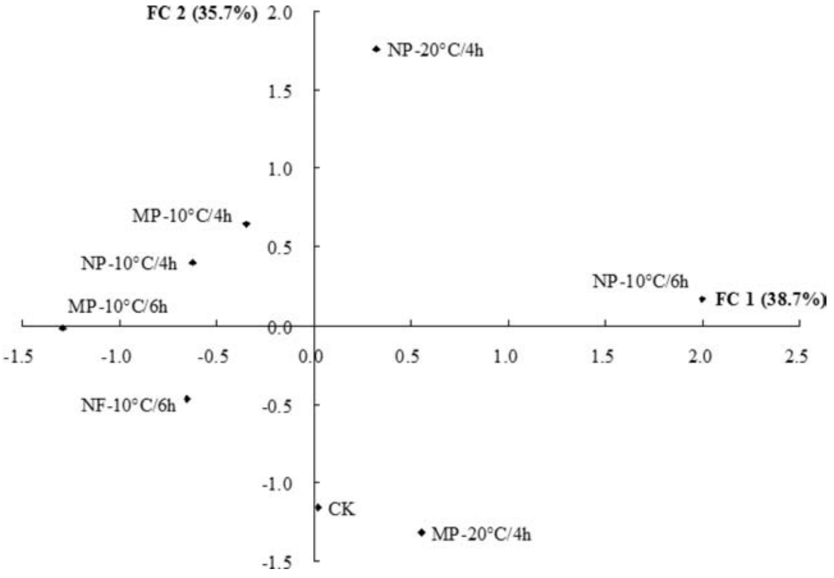

Figure 2. Distribution of the wine samples in the first two PCs of aromatic characteristics.

the tasters were still subjective.[19] To ensure the accuracy of sensory analysis, tasters should be trained with unified aromatic terms.[20] In this study, aromatic characteristics were analyzed by the method of "aroma sensing with quantified taste". Each panelist was told to describe the wine aromatic profile using five or six terms of Le Nez du Vin, and they needed to score the intensity of each term using a five-point scale.[16] MF% values of the wine samples are shown in Table 1. Some 28 aromatic characteristics from 6 aroma categories were detected in the wine samples by panelists, and 22 of them had values ≥20%.

Under the freezing treatments, using −20 °C would enhance wine aroma better than using −10 °C. This result accords with previous work.[3] The NP−20 °C/4 h treatment created a fruitier and more floral flavor, and there were 10 fruits and 2 florals of rose and violet in the wine. The wine from the MP−20 °C/4 h treatment had only an obvious vegetable flavor, whereas the NF−10 °C/6 h treatment added only three fruits. The NP−10 °C/6 h wine was fruitier than the control, except for tropical fruits. It had floral of rose, and its vegetal flavor was also the heaviest in all treatments. The NP−10 °C/4 h wine had several better fruits than the control; there was no floral fragrance, but it did have a green odor. The MP−10 °C/4 h wine was a little fruitier than the control, and it had rose and green flavors. Previous experiences with this technique proved an increase in cassis and strawberry notes for Pinot noir, an increase in fruity notes such as cherry, plum, and jam for Nebbiolo and other varieties,[21] and an increase in complexity and aromatic intensity for Sangiovese.[3]

The Principal Component Analysis (PCA) is used as a tool for screening, extracting and compressing data. PCA employs a mathematical procedure that transforms a set of possibly correlated response variables into a new set of noncorrelated variables called principal components.[22] PCA and correlation analysis were used to screen typical aromatic characteristics of Chinese Chardonnay white wines.[23] Variance analysis and multiple regression analysis were used to choose typical aromatic characteristics of Cherry wine.[24]

In this work, the frequency of each aroma term used by the sensory panel and the intensity percent of each term were calculated first, and then the geometrical mean of $F(\%)$ and $I(\%)$ were given as MF% to express the quantitative score of each aroma term. The PCA of MF% data was carried out.

After deleting some characteristics with little importance in loading, 17 characteristics were selected to build the principal components. The first two components accounted for 38.7 and 35.7% of total variance, respectively. Figure 1 shows the loadings of important aromatic characteristics in the first two PCs. Figure 2 is the map of distribution of the wine samples in the first two PCs. In Figure 1, some florals, berries, and sweet fruits were located in the positive part of PC 2, whereas vegetals and acid fruits lay in the positive part of PC 1. The wine samples were distributed in Figure 2. In general, the freezing treatment could enhance wine aroma. This is in agreement with the results of previous studies with a large improvement in all sensory characteristics of Pinot noir wines,[25,26] especially for NP−20 °C/4 h and NP−10 °C/6 h. The former had more floral and fruity characteristics, and the latter had more vegetal.

Aromatic Compounds Detected by Instruments. Aromatic compounds in the wine samples detected by SBSE-GC-MS are shown in Table 2. There are 55 aromatic compounds. Their concentrations varied from 192.2 to 205.3 mg/L. Some parts of aroma components were derived from grape berries, which played a decisive role in wine varieties and regional typicality, known as varietal aroma. Other parts of components were generated in the winemaking process, such as fermentation.

In this work, freezing treatment was performed before alcohol fermentation, so it is better to analyze and discuss varietal components and fermentation volatile compounds separately.

Varietal Compounds. It is considered that wine varietal aroma components are composed of C_6 compounds, terpenols, norisoprenoids, benzyl, and β-phenylethanols.[5,27] The amounts of these components can be influenced by various factors, such as climate, soil, cultivars, ripeness, viticulture patterns, and winemaking process.[28] In our work, the grape materials were the same, and the prefermentative freezing process was designed to extract more varietal compounds. Some 19 varietal compounds were detected and are quantified in Table 2, including 2 C_6 compounds, 6 terpenols, 3 norisoprenoids, 4 compounds of phenylethanol and its derivatives, and 4 others.

Table 2. Aromatic Compounds Quantified by SBSE-GC-MS in the Wine Samples

					concentration (μg/L)							
no.	compound	abbrev	odor threshold[a] (μg/L)	description	CK	MP−20 °C/4 h	NP−20 °C/4 h	NF−10 °C/6 h	NP−10 °C/6 h	MP−10 °C/6 h	NP−10 °C/4 h	MP−10 °C/4 h
varietal components												
	C-6 alcohols				109	242	259	213	195	176	167	152
1	hexanal	hexanal	5−15	apple, green, grassy	12	11	14	16	11	12	13	12
2	hexan-1-ol	hexanol	8000	green, grass	97	231	245	197	184	164	154	139
	terpenols				166.6	228.1	260.2	165.4	246.8	214.5	232	199.6
1	limonene	limonene	15	flowery, green, citrus	0.3	0.5	0.6	0.2	0.7	0.4	0.5	0.4
2	linalool	linalool	25	flowery, fruity, muscat	59.6	67.5	78.8	61.2	74.9	65.7	63.4	65.4
3	citronellol	citronellol	100	green lemon	3.7	0	0	0	2.8	0	0	0
4	geraniol	geraniol	30	citric	26.5	13.4	17.5	0	15.9	20.4	21.4	19.8
5	nerolidol	nerolidol	700	rose, apple, green, citrus	76	146	162	104	152	128	146	114
6	geranyl acetone	ger.acet	60	floral	0.5	0.7	1.3	0	0.5	0	0.7	0
	norisoprenoids				4.6	7.4	9.9	5.7	9.4	7.4	5.6	5.6
1	vitispirane	vitispirane	800	eucalyptus, woody, spicy	1	2	3	1	4	3	1	1
2	β-damascenone	damas	0.05	floral; sweet, honey, apple	3.4	5.4	5.9	4.2	4.9	4.4	4.6	4.1
3	β-ionone	ionone	0.09	balsamic, rose, violet	0.2	0	1.0	0.5	0.5	0	0	0.5
	other components				34677	30820	38761	33184	39934	34522	35720	31578
1	ethyl 2-phenylacetate	eth.phenylacet	73	floral, honey	0	0	2	0	0	0	0	0
2	phenethyl acetate	pheneth.acet	250	pleasant, floral; pleasant, flowery	495	447	394	472	406	487	441	463
3	ethyl dihydrocinnamate	Eth.Dh.Cinn	1.6	strawberry, plum, flowery	1	2	2	1	2	2	2	2
4	ethyl cinnamate	Eth.Cinn	1.1	strawberry cream	0	1	1	0	1	1	0	1
5	ethyl vanillate	Eth.Van	3000	vanilla, chocolate	175	245	184	164	369	49	120	105
6	methyl dihydrojasmonate	Meth.Dh.Jas			1	0	1	0	1	0	1	0
7	2-phenylethanol	Phenyleth	14000	roses	34004	30124	38175	32547	39154	33981	35156	31006
8	benzaldehyde	benzaldehyde	2000	almond	1	1	1	0	1	2	0	1
fermentation components												
	esters				39748	37256	36979	39491.4	40292	38289.9	39783	40742
1	ethyl acetate	Eth.Acet	7500	pineapple, fruity, balsamic	30712	25424	24904	28431	27507	26922	28431	29187
2	ethyl propanoate	Eth.Pro	1800	banana, apple	1604	1501	1447	2145	1884	2216	1607	1717
3	ethyl 2-methylpropanoate	Eth.2M.Pro	15	fruity, banana	150	171	182	144	203	164	157	164
4	isobutyl acetate	IsoBut.Acet	1600	waxy, fruity, apple, banana	111	183	164	122	174	97	116	151

Table 2. continued

					concentration (μg/L)							
no.	compound	abbrev	odor threshold[a] (μg/L)	description	CK	MP−20 °C/4 h	NP−20 °C/4 h	NF−10 °C/6 h	NP−10 °C/6 h	MP−10 °C/6 h	NP−10 °C/4 h	MP−10 °C/4 h
5	ethyl butyrate	Eth.But	20	strawberry, apple, banana	2327	2456	2571	1941	2639	1997	2334	2487
6	ethyl 2-methylbutyrate	Eth.2M.But	18	sweet fruit	21	64	75	35	76	49	56	43
7	ethyl 3-methylbutyrate	Eth.3M.But	3	berry, blackberry	11	32	44	45	49	37	44	38
8	isoamyl acetate	IsoamylAcet	30	banana, fruity, sweet	2357	4187	4237	3678	4458	3991	4123	4201
9	2-methylbutyl acetate	MBut.Acet	20−50	fruity, fatty, pleasant	169	179	210	234	217	154	99	185
10	ethyl pentanoate	Eth.Pent	>200	fruity, ester	1	1	1	0	1	0	0	1
11	ethyl hexanoate	Eth.Hex	5	fruity, green apple; floral, violet	827	1546	1601	1402	1531	1246	1209	1117
12	hexyl acetate	Hex.Acet	670	pleasant fruity, pear,cherry	68	48	51	43	41	46	34	38
13	ethyl heptanoate	Eth.Hep	220	pineapple, fruity	1.1	0	0	1.4	0	0.9	0	0
14	methyl octanoate	Met.Oct	100−400	waxy, apple skin, fruity	0	0	1	0	1	0	1	0
15	diethyl succinate	Dieth.Succ	6000	light fruity; wine	366	378	394	348	421	346	379	375
16	ethyl octanoate	Eth.Oct	2	fruity, pineapple, pear, floral	689	734	799	684	787	736	844	697
17	ethyl nonanoate	Eth.Non	1300	waxy, fruity	1	0	0	2	0	1	0	0
18	methyl decanoate	Met.Dec	1200	waxy, soap, fruity	0	0	0	1	1	0	0	0
19	octyl 2-methylpropanoate	Oct.2MPro	100−400	fruity, sweet	0	1	1	1	1	0	0	0
20	ethyl decanoate	Eth.Dec	200	fruity, fatty, pleasant	333	351	297	234	301	287	349	341
	high alcohols				125759	127081	114635	114353	109206	122592	124562	122609
1	isobutyl alcohol	Isobut	40000	fusel, alcohol	23204	14817	15107	16411	17101	17027	20112	21807
2	isoamyl alcohol	Isoamyl	30000	whiskey, nail polish	102417	112123	99387	97849	91975	105464	104319	100712
3	heptan-1-ol	Heptanol	1000	grape, sweet	84	92	74	49	64	38	87	26
4	2-ethylhexanol	EHexanol	8000	mushroom, sweet fruity	7	6	8	5	4	7	6	9
5	octan-1-ol	octanol	120	intense citrus, roses	16	21	15	12	6	11	9	14
6	nonan-1-ol	nonanol	600	green	4	5	6	3	2	1	0	4
7	decan-1-ol	decanol	400	orange flowery, special fatty	27	17	38	24	54	44	29	37
	carbonyl				5.4	12.5	20	3.7	23	27.7	27	17
1	2-nonanone	nonanone	15−50	fruity, floral, fatty	0.7	0.5	0	0.4	0	0.7	0	0
2	nonanal	nonanal	15	green, slightly pungent	1.7	10	17	2.3	21	24	26	16
3	δ-dodecalactone	dodecalactone	200−500	coconut fruity	3	2	3	1	2	3	1	1

Table 2. continued

no.	compound	abbrev	odor threshold[a] (μg/L)	description	concentration (μg/L) CK	MP−20 °C/4 h	NP−20 °C/4 h	NF−10 °C/6 h	NP−10 °C/6 h	MP−10 °C/6 h	NP−10 °C/4 h	MP−10 °C/4 h
	fatty acids				3423	4960	5107	4742	4439	4480	4829	4024
30	octanoic acid	octanoic	500	rancid, harsh, cheese, fatty acid	2486	3879	3795	3429	3034	3547	3461	3268
36	nonanoic acid	nonanoic	500−800	cheese, waxy flavor	355	298	324	267	319	267	337	129
45	decanoic acid	decanoic	1000	fatty, unpleasant	551	712	897	1004	1021	632	975	598
51	dodecanoic acid	dodecanoic	1000	dry, metallic, laurel oil flavor	31	71	91	42	65	34	56	29
	volatile phenols				7	24	26	13	22	20	14	15
40	4-vinyl-2-methoxyphenol	V2MPhenol	1100	phenolic, pleasant	6	23	24	12	22	19	14	15
44	eugenol	eugenol	6	clove	1	1	2	1	0	1	0	0

[a] Calculated in the laboratory: odor thresholds were calculated in 12% ethanol/water mixture containing 5 g/L tartaric acid at pH 3.2.

Considering their concentrations and respective odor thresholds, 10 of them had OAVs ≥ 0.1, namely, linalool, geraniol, nerolidol, β-damascenone, β-ionone, 2-phenylethanol, phenethyl acetate, ethyl dihydrocinnamate, ethyl cinnamate, and ethyl vanillate.

Terpenols are generally associated with floral and citric aromas, located in the skin and solid parts of the cells in the berries. So it can be imagined that wines with higher content of terpenols had more floral flavor and sweet fruit. The C_{13} norisoprenoid compounds are trace compounds in wine and are found at concentrations below 10 μg/L. However, their perception thresholds are also very low, between 0.05 and 0.09 μg/L, so norisoprenoids usually have odor activities.[29,30] They would give wine floral and sweet fruit. 1-Hexanol and hexanal were detected in the wine sample. Although 1-hexanol accounted for the vast majority of the total amount of C_6 compounds, it did not have an odor activity for the higher threshold. Hexanal was active and had a green trait.

As can be seen in Table 2, in addition to NF−10 °C/6 h, terpenols had a significant increase in freezing treatments, in agreement with the study carried out by Radeka et al.;[31] C_6 alcohols and norisoprenoids increased in some treatments. After prefermentative freezing, ethyl 2-phenylacetate and ethyl cinnamate could be detected, and ethyl dihydrocinnamate increased in wine. Values of 2-phenylethanol increased largely in NP−20 °C/4 h and NP−10 °C/6 h treatments; the rest of the compounds were little changed. Therefore, prefermentative freezing treatment could be used to extract more varietal aromatic compounds.

To reveal the influence of prefermentative freezing process on the varietal compounds, the data of varietal components were also processed by PCA. According to their loadings in PCA, 20 components were selected as important ones to build principal components. Figure 3 is the loading map of these 20 compounds in the first two PCs. In the positive part of PC1 exist most of the varietal compounds. They almost had activity. In Figure 4 of the sample distribution, control wine lies in the third quadrant. There are no compounds at the same place as in Figure 3, so it could be deduced that the prefermentative freezing process could enhance varietal compounds in wine. This fact could be of great importance in the fruity and floral aroma of the wines, which could reinforce the varietal character of the Meili wines. Wines of NP−20 °C/4 h and NP−10 °C/6 h located in the positive part of PC1 had much higher contents of varietal compounds.

Fermentation Volatile Compounds. Alcohol fermentation generates many more volatile compounds, which usually account for most of the total content of aroma compounds in wine. Fermentation volatile compounds mainly consist of esters, higher alcohols, fatty acids, carbonyl compounds, and volatile phenols.[32,33] In this work, esters, high alcohols, and organic acids were the main volatile compounds of the wine samples. Some 36 fermentation volatile compounds were quantified in total, including 26 esters, 8 higher alcohols, and another 2 carbonyl compounds. The prefermentative freezing process changed the total content of esters or high alcohols little, but some individuals changed significantly. Compared with the control, the total content of organic acids in treated wines increased. In the fermentation volatile compounds, 20 compounds had OAVs ≥ 0.1, including 12 esters, 4 alcohols, 2 organic acids, 1 aldehyde, and 1 volatile phenol. They were ethyl acetate, ethyl propanoate, ethyl 2-methylpropanoate, isobutyl acetate, ethyl butanoate, ethyl 2-methylbutanoate, ethyl

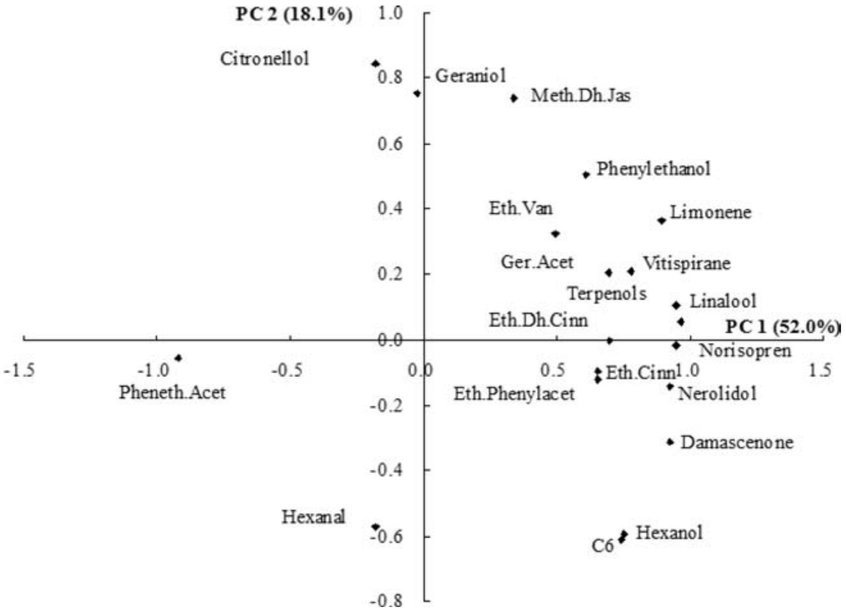

Figure 3. Loadings of varietal aromatic compounds in the first two PCs.

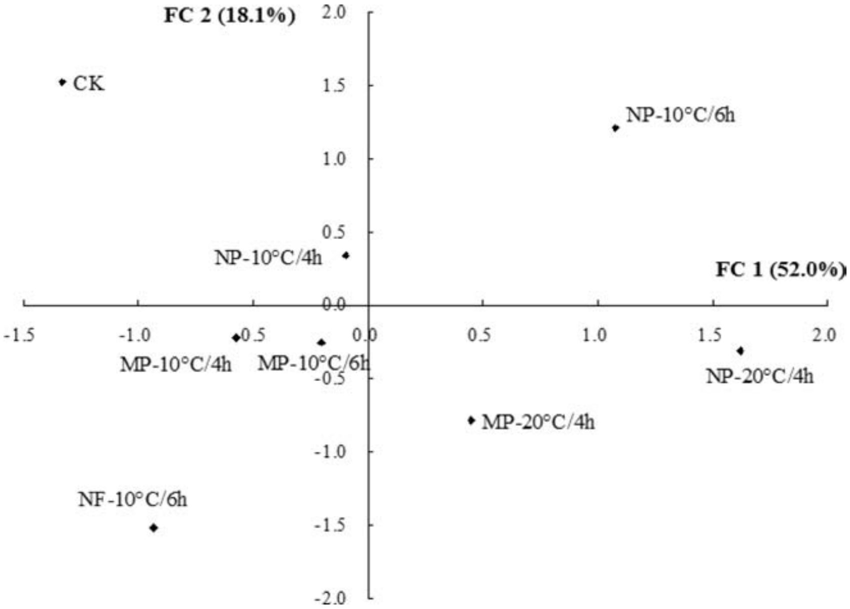

Figure 4. Distribution of the wine samples in the first two PCs of varietal aromatic compounds.

3-methylbutanoate, isoamyl acetate, ethyl hexanoate, hexyl acetate, ethyl octanoate, ethyl decanoate, isobutyl alcohol, isoamyl alcohol, octan-1-ol, decan-1-ol, nonanal, octanoic acid, decanoic acid, and eugenol.

Esters are very important compounds of wine flavor, giving it a fruity odor. Van der Merwe[34] found that in the perception of aroma, the role of the acetate esters was greater than that of the fatty acid ethyl esters and the odor intensity of mixed esters was higher than that of single components. Among the higher levels of esters in this work, isoamyl acetate, ethyl hexanoate, ethyl octanoate, and isobutyl acetate increased with the frozen macerations. However, ethyl acetate decreased and other ester compounds changed little.

Higher alcohols accounted for the largest part of the total aromatic compounds in wine. They accounted for >60% of the total in this study, but their concentrations were much lower than their thresholds. After freezing, higher alcohol compounds showed a slight decline. It is said that higher alcohols give wine quality a positive effect when they are below 400 mg/L. The total concentration of higher alcohols in the wine samples was below 400 mg/L.

It was found that grape juice compositions and fermentative conditions affected the fatty acid content in wine.[35] This work showed that prefermentative freezing treatment could enhance the content of fatty acids in wine, especially octanoic acid and decanoic acid, in agreement with Esti et al.[36] for Italian wines and Caudal et al.[37] for Airén white wines.

Volatile phenols are the products of alcoholic fermentation, and they would contribute positively or negatively to wine aroma depending on concentration.[38] Two volatile phenols were detected in the wine samples, but they were odorless. There were also three carbonyl compounds, 2-nonanone,

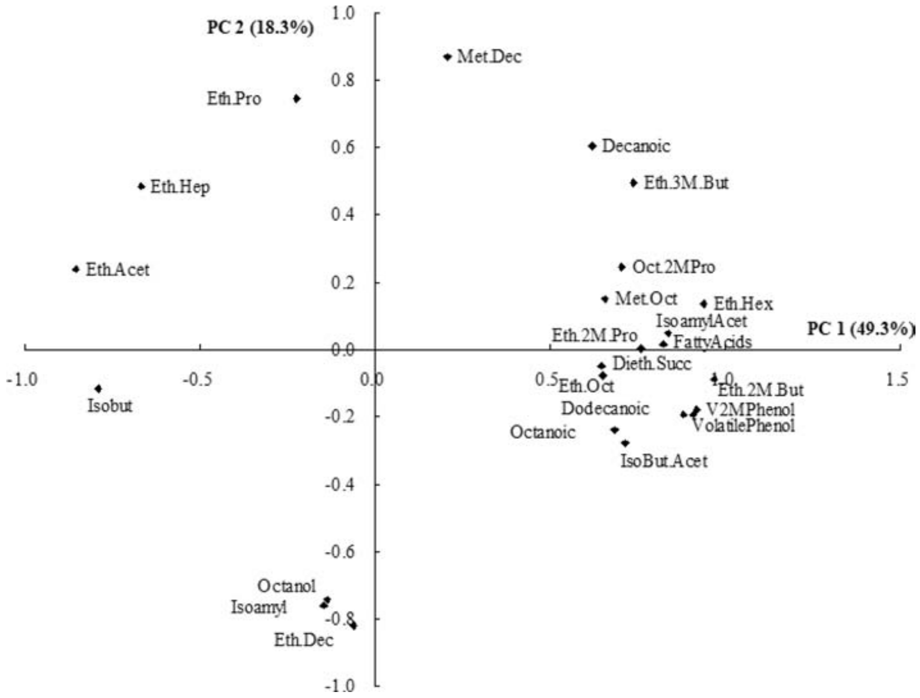

Figure 5. Loadings of fermentation aromatic compounds in the first two PCs.

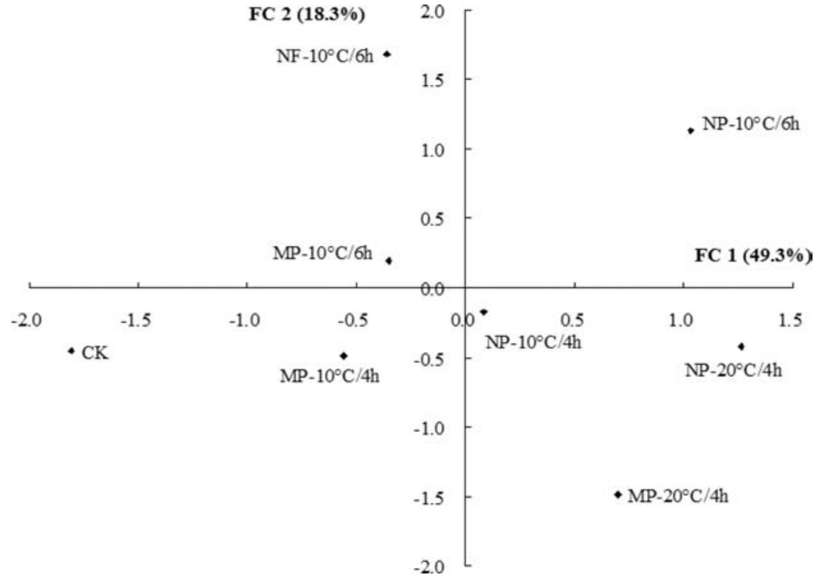

Figure 6. Distribution of the wine samples in the first two PCs of fermentation aromatic compounds.

nonanal, and δ-dodecalactone, detected in the wine samples. Nonanal had a concentration above its threshold in the same treatments.

The data of fermentation volatile compounds were also performed with PCA. After deleting some components with little contribution to the total variance, 24 volatile compounds were chosen to build PCs. The first two PCs had 49.3 and 18.3% of the total variance, respectively. Figure 5 is the loadings of 24 volatile compounds in the first two PCs. A mass of esters, organic acids, and volatile phenols located at the positive part of PC1. Figure 6 is the distribution of the wine samples in the first two PCs. The control wine was at the negative part of PC1, and all of the freezing treatments lie at the right part of the control. Wines of NP−20 °C/4 h and NP−10 °C/6 h located at the zone where there was a mass of impact fermentation volatile compounds in the corresponding place in Figure 5, so it could be deduced that these two wines had more of those impact volatile compounds.

Correlation between Aromatic Characteristics and Impact Components. Chemical compounds are the material base of wine sensory characters. Tao et al.[23] found that correlation between the typical aromatic characteristics and aromatic components was closely linked, but the relationship was complex. Not only did the components of OAV ≥ 1 enter into aroma prediction models, but also some compounds with OAV < 1 had aroma contributions. Recent research has indicated that the nonvolatile matrix of wine can also exert a powerful effect on the perception of aroma at either a physical−

Table 3. Regression of Aromatic Categories and Characteristics by Impact Varietal Components[a]

no.	compd	floral	sweet fruity	temperate fruity	vegetal	rose	strawberry
1	linalool	**0.119**	**0.163**	**0.166**	**0.158**	**0.232**	**0.164**
2	geraniol	0.011	0.099	**0.101**	0.036	**0.259**	**0.294**
3	nerolidol	0.084	−0.005	0.010	−0.063	**-0.110**	0.069
4	*β*-damasceone	0.071	**-0.098**	−0.057	−0.011	−0.057	−0.021
5	*β*-ionone	0.088	**0.461**	**0.187**	0.087	**0.558**	**0.272**
6	phenethyl acetate	−0.094	**-0.242**	**-0.179**	**-0.129**	**-0.214**	**-0.119**
7	ethyl dihydrocinnamate	0.079	−0.033	0.027	**-0.135**	0.005	**0.247**
8	ethyl cinnamate	0.092	**-0.130**	0.078	**0.100**	**0.140**	**0.155**
9	ethyl vanillate	0.032	−0.013	**0.289**	**0.557**	0.067	**-0.275**
10	2-phenylethanol	**0.101**	**0.415**	**0.260**	**0.183**	**0.152**	**0.168**
11	C_6 compounds	0.048	**-0.168**	**-0.128**	−0.032	**-0.163**	**-0.156**
12	terpenols	0.095	0.055	0.077	0.012	0.023	**0.150**
13	norisoprenoids	**0.113**	0.036	**0.116**	**0.172**	0.030	0.041
B_{0W}		−1.244	0.380	1.519	−0.981	1.201	0.271
R^2 calibration/validation		0.978/0.548	0.981/0.683	0.999/0.821	0.997/0.827	0.994/0.857	0.986/0.699

[a] Coefficients were standard ones.

Compounds	Coefficient
Eth.Acet	-0.024
Eth.Pro	-0.080
Eth.2M.Pro	**0.213**
IsoBut.Acet	**0.133**
Eth.But	**0.210**
Eth.2M.But	**0.120**
Eth.3M.But	0.027
IsoamylAcet	0.035
MBut.Acet	**0.120**
Eth.Hex	0.046
Hex.Acet	0.061
Eth.Oct	0.057
Eth.Dec	0.012
Isobut	0.016
isoamyl	**-0.188**
Octanol	-0.070
Decanol	**0.197**
Nonanal	0.041
Octanoic	-0.094
Nonanoic	0.024
Decanoic	0.022
Eugenol	0.014
B0W	2.201

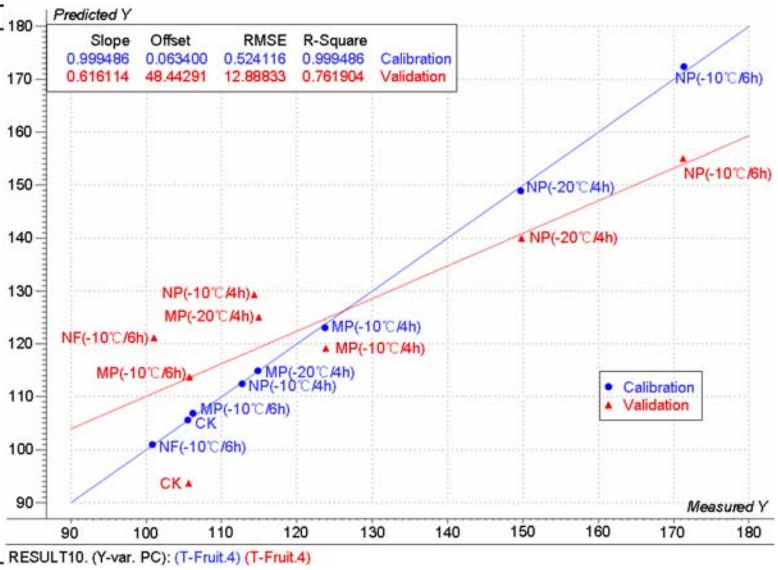

Figure 7. PLS regression of temperate fruity from fermentation volatile compounds.

chemical or percenptive level.[8,9] This indicated that OAV theory has its limitations when predicting aromatic characteristics.[39] We have used PLSR to show the relationship between the flavor components and sensory properties. Compounds were selected according to OAVs and PCA results. Components with OAV ≥ 0.1 and their chemical groups were selected to regress aromatic characteristics considering their importance in PCA. This technique has been previously used in the modeling of the aroma of wines of the variety *V. vinifera*,[39] in aged Spanish red wines,[40] in Australian Riesling and Chardonnay wines,[41] and in Spanish Albariño wines.[14]

Table 3 is the PLSR results of wine aroma by impact varietal compounds. Four aroma categories could be regressed well by varietal compounds, whereas only two models could be built for characteristics of rose and strawberry. In the table, at least three components had values ≥0.1 for one model. In one model, some compounds had coefficients >0 and others had coefficients <0, which indicated some compounds contributed to the odor positively and some, negatively. The correlations are positive as well as negative, which suggests that the perception of an aromatic note is influenced not only by the presence of a few components the aroma of which form the note but also by the presence of other odorants that negatively affect the perception of such an aromatic note.[40] Linalool and 2-phenylethanol were almost important positively for all aroma terms in models. Phenethyl acetate and C_6 compounds were negative to all aroma terms. Recent studies carried out in red wines[42] have shown that *β*-damascenone would have a more indirect rather than direct effect on aroma, enhancing fruity notes. However, in our study *β*-damascenone has some negative impact on fruity notes.

PCA showed that fermentation volatile compounds were influenced by prefermentative freezing process, so the aroma regression was also performed using impact fermentation volatile compounds. However, only wines from temperate fruits could be regressed. Figure 7 is the PLSR result of temperate fruit by fermentation compounds. In the model, seven components have coefficients with absolute values >0.1. Ethyl 2-methylpropanoate, isobutyl acetate, ethyl butyrate, ethyl 2-methylbutyrate, 2-methylbutyl acetate, and decanol gave temperate fruits important positive contribution, and isoamyl alcohol had the negative effect. From the odor description of aroma components in Table 2, important esters had fruity flavor,[43,44] and isoamyl alcohol had an alcohol scent like whiskey. Decanol gave orange flowery and special fatty odor. Prefermentative freezing treatment would change the chemical compositions in grape juice, and then the fermentation volatile compounds were changed. This work proved that changed fermentation volatile compounds only reinforce the temperate fruit wines.

To sum up, creation of a wine aroma was influenced by a prefermentative freezing process, which was designed considering four factors, namely, freezing temperature, freezing time, grape state, and thawing method. Wine aromatic characteristics were evaluated by trained panelists using sensory quantitative analysis. Aroma compounds were quantified by SBSE-GC-MS. The prefermentative freezing process could enhance wine aroma intensity and its complexity. In our work, using −20 °C was better than −10 °C for enhancing aroma effects, and frozen must was better than frozen berries at the freezing temperature of −10 °C. Treatment for 6 h was better than for 4 h. Microwave thawing could lower some vegetal flavors, but the fruity and floral characteristics were also lessened. Wines from the NP−20 °C/4 h and NP−10 °C/6 h treatments had better aromas than the control. The former had better fruity and floral characteristics, and the latter was better in vegetal flavor.

The prefermentative freezing process could improve the content of varietal compounds in wine. The NP−20 °C/4 h and NP−10 °C/6 h wines had more terpenols, norisoprenoids, phenylethanol and its derivative esters, and ethyl cinnamate and its derivatives. The freezing process could also raise some fermentation volatile compounds, such as esters and organic acids.

Aroma regression by impact aroma compounds showed that the aroma categories of floral, sweet fruity, temperate fruity, and vegetal were regressed well by impact varietal compounds. However, two specific characteristics of rose and strawberry could be regressed by varietal compounds. Although some fermentation volatile compounds were influenced by freezing process, only temperate fruits could be regressed by impact fermentation components.

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Notes

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