# Characterization of the differences in the aroma of cherry wines from different price segments using gas chromatography–mass spectrometry, odor activity values, sensory analysis, and aroma reconstitution

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**Abstract** The aroma composition, aroma-active compounds, and sensory attributions of cherry wines from three different price segments were investigated. A total of 48 aroma compounds were identified and quantified using headspace solid-phase microextraction (HS-SPME)/gas chromatographymass spectrometry (GC–MS), among which 23 aroma compounds were further screened out as important odorants based on their odor activity values (OAVs); then, the previously mentioned 23 volatiles were correlated to sensory attributes using partial least-squares regression (PLSR). The result indicates that the differently priced wines were associated with different compounds and aroma attributions. Finally, aroma reconstitution was performed by mixing odor-active aroma compounds (OAVs>1) on the basis of their measured concentrations in the original sample. The result indicated that the aroma profile of the reconstituted sample was similar to that of the original sample.

**Keywords:** cherry wine, different quality, odor activity value, partial least-squares regression, aroma reconstitution

## Introduction

Fruit wine prepared from various fruits such as apple, grape, and strawberry has gained popularity over the years owing to its several beneficial health effects. Cherry is a newly adopted raw material for wine production (1). The special flavor of cherry wine is derived from its specific traditional preparation processes. According to consumers, aroma profile is one of the major determinants of the quality of wine (2,3).

Although over 1000 aroma compounds have been identified in wines, only some complex aroma-active compounds play noticeable roles in sensory perception (4,5). It is obvious that sensory properties can be very different from one another because of these aroma-active compounds. Several factors affect the composition of aroma-active compounds, such as raw materials, processing method, and fermentation and aging processes (6,7); these factors may also determine the final quality and price of wine. Expensive wines are logically produced following a more careful process that allows for greater aromatic quality. Therefore, similar-quality wines are expected to share similar characteristics, including aroma profile, sensory attributions, and active-aroma compounds (5).

compounds significantly contribute to the aroma properties of wine, e.g., olfactometry, odor activity value (OAV) analysis, descriptive profile testing, aroma reconstitution, and omission tests. Gao et al. (6) identified 66 aroma compounds in light-aroma-type Chinese liquor using gas chromatography-olfactometry (GC-O) and further determined 27 odorants as important odorants based on their OAVs. Additionally, via omission experiments, they further confirmed  $\beta$ damascenone and ethyl acetate as the key odorants. Chen et al. (8) determined 73 aroma-active compounds using GC-O and gas chromatography-mass spectrometry (GC-MS) in Chinese rice wine and prepared a reconstitution model whose results showed good similarity to the aroma of the original Chinese rice wine by mixing 34 aroma compounds with OAVs>1. Langos et al. (9) studied the key aroma compounds in two Bavarian wheat beers using aroma extract dilution analysis (AEDA) and OAVs; consequently, they successfully simulated the overall aroma of wheat beer for the first time. Thus far, only a few studies have investigated aroma-active compounds in cherry wines.

Several techniques have been used to investigate which aroma

To the best of our knowledge, several studies on the aroma fractions of cherry wine have been reported in recent years (10-12).

However, the differences in the aroma of cherry wines of different qualities have not yet been investigated, including their aroma profiles, sensory attributions, and types and compositions of aromaactive compounds. This study attempted to clarify the above mentioned differences with the following five steps: (1) clarification of the differences in the aroma composition of different-quality wines via comparison using GC–MS, (2) determination and comparison of aroma-active compounds based on their OAVs, (3) comparison of the sensory attributions of different-quality cherry wines via a sensory analysis; (4) investigation of the relationships between different-quality wines, their sensory attributes, and aroma-active compounds using a multivariate analysis of PLSR, and (5) aroma reconstitution to verify the availability of the OAV method. These steps are expected to improve the quality of cherry wines and clarify the differences between different-quality cherry wines.

#### **Materials and Methods**

Cherry wine samples Four low-price cherry wines (50-98 RMB), five medium-price wines (120-199 RMB), and four high-price wines (230-540 RMB) were analyzed in this study. The four low-price cherry wines were supplied by Dalian yushengyuan Wine Co., Ltd. with 11% (vol) (L1, 375 mL), Jiangsu hongxiangyi Wine Co., Ltd. with 8% (vol) (L2, 375 mL), Jiangsu hongxiangyi Wine Co., Ltd. with 8% (vol) (L3, 750 mL), and Jiangsu hongxiangyi Wine Co., Ltd. with 9.5% (vol) (L4, 750 mL). The five medium-price wines were purchased from Jiangsu hongxiangyi Wine Co., Ltd. with 10.5% (vol) (M1, 750 mL), Dalianbeiguo Manor Wine Co., Ltd with 12% (vol) (M2, 375 mL), Yantaitongxin Wine Co., Ltd. with 10.5% (vol) (M3, 375 mL), Yantaitongxin Wine Co., Ltd. with 10% (vol) (M4, 375 mL), and Shandong jingqi Manor Wine Co., Ltd. with 16% (vol) (M5, 750 mL). The four high-price wines were purchased from Dalian beiguo Manor Wine Co., Ltd. with 12% (vol) (H1, 375 mL), Jiangsu hongxiangyi Wine Co., Ltd. with 10.5% (vol) (H2, 750 mL), Jiangsu hongxiangyi Wine Co., Ltd. with 11% (vol) (H3, 750 mL), and Yantai tongxin Wine Co., Ltd. with 18% (vol) (H4, 375 mL). All wines were stored at 4°C until analysis.

**Chemicals** The sources of 48 reference compounds are listed in Table 1s (data not shown). Analytical-grade ethanol [99.7% (v/v)], sodium hydroxide, and sodium chloride were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Tartaric acid ( $\geq$ 99.5%) was purchased from Merck (Darmstadt, Germany); 2-Octanol (internal standard) and n-alkane standards (C<sub>7</sub>-C<sub>30</sub>) were purchased from Sigma-Aldrich (St. Louis, MO, USA). All of them were analytical reagents. Pure water was prepared using the Milli-Q purification system (Millipore, Bedford, MA, USA).

Aroma extraction using solid-phase microextraction (SPME) Herein, 8 mL of the sample was placed in a 15-mL headspace vial (Reference 27385; Supelco, Bellefonte, PA, USA) along with PTFE (Polytetrafluroethylene)-silicone septa (Supelco), 2 g of sodium chloride and 50  $\mu$ L of 2-octanol (400 mg L<sup>-1</sup>). The fiber coated with divinylbenzene/ carboxen/polydimethylsiloxane (DVB/CAR/PDMS, 1 cm, film thickness 50/30  $\mu$ m) was exposed to the headspace of the sample for 45 min in a thermostatic water bath at 50°C without stirring and then desorbed into the injection port of the GC apparatus for 5 min. After each analysis, the fiber was inserted into a thermal heater for 20 min at 250°C to recondition the fiber and eliminate the carryover effects (13). All samples were used in triplicate.

Identification of aroma compounds using GC-MS Separation and detection analyses were performed using a 7890A gas chromatograph coupled to a 5973C mass selective detector (Agilent Technologies, Santa Clara, CA, USA). The transfer-line temperature was 250°C. The HP-INNOWAX (chromatographic column) fused-silica capillary column (60 m×0.25 mm ID, 0.25-µm film thickness) and DB-5 (60 m  $\times 0.25$  mm ID, 0.25- $\mu m$  film thickness, Agilent Technologies) were used to perform chromatographic separations. The oven temperature program was as follows: 40°C for 2 min and then ramped up to 230°C for 2 min at a rate 3°C min<sup>-1</sup>. The parameters of the mass selective detector included electron ionization at an electron energy of 70 eV, an ion-source temperature of 230°C, and a mass filter temperature of 150°C. For identification, the scan mode was used with a mass range of m/z 30–350. The injector temperature was set at 230°C. The SPME fiber was inserted the injector 5 min for flavor desorption in the splitless mode. Helium was used as the column carrier gas at a constant flow rate of 1 mL min<sup>-1</sup>.

The volatiles were identified by comparing their RIs (retention indices) (on two different gas chromatograph column phases), molecular weights, and mass fragmentation patterns in the Wiley7n.L Database and NIST Database (Hewlett-Packard, Palo Alto, CA) to those of the chemical standards.

**Determination of odor thresholds** OAVs can be influenced by matrix, such as water, air, oil or solvent, as reported by previous studies (14-16). To consider the effect of the matrix, all the thresholds were calculated in a 12% water-ethanol mixture and determined using a forced-choice method comprising seven concentration steps. A certain amount of the odorant diluted stepwise (1:3 by volume, with the 12% hydroalcoholic solution).

The dilution and two glasses of the 12% hydroalcoholic solution were prepared and taken to the panelists, who were asked to select the dilution. Additionally, the minimum concentration that the assessors selected correctly and the maximum concentration that they selected incorrectly were recorded. The odor threshold of each odorant was calculated based on the formulas described in previous work (17).

Quantitative analysis and OAVs of aroma compounds A stock solution of mixed standards was prepared by adding a certain

amount of each standard. The matrix was adjusted to 12% ethanol and contained 2 g  $L^{-1}$  tartaric acid with pH 3.5; it was then used to construct calibration curves.

The volatiles were quantified based on the calibration curves obtained by using each compound at five different concentrations in the SIM mode. The equations of the calibration curves are shown in Table 1s (data not shown).

OAVs provide a more accurate estimation of aroma contribution (18) and are usually used to evaluate the potential sensory contribution of a chemical compound (19). The OAV of a compound is calculated as the ratio of its concentration in wine to its odor threshold (20).

**Sensory analysis** A quantitative, descriptive sensory analysis was performed for evaluating three sets of wine samples and completed by a well-trained panel comprising six females and males, 20–30 years old, as reported previously (21). All panel members were trained on the basis of the ISO 4121 standard. The samples were presented to the panelists, and the descriptive terms of sample wines were given. After all the samples were evaluated, the aroma standards were discussed by the panelists until their attributes were agreed upon by all judges. Finally, fruity, floral, fermented, spicy, caramelized, woody, sour, and inharmonious attributes were confirmed. A 10-point scale (0=none, 9=very strong) was adopted in this paper. Then, the sensory scores from the panelists were averaged to calculate the mean value.

Aroma reconstitution test To confirm that the volatile compounds with high OAVs were actually the important odorants of cherry wine, aroma recombination was performed. A 12% hydroalcoholic solution was prepared as the matrix for recombination. Then, the volatile compounds with OAVs  $\geq$ 1 were mixed and dissolved in the matrix at their quantified concentrations in the H4 sample. Thus, a complete recombinate was obtained, resulting in Model B, whereas the H4 sample was acted as Model A.

**Statistical analysis** Analysis of variance (ANOVA) was performed using SAS V8 (SAS Institute Inc., Cary, NC, USA). One-way ANOVA with Duncan's multiple-range tests was used to evaluate the significant differences in the average scores and concentrations among the three groups of wines. A significant difference was identified at p<0.05.

Partial least-squares (PLS) regression analysis is the most powerful multivariate calibration technique in chromatography, spectroscopy, and sensory sciences (22). It was expected to present an overview of potential connections between the samples, aroma-active compounds, and sensory attributes. A multivariate analysis was performed using Unscrambler version 9.7 (CAMO ASA, Oslo, Norway). To make each variable with variance and zero mean before applying PLS analysis in order to obtain unbiased contribution of each variable to the criterion, all variables were centered and standardized (1/SD). Additionally, a

full cross-validation was performed to validate the prediction ability of the models.

#### **Result and Discussion**

**Identification of volatile compounds in cherry wines** The mean concentrations and standard deviation for all volatile compounds identified in cherry wines are presented in Table 1. A total of 48 compounds were positively identified and quantified using calibration curves, including 19 esters, 12 alcohols, 3 acids, 4 aldehydes, 3 ketones, 4 phenols, 2 terpenes, and 1 lactone, among which 23 volatile compounds showed significant differences (*p*<0.05).

Esters: As shown in Table 1, esters play an important role in the aroma characteristic of cherry wine. A total of 19 esters were identified. Most of them contribute toward the fruitiness of cherry wine. Among the esters, ethyl acetate was most abundant and contributed toward the wines' pleasant and fruity fragrance. A similar result was found in a previous report (13). Ethyl acetate was richest in the high-price wines (95.860 mg L<sup>-1</sup>), and it exhibited significantly different levels (p<0.05) among the three wine sets. In addition, ethyl butyrate, ethyl lactate, ethyl decanoate, phenethyl acetate, and ethyl 3-phenyl propanoate were richest in high-piece wines. They all exhibited significantly different levels (p<0.05) among the three wine sets except for ethyl decanoate and ethyl 3phenylpropanoate. The contents of ethyl butyrate and ethyl decanoate kept increasing with the price of cherry wines, whereas the contents of ethyl isovalerate and ethyl 2,4-hexadienoate kept reducing with an increase in the price. Methyl salicylate was only detected in the lowprice wines, whereas hexyl acetate and methyl octanoate were only found in the medium-price wines. Anisyl formate was only absent in the low-price wines and reached the highest levels in the mediumprice wines (0.056 mg L<sup>-1</sup>). The total concentration of all these ester compounds was highest in the high-price wines (101.524 mg  $L^{-1}$ ) and lowest in the medium-price wines (37.006 mg  $L^{-1}$ ).

Alcohols: Twelve types of alcohols were identified in this study. Six of them varied significantly (p<0.05) among the three groups. A small amount of fusel alcohols, such as 1-propanol, 2-methyl-1-butanol, and 3-methyl-1-butanol. produced during alcoholic fermentation can impart fermented aroma in wine. All of these alcohol volatiles reached the highest levels in the high-price wines except for 1hexanol and 2-ethyl-1-hexanol; 1-hexanol was most abundant in the medium-price wines. The content of 2-ethyl-1-hexanol was similar in the medium-price and high-price wines (0.023 mg  $L^{-1}$ ); It was reported that yeasts have a significant effect on the content of  $\alpha$ terpineol (1). Linalool and  $\beta$ -citronellol were only found in the medium-price and high-price wines, and their content kept increasing from the medium-price wines to high-price wines. The contents of linalool and  $\beta$ -citronellol can be influenced by the cherry variety (5). The differences in cherry variety significantly affect cherry wines in terms of the final quality. The total contents of the aforementioned

Table 1. Identification and quantitation of volatile compounds (mg  $L^{-1}$ ) in cherry wines

Compounds	RI		5	15	Average concentration and significant differences						
	Innowax	DB-5	Descriptors	ID	L	SD	М	SD	Н	SD	Р
Esters											
Ethyl acetate	897	598	pineapple	MS,RI,Std	58.890b	6.552	33.070b	2.683	95.860a	6.642	0.0087
Ethyl butyrate	1041	801	apple	MS,RI,Std	0.075b	0.013	0.097b	0.005	0.393a	0.018	0.0046
Ethyl isovalerate	1072	852	fruity	MS,RI,Std	0.020a	0.003	0.014a	0.002	nd		0.0143
Isoamyl acetate	1123	876	banana	MS,RI,Std	0.042	0.02	0.126	0.014	0.076	0.004	0.5237
Ethyl hexanoate	1233	998	apple peel, fruit	MS,RI,Std	0.131	0.002	0.244	0.005	0.189	0.009	0.7487
Hexyl acetate	1273	1013	pleasant fruity	MS,RI,Std	nd		0.011a	0.001	nd		0.0375
Ethyl lactate	1360	814	green fruity	MS,RI,Std	1.256a	0.107	0.338b	0.035	1.281a	0.092	0.0263
Ethyl 2,4-hexadienoate	1512	1066	fruity	MS,RI,Std	1.279	0.192	1.224	0.224	0.929	0.138	0.9371
Methyl octanoate	1391	1122	orange	MS,RI,Std	nd		0.004a	0	nd		0.0035
Ethyl octanoate	1435	1196	fruity, fat	MS,RI,Std	0.231b	0.002	0.820a	0.014	0.461ab	0.015	0.0755
Ethyl decanoate	1637	1394	fruity	IVIS, RI, Std	0.033	0.002	0.102	0.002	0.182	0.006	0.4055
Ivietnyi benzoate	1633	1175	Flowery, noney		0.046a	0.001	0.008D	0.001	0.0190	0.001	0.0041
Diothyl sussinate	1607	1170	noral wino fruit	MC DI C+d	4.590a	0.050	0.5150	0.004	0.0990 1.026ab	0.029	<0.0001 0.0122
Mothyl salicylate	1700	11/0	wille, Itult	MC DI C+d	1.459a	0.074	0.4790 nd	0.027	1.050aD	0.014	0.0155
Phonothyl acetate	1810	1270	rose floral	MS RI Std	0.045a	0.001	0.007b	0 002	0.0/12	0.001	0.0131
Fthyl laurate	1849	1270	leaf	MS RI Std	0.01485	0.002	0.0075	0.002	nd	0.001	0.0200
Anisyl formate	1868	1317	sweet snice herh	MS RI Std	nd	0	0.005	0.01	0.031	0.019	0 3004
Ethyl 3-phenylpropanoate	1897	1353	floral	MS.RI.Std	0.093	0.008	0.088	0.007	0.127	0.01	0.7336
totals					68.187		37.006		101.524		
Alcohols											
1-propanol	1049	546	alcoholic	MS,RI,Std	15.52	1.443	8.53	0.324	40.92	3.699	0.1515
2-methyl-1-butanol	1220	739	alcoholic, nail polish	MS,RI,Std	0.312b	0.026	0.410ab	0.018	1.164a	0.045	0.0708
3-methyl-1-butanol	1227	736	whiskey, malt	MS,RI,Std	5.29	0.611	14.64	0.824	32.5	1.697	0.1439
1-hexanol	1363	873	fruity	MS,RI,Std	0.172	0.004	0.496	0.008	0.443	0.012	0.4226
1-heptanol	1461	973	chemical, green	MS,RI,Std	0.014	0.001	0.011	0.001	0.026	0.002	0.1871
(E)-linalool oxide	1450	1090	flower, sweet	MS,RI,Std	0.065	0.003	0.036	0.001	0.08	0.004	0.4866
2-ethyl-1-hexanol	1492	1030	rose, green	MS,RI,Std	0.015	0.002	0.023	0.001	0.023	0.003	0.8046
Linalool	1551	1102	flower, lavender	MS,RI,Std	nd		0.150a	0.007	0.153a	0.003	0.0387
$\alpha$ -terpineol	1705	1201	oil, anise, mint	MS,RI,Std	0.242b	0.017	0.222b	0.012	0.446a	0.013	0.0202
	1//0	1232	rose	MS,RI,Std	nd	1 455	0.051a	0.003	0.055a	0.003	0.031
Benzyl alconol	1890	1045	floral, sweet		42.075a	1.455	17.828D	0.787	44.094a	1.394	0.0126
totals	1926	1110	noral, rose-like	IVIS,RI,SLU	4.7940	0.343	9.18330	0.335	10.4578	0.754	0.0605
					00.499		51.560		130.301		
Acetic acid	1457	627	sour	MS RI Std	4 416h	0 279	3 728h	0 101	17 742a	0 527	0 024
Hexanoic acid	1853	980	sweat acidic	MS RI Std	0.43	0.098	1 171	0.101	4 219	0.014	0.3563
Octanoic acid	2071	1270	cheesy, sweaty	MS.RI.Std	0.573	0.111	0.77	0.098	4.789	0.178	0.1246
totals			,, , , , , , , , , , , , , , ,	, , ,	5.419		5.669		26.750		
Aldehydes											
Furfural	1476	834	almond, bread	MS,RI,Std	0.431b	0.187	3.183ab	0.186	9.209a	0.476	0.0509
Benzaldehyde	1539	970	almond, burnt sugar	MS,RI,Std	17.49	0.819	2.31	0.085	22.68	0.729	0.2554
5-methyl-2-furfural	1587		almond, caramel	MS,RI,Std	0.049b	0.014	0.060b	0.002	0.404a	0.015	0.0001
5-(hyddroxymethyl)furfural	2545		floral	MS,RI,Std	0.542	0.04	nd		0.093	0.009	0.2271
totals					18.512		5.553			32.386	
Ketones	1200				0.067	0.004	0.000	0.004	0.050	0.005	0 2055
2-octanone	1288	720	soap, gasoline	MS,RI,Std	0.067	0.004	0.083	0.004	0.059	0.005	0.3055
3-hydroxy-2-butanone	1297	/20	flowery, butter	IVIS, RI, Std	0.028a	0.001	nd 0.002a	0	0.014ab	0.002	0.0326
z-nonanone	1391	1092	not mik, green	IVIS,RI,SLU	0.004a		0.003a	0	nu 0.072		0.0012
Phonois					0.099	0.005	0.065		0.075		
A-methyl guaiacol	1969	1193	smoky	MS BI Std	0.024b	0.005	0 2352	0 023	0 2352	0 022	<0.0001
4-methyl guaiacol	2045	1279	snice clove	MS RI Std	0.0240	0.005	0.2358	0.023	0.2358	0.022	0.7974
Fugole	2185	1359	clove honey	MS RI Std	0.001	0.003	0.020	0.001	0.023	0.002	0.8048
4-ethyl phenol	2198	1000	must	MS.RI.Std	0.613	0.081	0.553	0.088	0.552	0.073	0.9963
totals					0.754		0.879		0.864		
Terpenes											
Myrcene	1157	991	balsamic	MS,RI,Std	nd		0.125a	0.008	0.087a	0.005	0.0139
DL-limonene	1184	1033	citrus, mint	MS,RI,Std	0.005b	0.001	0.013ab	0.002	0.036a	0.002	0.0353
totals					0.05		0.138		0.123		
Lactones											
γ-butyrolactone	1648	918	caramel, sweet	MS,RI,Std	0.021	0.002	0.036	0.001	0.057	0.004	0.5932
totals					0.021		0.036		0.057		

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*Acids*: Three acids, namely, acetic acid, hexanoic acid, and octanoic acid, were identified. Acetic acid and hexanoic acid were the likely contributors to the sour aroma of the wines. Only acetic acid exhibited significantly different levels (p<0.05) among the three wine sets. Its content was richest in the high-price wines (17.742 mg L<sup>-1</sup>) and poorest in the medium-price ones (3.728 mg L<sup>-1</sup>). The content of acetic acid depends on the strains applied and the raw material (23). The content of hexanoic acid ranged from 0.430 (low-price) to 4.219 mg L<sup>-1</sup> (high-price), and it has a negative impact at concentrations higher than 20 mg L<sup>-1</sup> (24). Octanoic acid content increased from the low-price to high-price wines and showed the highest level in the high-price wines (4.789 mg L<sup>-1</sup>). The total contents of these acid volatiles were richest in the high-price wines (26.75 mg L<sup>-1</sup>) and moderate levels were found in the low-price (5.419 mg L<sup>-1</sup>) and medium-price (5.669 mg L<sup>-1</sup>) wines.

**Aldehydes:** A total of four aldehydes were determined: furfural, benzaldehyde, 5-methyl-2-furfural, and 5-(hyddroxymethyl) furfural. Among them, only 5-methyl-2-furfural showed a significant difference (*p*<0.05) among the three groups. The content of furfural and 5-methyl-2-furfural reached the highest level in the high-price wines and the lowest level in the low-price wines. The total contents of these aldehydes were rich (32.386 mg L<sup>-1</sup>) in the high-price wines and poor (5.553 mg L<sup>-1</sup>) in the medium-price wines.

**Ketones:** Three ketones were identified; two of them, namely, 3hydroxy-2-butanone and 2-nonanone, showed a significant difference (p<0.05) among the three groups. The low-price wines accounted for a higher concentration of 3-hydroxy-2-butanone, which was not detected in the medium-price wines. The content of 2-nonanone reached a similar level in the low-price wines (0.004 mg L<sup>-1</sup>) and medium-price wines (0.003 mg L<sup>-1</sup>). The total contents of the ketones were richest in the low-price wines (0.099 mg L<sup>-1</sup>) and lowest in the high-price wines (0.073 mg L<sup>-1</sup>).

**Phenols:** Four phenols were identified, of which only 4-methyl guaiacol showed a significant difference (p<0.05) among the three groups. Eugole reached the highest concentration in the medium-price wines; however, there was no significant difference among the three groups, with their values being 0.056 (low-price wines), 0.065 (medium-price wines) and 0.054 mg L<sup>-1</sup> (high-price wines), respectively. The most inexpensive wine set showed the highest contents in 4-ethyl guaiacol and 4-ethyl phenol. These phenolics are originally present in cherry fruits (7). Moreover, fermentation and wine aging decreased the content of polyphenols (25). The high levels of 4-ethyl guaiacol and 4-ethyl phenol in inexpensive wines indicated that polyphenol was insufficient in the process of fermentation and wine aging. However, the total contents of these phenol volatiles were similar in the medium-price and high-price wines, i.e., 0.879 and 0.864 mg L<sup>-1</sup>, respectively.

Terpenes: Myrcene and dl-limonene all showed significant differences

(*p*<0.05) among the three groups. In addition, dl-limonene was associated with imparting citrus and minty smell. Its content in the high-price wines was high (0.036 mg L<sup>-1</sup>), whereas it was low in the low-price wines (0.005 mg L<sup>-1</sup>). Myrcene was only absent in the low-price wines and reached the highest level in the medium-price wines (0.125 mg L<sup>-1</sup>). The total contents of these terpene volatiles were high in the medium-price and high-price wines, i.e., 0.138 and 0.123 mg L<sup>-1</sup>, respectively.

**Lactones:**  $\gamma$ -Butyrolactone was a desirable compound and imparted the aroma of caramel and sweetness to the wines. However, it did not show a significant difference (p>0.05) among the three groups. Its content kept increasing from the low-price to high-price wines and showed the highest level in the high-price wines (0.057 mg L<sup>-1</sup>). Among these volatiles, anisyl formate and 1-heptanol were reported in cherry wines for the first time.

Sensory analysis ANOVA was used to distinguish different sample sets on the basis of their sensory evaluation scores, which are shown in Table 2s (data not shown) and Fig. 1. The low-price wines received the highest scores for inharmonious aroma properties, the mediumprice wines had the highest sour, floral, woody, and spicy aroma, and the high-price wines received the highest scores in fruity, fermented, and caramelized aroma. The differences in the sensory analysis results may be caused by fermentation as yeasts have a significant effect on the sensory characteristics of wines (7). According to the quantitative result (Table 1), the high-price wines are the richest ones in all of the sensory attributes except for inharmonious aroma, which was contradictory the result of the sensory evaluation. It is known that only dozens of volatiles with low sensory thresholds can be impact odorants (26). The various chemical classes instead of one compound, such as esters, alcohols, carboxylic acids, ketones, aldehydes, and phenols, influence each other and are responsible for the overall odor perception (12). Thus, the difference between the sensory analysis and quantitative analysis can be explained.

Odor active values OAVs are an effective tool for evaluating the contribution of each aroma compound to the overall aroma (2). Compounds with OAVs $\geq$ 1 are commonly at the perception level and usually determined to be the aroma-active compounds contributing to the aroma of wines (19). The data on volatile compounds with OAVs≥1 and their odor thresholds are shown in Table 2. Twentythree volatile compounds had a concentration above the odor thresholds (OAV≥1). Ethyl hexanoate and ethyl octaneoate exhibited the highest OAVs (OAV>100), which were revealed as the most important contributor to the aroma of cherry wines. Ethyl octaneoate has been considered as one of the most important compounds in young red wines (27), aged red wines (28,29), Zalema white wines (30), and light-aroma liquors (6). Compounds such as ethyl acetate, (E)-linalool oxide, octanoic acid, and eugole are another important volatile with OAV 10. Additionally, there were 18 volatiles with OAVs ranging between 1 and 10 that were potential aroma contributors.



Fig. 1. Sensory profile of cherry wines from three different price categories.

Table 2. OAVs (>1) of the volatile compounds in cherry wines

NO	Compounds	Odor throshold (mg $1^{-1}$ )	OAVs					
NO.	compounds		Low-price Wines	Medium-price Wines	High-price Wines			
1	Ethyl acetate	7.5	7.3	4.3	12.8			
2	Ethyl butyrate	0.044	1.7	2.2	8.9			
3	Ethyl isovalerate	0.015	1.3	0.9	-			
4	Isoamyl acetate	0.025	1.7	5.0	3.0			
5	DL-limonene	0.01	0.5	1.3	3.6			
6	Ethyl hexanoate	0.0015	86.7	162.7	126.0			
7	Ethyl octanoate	0.005	46.2	164.0	92.2			
8	(E)-Linalool oxide	0.005	13.0	7.2	16.0			
9	Linalool	0.018	0.0	8.3	8.5			
10	Ethyl benzoate	0.575	8.0	0.5	1.6			
11	Ethyl 3-phenylpropanoate	0.13	0.7	0.7	1.0			
12	Phenylethyl alcohol	12	0.4	0.8	1.5			
13	Eugole	0.005	11.2	13.0	10.8			
14	3-Methyl-1-butanol	30	0.2	0.5	1.1			
15	Octanoic acid	0.5	1.1	1.5	9.6			
16	Myrcene	0.07	0.0	1.8	1.2			
17	4-Ethyl guaiacol	0.036	1.7	0.7	0.6			
18	lpha-terpineol	0.25	1.0	0.9	1.8			
19	Benzaldehyde	5	3.5	0.5	4.5			
20	4-Ethyl phenol	0.5	1.2	1.1	1.1			
21	Hexanoic acid	1.4	0.3	0.8	3.0			
22	2-Octanone	0.05	1.3	1.7	1.2			
23	4-Methyl guaiacol	0.025	1.0	9.4	9.4			

All the thresholds were calculated in a 12% water/ethanol mixture.

Among these 18 compounds, 12 volatiles exhibited significantly highest OAVs in the high-price wines, namely, ethyl acetate, ethyl butyrate, linalool, ethyl 3-phenylpropanoate,  $\alpha$ -terpineol, hexanoic acid, octanoic acid, benzaldehyde, 3-methyl-1-butanol, *(E)*-linalool oxide, phenylethyl alcohol, and dl-limonene. In the medium-price wines, the OAVs of isoamyl acetate, ethyl hexanoate, ethyl octanoate, 2-octanone, myrcene, and eugole were highest. The aroma volatiles of ethyl isovalerate, ethyl benzoate, 4-ethyl guaiacol, and 4-ethyl phenol had the highest OAVs in the low-price wines. Furthermore, 4-ethyl phenol and 4-methyl guaiacol exhibited similar OAVs in the

medium-price and high-price wines.

**Relationship between samples, OAVs, and sensory attribution** To study the relationships between the samples, their sensory attributes, and their aroma-active compositions (OAV $\geq$ 1), multivariate PLSR was performed. The PLSR model presented two principal components explaining 56% of the variance in X (volatile compounds) and 56% of that in Y (sensory attributes). Figure 2 shows a PLS2 score plot based on the major aroma-active compounds (OAV $\geq$ 1) and sensory analyses. As shown in Fig. 2, the wine samples can be clearly distinguished on the basis of their aroma characteristics. The low-



Fig. 2. Score plot obtained from partial least-squares regression (PLSR) based on the aroma active compounds (OAV>1) and sensory analyses.

price and medium-price wines were on the negative side of PC1, whereas, the samples belonging to the two different groups were separated by PC2. The high-price wine samples were on the positive side of PC1, which was separated from other wine sets. Figure 3 presents the correlation-loading plot of the first and the second principal. The inner and outer ellipses explain 50 and 100% of the variance, respectively. The sensory attributes and the aroma-active compounds between the two ellipses can be well explained by the PLS2 model (2). The variables marked with small circles were considered as significant, and those inside the inner ellipse were poorly explained.

As shown in Fig. 3, all the aroma-active compositions and sensory attributions except isoamyl acetate, ethyl hexanoate, ethyl 3-phenyl propanoate, linalool, methyl salicylate, 4-methyl guaiacol, 4-ethyl guaiacol, eugole, 4-ethyl phenol, and DL-limonene can be well explained by the PLS2 model. Figure 2 and 3 show that fermented, fruity, and caramelized aroma are located at the right-hand side of PC1 and are supposed to be the primary aroma of the high-price wines. The compounds of ethyl butyrate, phenylethyl alcohol, 3-methyl-1-butanol, ethyl acetate,  $\alpha$ -terpineol, octanoic acid, hexanoic acid, myrcene, benzaldehyde, and (*E*)-linalool oxide were highly



Fig. 4. Aroma profiles of H4 and the aroma reconstituted models.

associated with the high-price wines. Floral, sour, woody, and spicy aromas are located in the upper-left vertical axis and are considered to be the major aroma of the medium-price wines. The compounds of ethyl octanoate, isoamyl acetate and eugole were highly associated with the medium-price wines. The inharmonious note located in the lower-left quadrant was the major sensory attribution of the lowprice wines and associated with ethyl isovalerate and ethyl benzoate.

**Aroma recombination** The aroma reconstitution experiment was performed on the basis of the quantitative results of the H4 sample (Model A). All odorants with an OAV 1 were dissolved in a 12% hydroalcoholic solution; then, the recombination sample (Model B) and H4 sample were presented to the panelists for evaluation. The flavor profiles are shown in Fig. 4. The profiles of Model A and Model B were similar, especially for the fruity aroma. The woody, spicy, caramelized, and fermented aromas in Model A were slightly stronger than those in Model B, whereas the floral aroma was weaker in sample wine. The aroma reconstitution experiments successfully identified and quantitated the key aroma-active compounds in cherry wine.



Fig. 3. Correlation-loading plot obtained from partial least-squares regression (PLSR). The model was derived from aroma compounds (OAV>1) as the X-matrix and from sensory variables as the Y-matrix.

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