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Full Length Research Paper

Geographical differentiation of China's young 'Cabernet Sauvignon' Wines based on volatile compounds

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Volatile compounds of thirty Cabernet Sauvignon wines from different vineyards of China's five regions were analyzed and a total of 67 volatile components were quantified. The terpene types and the higher-alcohol concentrations presented significant difference between regions. Hierarchical cluster analysis (HCA) shows that wines from different vineyards of the same region can be well clustered together; Principal component analysis (PCA) can well separate wines from different regions; Stepwise linear discriminant analysis (SLDA) allows nine volatile compounds including 2-ethyl-1-hexanol, 4-methyl-3-ethyl-pentanol, 1-octanol, ethyl hexanoate, ethyl octanoate, ethyl dl-2-hydroxycaproate, linalool, geranyl acetone and nonanal, to get wine samples classified with 100% accuracy according to their provenances.

Keywords: geographical differentiation; volatile compounds; Cabernet Sauvignon wines

INTRODUCTION

The quality of wines mainly depends on three factors: the varieties of grape with the genetic potential, defined by the varietal and clonal origin of the grapevine; the climate and the soil affecting the quality of grape berries; human intervention such as vineyard management, wine-making techniques and aging methods. In particular, the *terroir* (climate-soil) is one of the key factors which influence exclusively and decisively the character, quality and typical attributes of a wine (Vilanova and Soto, 2005). Even the same varieties and the same brewing processes in different regions also will produce wine of different styles, which is considered as a regional typicality of wine. As this special geographical origin of a wine is a label for a particular taste and certain quality or reputation, it is used by producers as a good marketing tool to generate and consolidate markets, and meanwhile it is often made particularly valued by consumers. Thus, it is essential to develop an effective method to distinguish the geographical origin of a wine.

In recent years, the geographical differentiation of a wine has been researched using different analytical parameters and multivariate analysis techniques, such as sensory analysis (Vilanova and Soto, 2005; Vilanova and Vilariño, 2006), mineral elements (Capron et al., 2007; Iglesias et al., 2007), polyphenolic compounds (Kallithraka et al., 2007), organic acids (Sass-Kiss et al., 2008) and amino acids (Etiévant et al., 1988; Soufleros et al., 2003). The sensory analysis needs a panel and it cannot provide sufficient information to separate wines from various areas of France and USA (Frank and Kowalski, 1984), and the mineral elements of wines may be contaminated by fertilization, pesticides, machinery pipes, additives, etc. (Eschnauer, 1982). Therefore, soil chemistry pollution and wine manufacturing practices may as well affect the mineral finger print of a wine (Kment et al.,2005). Other methods can provide valuable information but they are time-consuming and labor-intensive.

Aroma is one of the most important factors determining wine character and quality. The varietal flavor of wines is

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mainly composed of monoterpenes, norisoprenoids and thiols, while the volatiles derived from yeast metabolism are alcohols and esters (Swiegers et al., 2005). Volatile compounds have been considered as the first choice because they are closely related to wine sensory characteristics, and besides, they are influenced by numerous factors, including grape variety, microorganism metabolism and environmental factors such as soil (Sabon et al., 2002), light environment (Bureau et al., 2000), and water status (Koundouras et al., 2006).

Several studies have been done to differentiate and classify monovarietal wines according to their geographic origins using volatile compound as variables.

Through investigating 40 wines of *Vitis vinifera* cv. Pinot Noir from France and the United States, 1–hexanol, cyclohexane, *p*–hydroyxbenzaldehyde and 2–phenylethanol were found to be the major components for classification (Kwan and Kowalski, 1980).

Vilanova *et al.* (2007) analyzed the volatiles of *Vitis vinifera* cv Albariño from northern and southern parts of Galicia, and found that β–pineno, free linalool, free nerol, free β-ionona, bound terpinen-4-ol, acetal and 2-phenylethanol could be used for the separation between the Albariño wines. The geographic origin of wines from three subregions of Rías Baixas could be defined according to terpenes, ethyl esters and C_{13}–norisoprenoids (Zamúz and Vilanova, 2006).

Nineteen wines of the Grenache Noir cultivar obtained from representative soils of Rhone Valley could also be differentiated according to their producing regions on the basis of β–damascenone, β–ionone, geraniol, hexenols and methanol (Sabon et al., 2002).

In a word, these results all indicate that volatile components can be used as regional wine indicators. There exists a great deal of difference in ecological conditions across the wine-making regions of China. Unlike other countries in the world, where wine producing regions are centralized, the wine-making regions of China are widely scattered, of which the longest distance of over 2,000 kilometers can be found either from east to west or from south to north. Besides, each wine-making region is unique in its ecological conditions. The ecological diversity bestows China on the capability of producing various wines with different styles and flavors. In recent years, the wine industry is growing fast and the wine market has a wider space to develop in China, and it will be still more prosperous in the future. The Cabernet Sauvignon belongs to the red grape variety of *Vitis vinifera* widely grown in China. During the last few years, intensive studies have been done on the volatile compounds of the Cabernet Sauvignon wines produced in China, which focused on the sensory characters (Tao et al., 2009a) or volatile compounds (Tao et al., 2009b) of Cabernet Sauvignon wines in a certain region, or the comparative study of aromatic compounds between wines of Cabernet Sauvignon and other varieties (Zhang et al., 2007), as well as the comparative study of volatile compounds of Cabernet Sauvignon wines from different regions of China using the data visualization by computer (Tao et al., 2008). However, there have been, to date, no published research reports on the geographical differentiation of wines with detailed volatile information in China.

In this study, the volatile components of thirty Cabernet Sauvignon wines from five geographic areas of China were analyzed, to determinate the influence of *terroir* on wine volatiles. One way–ANOVA (analysis of variance) and multivariate analysis of cluster and principle component analysis (PCA) were used for these comparisons.

The present paper will help to understand better the volatile properties of wines from China's main production regions.

MATERIALS AND METHODS

Wine Samples

Five grape-producing regions with distinct *terroir* characters were selected for collecting wine samples, which include Helanshan (HLS), Shacheng (SC), Yantai (YT), Changli (CL) and Chateau Huaxia (CH). Helanshan region is located in northwestern China and has a cool and semi-arid climate with a big temperature difference between daytime and night time, the accumulated temperature being 3289°C from April to September, with abundant sunshine and an annual rainfall of 150–200 mm. The vineyards there include gravel-type soils. Shacheng region has a cool-warm and semi-arid climate with a big temperature difference between daytime and night time, the annual accumulated temperature being 3532°C, with adequate sunshine and an annual rainfall of about 400 mm. The soils of this region are composed of cinnamon with partial sands. Yantai region shows a warm, semi-humid climate with a slight temperature difference between daytime and night time, the accumulated temperature being 3800–4200°C, with an annual rainfall of 750–800mm and appropriate sunshine. The Yantai vineyards are mainly composed of sandy soils.

Both Chateau Huaxia and Changli regions are located in Hebei Province China, and have a . cool-warm, semi-humid continental climate with an annual effective temperature of 3940°C, an annual rainfall of about 700

mm, and an annual sunshine time of 2600–2800 hours. These two regions were under our study because their terrain and soil condition show a considerable difference, and the soil of Chateau Huaxia region is mainly characterized by gravel on the base and the sands on the surface, while the soil in Changli region mainly comprises clay and sand.

Thirty Cabernet Sauvignon monovarietal wines were made in the year of 2007, and all wines were guaranteed to be made of 100% of grapes from specified regions.

To minimize the possibility of aromatic difference between wines from different regions that might be caused by Cabernet Sauvignon clones, vineyard artificial practice and enological means, these samples were produced from grapes with different clones or vineyards in the same region but from different manufacturers. All the wines were made through the manufacture techniques of red wine made from Cabernet Sauvignon in China.

At the end of fermentation (including alcohol and malolactic fermentations), some conventional parameters were assessed, including alcohol degree, residual sugar, total acids, volatile acids, free SO_2, total SO_2 and dry extracts.

After wines were verified to have reached the national standard, each sample of about 500 mL was collected and used for analysis of volatile components.

Solid Phase Microextraction

Volatile compounds of the wine samples were extracted by headspace-solid phase microextraction (HS-SPME) as described by Zhang *et al.* (2007).

5 mL of wine sample and 1 g NaCl were placed in a 15-mL sample vial. The vial was tightly capped with a PTFE-silicon septum and heated at 40°C for 30 min on a heating platform agitation at 400 rpm. Then the SPME (50/30-µm DVB/Carboxen/PDMS, Supelco, Bellefonte, Pa., U.S.A.) was inserted into the headspace, where extraction lasted for 30 min with heating and agitation by a magnetic stirrer. For each wine sample, three independent extractions were performed to minimize the deviation of this procedure.

Gas Chromatography-Mass Spectrometry (GC-MS) Analysis

The GC–MS system used was an Agilent 6890 GC equipped with an Agilent 5975 mass spectrometry. The column used was a 60 m×0.25 mm HP–INNOWAX capillary with 0.25µm film thickness (J &W Scientific, Folsom, Calif., U.S.A.). The carrier gas was helium with a flow rate of 1 mL/min. Samples were injected by placing the SPME fiber at the GC inlet for 25 min with the splitless mode. The chromatographic program was set at 50°C (maintained for 1 min), raised to 220°C at 3°/min and maintained for 5 min. The mass spectrometry in the electron impact mode (MS/EI) at 70eV was recorded in the range m/z 20 to 450U. The mass spectrophotometer was operated in the selective ion mode under autotune conditions and the area of each peak was determined by Chem Station software (Agilent Technologies). Standards include isoamyl acetate, ethyl hexanoate, hexyl acetate, 1-hexanol, (*E*)-3-hexen-1-ol, (*Z*)-3-hexen-1-ol, (*E*)-2-hexen-1-ol, (*Z*)-2-hexen-1-ol, methyl octanoate, linalool, 1-octanol, 2,3-butandiol, ethyl decanoate, diethyl succinate, 3-(methylthio)-1-propanol, 1-decanol, phenylethyl acetate, hexanoic acid, benzyl alcohol, 2-phenylethanol and octanoic acid . Standard volatile compounds were extracted using the same SPME fiber and GC conditions as the wine samples.

All standards were purchased from Aldrich (Milwaukee, Wis., USA) and Fluka (Buchs, Switzerland), and their purity was above 99%. Volatile compounds in wine sample were identified by comparing retention times with their corresponding standards, and other compounds that have not corresponding standards were tentatively identified by comparing the mass spectral data with the NIST 05 library. For quantification, model solutions were prepared using the methods reported by Howard *et al.* (2005). Five-point calibration curves for each compound were prepared using the method described by Ferreira *et al.* (2000), which was also used as a reference to determine the concentration range of standard solutions. The regression coefficients of calibration curves were above 96%. The standard deviation for the SPME method was below 10%. Duplicate analysis was done for each sample following the extraction and analytic procedures mentioned above.

Statistical Analysis

PASW Statistics 18.0 for Windows was used for all statistical analysis. Significant differences between wines for each of the compounds were determined by Analysis of variance (ANOVA). For each volatile compound, a total of five to six data were applied for ANOVA. Hierarchical cluster analysis was calculated as classificatory procedure, based on a similarity matrix constructed using Euclidean distance. Hierarchical cluster analysis (HCA), Principal component analysis (PCA) and Stepwise linear discriminant analysis (SLDA) were respectively performed

Table 1. Range of concentration of volatile compounds in Cabernet Sauvignon wines from China's five wine-growing regions (μg/L)[a].

Compound	Shacheng	Huaxia Chateau	Changli	Yantai	Helanshan
1-Propanol	14.30-57.20 a	11.60-59.20 a	10.90-81.40 a	35.3078.80 a	17.20-36.10 a
2-Methyl-1-propanol*	1.66-3.08 c	0.18-7.00 a	0.13-0.66 a	0.87-1.62 b	0.38-0.78 a
3-Methyl-butanol*	12.97-19.46 b	11.59-21.23 b	10.45-17.36 b	13.60-26.06 b	5.60-7.80 a
1-Butanol	34.10-42.00 a	44.90-173.50 a	44.90-173.50 a	44.30-111.70 a	25.70-36.40 a
1-Pentanol	0.00-11.40 a	7.10-14.90 a	1.80-10.40 a	7.00-14.60 a	3.60-9.00 a
3-Methyl-3-buten-1-ol	0.00-31.30 a	0.00-29.20 a	0.00-36.00 a	0.00-31.60 a	nq
4-Methyl-pentanol	28.30-32.30 a	39.80-51.10 c	35.50-58.10 bc	31.50-40.00 abc	31.00-33.50 ab
3-Methyl-pentanol	20.20-29.80 a	34.80-64.90 b	21.50-41.40 a	18.80-46.80 a	11.20-15.60 a
1-Hexanol	423.60-906.30 b	89.60-433.90 a	219.80-643.10 ab	104.70-435.00 a	104.20-313.10 a
E-3-hexen-1-ol	17.70-23.70 a	0.00-9.80 c	0.00-17.80 ab	8.00-16.80 abc	7.30-20.80 bc
Z-3-hexen-1-ol	15.60-24.80 a	0.00-29.60 a	3.70-15.80 a	15.50-21.20 a	8.50-13.90 a
E-2-hexen-1-ol	Nq	8.30-26.70 b	0.00-7.70 a	nq	0.00-6.20 a
1-Octen-3-ol	0.00-11.80 a	4.50-16.50 a	5.70-13.70 a	7.80-12.10 a	0.00-7.50 a
Heptanol	90.70-147.70 c	86.40-137.20 c	33.90-48.40 ab	51.10-75.00 b	33.20-38.40 a
2-Ethyl-1-hexanol	Nq	0.00-1.10 a	2.30-15.40 b c	nq	0.00-1.30 a
4-Methyl-3-ethyl-pentanol	2.80-3.60 ab	0.00-2.60 a	3.20-8.00 c	3.10-5.10 bc	3.70-5.80 bc
1-Octanol	3.50-7.00 a	10.10-32.40 b	6.80-19.20 a	8.70-9.50 a	8.40-10.10 a
2,3-Butanediol	0.92-1.09 c	0.82-0.96 a	0.77-0.97 a	0.87-0.96 ab	1.01-1.03 c
1-Nonanol	1.00-3.30 a	0.00-5.60 a	0.00-4.20 a	1.00-4.50 a	0.00-5.80 a
1-Decanol	0.00-1.70 a	1.90-3.20 c	1.70-3.20 bc	0.00-1.80 ab	2.00-2.30 bc
2-Phenyl-alcohol*	19.44-23.43 bc	16.95-35.33 c	9.43-16.87 ab	10.44-29.69 bc	4.97-6.83 a
Ethyl acetate*	0.89-1.01 a	0.98-1.49 a	0.83-1.94 a	0.92-1.86 a	0.82-2.38 a
2-Methylproply acetate	187.77-219.59 b	114.39-155.76 a	110.77-184.40 a	110.03-142.52 a	108.59-126.68 a
3-Methylbutyl acetate*	0.68-1.08 a	0.31-1.52 a	0.13-2.83 a	0.24-0.65 a	0.00-0.71 a
Hexyl acetate	119.21-131.56 a	2.54-108.30 a	9.47-537.25 a	18.63-42.94 a	0.00-160.88 a
Phenylethyl acetate	16.61-20.41 a	12.90-26.40 a	12.31-40.29 a	13.43-26.54 a	0.00-13.14 a
Octyl acetate	Nq	0.00-89.91 a	0.00-92.09 a	nq	nq
Ethyl butanoate	5.87-10.13 a	7.84-13.23 ab	4.48-15.28 a	4.62-8.47 a	11.63-20.38 c
Ethyl hexanoate	0.66-0.75 c	0.46-1.01 ab	0.29-0.81 ab	0.22-0.44 a	0.20-0.65 ab
Ethyl heptanoate	0.00-7.95 ab	0.00-11.47 ab	0.00-3.45 a	0.00-28.00 b	0.00-5.44 ab
Ethyl 2-hexenoate	0.00-123.88 a	91.36-101.43 b	91.79-111.74 b	93.41-106.26 b	0.00-99.25 ab
Ethyl lactate	347.27-562.34 c	nq	0.00-21.77 a	313.63-347.18 c	4.36-315.33 b
Ethyl octanoate*	1.18-1.30 ab	1.54-2.75 b	0.68-2.50 ab	0.84-1.24 a	0.88-2.33 ab
Ethyl dl-2-hydroxycaproate	95.44-102.58 bc	Nq	nq	96.05-113.37 a	0.00-101.07 b
Ethyl decanoate	0.21-0.26 a	0.29-0.57 a	0.21-1.05 a	0.24-0.30 a	0.27-0.42 a
Diethyl succinate	224.04-258.77 ab	222.23-284.06 ab	168.37-227.10 a	271.27-387.74 b	174.11-502.31 ab
Ethyl 9-decenoate	109.70-141.97 b	109.45-146.26 b	0.00-120.51 a	nq	nq
Ethyl phenylacetate	Nq	0.00-10.80 ab	nq	0.00-11.95 b	nq
Ethyl dodecanoate	91.63-92.42 a	91.40-108.91 a	0.00-162.96 a	94.04-103.07 a	92.25-99.92 a
Methyl hexanoate	34.18-47.44 b	33.39-42.97 b	28.59-35.84 b	0.00-31.61 a	nq
Methyl octanoate	0.00-0.99 a	6.83-27.75 b	0.00-12.77 ab	0.00-0.62 a	2.31-9.65 ab
Isopentyl hexanoate	104.00-107.76 a	0.00-101.93 a	0.00-103.58 a	91.50-94.31 a	0.00-96.07 a

Table 1 Continue

Isoamyl lactate	95.44-102.58 ab	Nq	nq	96.05-113.37 b	0.00-101.07 a
Butyrolactone	0.94-0.98 a	0.79-3.10 a	0.00-1.19 a	0.00-1.43 a	0.00-0.86 a
3-Methylbutyl octanoate	Nq	0.00-95.87 a	0.00-66.06 a	0.00-90.60 a	0.00-103.37 a
Linalool	nq	6.69-7.74 b	6.86-8.64 b	nq	0.00-7.12 a
4-Terpinenol	nq	Nq	0.00-14.66 a	0.00-14.46 b	nq
Citronellol	14.14-14.73 a	14.15-15.66 a	0.00-14.52 a	0.00-14.48 a	0.00-14.30 a
Geraniol	nq	0.00-14.67	nq	nq	nq
Geranyl acetone	nq	Nq	nq	nq	14.70-16.76
Acetic acid*	2.98-3.27 bc	2.17-2.99 a	2.15-3.66 ab	2.97-3.61 c	2.25-3.38 abc
Hexanoic acid*	2.17-2.28 a	2.09-2.36 a	2.03-2.26 a	2.05-2.16 a	2.06-2.12 a
Octanoic acid*	6.18-6.23 a	6.18-6.59 a	6.11-6.40 a	6.14-6.23 a	6.17-6.18 a
Decanoic acid	nq	0.00-6.13 a	0.00-6.13 a	nq	nq
3-Hydroxy-2-butanone	11.15-35.07 b	Nq	0.00-2.79 a	0.00-47.03 b	0.00-1.59 a
β-damascenone	7.01-7.87 a	0.00-6.50 a	0.00-8.44 a	7.05-7.32 a	7.16-7.54 a
Nonanal	nq	Nq	nq	nq	0.00-6.84 b
Benzaldehyde*	0.89-0.92 ab	0.00-0.88 a	0.00-0.96 a	1.33-3.49 c	1.29-1.97 bc
3-(methylthio)-1-propanol	18.52-19.08 c	15.59-20.12 bc	15.02-17.35 ab	14.97-19.69bc	14.08-14.28 a
N-(3-methylbuty)acetamide	nq	Nq	1.69-2.51a	0.00-3.06 a	nq

[a] Values (range of concentration) of the same compounds followed by different letters are significantly different ($P < 0.05$). * Values at concentration of 1mg/L. nq: Not quantified.

to find homogeneous clusters of wine sample based on volatile compounds, to illustrate the differentiation between regional wines and to select discriminant variables.

A general approach to cluster analysis is hierarchical cluster analysis (HCA), the purpose of which is to group together objects or records that are 'close' to one another. The cluster method of complete linkage and the distance measured by the Euclidean squared distance were used. The dendrogram is a tree-like plot where each step of hierarchical clustering is represented as a fusion of two branches of the tree into a single one. The branches represent clusters obtained from each step of hierarchical clustering.

RESULTS AND DISCUSSION

Comparison Of Volatile Compounds between Regional Wines

A total of 67 volatile compounds were detected in all the wines analyzed. ANOVA analysis showed that 43 volatiles presented significant difference among the regional wines, including 14 higher alcohols, 15 esters, 5 terpenes, 3 acids, 4 carbonyl compounds, 3-(methylthio)-1-propanol and N-(3-methylbutyl) acetamide (Table1).

Among the volatile compounds, 23 higher-alcohols were found in the Cabernet Sauvignon wines analyzed, of which 21 higher-alcohols concentration ranges in the wines from five regions were shown in Table 1, whereas 3-ethoxy-1-propanol and benzyl alcohol were not presented due to their trace levels. Among the components, both (*E*)-2-hexen-1-ol and 2-ethyl-hexanol were found in all wines from a given region: (*E*)-2-hexen-1-ol in all CH-originated wines and 2-ethyl-hexanol in all CL-originated wines, but in other regions, they were detected in only a few wines. 3-Methyl-3-buten-1-ol was found only in a small number of samples from SC, CH, CL and YT. Besides, wines from SC were characterized by their relatively high concentrations of 2-methyl-1-propanol and 1-heptanol. The CH wines also had relatively high concentrations of 1-octanol and 3-methyl-1-pentanol. The HLS wines were characterized by the relatively low concentration of 3-methyl-butanol.

The higher-alcohols can be divided into three groups: C_6 alcohols, aliphatic alcohols and aromatic alcohols. In general, the higher-alcohols in wines generate mainly from yeast metabolism. But some research findings show that the C_6 alcohols (1-hexanol, (*E*)-3-hexen-1-ol, (*Z*)-3-hexen-1-ol, and (*E*)-2-hexen-1-ol) are from the

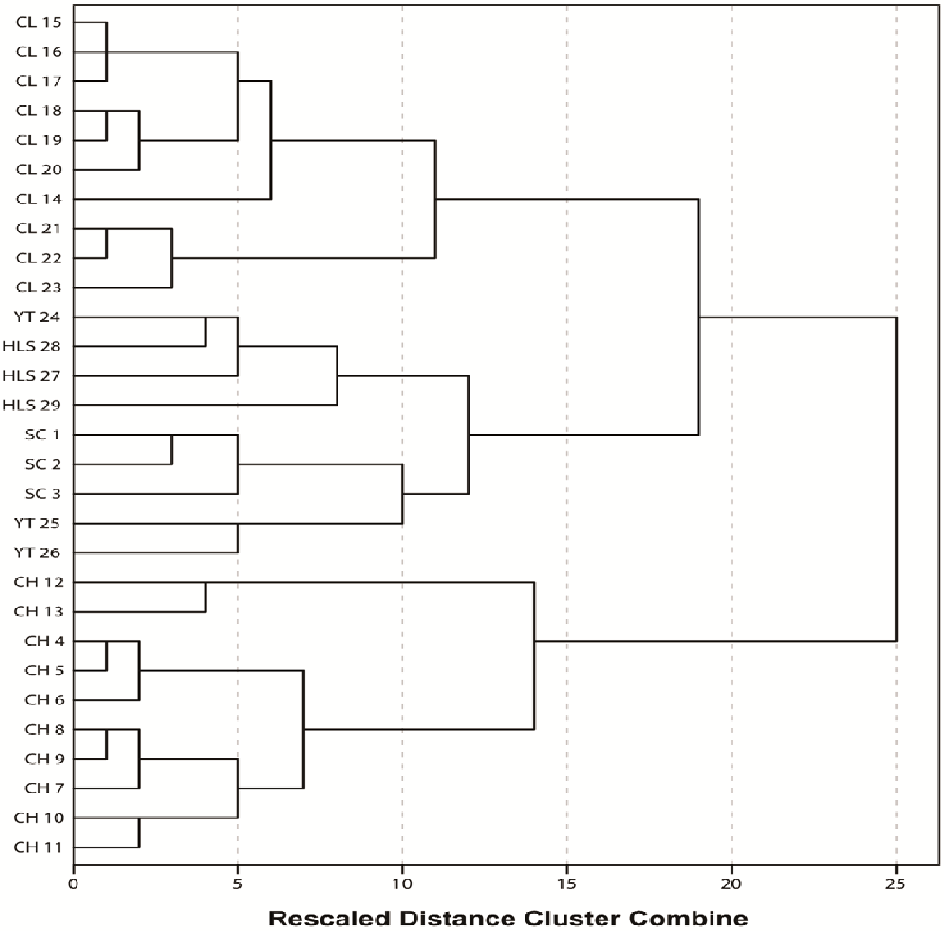

Figure 1. Dendrogram built with all variables using complete linkage and Euclidean squared distance of hierarchical cluster analysis of wine samples, using 60 variables shown in Table 1. CL: Changli; HLS: Helanshan; SC: Shacheng; YT: Yantai; CH: Huaxia Chateau

enzymatic oxidation of linoletic and linolenic acids that occurs during grape pressing before fermentation. And the aliphatic alcohols and aromatic alcohols, such as 3-methyl-butanol, 2-methyl-propanol and 2-phenylethanol, are originated from leucine, isoleucine, valine and phenylalanine via oxidative deamination, and the 1-butanol and 1-pentanol, from a keto acid that takes part in cell glucidic metabolism (Mauricio et al., 1997). That is, some aliphatic alcohols and aromatic alcohols are derived from amino acids in grapes used for winemaking, and thus the concentrations of these compounds may be more influenced by the ecological condition of their geographic origins. It has been reported that when the higher-alcohols of Albarinõ wines from different sub-regions of Certified Brand of Origin “Rías Baixas” were selected to perform PCA, and the wine samples clustered in accordance with their geographic origin (Falqué et al., 2008).

A total of 28 esters were found in the Cabernet Sauvignon wines, among which ethyl 4-octenoate, ethyl nonanoate, methyl salicylate and methyl decanoate were not shown because of their extremely trace level. As can be seen from Table 1, Methyl hexanoate was not detected in HLS wines, but detected in wine samples from other origins.

Ethyl dl-2-hydroxycaproate was absent only in CH and CL wines. Ethyl 9-decenoate was detected in CH, CL and SC wines. In all wines analyzed, SC wines contained the highest concentration of 2-methylpropyl acetate; CH wines showed the highest concentration of methyl octanoate and HLS wines had the highest concentration of ethyl butanoate. CH wines contained higher ethyl octanoate concentration than CL and YT wines. These indicated that there existed certain differences in some

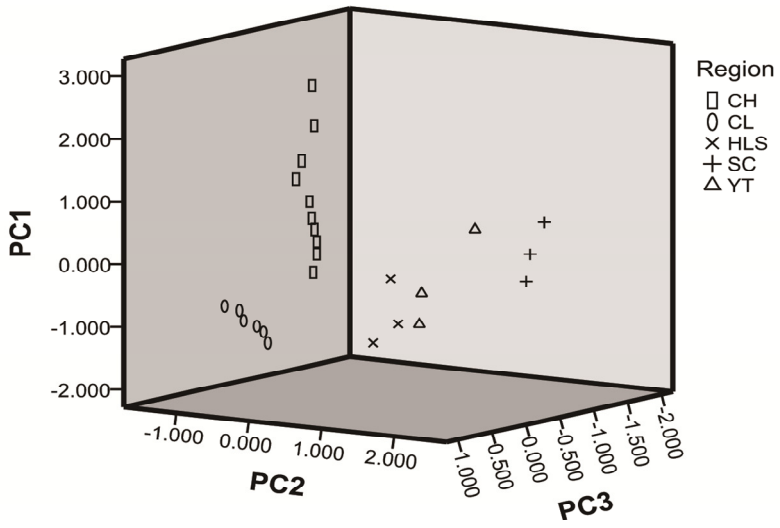

Figure 2. Score plot of the first three principal components for classification of Cabernet Sauvignon wines originated from different geographic areas. CH: Huaxia Chateau; CL: Changli; HLS: Helanshan; SC: Shacheng; YT: Yantai;

ester components between the regional wines.

Esters were derived mainly from yeast fermentation and it has been reported that esters have a significant effect on the fruity flavors in wine (Swiegers et al., 2005). Few reports showed that esters were used for classification of regional monovarietal wines.

A total of five terpenes were found in the analyzed wines, which were linalool, 4-terpinenol, citronellol, geraniol and geranyl acetone. As shown in Table 1, some compounds had significantly regional dependence. For example, linalool was found in CH and CL wines, but not in SC and YT wines; 4-terpinenol was observed in CL and YT wines, but not in the other regional wines. Geraniol was detected only in CH wines, and geraniol acetone only in HLS wines. So, it is suggested that the kinds of terpenes might be influenced by the factor of origin. This did not consist with previous studies that showed that *terroir* influenced the concentrations rather than the types of terpene compounds (Sabon et al., 2002; Sabon et al., 2002; Cabrita et al, 2007). Such inconsistence may be due to the fact that the wines in their studies came from sub-regions of the same region where there appeared to be similar climate and soil conditions, but in our study, the Cabernet Sauvignon wines were selected from representative regions of China where climate and soil conditions differ considerably. Vilanova *et al.* (2007) also observed that some terpenes existed only in the south or only in the north of Galicia, and the north is cold and have alluvial top soils while the south is hot and slate comes to the surface. The grapes may respond to the different climate and soil conditions of the geographic origins and showed the different kinds of some terpenes in wines detected ultimately.

A total of four volatile acids were detected in the Cabernet Sauvignon wines from the five regions. These volatile acids were acetic acid, hexanoic acid, octanoic acid and decanoic acid (Table 1). Volatile acid profiling showed regional difference. Decanoic acid was found only in individual wine samples from CH and CL regions, but acetic acid, hexanoic acid and decanoic acid in all the wine samples. The YT and SC wines contained higher level of acetic acid than the CH and CL samples. The CH wines showed higher octanoic acid than the CL wines. The CH and SC wines had higher hexanoic acid concentration than the CL wines.

A total of five carbonyl compounds were found in the Cabernet Sauvignon wines analyzed. The five carbonyl compounds were 3-hydroxy-2-butanone, β-damascenone, nonanal, furfural and benzaldehyde (Table 1). 3-Hydroxy-2-butanone was detected in the SC, CL, YT and HLS wines, but its concentration showed great difference between these regional wines. The YT and HLS wines presented significantly higher concentration of benzaldehyde than the CH and CL wines. The CH wines contained lower concentration of β-damascenone than the wines from the other four regions.

These results indicated that a certain difference also existed in carbonyl compounds of Cabernet Sauvignon

wines from different regions.

Only one sulfur compound, 3-(methylthio)-1-propanol showing significant difference between regions, was detected in all the wine samples (Table 1). The nitrogen compound N-(3-methylbutyl) acetamide was found only in all the CL wines and a small part of YT wines (Table 1).In the other regional wines, this compound was undetectable.

Statistical Analysis

Hierarchical cluster analysis (HCA) was applied to find homogeneous clusters of wine samples from five regions of China. Samples were clustered into different groups at different distance as the volatile profiles in wines varied from one sample to another.

As can be seen from Figure 1, the wine samples from the same region were clustered well together, indicating that the volatiles have significant regional characteristics, that is, these regional wines possess their own unique volatile constitutes.

Principle component analysis (PCA) was used for wine classification in terms of volatile compounds, with the 60 variables shown in Table 1 subjected to the analysis. As can be seen from Figure 2, wine samples can be well separated according to their provenances by the first three principal components accounting for 67% of the total variance. Among the three principal components, the first one was well associated with 1-pentanol, 3-methyl-pentanol, 1-octanol, 2-phenyl-alcohol, 3-methylbutyl acetate, ethyl hexanoate, ethyl octanoate, ethyl decanoate, methyl octanoate, butyrolactone, hexanoic acid and octanoic acid, the second one with *E*-3-hexen-1-ol, ethyl lactate, ethyl dl-2-hydroxycaproate, isamyl lactate, acetic acid and benzaldehyde, and the third one with *E*-3-hexen-1-ol, ethyl lactate, ethyl dl-2-hydroxycaproate, isamyl lactate, acetic acid and benzaldehyde.

Stepwise linear discriminant analysis (SLDA) was employed to select reliable variables that can differentiate wines from different regions.

The result allowed nine volatile compounds to get wine samples classified with 100% accuracy according to their provenances.

These compounds were 2-ethyl-1-hexanol, 4-methyl-3-ethyl-pentanol, 1-octanol, ethyl hexanoate, ethyl octanoate, ethyl dl-2-hydroxycaproate, linalool, geranyl acetone and nonanal, of which three were higher alcohols, three were esters, two were terpenes, and one was carbonyl compounds.

The analysis above indicates that volatile compounds can be considered as reliable descriptors for discriminating wines of different provenances

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