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Characterization of odor-active compounds of various cherry wines by gas chromatography–mass spectrometry, gas chromatography–olfactometry and their correlation with sensory attributes

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ABSTRACT

To characterize the aroma of cherry wine, five samples were analyzed by quantitative descriptive sensory analysis, gas chromatography–mass spectrometry (GC–MS) and gas chromatography–olfactometry (GC–O). The aroma of cherry wines was described by 6 sensory terms as fruity, sour, woody, fermentation, cameral and floral. Fifty-one odor-active (OA) compounds were detected by GC–O and quantified by GC–MS, and 45 of them were identified. Twenty-nine OA compounds having more than 50% detection frequency were selected as specific compounds correlated to sensory attributes by partial least squares regression (PLSR). The correlation result showed ethyl 2-methyl propionate, 2,3-butanedione, ethyl butyrate, ethyl pentanoate, 3-methyl-1-butanol, ethyl hexanoate, 3-hydroxy-2-butanone, ethyl lactate, 1-hexanol, (Z)-3-hexen-1-ol, ethyl hydroxyacetate, acetic acid, furfural, 2-ethyl-1-hexanol, benzaldehyde, propanoic acid, butanoic acid, guaiacol, beta-citronellol, hexanoic acid, 2-methoxy-4-methylphenol, 2-ethyl-3-hydroxy-4H-pyran-4-one, ethyl cinnamate, 2-methoxy-4-vinylphenol were typical OA compounds, which covaried with characteristic aroma of cherry wines.

1. Introduction

Cherry is one of the most popular fruits cultivated and consumed worldwide. Besides some essential dietary components such as vitamins, minerals, protein and carbohydrates, cherries also contain other phytonutrients that may prevent some dietary deficiencies and multiple diseases [1]. Cherry wine, one of the products made from cherry, has a unique color and flavor, derived from its specific traditional processes. Cherry wines are very popular in China and other countries.

Volatile compounds play an important role for the quality of wine. Recent sensory studies based on consumer preference proved that wine flavor was one of the crucial factors [2]. More than 800 volatiles have been identified in wines including alcohols, esters, organic acids, aldehydes, ketones and monoterpenes [3–5]. Through GC–MS and gas chromatography-flame ionization detection (GC-FID) analysis, Duarte et al. [6] characterized the aroma compounds of various fruit wines which made from cocoa, cupuassu, gabiroba, jaboticaba and umbu; Pino et al. [7] analyzed volatile compounds of mango wine, and estimated the contribution of the identified compounds to the aroma of the wine using odor activity value. Rocha et al. [8] identified the volatile compounds of Baga red wine, and assessed the identification of the would-be impact odorants by aroma index. The concentration of these compounds in wines varies from a few mg L^{-1} to hundreds of mg L^{-1} [9,10].

The combination profile of all these compounds forms the characteristic of wine and distinguishes one from others. Among hundreds of volatile compounds present in wine, however, only few of them contribute actively to flavor [11]. GC–MS is an effective method to identify and quantify flavor substances, but it cannot identify odor-active compounds. Gas chromatography–olfactometry (GC–O) provides a valuable tool for investigating the pattern of odorants in terms of both their odor descriptors and activity. Many studies have been done to identify typical aroma compounds in fruit wines via GC–MS and GC–O. Campo et al. [12] characterized four Madeira wines from different grape varieties by sensory analysis, GC–MS and GC–O, and identified a large number of potential odorants. Denise Falcão et al. [13] evaluated the difference of Brazilian Cabernet Sauvignon wines produced from

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different regions by GC–O. Janáčová et al. [14] identified key odorants of Slovak Brandies using GC–MS and GC–O. However, few studies have been done so far on the typical aroma of cherry wines.

Recently, multivariate statistical methods have been used to explore the relationships between sensory profiles and wine volatiles, such as principal component analysis [15], partial least squares regression (PLSR) [16] and generalized procrustes [17]. However, there is still a lack of systematic study on the relationship between cherry wine samples, sensory attributes and odor-active (OA) compounds.

The primary aim of the present study was to (a) apply descriptive sensory analysis to describe the aroma attributes of different cherry wines; (b) analyze the typical OA compounds; and (c) identify which OA compounds have significant influence on individual sensory of wine samples through PLSR analysis. A better understanding of this knowledge will be helpful for the improvement of characteristic aroma of cherry wine through adjusting fermentation parameters or compensating typical aroma compounds after alcoholic fermentation.

2. Materials and methods

2.1. Materials

Five cherry wines obtained from different wine companies were studied. They were purchased from Yantai Hualong Wine Co., Ltd. (W1 cherry wine), Shan Dong Linqu Sanxin Food Co., Ltd. (W2 cherry wine), Shan Dong Zunhuang Cherry Wine Co., Ltd. (W3 cherry wine), Laizhou Yinghong Wine Co., Ltd. (W4 cherry wine) and Si Chuan Hanyuan fruit wine company (W5 cherry wine), respectively.

Absolute ethanol, dichloromethane and sodium sulfate were purchased from Sinopharm Chemical Reagent Co. Ltd., and all of them were ARG quality. 2-Octanol (internal standard) was chromatography grade and obtained from Sigma–Aldrich Chemical Co. (St. Louis, MO). Other authentic reference compounds were obtained from commercial source. Pure water was obtained from a Milli-Q purification system (Millipore, Bedford, MA).

2.2. Extraction of wine volatiles

Before extraction, 100 μL of 2-octanol (400 mg L^{-1} in absolute ethanol) was added to 50 mL cherry wine as internal standard. Three consecutive extractions were then carried out using 20 mL, 20 mL and 10 mL dichloromethane. The aromatic extract was dried with 3 g anhydrous sodium sulfate overnight, and concentrated to 1 mL in a micro-Kuderna–Danish concentrator (Afora S.A., Spain) under a stream of pure N_2.

2.3. Gas chromatography–mass spectrometry (GC–MS)

One microliter of concentrated extract of wine was analyzed on a Hewlett-Packard 6890 gas chromatograph coupled to a 5973C mass selective detector (MSD) (Agilent Technologies, USA). HP-INNOWAX analytical fused silica capillary column was used (Agilent, Santa Clara, CA), with 60 m × 0.25 mm with 0.25 μm film thickness. The injection was conducted in a splitless mode for 3 min at 250 °C. The carrier gas was helium at 1 mL min^{-1}. Mass spectrum in the electron impact mode was generated at 70 eV and ion source temperature was 230 °C. The quadrupole mass filter was operated at 150 °C. The transfer line temperature was at 250 °C. The chromatograms were recorded by monitoring the total ion currents in 30–450 mass range. The oven temperature had been held at 40 °C for 5 min, then ramped to 230 °C at the rate of 3 °C min^{-1} and maintained for 5 min.

The identification of volatile compounds were made by comparing Kovats retention indices (KI) and MS fragmented patterns with those of reference compounds, or with mass spectra in the Wiley7n.l Database (Hewlett-Packard, Palo Alto, CA) and previously reported Kovats retention indices. The KI of compounds were determined via sample injection with a homologous series of alkanes (C6–C30) (Sigma–Aldrich, St. Louis, MO). To quantify the volatiles, the samples were run in triplicate, and the integrated areas based on the total ion chromatograms were normalized to the areas of the internal standard and averaged. The relative volatile concentrations in the cherry wines were determined by comparison with the concentration of the internal standard (2-octanol).

2.4. Gas chromatography–olfactometry (GC–O)

One microliter of concentrated extract of wine was injected on a Hewlett-Packard 6890 gas chromatograph equipped with a flame ionization detection (FID) system and a sniffing port (ODP 2, GERSTEL). At the end of the capillary column, the effluent was split 1:1 for FID and sniffing port, respectively, using deactivated and uncoated fused silica capillaries as transfer lines, and the sniffing cone was purged with humidified air to help in maintaining olfactory sensitivity by reducing dehydration of mucous membranes in the nasal cavity. The sniffing port was held at 250 °C to prevent any condensation of volatile compounds. The column and operating conditions were the same as those used for GC–MS. The analysis was carried out in duplicate.

Detection frequency method (DFA) using a panel of six panelists was applied to obtain the odor profile of cherry wines. Each of the six panelists participated in perceiving the aroma compounds separated from cherry wines at the sniffing port. An “olfactometer button” was depressed when the aroma was detected. The panelists were asked to give verbal description of perceived odors that was recorded.

2.5. Sensory evaluation

Quantitative descriptive sensory analysis was applied for evaluation of the wine samples, using a 10-point interval scale (0 = none, 9 = extremely strong). The sensory evaluation was done by a well-trained panel made of 4 females and 4 males, 23–30 years old. The panel has previously been trained according to ISO 4121, ASTM-MNL 13 and DIN 10964 [18]. Sensory sessions took place in a sensory laboratory, which complied with international standards for test room [19]. Five specific training sessions were carried out. In the first session, panelists generated descriptive terms for the cherry wines; in the second and third, different aroma standards were presented and discussed by panelists. From these discussions, the six aroma terms (fruity, sour, woody, fermentation, cameral and floral) as shown in Fig. 1 were selected for further descriptive analysis. In the fourth and fifth sessions, the cherry wines were evaluated in duplicate using the 10-point interval scale mentioned above. Then, the reference materials of aroma were as follow: fruity (crushed strawberries, raspberries and blackberries), sour (Shanghai fragrant vinegar, obtained from Shanghai Beau Ideal Fermentation Co., Ltd.), woody (5 g oak wood chips in 100 mL 10% ethanol–water solution), fermentation (0.5 g dry yeast in 100 mL sugar solution after overnight), cameral (5 g crushed caramel in 100 mL 10% ethanol–water solution), floral (1 mg L^{-1} aqueous solution of 2-phenyl ethanol). Sensory evaluation was performed in coded, tulip glass containing 20 mL of cherry wines. Samples were presented in a random order.

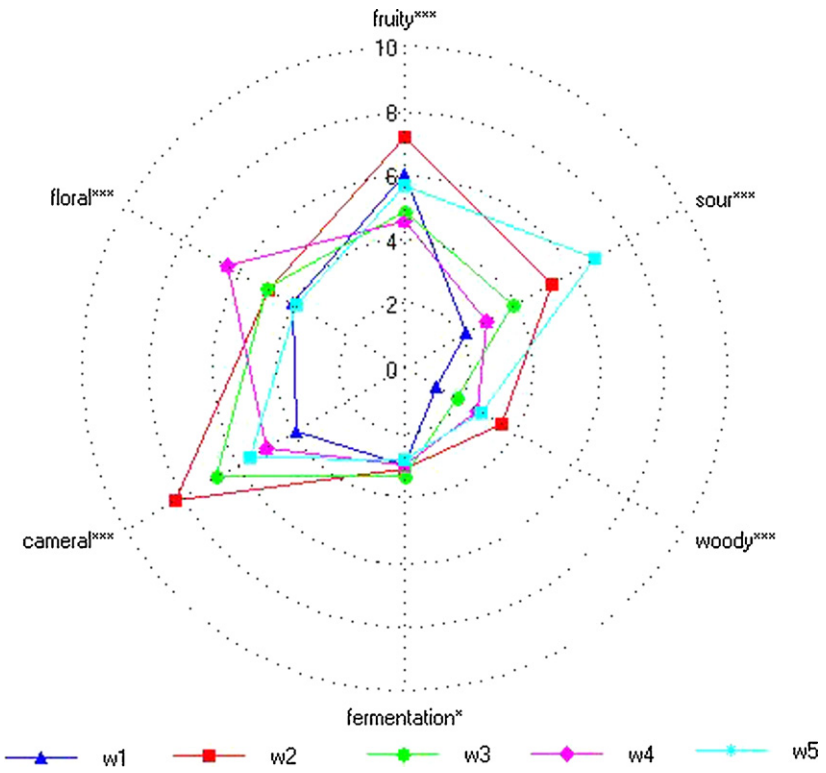

Fig. 1. Graph of the mean sensory scores of the five cherry wines studied. Notations * and *** indicate significance at $p < 0.05$ and $p < 0.001$, respectively.

2.6. Statistical analysis

Data from the descriptive analysis was evaluated by analysis of variance (ANOVA) using SPSS v13.0 (SPSS Inc., Chicago, IL, USA). ANOVA with Duncan's multiple comparison tests were performed to determine the difference among individual sample for each sensory attribute.

Partial least squares regression analysis (PLSR) was used to explore the relationship between wine samples, sensory attributes data and the odor-active volatiles of 5 cherry wines through UNSCRAMBLER ver. 9.8 (CAMO ASA, Oslo, Norway). All variables were centered and standardized (1/Sdev) so that each variable has a unit variance and zero mean before applying PLSR analyses. By applying PLSR analysis to standardized data, importance of peaks for each attribute could be compared quantitatively based on regression coefficients and loading weights for each predictor or *X* variable used in PLSR models.

3. Results and discussion

3.1. Sensory analysis

The aromatic characteristics of five different cherry wines were described by six different sensory panelists. The results of sensory analysis were shown in Fig. 1 and Table 1. As shown in Fig. 1, cherry wines aroma was described as fruity, sour, woody, fermentation, cameral and floral.

ANOVA analysis revealed that the most discriminative terms were fruity, sour, woody, cameral and floral among cherry wines ($p < 0.001$), followed by fermentation ($p < 0.05$) (Fig. 1). Duncan's multiple comparison test results (Table 1) indicated that sour and cameral aroma had most significant difference, with different superscripts for each sample. However, fermentation attribute had a little difference. Therefore, the five attributes sour, cameral, fruity, woody and floral seemed to well explain their aroma characteristics of different samples. As shown in Fig. 1 and Table 1, W1 had the least sour, woody and cameral aroma. W2 presented the highest fruity, woody and cameral aroma. W3 had almost the same score in fruity, sour, woody, cameral and floral, a little higher score in fermentation aroma than others. W4 had the strongest floral attribute, but it had the least weak fruity attribute. W5 showed the highest score in sour aroma.

3.2. Characterization of odor-active compounds by GC–O analysis

The five cherry wines were subjected to GC–O analysis, based on the detection frequency method, to identify the OA compounds from volatile compounds. A summary of the GC–O analysis results were shown in Table 2. Fifty-one OA compounds were detected by six panelists, but only 45 odorant compounds were identified by GC–MS, and other six compounds' structure were unknown, it might be due to their lower concentration or their higher detection limit of MS or not finding these compounds in Wiley7n.l Database.

Twenty-nine OA compounds were characterized in the five cherry wines with more than 50% detection frequency (more than 3 sniffing among 6 panelists on average). These compounds had

Table 1
The mean scores of the six attributes for the five cherry wines in descriptive sensory evaluation.*

Sample	Mean score					
	Fruity	Sour	Woody	Fermentation	Cameral	Floral
W1	6.06^{b}	2.19^{a}	1.31^{a}	3.00^{a}	3.88^{a}	4.00^{a}
W2	7.19^{c}	5.25^{d}	3.50^{d}	3.13^{ab}	8.19^{e}	4.88^{b}
W3	4.88^{a}	3.88^{c}	1.88^{b}	3.38^{b}	6.75^{d}	4.94^{b}
W4	4.56^{a}	2.94^{b}	2.63^{c}	3.00^{a}	4.94^{b}	6.31^{c}
W5	5.69^{b}	6.81^{e}	2.75^{c}	2.81^{a}	5.56^{c}	3.88^{a}

* Mean scores for each attribute within a column with different letters are significantly different ($p < 0.05$) using Duncan's multiple comparison tests ($n = 16$: 8 panelists with 2 replications).

Table 2
Odor-active compounds of five cherry wines, determined by gas chromatography–olfactometry, frequency of detection (six assessors, average of two sessions) and odor description.

Code	KI[b]	Compound	Detection frequency					Odor description[c]	ID[d]
			W1	W2	W3	W4	W5		
		Esters							
1	890	Ethyl acetate	0	1	2	1	1	Fruity, pineapple	A
2[a]	977	Ethyl 2-methyl propionate	5	6	0	0	6	Alcoholic-fruity, sweet	B
3	985	Propyl acetate	0	1	1	2	2	Fruity, Sweet	A
4[a]	1045	Ethyl butyrate	4	6	4	5	6	Fruity, banana	A
5	1131	Isoamyl acetate	2	1	2	0	0	Banana, sweet	B
6[a]	1143	Ethyl pentanoate	0	6	0	0	5	Fruity, apple	A
7[a]	1241	Ethyl hexanoate	4	6	5	4	4	Fruity, anise	B
8[a]	1363	Ethyl lactate	3	5	6	3	4	Sweet, fatty	B
9[a]	1430	Ethyl hydroxyacetate	4	5	3	5	5	Fruity, floral	B
10	1530	Ethyl 3-hydroxybutyrate	1	0	2	1	0	Fresh, fruity	B
11	1685	Ethyl benzoate	0	0	0	0	6	Fruity	A
12	1688	Diethyl succinate	0	0	2	0	1	Fruity, sweet	A
13	2065	Diethyl malate	0	0	0	2	1	Brown sugar	B
14[a]	2161	Ethyl cinnamate	0	0	0	6	0	Floral	A
		Alcohols							
15	1114	2-Methyl-1-propanol	1	0	0	0	0	Malty	A
16	1153	1-Butanol	0	0	1	0	2	Spicy	A
17[a]	1220	3-Methyl-1-butanol	5	3	6	6	6	Cheese	A
18	1335	3-Methyl-1-pentanol	0	0	0	1	0	Fruity, cocoa	B
19[a]	1394	1-Hexanol	5	0	2	6	0	Green, floral	A
20[a]	1391	(Z)-3-hexen-1-ol	3	6	0	2	0	Fruity, plant	B
21	1412	(E)-2-Hexen-1-ol	0	0	0	2	0	Grass, vegetable	B
22[a]	1494	2-Ethyl-1-hexanol	5	5	5	0	3	Fruity, green cucumber	A
23	1675	Furfuryl alcohol	0	2	0	0	0	Camarel, sweet	B
24	1903	Benzyl alcohol	0	0	2	1	1	Floral, sweet	A
25[a]	1938	Phenylethyl alcohol	6	5	6	6	4	Rose, sweet	B
		Acids							
26[a]	1459	Acetic acid	1	6	3	3	6	Vinegar	A
27[a]	1559	Propanoic acid	0	4	0	0	6	Soy	A
28[a]	1645	Butanoic acid	2	3	2	1	5	Cheese, stinky	B
29	1754	Valeric acid	0	0	0	0	2	Sweaty	A
30	1819	Pentanoic acid	0	0	0	0	1	Cheese	A
31[a]	1864	Hexanoic acid	1	5	2	2	1	Unplesant, metallic	A
32	1970	Heptanoic acid	0	0	0	0	2	Sweaty, cheese	A
33	2077	Octanoic acid	1	1	0	2	0	Fatty	A
34	2192	4-Hydroxy-3-methoxy-benzoic acid	0	0	0	2	0	Camarel, sweet, vanilla	B
		Ketones							
35[a]	991	2,3-Butanedione	5	6	6	4	5	Sweet, caramel	A
36[a]	1294	3-Hydroxy-2-butanone	6	6	5	4	5	Fatty	A
37	1310	1-Hydroxy-2-Propanone	0	2	0	1	0	Alcoholic-fruity, malty	B
38[a]	2046	2-Ethyl-3-hydroxy-4H-pyran-4-one	2	6	0	2	1	Camarel, sweet	B
		Phenols							
39[a]	1884	Guaiacol	6	0	0	0	0	Smoky	B
40[a]	1981	2-Methoxy-4-methylphenol	0	0	5	0	0	Spicy, herbal	B
41	2110	p-Cresol	0	0	0	0	2	Stinky	B
42[a]	2227	2-Methoxy-4-vinylphenol	5	0	0	5	0	Smokey, nutty	B
		Aldehydes							
43[a]	1479	Furfural	3	4	6	5	6	Sweet	B
44[a]	1541	Benzaldehyde	4	6	4	5	5	Fruity, almond	B
		Terpene							
45[a]	1774	Beta-citronellol	0	0	0	6	0	Sweet, floral	B
		Unknown compounds							
46[a]	1248	Unknown	0	0	0	0	5	Sweet, plant	
47[a]	1374	Unknown	0	0	5	0	0	Woody, herbal	
48[a]	1571	Unknown	5	0	0	0	0	Nutty	
49	2032	Unknown	0	0	0	3	0	Mushroom, fermented	
50	2068	Unknown	0	0	0	0	3	Nutty	
51[a]	2180	Unknown	0	5	0	0	0	Cameral, sweet	

[a] Code representing the 29 odor-active compounds using in the PLSR analysis.
[b] Kovats indices of unknown compounds on INNOWAX column.
[c] Odor description as perceived by panelists at a given retention index during GC–O.
[d] Identification method: A, mass spectrum and KI agree with that of the authentic compound run under similar GC–MS conditions; B, mass spectrum and KI agree with literature data.

a great contribution on cherry wine aroma. Sixteen of them have already been reported as wine aroma contributor: 2,3-butanedione (lactic, strawberry), ethyl butyrate (fruity), 3-methyl-1-butanol (cheese), ethyl hexanoate (fruity, anise), ethyl lactate (acid, plastic), (Z)-3-hexen-1-ol (grass), acetic acid (vinegar), furfural (sweet, wood), 2-ethyl-1-hexanol (green, flowery), propanoic acid (soy), butanoic acid (cheese), guaiacol (phenolic and chemical), hexanoic acid (cheese), phenylethyl alcohol (flowery, fresh, green), ethyl cinnamate (floral, sweet), 2-methoxy-4-vinylphenol (phenolic, smoky) [3,20–22]. Thirteen compounds were detected in every cherry wine samples. Thus, these thirteen compounds were identified to contribute to the body note of cherry wines rather

Table 3
Mean concentrations (mg L^{-1}) of odor-active in five cherry wines.

Code	KI[b]	Compound	W1	W2	W3	W4	W5
		Esters					
1	890	Ethyl acetate	0.104 ± 0.01[c]	0.178 ± 0.01	0.267 ± 0.02	0.126 ± 0.03	0.160 ± 0.01
2[a]	977	Ethyl 2-methyl propionate	0.278 ± 0.05	0.356 ± 0.05	ND	ND	0.880 ± 0.11
3	985	Propyl acetate	ND	0.036 ± 0.01	0.053 ± 0.03	0.337 ± 0.10	0.560 ± 0.10
4[a]	1045	Ethyl butyrate	0.139 ± 0.02	3.111 ± 0.29	0.267 ± 0.02	0.211 ± 0.02	4.960 ± 0.72
5	1131	Isoamyl acetate	0.466 ± 0.05	0.267 ± 0.03	0.400 ± 0.14	0.126 ± 0.03	ND
6[a]	1143	Ethyl pentanoate	ND	0.178 ± 0.04	ND	ND	0.160 ± 0.02
7[a]	1241	Ethyl hexanoate	0.452 ± 0.05	11.200 ± 0.05	0.800 ± 0.05	0.463 ± 0.01	0.320 ± 0.01
8[a]	1363	Ethyl lactate	7.965 ± 0.02	201.333 ± 0.01	358.000 ± 0.02	23.032 ± 0.01	121.760 ± 0.08
9[a]	1430	Ethyl hydroxyacetate	0.174 ± 0.01	0.533 ± 0.03	0.053 ± 0.01	0.253 ± 0.04	0.480 ± 0.08
10	1530	Ethyl 3-hydroxybutyrate	0.278 ± 0.04	0.089 ± 0.03	0.667 ± 0.05	0.337 ± 0.04	ND
11	1685	Ethyl benzoate	ND	ND	ND	ND	0.712 ± 0.02
12	1688	Diethyl succinate	ND	ND	1.253 ± 0.07	ND	0.624 ± 0.02
13	2065	Diethyl malate	ND	ND	ND	1.070 ± 0.12	0.048 ± 0.02
14[a]	2161	Ethyl cinnamate	ND	ND	ND	4.200 ± 0.09	ND
		Alcohols					
15	1114	2-Methyl-1-propanol	0.020 ± 0.01	ND	ND	ND	ND
16	1153	1-Butanol	0.097 ± 0.06	0.533 ± 0.06	0.933 ± 0.37	0.337 ± 0.08	3.040 ± 0.35
17[a]	1220	3-Methyl-1-butanol	29.078 ± 0.07	3.378 ± 0.05	201.067 ± 0.05	102.316 ± 0.03	128.160 ± 0.03
18	1335	3-Methyl-1-pentanol	ND	ND	ND	0.168 ± 0.02	ND
19[a]	1394	1-Hexanol	5.113 ± 0.10	ND	0.053 ± 0.01	5.895 ± 0.09	ND
20[a]	1391	(Z)-3-hexen-1-ol	0.243 ± 0.02	2.577 ± 0.16	ND	0.211 ± 0.02	ND
21	1412	(E)-2-Hexen-1-ol	ND	ND	ND	0.084 ± 0.01	ND
22[a]	1494	2-Ethyl-1-hexanol	1.530 ± 0.01	1.662 ± 0.02	3.520 ± 0.01	ND	0.088 ± 0.02
23	1675	Furfuryl alcohol	ND	0.050 ± 0.01	ND	ND	ND
24	1903	Benzyl alcohol	0.108 ± 0.02	1.742 ± 0.06	9.360 ± 0.11	3.646 ± 0.05	2.408 ± 0.11
25[a]	1938	Phenylethyl alcohol	2.442 ± 0.04	0.178 ± 0.03	2.280 ± 0.08	1.478 ± 0.13	0.976 ± 0.04
		Acids					
26[a]	1459	Acetic acid	1.704 ± 0.06	45.955 ± 0.01	11.600 ± 0.22	9.811 ± 0.01	48.240 ± 0.07
27[a]	1559	Propanoic acid	ND	2.053 ± 0.02	ND	ND	10.296 ± 0.08
28[a]	1645	Butanoic acid	0.073 ± 0.01	0.560 ± 0.07	0.133 ± 0.01	0.063 ± 0.01	2.296 ± 0.04
29	1754	Valeric acid	ND	0.053 ± 0.01	ND	ND	0.176 ± 0.06
30	1819	Pentanoic acid	ND	ND	ND	ND	0.048 ± 0.01
31[a]	1864	Hexanoic acid	0.268 ± 0.07	2.587 ± 0.09	0.307 ± 0.02	0.286 ± 0.05	0.264 ± 0.03
32	1970	Heptanoic acid	ND	0.004 ± 0.00	ND	ND	0.040 ± 0.02
33	2077	Octanoic acid	0.289 ± 0.06	0.133 ± 0.02	ND	0.387 ± 0.05	0.040 ± 0.02
34	2192	4-Hydroxy-3-methoxy-benzoic acid	ND	ND	ND	0.535 ± 0.07	ND
		Ketones					
35[a]	991	2,3-Butanedione	0.695 ± 0.01	1.244 ± 0.12	1.733 ± 0.41	0.379 ± 0.05	0.480 ± 0.09
36[a]	1294	3-Hydroxy-2-butanone	5.579 ± 0.09	47.377 ± 0.03	2.933 ± 0.04	1.030 ± 0.01	1.920 ± 0.01
37	1310	1-Hydroxy-2-Propanone	ND	0.356 ± 0.00	0.053 ± 0.01	0.211 ± 0.01	ND
38[a]	2046	2-Ethyl-3-hydroxy-4H-pyran-4-one	0.061 ± 0.02	42.000 ± 0.11	ND	0.143 ± 0.02	0.048 ± 0.01
		Phenols					
39[a]	1884	Guaiacol	7.000 ± 0.12	ND	ND	ND	ND
40[a]	1981	2-Methoxy-4-methylphenol	ND	ND	0.080 ± 0.03	ND	ND
41	2110	p-Cresol	ND	ND	ND	ND	0.016 ± 0.01
42[a]	2227	2-Methoxy-4-vinylphenol	1.103 ± 0.14	ND	ND	0.320 ± 0.09	ND
		Aldehydes					
43[a]	1479	Furfural	0.883 ± 0.04	1.244 ± 0.01	9.467 ± 0.07	2.400 ± 0.15	11.120 ± 0.01
44[a]	1541	Benzaldehyde	1.035 ± 0.07	7.528 ± 0.02	2.733 ± 0.02	7.365 ± 0.07	5.544 ± 0.06
		Terpene					
45[a]	1774	Beta-citronellol	ND	ND	ND	16.800 ± 0.10	ND
		Unknown compounds					
46[a]	1248	Unknown	ND	ND	ND	0.084 ± 0.01	0.080 ± 0.01
47[a]	1374	Unknown	ND	ND	53.333 ± 0.03	ND	ND
48[a]	1571	Unknown	0.017 ± 0.01	ND	ND	ND	ND
49	2032	Unknown	ND	ND	ND	0.110 ± 0.08	ND
50	2068	Unknown	0.004 ± 0.00	ND	0.005 ± 0.00	ND	56.000 ± 0.12
51[a]	2180	Unknown	ND	0.080 ± 0.08	ND	ND	ND

[a] Code representing the 29 odor-active compounds using in the PLSR analysis.
[b] Kovats indices of unknown compounds on INNOWAX column.
[c] Mean standard deviation (average of triplicate). ND: not found.

than individual nuance in cherry wines. Ethyl hexanoate has been described as fruity and anise aroma in cherry wines and was also detected in other wines. For instance, it was detected with higher 75% detection frequency in Califomian Chardonnay wine [3]. Ethyl hexanoate has also been identified as a key OA compound with high intensity in cashew apple-based alcoholic beverage [23], high FD value in botrytized wines [24] or high GC–O score in Desert and Sparking white wines [25], respectively.

Guaiacol, which contributed to smoky aroma, was only detected in W1. It was also detected with high frequency in two of Califomian Chardonnay wines [3] and some sparkling white wines [25]. Unknown compound 51 (Table 2, KI = 2180) exhibited caramel and sweet aroma was only detected in W2. 2-methoxy-4-methylphenol (spicy, herbal aroma) and unknown compound 47 (Table 2, KI = 1374) were only detected in W3. Beta-citronellol (sweet and floral aroma) and ethyl cinnamate (floral aroma) were only detected in W4. Ethyl cinnamate has also been described as key OA compound in Californian Chardonnay Wines for the raisin aroma [3]. It might be formed during a slow esterification of some wine organics [12]. Ethyl benzoate (fruity aroma) was only present

in W5. Therefore, those compounds would be uncommon typical OA compounds in cherry wines.

Moreover, ethyl 2-methyl propionate was detected in W1, W2 and W5. Ethyl pentanoate and propanoic acid were present in W2 and W5. 1-hexanol was detected in W1, W3 and W4. (Z)-3-hexen-1-ol was detected in W1, W2 and W4. 2-methoxy-4-vinylphenol was found in W1 and W4.

Among the five cherry wines, W2 showed high significant detection frequency score of OA compounds than other samples, especially for ethyl 2-methyl propionate, ethyl pentanoate, (Z)-3-hexen-1-ol, acetic acid, hexanoic acid, 2-ethyl-3-hydroxy-4H-pyran-4-one and unknown compound 51. 2,3-Butanedione, ethyl butyrate, ethyl hexanoate, 3-hydroxy-2-butanone, ethyl hydroxyacetate, benzaldehyde and phenylethyl alcohol exhibited sweet/caramel, fruity/banana, fruity/anise, fatty, fruity/floral, fruity/almond and rose/sweet notes, respectively. They were not OA compound which differentiated W2 from other wines.

3.3. Quantitative analysis of odor-active compounds

The mean concentration of 51 OA compounds, including 14 esters, 11 alcohols, 9 acids, 4 ketones, 4 phenols, 2 aldehydes, 1 terpene and 6 unknown compounds were shown in Table 3. Quantitatively, the volatile profiles were dominated by ethyl lactate (7.965–358 mg L^{-1}), 3-methyl-1-butanol (3.378–201.067 mg L^{-1}), acetic acid (1.704–48.24 mg L^{-1}), 3-hydroxy-2-butanone (1.03–47.377 mg L^{-1}), furfural (0.883–11.12 mg L^{-1}), benzaldehyde (1.035–7.528 mg L^{-1}), respectively. Meanwhile, most of the compounds were detected with high detection frequency in all five cherry wines. Therefore, these OA compounds might play a key role in the characterization of cherry wines. However, the concentrations of these compounds in cherry wines differed greatly from each other. This might be due to their different processing techniques and/or the different origin of cherry.

Esters and alcohols were the largest groups which accounted for 74.68% of the OA compounds on average. They were produced during alcoholic fermentation, and played an essential role in wines flavor, depending on types of compounds and their concentrations [26]. Esters of cherry wines were mainly composed of acetate esters and ethyl esters including ethyl acetate, propyl acetate, isoamyl acetate, ethyl 2-methyl propionate, ethyl butyrate, ethyl pentanoate, ethyl hexanoate, ethyl lactate, ethyl hydroxyacetate and ethyl 3-hydroxybutyrate. Acetate esters showed lower concentration than ethyl esters in wine samples. Ethyl esters might be produced enzymatically during yeast fermentation and from ethanolysis of acyl-CoA that was formed during fatty acids synthesis or degradation. Their concentration relied on several main factors including yeast strain, fermentation temperature, aeration degree and sugar contents [27]. Ethyl lactate was the most abundant compound with 42.05% of the total OA compounds and reached the highest level of 358 mg L^{-1} in W3. Similarly, it was detected with high concentration in young Cabernet Sauvignon red wine [28], various liqueurs [29] and young wines from the Denomination of Origin "Vinos de Madrid" [30]. Alcohols have been reported in cherry fruits [31,32]. 3-methyl-1-butanol was ranged from 3.378 to 201.067 mg L^{-1}. Some alcohols were not identified in cherry wine such as 2-methyl-1-propanol, 3-methyl-1-pentanol, 2-ethyl-1-hexanol and furfuryl alcohol.

Acids accounted for 8.17% of the total volatile compounds. The fatty acids may arise from the autoxidation of saturated lipids present in fruits, whose production increased with the thermal treatment [7]. Acetic acid (1.704–48.24 mg L^{-1}), butanoic acid (0.063–2.296 mg L^{-1}) and hexanoic acid (0.264–2.587 mg L^{-1}) were the major compounds quantified in the samples. However, propanoic acid, valeric acid and heptanoic acid were detected in W2 and W5, and described as soy, sweaty and sweaty/cheese notes, respectively.

Four ketones were quantified, including 3 aliphatic ketones and 1 pyran ketone, 2,3-butanedione and 3-hydroxy-2-butanone had a great contribution to cherry wine aroma. Their individual concentrations in each sample were found higher than their odor threshold 0.0011 and 0.014 mg kg^{-1} (in aqueous solution), respectively, the result was consent with the report by Boonbumrung et al. [33]. Four phenol compounds were detected in W1, W3 and W5 samples. They were guaiacol (7 mg L^{-1}), 2-methoxy-4-methylphenol (0.08 mg L^{-1}) and p-cresol (0.016 mg L^{-1}), respectively. Although their total concentration was low, these compounds had high detection frequency in GC–O analysis due to their low odor threshold. For example, Gerny and Grosch [33] reported guaiacol with a very low odor threshold 0.0025 mg kg^{-1} (in aqueous solution). 2-methoxy-4-vinylphenol was found in W1 and W4 with the concentration of 1.103 mg L^{-1} and 0.32 mg L^{-1}, respectively. Two aldehydes were quantified in cherry wines, i.e. furfural and benzaldehyde. The average concentration of two compounds was 5.023 mg L^{-1} and mg L^{-1}, respectively. And benzaldehyde had been previously reported in sweet cherries [34]. Beta-citronellol, one of terpene compounds, was only detected in W4 cherry wine with the concentration of 16.8 mg L^{-1}.

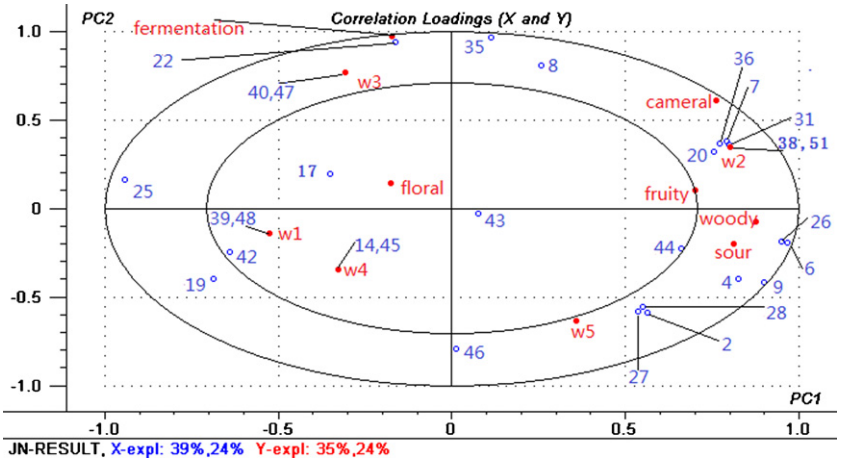

Fig. 2. An overview of the variation found in the mean data from the partial least squares regression (PLSR) correlation loadings plot for cherry wine samples. The model was derived from GC–MS isolated compounds as the *X*-matrix and samples and sensory attributes as *Y*-matrix. Elipses represent r^2 = 0.5 and 1.0, respectively.

3.4. Relationship between wine samples, sensory attributes and odor-active compounds

ANOVA-PLSR was used to process the mean data accumulated from sensory evaluation by the panelists and GC–MS analysis. Twenty-nine OA compounds were used as variables in the subsequent PLSR analysis. The *X*-matrix was designed as GC–MS measurements; the *Y*-matrix was designed as wine samples and sensory variables. The optimal number of components in the APLSR model presented was determined as 3 Principal Components. PC1 versus 2 (Fig. 2) and PC2 versus 3 were explored. PC2 versus 3 results was not presented here, as the additional information was not gained through their examination. Further, PCs did not provide any predictive improvement in the *Y*-matrix obtained. The calibrated explained variance for this model was PC1 = 39% and PC2 = 24%. Fig. 2 was presented as correlation loadings plot. The big circles indicated 50% and 100% explained variances, respectively [35]. Seven *Y* variables (W2, W3, W5, sour, woody, cameral, and fermentation) and twenty one *X* variables including ethyl 2-methyl propionate, 2,3-butanedione, ethyl butyrate, 1-butanol, ethyl hexanoate, unknown compound 46 (Table 2, KI = 1248), 3-hydroxy-2-butanone, ethyl lactate, unknown compound 47, 1-hexanol, (Z)-3-hexen-1-ol, ethyl hydroxyacetate, acetic acid, 2-ethyl-1-hexanol, propanoic acid, butanoic acid, hexanoic acid, phenylethyl alcohol, 2-methoxy-4-methylphenol, 2-ethyl-3-hydroxy-4H-pyran-4-one and unknown compound 51 were placed between the inner and outer ellipses, $r^2 = 0.5$ and 1.0, respectively, indicating they were well explained by the PLSR model.

As indicated from Fig. 2, W1 did not covary well with any sensory attribute. This was in agreement with the sensory evaluation results (Fig. 1), where W1 did not have highest score in some sensory attributes. Nevertheless, it covaried with some of the identified OA compounds like 1-hexanol, 2-methoxy-4-vinylphenol, unknown compound 48 (Table 2, KI = 1571), guaiacol. W2 located in the upper right hand quadrant, correlated to cameral, fruity and woody notes. It also had good correspondence to the sensory evaluation results that W2 had the strongest aroma intensities in cameral, fruity and woody attributes. In addition, cameral and fruity attribute were associated with some identified OA compounds like hexanoic acid, (Z)-3-hexen-1-ol, 3-hydroxy-2-butanone, ethyl hexanoate, 2-ethyl-3-hydroxy-4H-pyran-4-one and unknown compound 51. Woody attribute covaried with ethyl butyrate, ethyl hydroxyacetate, ethyl pentanoate, acetic acid and benzaldehyde. W3 was in the upper left hand quadrant, covaried only with fermentation note. This attribute had a greater association with 2,3-butanedione, 2-ethyl-1-hexanol, 2-methoxy-4-methylphenol, unknown compound 47 and ethyl lactate. W4 was only associated with floral note with the highest score. Additionally, W4 covaried with two OA compounds including beta-citronellol and ethyl cinnamate. Floral attribute covaried with two OA compounds 3-methyl-1-butanol and furfural. W5 was in the lower right hand quadrant, covaried with sour note. Sour attribute was associated with ethyl butyrate, ethyl hydroxyacetate, ethyl pentanoate, acetic acid and benzaldehyde. It was observed that phenylethyl alcohol and unknown compound 46 did not covary with any sensory attribute. It showed that phenylethyl alcohol and unknown compound 46 had no significant impact on cherry wine aroma. From the above results, it was revealed that most OA compounds which had higher detection frequency, made a great contribution to cherry wine except phenylethyl alcohol and unknown compound 46. Therefore, the aroma characteristics of cherry wine could be improved by compensating some OA compounds. For instance, the fermentation aroma could be improved by adding suitable amount of 2-ethyl-1-hexanol.

4. Conclusions

Quantitative descriptive sensory analysis succeeded in identification of the aroma characteristics of 5 cherry wines using 6 sensory attributes (fruity, sour, woody, fermentation, cameral and floral). The result showed that 5 cherry wines had different aroma characteristics. OA compounds were detected by GC–O and quantified by GC–MS, and most of them were identified with more than 50% detection frequency and selected as specific compounds correlated to wines, sensory attributes. PLSR analysis clearly revealed that the most OA compounds with higher detection frequency were associated with characteristic aroma of cherry wines. In conclusion, the aroma characteristic of cherry wines could be improved by adjusting fermentation parameters or compensating these typical aroma compounds after alcoholic fermentation.

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