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ORIGINAL PAPER

Impact odorants of Chardonnay dry white wine from Changli County (China)

Hua Li · Yong-Sheng Tao · Hua Wang · Li Zhang

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Abstracts Effect of volatile compounds' contribution to the overall aroma of Chardonnay wines from Changli County was first investigated in this research. Wine aroma compounds were extracted by solid-phase micro-extraction fibers, then they were submitted to gas chromatography-mass spectrometry (GC–MS). A total of 41 volatile compounds were identified and quantified. In the volatiles detected, higher alcohols, esters and fatty acids are the main chemicals. According to their odor active values (OAVs), 13 volatile compounds were considered to be the powerful impact odorants of this wine. They are β-damascenone, isopentyl acetate, phenethyl acetate, ethyl butyrate, ethyl hexanoate, ethyl octanoate, ethyl lactate, ethyl decanoate, isopentyl alcohol, 2-phenyl-ethanol, hexanoic acid, octanoic acid and *n*-decanoic acid. Odor descriptions of the impact volatiles suggested that Chardonnay wines from Changli County was a pleasant floral and fruity odor product.

Keywords Chardonnay · White wine · Aroma compounds · GC–MS

Introduction

Changli County, a region of North China, has become a famous wine product district in China. It is one of the four districts of Wine Denomination of Origin in China. The winemaking sector is the principal economic source of this county. The main white grape variety used in the wine production is Chardonnay, a *Vitis vinifera*. L.

Wine aroma is an important aspect of wine quality. Volatile compositions influence the organoleptic characteristics of the wines, particularly the aromatic characteristics. Aroma constituents of different grapes and wines have been extensively studied in the last few years. More than 800 volatile compounds, such as alcohols, esters, organic acids, phenols, thiols, monoterpenes and norisoprenoids have been found in wines, only several tens of which can be impact odorants. Volatiles of wines can reflect the influence of variety, climate and soil, etc. So they play a decisive role in wine quality and regional character [1–3].

A total of 140 aroma compounds have been identified in Chardinnay wines, of which only tens of these volatiles are responsible for odors, whereas others might not produce noticeable odors at all [4, 5]. The contribution of volatiles to the final aroma depends on whether their concentration in the wine is above the perception threshold; so, odor activity value (OAV) was introduced to choose impact odorants [6, 7]. OAV calculation depends both on measuring concentration and on odor threshold in the same matrix. Only those odorants with OAV > 1 can be perceived.

Volatiles of Chardonnay grapes and wines have been studied using a variety of techniques. Principal component analysis (PCA) of headspace volatiles of three white varieties was used to cluster wines by grape varieties. Chardonnay wines were higher in esters [8]. Research on Californian Chardonnay wines showed that the fruity and floral terms were associated with isopentyl acetate, 2-phenylethyl acetate and linalool [9]. Dichloromethane extracts of seven Chardonnay wines from Burgundy were analyzed by GC–O, results showed 11 compounds as the

H. Li · Y.-S. Tao (✉) · H. Wang · L. Zhang
College of Enology, Northwest A& F University,
Yangling, Shaanxi Province 712100, China
e-mail: taoyongsheng@nwsuaf.edu.cn

potential contributors to the distinctiveness of the wine's aroma. In these compounds, seven were identified: vanillin, diacetyl, 4-vinylguaiacol, ethyl cinnamate, ethyl hexanoate, ethyl 2-methyl butanoate, ethyl butanoate and guaiacol [10]. Another study on potential impact odorants in Chardonnay wines with GC–O and GC–MS indicated that 10 compounds may be quite representative of the Chardonnay concept [11].

This work reports the results of the first study on volatile compounds of the Chardonnay wine from Changli County (China). The aim was to define the profile of the major volatile compounds and impact odorants in Chardonnay wines from this region.

Materials and methods

Wine samples

Changli Chardonnay wine 2004, 2005 (supplied by Huaxia Winemaking Company, Yueqiannian Winemaking Company, Changli County) was used to analyze the volatile compositions. Wine samples were collected 6 months after winemaking and then analyzed.

Winemaking: sound grapes of Chardonnay were obtained from the vineyard. Then the grapes were destemmed and crushed on a commercial grape destemmer-crusher and then pressed to get juice. The juice was treated with sulfur dioxide (45 mg/L) in stainless-steel tank and allowed to settle about 24 h. Fermentation was carried out at 18–20 °C. After fermentation, the wines were then racked and sulfur dioxide was added (75 mg/L). They were stored at 15 °C in a stainless-steel tank. Racking and stabilizing processes prior to analysis were carried out.

Reducing sugars, density, ethanol, extract, titratable acidity, pH, volatile acidity and total and free SO_2 were analyzed [12] (Table 1).

Table 1 General composition of Chardonnay must and wine

	2004	2005
Must composition		
Titratable acidity[a] (g/L)	9.3	9.7
pH	3.4	3.4
Reducing sugars (g/L)	191	195
Wine composition		
Density (20 °C)	0.994	0.993
Ethanol (%, v/v)	10.9	11.3
Reducing sugars (g/L)	1.54	0.89
Extract (g/L)	19	20
Titratable acidity[a] (g/L)	6.9	7.1
pH	3.2	3.3
Volatile acidity[b] (g/L)	0.30	0.34
Free SO_2 (mg/L)	12	15
Total SO_2 (mg/L)	115	109

[a] As tartaric acid

[b] As acetic acid

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). Water was obtained from a Milli-Q purification system (Millipore). Solvents did not require additional distillation. A total of 32 pure reference compounds were from Sigma-Aldrich (China sector). They are ethyl acetate, ethyl butyrate, 1-propanol, 2-methyl thiophene, 2-methyl-1-propanol, isopentyl acetate, 1-butanol, 2,5-dimethyl-tetrahydro-furan, isopentyl alcohol, ethyl hexanoate, ethenyl benzene, ethyl lactate, 1-hexanol, 3-octanol, ethyl octanoate, furfural, decanal, *cis*-geraniol, *β*-ionone, linalool, *β*-damascenone, ethyl decanoate, phenethyl acetate, 1-decanol, hexanoic acid, benzyl alcohol, 2-phenyl-ethanol, ethyl dodecanoate, ethyl hexadecanoate, octanoic acid, decanoic acid, *p*-ethyl-phenol.

Standard solutions

Octan-3-ol was employed as internal standard. Exact volumes of octan-3-ol was dissolved in absolute ethanol and made up to a volume of 50 mL. Exact volumes of all chemical standard compounds were dissolved in synthetic wines to calculate the emendation factor to octan-3-ol. These standard compounds dissolved in synthetic wines at typical concentration found in wines. The final alcohol content of the synthetic wine is 11% (v/v). The synthetic wine has 6 g/L of tartaric acid and its pH is 3.3–3.4, adjusted with 1 M NaOH (synthetic wine matrix). All these solutions were stored at 4 °C [1, 13].

SPME sampling conditions

SPME were carried following the method below. Both wine samples and model solutions were analyzed in 15 ml glass vials, filled with 10 ml of each sample and 2 g of NaCl added. For SPME analyses, the vials were dipped in a thermostatic water bath. A magnetic stirring bar was put in the vial and it provided the sample with agitation. The solid-phase fiber for micro-extraction was PDMS (100 μm Polydimethylsiloxane). The vial was equilibrated at 40 °C for 10 min, then powered magnetic

stirrer, the Solid-phase micro-extraction was performed at 40 °C for 30 min, and immediately followed by the desorption of the analytes into the gas chromatograph injector, the solid-phase fiber remained into the injector for about 3 min [14, 15].

GC–MS analysis

GC–MS apparatus: TRACE DSQ (Thermo-Finnigan, USA). Analytical column: DB-Wax capillary column (30 m × 0.32 mm i.d., 0.25 μm film thickness), J&W (Folsom, USA). Carrier: He at 1 ml/min. Temperature program: 40 °C for 3 min, then raised to 160 °C at 4 °C / min, then raised to 230 °C at 7 °C /min for 8 min. Transfer line temperature was 230 °C. Injection temperature was 250 °C. Mass spectra were recorded in electron impact (EI) ionization mode. Mass spectrometry: mass range was 33–450 amu, scanned at 1s intervals. Ion source temperature was 230 °C.

Qualitative analysis and quantification

Identification was achieved by comparing the mass spectra obtained from the sample with those from the pure standards injected under the same conditions and by comparing the Kováts index and the mass spectra present in the NIST2.0 MS library database or in literature.

The quantification was carried out following the internal standard quantification method. Thus, octan-3-ol was chosen as the internal standard. Quantitative data of the identified compounds were obtained by the formula:

$$\begin{aligned}\text{Analyte's concentration} &= (\text{analyte's area}/\text{octan-3-ol's area}) \\ &\times \text{emendation factor to octan-3-ol} \\ &\times \text{octan-3-ol's concentration}\end{aligned}$$

The concentration of volatile compounds for which there was no pure reference available was obtained by using the same emendation factor as one of the compounds with the most similar chemical structure [3, 6].

Results and discussion

The analytical method proposed allowed the correct identification and quantification of 41 compounds in the volatile fraction of Chardonnay wines in Changli County (Table 2). The majority were higher alcohols, esters and fatty acids. Other minor compounds identified were three terpenes, one norisoprenoids and two volatile phenols.

Esters

Acetate esters are the result of the reaction of acetyl-CoA with higher alcohols that are formed from degradation of amino acids or carbohydrates [3]. The Chardonnay wine in Changli County showed the lowest concentration of acetate esters. Five acetate esters were detected. The subtotal concentration is 5,800 μg/L, which is 2.2% of the total volatile compounds detected. Only isopentyl acetate and phenethyl acetate have an OAV above 1. Isopentyl acetate gives a fresh and banana flavor, and phenethyl acetate has a pleasant floral aroma.

Ethyl esters of fatty acids are produced enzymatically during yeast fermentation and from ethanolysis of acylCoA that are formed during fatty acids synthesis or degradation. Their concentration is dependent on several main factors: yeast strain, fermentation temperature, aeration degree and sugar content [3]. A total of 12 ethyl esters were identified and quantified. The subtotal concentration was 28,000 μg/L, 11% of the total volatiles. The esters of this group make a positive contribution to the general quality of wine. Most of them have nuances of mature fruit flavor. Ethyl butyrate (sour fruit, strawberry, fruity), ethyl hexanoate (green apple, fruity, strawberry, anise), ethyl octanoate (pineapple, pear, floral), ethyl decanoate (fruity, fatty, pleasant) and ethyl lactate (lactic, raspberry) have OAV above 1. These five ethyl esters are responsible for the "fruity" and "floral" sensory properties of wine.

Besides the ethyl esters, some other fatty acid esters of higher alcohols were also identified, which were isopentyl hexanoate, isobutyl octanoate, methyl decanoate and isopentyl octanoate. Their subtotal concentration is 90 μg/L, which accounts for 0.03% of the total. These esters that were detected may have an OAV lower than 1, and so they play a lesser role in the overall aroma profile of wine.

Higher alcohols

Those aromatic compounds, which are released to the medium as secondary products of metabolism of yeasts, are the fusel alcohols: iso-butanol, iso-pentyl alcohol, 2-phenyl-ethanol and 1-propanol. These compounds can be synthesized by the action of yeast through two mechanisms: anabolic pathway from glucos, or catabolic pathway from their corresponding amino acids (valine, leucine, iso-leucine and phenylalanine). Another compound related with the catabolic pathway is methionol [3-(methylthio)-propan-1-ol], formed from the amino acid methionine [3, 6]. It should be remembered that the composition of amino acids depends on the variety of grape and for that reason all these volatile compounds are related to the variety of grape used.

Table 2 Concentrations of volatile compounds from Chardonnay wines from Changli County (Mean of three repetitions)

NO.	KI[a]	Compounds	Emendation factor	Concentration (μg/L)	RSD[b] (%)	Odor threshold[c] (μg/L)	OAV[d]	Odor description[c]
1	885	ethyl acetate	4.671	5,000	1.8	7,500 [1]	<1	Fruity, sweet
2	1026	ethyl butyrate	7.030	680	58	20 [17]	34	Sour fruit, strawberry, fruity
3	1036	1-propanol	17.052	770	87	50,000 [2]	<1	Fresh, alcohol
4	1108	isobutyl alcohol	9.645	4,900	60	40,000 [17]	<1	Fusel, alcohol
5	1132	isopentyl acetate	0.880	60	24	30 [17]	2	Fresh, banana
6	1165	1-butanol	21.727	240	60	150,000 [17]	<1	Medicinal, alcohol
7	1230	isopentyl alcohol	53.089	150,000	75	30,000 [17]	5	Alcohol, harsh, bitter
8	1244	ethyl hexanoate	0.816	650	31	14 [17]	46	Green apple, fruity, strawberry, anise
9	1287	hexyl acetate	0.816	150	26	1,500 [17]	<1	Pleasant fruity, pear
10	1363	ethyl lactate	92.459	24,000	36	14, 000 [2]	2	Lactic, raspberry
11	1392	1-hexanol	8.109	1,200	32	8,000 [17]	<1	Green, grass
12	1446	ethyl octanoate	0.218	1,200	25	5 [17]	240	Pineapple, pear, floral
13	1450	isopentyl hexanoate	0.208	2	22	1,000 [21]	<1	Pineapple, cheese
14	1467	octyl acetate	0.218	1	24	50,000 [2]	<1	Orange floral, jasmine, pear
15	1581	ethyl nonanoate	0.208	2	28	1,300 [2]	<1	Rose, fruity
16	1599	ethyl 2-hydroxy-4-methyl pentanoate	0.816	40	21	Unknown		
17	1602	isobutyl octanoate	1.307	20	46	800*	<1	
18	1620	2,3-butanediol	72.298	1,200	2.5	120,000 [19, 2]	<1	Butter, creamy
19	1628	methyl decanoate	0.041	2	40	1,200*	<1	
20	1651	ethyl decanoate	0.041	300	6	200 [17]	2	Fruity, fatty, pleasant
21	1674	isopentyl octanoate	1.307	70	72	~1,000 [18]	<1	Sweet, light fruity, cheese, cream
22	1701	diethyl succinate	22.685	1,700	38	200,000 [17]	<1	Light fruity
23	1712	ethyl 9-decenoate	0.041	20	42	Unkown		
24	1718	terpineol	1.306	40	69	250 [17]	<1	Pleasant, sweet, anise
25	1781	1-decanol	1.063	30	38	400 [2]	<1	Orange flowery, special fatty
26	1829	phenethyl acetate	4.190	650	11	250 [17]	3	Pleasant, floral
27	1832	*β*-damascenone	1.113	2	4.5	0.05 [17]	40	Bark, canned peach, baked apple, dry plum
28	1849	ethyl laurate	0.114	90	34	>800 [2]	<1	Sweet, floral, fruity, cream
29	1863	hexanoic acid	15.388	5,300	14	420 [17]	13	Cheese, rancid
30	1927	2,6-di-ter-butul-4-methyl-phenol	0.100	3	9	~200 [19,2]	<1	Phenolic
31	1931	2-phenyl-ethanol	72.065	34,000	4	14,000 [17]	2	Flowery, pollen, perfume
32	1981	dodecan-1-ol	1.063	40	3	1,000 [2]	<1	Unpleasant in higher concentration, flowery in low concentration
33	2058	[*E*]-nerolidol	1.306	70	23	>100 [2]	<1	Floral, fruity, orange, light flavor
34	2065	ethyl tetradecanoate	0.059	1	2.5	800 [2]		
35	2083	octanoic acid	7.782	26,000	27	500 [17]	50	Rancid, harch, cheese, fatty acid
36	2274	ethyl hexadecanoate	0.059	2	105	1,500 [20, 2]	<1	Fatty, rancid, fruity, sweet
37	2296	n-decanoic acid	0.717	2,600	14	1,000 [17]	3	Fatty, unpleasant
38	2330	2,4-di-tert-butyl-phenol	0.100	60	22	~200 [19,2]	<1	Phenolic
39	2356	9-decenoic acid	0.717	40	54	Unknown		
40	2373	[*E,E*]-farnesol	1.306	6	78	>100 [2]	<1	Lemon, anise, floral, peach, honey, pollen, raspberry
41	2517	dodecanoic acid	0.369	90	80	1,000 [21]	<1	Dry, metallic, laurel oil flavor

* Calculated in the laboratory, orthonasal thresholds were calculated in a 12% ethanol/water mixture containing 5 g/L tartaric acid at pH 3.2

[a] Retention indices on a DB-Wax column

[b] RSD = (standard deviation (SD)/mean) × 100%

[c] In reference, thresholds were calculated in a 12% ehanol/water mixture, the reference from which the odor threshold and odor description have been taken is given in parentheses

[d] OAV (odor active value) = concentration/odor threshold

In our work, nine higher alcohols were identified and quantified in Changli Chardonnay wines. They are the largest group of volatile compounds. The subtotal concentration of higher alcohols is 200,000 μg/L, which makes up 74% of the total volatile compounds detected. However, only isopentyl alcohol and 2-phenyl-ethanol have OAV more than 1. Isopentyl alcohol has "alcohol, harsh, bitter" odor, which has a negtive effect on wine aroma; 2-phenyl-ethanol gave nuances of "flowery, pollen, perfume", which is flowery in character.

Fatty acids

The concentration of fatty acids detected in the wine was 30,000 μg/L. In the five acids, hexanoic acid, octanoic acid and decanoic acid have OAV more than 1, especially octanoic acid. Hexanoic acid gives a cheese character, but the other two have a bad effect on the overall wine aroma.

Minor compounds

Numerous studies have reported that the terpenoid compounds could be used analytically for varietal characterization. Terpene compounds belong to the secondary plant constituents, of which biosynthesis begins with acetyl-coenzyme A (CoA). Microorganisms are also able to synthesize terpene compounds, but the formation of terpenes by *Saccharomyces cerevisiae* has not yet been observed. Terpenes are not changed by the metabolism of yeasts during fermentation [16]. Three terpenes were detected in the sample wine. They are terpineol, [*E*]-nerolidol and [*E,E*]-farnesol. They all have OAVs lower than 1. For norisoprenoids, only β-damascenone was detected in our work. It has an OAV of 50 and gives the nuances of "bark, canned peach, baked apple and dry plum" to the wine. Only two phenols were detected, but they have low OAV and their contribution to wine aroma is little.

Conclusion

In the 41 volatile compounds detected in the Chardonnay wine from Changli County, higher alcohols, esters, and fatty acids are the main chemical groups. A total of 13 volatile compounds were considered to be the powerful impact odorants of this wine, because their OAVs were more than 1. They are β-damascenone, isopentyl acetate, phenethyl acetate, ethyl butyrate, ethyl hexanoate, ethyl octanoate, ethyl lactate, ethyl decanoate, isopentyl alcohol, 2-phenyl-ethanol, hexanoic acid, octanoic acid and *n*-decanoic acid. Seven esters and 2-phenyl-ethanol give a fruity and floral odor. β-damascenone has a flavor, which is of dry fruit in character. Isopentyl alcohol and three fatty acids contribute a negative effect to the whole wine aroma; they give a "harsh, rancid, fatty and unpleasant odor" to the wine. This is the first study on aroma compounds of Chardonnay wines from Changli County (China). From the result of this study, aroma recombination or omission experiment could be designed to find the more exact aroma contribution of detected odorants.

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