Evolutions of volatile sulfur compounds of Cabernet Sauvignon wines during aging in different oak barrels

Dong-Qing Ye a,b, Xiao-Tian Zheng b, Xiao-Qing Xu b, Yun-He Wang b, Chang-Qing Duan b, Yan-Lin Liu a,*

a College of Enology, Northwest A&F University, Yangling, Shaanxi 712100, China
b Centre for Viticulture and Enology, College of Food Science and Nutritional Engineering, China Agricultural University, Beijing 100083, China

Article info
Article history:
Received 29 October 2015
Received in revised form 28 January 2016
Accepted 29 January 2016
Available online 4 February 2016

Keywords:
Volatile sulfur compounds
Oak barrel aging
Wine
HS-SPME/GC-FPD

Abstract
The evolution of volatile sulfur compounds (VSCs) in Cabernet Sauvignon wines from seven regions of China during maturation in oak barrels was investigated. The barrels were made of different wood grains (fine and medium) and toasting levels (light and medium). Twelve VSCs were quantified by GC/FPD, with dimethyl sulfide (DMS) and methionol exceeding their sensory thresholds. Most VSCs tended to decline during the aging, while DMS was found to increase. After one year aging, the levels of DMS, 2-methyltetrahydrothiophen-3-one and sulfur-containing esters were lower in the wines aged in oak barrels than in stainless steel tanks. The wood grain and toasting level of oak barrels significantly influenced the concentration of S-methyl thioacetate and 2-methyltetrahydrothiophen-3-one. This study reported the evolution of VSCs in wines during oak barrel aging for the first time and evaluated the influence of barrel types, which would provide wine-makers with references in making proposals about wine aging.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Volatile sulfur compounds (VSCs) have a strong impact on wine aroma and mostly responsible for possible “reduced” flavor resembling rotten eggs, cooked cabbage, onion, garlic and rubber (Moreno-Arribas, Polo, & Polo, 2009, Chap. 8). It is usually caused by the presence of excessive concentrations of short-chain thiols, sulfides, disulfide, thioesters and heterocyclic compound (Mestres, Busto, & Guasch, 2000). However, it may have possible positive contributions to wine quality when some VSCs presented at relatively low concentrations. For example, Segurel, Razungles, Riou, Salles, and Baumes (2004) reported that dimethyl sulfide (DMS) levels near 100 μg/L enhanced the fruity notes of Grenache Noir and Syrah wines. There is an ongoing endeavor to establish the relationship between the chemistry and sensory contributions of VSCs to wine aroma. The relationship was report to be influenced by the complex interactions between various wine constituents (McGorrin, 2011). Recently, Coetzee et al. (2015) demonstrated that methional can suppress pleasant aroma attributes linked to volatile thiols, while contributing negative attributes especially in the presence of 3-isobutyl-2-methoxypyrazine in Sauvignon Blanc wine. Lytra, Tempere, Marchand, de Revel, and Barbe (2015) used dynamic analytical and sensory methods to reveal the variations of wine’s fruit notes contributed by DMS and esters during wine tasting and highlighted significant differences for red-berry and fresh fruit after 5 min, black berry and jammy fruit after 15 min.

Sulfur compounds can be generated through the biological or chemical processes, that is, the enzymatic pathway in microorganisms metabolism during wine fermentation involves sulfates, sulfites and sulfur containing amino acids (Landaud, Helinck, & Bonnarme, 2008), or non-enzymatic mechanisms as photochemical and thermal reaction occurring in winemaking and storage (Robinson et al., 2013). Therefore it is not surprising that VSCs are found at various stages of wine production and storage (Fedrizzi, Magno, Finato, & Versini, 2010; Kinzurik, Herbst-Johnstone, Gardner, & Fedrizzi, 2015; Landaud et al., 2008; Moreira et al., 2002; Robinson et al., 2013). However, apart from the production of H2S in yeast, few of the chemical and/or metabolic pathways for the formation of other VSCs have been reported or verified during winemaking (Moreno-Arribas et al., 2009).

The effects of wine aging conditions on the evolution of VSCs have previously been investigated. McCord (2003) demonstrated that Cabernet Sauvignon wines aged in the stainless steel tanks with micro-oxygenation had a significantly lower level of free mercaptans. Meanwhile there was no increase of DMS concentration with the addition of oxygen and significant decrease in all treatments with adding toasted oak products. Nguyen, Nicolau, Dykes,
and Kilmartin (2010) reported similar results that DMS and thiocysters were not affected by oxygen while other compounds were changed. The work of Ferreira, Rodrigues, Hogg, and De Pinho (2003) also found that old port wine (barrel aged) contained fewer VSCs than young port wines due to the decrease of thioalcohols during the aging. Although those studies had discussed the various factors to the respective aging, oxygen in particular, which greatly influence the profile of VSCs during aging. However it is still not well documented that the VSCs variation in such a complex wine matrix. Nevertheless, the information is practically significant to understand the contribution of VSCs on wine quality during different vinification processes.

Maturation of the wine in oak barrel is commonly in the red wine making and a complex process accompanied by the development of color, aroma and flavor (Moreno-Arribas et al., 2009; Ribéreau-Gayon, Glories, Maujean, & Dubourdieu, 2006). In the aspect of volatile composition, the wines aged in oak barrel can acquire a complex aroma by extracting some substances such as oak lactone and phenolic aldehydes from oak wood. Meanwhile the oxygen permeation of natural barrel can modify the intrinsic wine volatile compounds and those extracted from wood (Garder-Cerdan & Ancin-Azpilicueta, 2006; Jackson, 2008; Ortega-Heras, Gonzalez-Sanjose, & Gonzalez-Huerta, 2007). Although the low oxidation conditions of oak barrel was reported to accelerate the wine oxidation and eliminate VSCs (Jackson, 2008, Chap. 6 and 8), there are few quantitative studies regarding the evolution of VSCs in wines during oak barrel aging. It’s well known that wine is a complex mixture of several hundred compounds present at different concentrations (Jackson, 2008). The wine-production regions in China are scattered and have different ecological conditions to enable the winemakers to produce various types of wines with different styles and flavors. In this study, the wine samples from seven regions of China in two consecutive years maturated in four types of oak barrels was investigated to evaluate a wide range of VSCs in those wines. It is the first time to provide the information of their profiles affected by the oak barrel aging.

2. Materials and methods

2.1. Wine samples and aging conditions

The Cabernet Sauvignon base wines were produced at an industrial scale by four wine regions of China: Manasi County, Xinjiang (44°18’ N, 86°24’ E); Hexi Corridor, Gansu (36°04’ N, 103°47’ E); Shacheng County, Hebei (40°25’ N, 115°31’ E); Changli County, Hebei (39°44’ N, 119°11’ E) in 2010 and five wine regions Manasi County, Xinjiang; Hexi Corridor, Gansu; Helanshan, Ningxia (38°34’ N, 106°02’ E); Yanqing County, Beijing (40°27’ N, 115°59’ E); Deqin County, Yunnan (28°29’ N, 98°55’ E) in 2011 (Fig. 4B). The nine wines were abbreviated as 10MNS, 10HXC, 10SC, 10CL, 11MNS, 11HXC, 11HLS, 11YQ and 11DQ. After alcoholic fermentation, the wines were placed in stainless steel tanks until they were transported to Beijing. The physicochemical parameters of those wines were shown in Table S1 (Supplementary Table). The contents of reducing sugar were below 4.0 g/L and the alcoholic degrees were between 13% and 14% (v/v) for all wines. Other physicochemical parameters of those wines met the Standards of Wine Product in China (GB/15037-2006).

The wines were aged in four types of oak barrels which were two wood grains (fine: 1–3 mm or medium: 3–5 mm) with two toasting levels (light: toasting at 150 °C for 15 min or medium: toasting at 175 °C for 15 min). These four oak barrels were (1) fine wood grains and light toasting (FG_LT); (2) fine wood grains and medium toasting (FG_MT); (3) medium wood grains and light toasting (MG_LT); (4) medium wood grains and medium toasting (MG_MT). The new 225 L barrels were made of 160-years old Quercus petrea obtained from the same forest located in the center region of France by Yantai Demptos Co., LTD (Yantai, China). The wines aged in stainless steel tanks (100 L) were used as control (abbreviated as SST).

The base wines were put into the barrels or stainless steel tanks in June 2011 and 2012 and kept for 12 months in a wine cellar where relative humidity and temperature conditions were controlled at 70–80% and 14–16 °C, respectively. The barrels and tanks were refilled every two months to compensate the losses of evaporation of water and ethanol. No racking was performed during aging. The corrections of SO2 were done when the free SO2 levels were below 30 mg/L.

Wine samples were collected after 0 (before putting in containers), 4, 8 and 12 months aging in each container. There were 144 samples corresponding to the nine wines in the five aging types to be used for following analysis. All samples were stored at –20 °C before analysis. Each analysis for every sample was carried out in triplicate. None of the samples presented reduced off-flavors in the sensory evaluation carried out by the experienced enologist of Centre for Viticulture and Enology during the aging period.

2.2. Chemicals

The sulfur compounds including (abbreviation and CAS number in brackets): dimethyl sulfide [DMT, 75-18-3], S-methyl thioacetate [MTA, 1534-08-3], S-ethyl thioacetate [ETA, 625-60-5], 2,5-dimethylthiophene [DMTh, 638-02-8], diethyl disulfide [DEDS, 110-81-6], 2-methyltetrahydrolatrophen-3-one [MTTHF, 13679-85-1], 3-(methylthio)propionaldehyde [methional] [MTPA, 3268-49-3], 2-mercaptoethanol [ME, 60-24-2], 2-(methylthio)ethanol [MTE, 5271-38-5], methyl-3-methylthio propionate [MMP, 13532-18-8], 3-(methylthio)propyl acetate [PMTE, 16630-55-0], 3-(methylthio)-1-propanol [methionol] [MTP, 505-10-2], 3-(ethylthio)-1-propanol [ETP, 18721-61-4], 4-(methylthio)-1-butanol [MTB, 20582-85-8], benzothiazole [BT, 95-16-9], and ethyl-3-methylthio propionate [EMTP, 13327-56-5] were purchased with a purity above 98% from Sigma-Aldrich (St. Louis, USA), Fluka (Buchs, Switzerland) and J&K Scientific Ltd. (Beijing, China).

Individual standard solution for each sulfur compound was prepared with HPLC grade ethanol obtained from Honeywell (New Jersey, USA). Charcoal and inorganic reagents were supplied by Beijing Chemical Works (Beijing, China). Purified water was generated using a Milli-Q purification system (Millipore, USA).

2.3. Volatiles extraction by HS-SPME method

The HS-SPME method for volatiles analysis was in accordance with the study of Fedrizzi, Magni, Moser, Nicolini, and Versini (2007). Since the mass spectrometer was used as detector in the exemplary method, the factors (fibre, time of equilibrium and adsorption, temperature of the sample, ionic strength) were studied to get the maximum signal for each compound on the FPD detector. The optimal operating conditions were summarized as follows. The SPME fibre was CAR/PDMS/DVB (50/30 μm × 2 cm) (Supelco, Bellefonte, PA, USA). For each analysis, 5.0 mL of the sample was placed in a 15 mL brown vial which contained 1.0 M MgSO4·7H2O and a magnetic stirrer and was capped with a PTFE–silicon septum. Then the sample vial was agitated at 500 rpm and incubated at 40 °C for 10 min. Afterwards, the SPME fibre was inserted through the vial septum and exposed to the headspace over the liquid sample for 50 min. Then, the fibre was immediately desorbed in the GC injection for 8 min. 
2.4. Analysis of volatile sulfur compounds by GC/FPD

The analyses were performed on an Agilent 7890 gas chromatography equipped with a H9261 flame photometric detection system (Varian, Walnut Creek, CA, USA) operating in the sulfur mode. The gas chromatography conditions were based on the study of Mestres, Marti, Busto, and Guasch (2000). The separation was performed by a HP-INNOWAX capillary column (60 m × 0.25 mm I.D., 0.25 μm film thickness, J&W Scientific, USA). The GC injection was in the splitless mode at temperature 250 °C. The oven temperature was programmed as follows: 40 °C (initial hold for 5 min), ramp at 8 °C/min to 150 °C, and next ramp at 2 °C/min to 180 °C, and then ramp at 15 °C/min to 220 °C (final hold for 5 min). The carrier gas was pure nitrogen with a constant flow rate at 60 mL/min. The FPD detector was set up at temperature 250 °C and supplied with 50 mL/min of hydrogen and 60 mL/min of air. All sulfur compounds were identified by comparing their retention times with the pure standards. A typical chromatogram was displayed in Fig. S1 (Supplementary Figure).

2.5. Quantification of the sulfur compounds

The standard solutions for the quantification were prepared following published method (Fedrizzi et al., 2007). A white wine (alcohol strength: 12.0% v/v; sugar content: 2.30 g/L) was treated twice with charcoal (3.0 g/L) to remove any sulfur compounds.
and used as a solution media. Because FPD response is a power function, the calibration curve was constructed by plotting the log [S-compound] peak area ratios against the log [S-compound] concentration ratios to obtain the VSCs linear calibration graphs.

As shown in Table S2 (Supplementary Table), the linearity and precision were verified and could satisfactorily quantify the wine samples. Also the recoveries were confirmed by spiking the red wine with each analyte at three different levels (low, middle and high concentration of the calibration graphs), and their ranges were between 70% and 130% for all analytes, which were satisfactory for analyzing those trace concentrations of sulfur compounds (Mestres, Busto, & Guasch, 2002; Mestres, Marti, et al., 2000).

2.6. Statistical analysis

Linear regression analysis of all calibration standard curves was carried out on Microsoft Excel 2010. The analysis of variance and Duncan’s multiple range test were carried out via SPSS 20.0 Software (SPSS Inc., Chicago, IL). The graphs were constructed using Origin 8.5. Hierarchical clustering and heatmap visualization were performed using ‘pheatmap’ package in R (3.0.3) (Team, 2012).

3. Results and discussion

The volatile sulfur compounds were commonly presented in wine, sixteen compounds presented in Table 1 were the analytes of interest in the current study. The ranges of the concentrations

Fig. 2. Evolution of MTP during maturation of wines aged in five different containers. Within a column of the grid, different letters denote statistically significant differences (p < 0.05) at each time point.
together with their perception thresholds, odor descriptions and typical concentration ranges of the nine types of wines were listed in Table 1 as well. DMTh, DEDS and ME were not detected in all samples. MTB was detected in 11YQ, but two times lower than its sensory threshold (28.44 μg/L). For ETA, PMTE, MTPA, ETP and BT, they were quantified in just one or two wine types from 2011 during the aging and had the level below thresholds. These results indicated that those compounds were not commonly in Chinese wines, compared with some wines in other countries (Belancic Majcenovic, Schneider, Lepoure, Lempereur, & Baumes, 2002; Burin, Marchand, de Revel, & Bordignon-Luiz, 2013; Fedrizzi, Magno, Badocco, Nicolini, & Versini, 2007; Ferreira et al., 2003; Moreira et al., 2002).

On the other hand, the other seven compounds (DMS, MTA, MMTP, MTE, 2MTHF, EMTP, MTP) were detected in almost all the samples of this study. They were also present in different wines from other countries, for example Merlot, Marzemino, Teroldego and Chardonnay wines (Fedrizzi et al., 2007), dry red Botrytis wines (Fedrizzi et al., 2011), port wines (Ferreira et al., 2003) and so on. Among these compounds, MTP was the most prominent VSC in all wine samples and reported as the most abundant VSC in wine at up to mg/L levels (Landaud et al., 2008). DMS and MET were the second most abundant VSCs in these wines. It’s worth noting that the DMS contents detected in the current study were remarkably higher than those reported in previous studies (Landaud et al., 2008; Mestres, Busto, et al., 2000). Especially after the one year

Fig. 3. Evolution of MTA during maturation of wines aged in five different containers. Within a column of the grid, different letters denote statistically significant differences (p < 0.05) at each time point. nq, not quantified.
aging, the concentration of DMS was over 100 μg/L in most wines. As shown in Table 1, except for DMS and MTP, other compounds presented below their perception thresholds. Nevertheless, they may act synergistically to augment the detection of other reduced-sulfur odorants (Coetzee et al., 2015; Jackson, 2008), so we should closely pay attention to those compounds.

3.1. Increase of DMS during the aging

DMS, a light volatile sulfur compound, is found in a wide range of beverages and foodstuffs and usually described as cabbage, asparagus and corn (Moreno-Arribas et al., 2009). It has a perception threshold of 27 μg/L in red wine. Some researchers confirmed that not only the DMS concentration but also the type of wine can affect the wine aroma (De Mora, Knowles, Eschenbruch, & Torrey, 1987; Segurel et al., 2004). It could enhance the fruity notes of Grenache Noir and Syrah wines at a level around 100 μg/L (Segurel et al., 2004), and contributed to additional truffle and quince notes in Port wines (Ferreira et al., 2003). In the work of Segurel et al. (2004), it was never perceived as off-flavor even though the DMS concentration reached 200 μg/L. In this study, the levels of DMS ranged from 52.34 to 157.27 μg/L in all samples. However, none of the wines had off-flavors. It indicates that the relatively high DMS concentration in Cabernet Sauvignon wines might improve the complexity of wine aroma rather than result in a negative note. However, further research would be conducted to understand the interaction of DMS with other compounds and their impact on wine aroma.

DMS was found to increase during the one year aging (Fig. 1), except that the 10MNS wine aged in FG_LT oak barrel showed no obvious change after aging for 12 months. The results were consistent with some previous findings (Fedrizzi et al., 2003; Segurel, Razungles, Riou, Trigueiro, & Baumes, 2005; Segurel et al., 2004). Although the DMS contents of most wines fluctuated during the aging process, they significantly increased by 9.42–142.44% at the end of the trial period, compared with their base wines (52.34–91.19 μg/L). This result confirmed the findings that DMS released from precursors presented in young wines during the aging (Nguyen et al., 2010; Segurel et al., 2005; Ugliano et al., 2012). DMS is usually generated by yeast from various sulfur amino acids and derived compounds during alcoholic fermentation (De Mora et al., 1987). Since DMS is quite volatile and could be stripped off by CO2, its levels in young wines are usually low (Moreno-Arribas et al., 2009). However, they can significantly increase through chemical pathways during wine aging (Segurel et al., 2005). Furthermore, Loscos et al. (2008) revealed that S-methyl methionine (SMM) was the principal precursor of DMS in grapes, accounting for more than 70% of the potential DMS (PDMS). Segurel et al. (2005) demonstrated the chemical reactivity of SMM converting into DMS during the model aging of wine. Recently, De Royer Dupré, Schneider, Payan, Salançon, and Razungles (2014) reported that vine water deficit could increase the accumulation of PDMS in berries to result in a better preservation of PDMS during winemaking. In this study, a large variation of DMS in different wines might correlate to their individual matrices and the content of SMM in individual base, although the reason resulting in is still not understood. The clear correlations between DMS and SMM in wine matrix have yet been fully elucidated.

During the aging process, the evolution pattern of DMS (Fig. 1) in wines aged in stainless steel tanks was obviously different from that in oak barrels, especially in the wines from 2011 vintage. For the major wine types, the contents of DMS were significantly lower in wines matured in oak barrels than in stainless steel tanks after aging for 8 months. However, the DMS level in wines from...
Table 1
Odor descriptors, thresholds and content ranges of volatile sulfur compounds in wines during aging.

<table>
<thead>
<tr>
<th>No.</th>
<th>Analytea</th>
<th>Odor descriptorsb</th>
<th>Thresholdb</th>
<th>Literature valuesc (µg/L)</th>
<th>Contents in wines (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>10MNS</td>
<td>10HXC</td>
<td>10SC</td>
<td>10CL</td>
</tr>
<tr>
<td>1</td>
<td>DMS</td>
<td>Cooked cabbage, canned corn, asparagus</td>
<td>1–62</td>
<td>3.76–7.78</td>
<td>nd</td>
</tr>
<tr>
<td>2</td>
<td>MTA</td>
<td>Sulfurous, cheesy, egg</td>
<td>50 (beer)</td>
<td>nd – 115</td>
<td>nd – 98</td>
</tr>
<tr>
<td>3</td>
<td>ETA</td>
<td>Sulfurous, garlic, onion</td>
<td>10 (beer)</td>
<td>nd – 180</td>
<td>nd – 76</td>
</tr>
<tr>
<td>4</td>
<td>DMTb</td>
<td>Green-like, nutty, sulfur</td>
<td>–</td>
<td>nd – 0.7</td>
<td>nd</td>
</tr>
<tr>
<td>5</td>
<td>DEDS</td>
<td>Onion, burnt rubber</td>
<td>4.3</td>
<td>nd – 85</td>
<td>nd</td>
</tr>
<tr>
<td>6</td>
<td>MTPA</td>
<td>Onion, mashed potatoes</td>
<td>250 (beer)</td>
<td>nd – 57.5</td>
<td>nd</td>
</tr>
<tr>
<td>7</td>
<td>ME</td>
<td>Poultry, farmyard, alliaceous</td>
<td>450–600</td>
<td>nd – 400</td>
<td>nd</td>
</tr>
<tr>
<td>8</td>
<td>MMTP</td>
<td>Sulfurous</td>
<td>–</td>
<td>nd – 0.4</td>
<td>nd</td>
</tr>
<tr>
<td>9</td>
<td>MTE</td>
<td>French bean</td>
<td>250</td>
<td>5–139</td>
<td>36.05–112.95</td>
</tr>
<tr>
<td>12</td>
<td>PMTE</td>
<td>Mushroom, onion, garlic</td>
<td>115 (red); 100 (white)</td>
<td>nd – 17</td>
<td>nd</td>
</tr>
<tr>
<td>14</td>
<td>ETP</td>
<td>Rancid, sweaty</td>
<td>–</td>
<td>11–88</td>
<td>nd</td>
</tr>
<tr>
<td>15</td>
<td>MTB</td>
<td>Metallic-bitter, earthy, chive-garlic</td>
<td>80</td>
<td>nd – 181</td>
<td>nd</td>
</tr>
<tr>
<td>16</td>
<td>BT</td>
<td>Smoky, flintstone</td>
<td>50</td>
<td>nd – 6</td>
<td>nd</td>
</tr>
</tbody>
</table>

nd, not detected; nq, not quantified.

a DMS, dimethyl sulfide; MTA, S-methyl thioacetate; ETA, S-ethyl thioacetate; DMTb, 2,5-dimethylthiophene; DEDS, diethyl disulfide; MTPA, S-(methylthio)propionaldehyde; ME, 2-mercaptoethanol; MMTP, methyl-3-methylthio propionate; MTE, 3-(methylthio)ethanol; 2MTHF, 2-methyltetrahydrotetriophen-3-one; EMTP, ethyl-3-methylthiopropionate; PMTE, 3-(methylthio)propyl acetate; MTP, 3-(methylthio)1-propanol; ETP, 3-(ethylthio)1-propanol; MTB, 4-(methylthio)-1-butanol; BT, benzothiazole.

b Reported odor descriptor, threshold and values (Mestres, Busto, & Guasch, 2000; Landaud et al., 2008; Burin et al., 2013; Moreira et al., 2010).

c Reported odor descriptor, threshold and values (Mestres, Busto, & Guasch, 2000; Landaud et al., 2008; Burin et al., 2013; Moreira et al., 2010).
10HXC was not significantly different between these two kinds of containers during the first 8 months, but it reduced in the one in stainless steel tank at 12th month, whereas it kept rising in oak barrel. These results suggested that the 8-month period might be a key turning point to the variation of DMS between the two kinds of aging wines. Although the evolution of DMS was not affected by oxygen exposure during microoxygenated tank (McCord, 2003; Nguyen et al., 2010) and bottle maturation (Ugliano et al., 2012), wines aged in oak barrels are not only exposed to small amounts of air that penetrates the wood pores but also in contact with oak staves. In such a natural micro-oxygenation, some substances formed by certain physical and chemical processes (Ortega-Heras et al., 2007) which possibly inhibited the formation of DMS from its precursors already presented in the wine, or catalyzed the degradation of DMS. McCord (2003) reported the similar results that lower concentration of DMS was observed in all treatments with added toasted oak products in the aging of Cabernet Sauvignon wine.

3.2. Decrease of thiaalcohols during the aging

MTP as an amino acid-related thiaalcohol, is considered the most important heavy volatile sulfur compound in wine, which can confer odors of cauliflower and cooked cabbage at a concentration above its perception threshold (1200 μg/L) (Mestres, Busto, et al., 2000). The contents of MTP in those base wines from different regions of China all reached its threshold, which indicated that it would contribute to aroma defects in wines if no effective control has been practiced during the following process.

The formation of MTP is clearly related to the catabolism of methionine via the Ehrlich pathway during alcohol fermentation (Landaud et al., 2008). As shown in Fig. 2, a great variety of MTP concentration was found in different base wines, this suggested the difference of methionine metabolism routes in wines from various regions. However, there was uninvolved biochemical process in the current study, so as expected, in most wines there was a propensity of decreasing of MTP during aging, although the trends were wine-dependent. In addition, this trend was much stronger in the cases of 11MNS and 11YQ, which showed a noticeable drop above 30 percent for the five aging containers at the end of the experiment period. Previous studies reported that MTP decreased with the presence of oxygen (Ferreira et al., 2003; Nguyen et al., 2010), likely due to the direct oxidation of MTP to form methional. Escudero, Hernandez-Orte, Caño, and Ferreira (2000) found a decline of methionol along with the formation of methional in a white wine. However, a study did not find that methional was present in a Port wine treated with oxygen (Ferreira et al., 2003). Furthermore, the Strecker mechanism was considered to be the main pathway for the formation of methional (Silva Ferreira, Guedes de Pinho, Rodrigues, & Hogg, 2002). For all the samples monitored in this study, methional was only found in 11HLS wines at a rather low level (approximately 20 μg/L) with less change during aging. Its acetate ester (PMTE) was only detected in the samples from 11YQ in low contents (below 2 μg/L), which were not enough to offset the decline of MTP. These results indicated that the decrease of MTP would lead to the formation of other unidentified compounds, such as methionol-S-oxide tentatively identified in a dry Botrytized red wine (Fedrizzi et al., 2011).

2MTHF as a food flavor constituent is observed in such foodstuffs as coffee, roasting peanuts and whisky and has a metallic bean-like odor (Mestres, Busto, et al., 2000). Karagiannis and Lanaridis (1999) considered that it is synthesized via a different biochemical path than that of methionol, after investigating the effect of some vinification parameters on it. However, its formation mechanism during winemaking is not well documented. Nguyen et al. (2010) reported that the concentration of MTE decreased during wine aging in stainless steel tanks, and higher oxygen dosage (20 mg/L/month) resulted in a greater drop. In the current study, except for 11MNS, other wines contained abundant contents of MTE, and the highest level was detected in the base wine from 11HXK (data was available in Supplementary Fig. S3). Besides slight accumulations of MTE were observed in 10MNS, MTE in other wines showed a downward trend during the whole aging period, even if the differences among containers were generally restricted by wine types. And interestingly, medium grain with light toasting barrels resulted in a general increase of MTE concentrations after 12 months aging, compared with fine grain with the same level of toasting.

3.3. Lower content of esters in wines aged in oak barrel than in stainless steel tank

MTA and ETA were found and monitored during the aging of the nine types of wine. ETA was only quantified in 11HLS and 11YQ wines. MTA was detected in all samples, but its level didn’t reach the limit of quantification (2.61 μg/L) in wines from Hexi Corridor in two vintages (Fig. 3). In wines with off-flavor, their concentrations can reach to 85 and 180 ppb, respectively (Mestres, Busto, et al., 2000). These compounds not only produce sulfurous or vegetable smells for wine, but also can be hydrolyzed to give free thiols at wine pH, which confer a poultry-like or rotten egg off-odors to wine (Landaud et al., 2008). The formation of these esters is attributed to the enzymatic esterification of methyl mercaptan via acetyl coenzyme A (acyetyl-CoA) (Landaud et al., 2008). In the case of MTA, a decline was observed for all cases across the whole period studied, especially for 10CL and 11MNS, which showed much greater decreases. After aging for 12 months, there was no significant effect of aging containers on MTA contents of 10CL, 11MNS and 11DQ, but in the case of 10MNS, 10SC, 11HLS and 11YQ, its content was significantly lower in wines aged in oak barrels than in stainless steel tanks. It seems that MTA was harder to be kept in wines aged in oak barrels. Though recent studies have shown that oxygen did not influence this hydrolysis during the aging (Nguyen et al., 2010; Ugliano et al., 2012), oak wood may have ability to sorb MTA like other esters (Garde-Cerdan & Ancin-Azpilicueta, 2006). As displayed in Fig. 3, the effects of types of oak barrel were significant only at some point of wine maturation, also there were inconsistencies among different wines. For example, after 4 months aging, the MTA contents of 10MNS wines
aged in oak barrels with medium grain were significantly higher than that with fine grain, whereas 11MNS wines showed opposite results. Furthermore, this difference didn’t remain later.

As other esters quantified in this study, MMTP and EMTP are considered to have a sulfurous or metallic odor and methionine may act as their precursors (Mestres, Bustó, et al., 2000; Moreira et al., 2002). Although Karagiannis and Lanaridis (1999) reported that concentration of EMTP could be raised by increasing bisulfite, fermentation temperature and time of wine contacted with yeast deposit during winemaking, much less information is available on the evolution of those compounds during wine aging. In the current study, their contents were in accordance with the previous reports (Karagiannis & Lanaridis, 1999; Mestres, Bustó, et al., 2000; Moreira et al., 2002), and the highest content of MMTP was found in wines from 10SC, while the most abundant EMTP appeared in wines from 11HLS (data was available in Supplementary Figs. S4 and S5). During the aging process, their evolution patterns were more restricted by wine types, compared with other sulfur compounds abovementioned. Moreover the differences of various aging treatments were generally smaller and not significant in all cases at any given time. But interestingly, similar to the result of MTA, in most cases the highest concentrations of MMTP and EMTP were observed in wines aged in stainless steel tanks at the end of aging, it seemed that these esters were also more difficult to be kept in oak barrel.

3.4. Factors influencing VSCs during the aging

Formation of VSCs during aging can be a challenge for winemakers to deal with. To date, however, little research has focused on the evolution of sulfur compound during aging in oak barrels, with the exception of some multifunctional thiols (Blanchard, Tominaga, & Dubourdieu, 2001; Piano et al., 2014) which are not so active, especially in the wines from Manasi County, which has the most important influence on the chemical composition of oak wood (Garde-Cerdan & Ancin-Azpilicueta, 2006). Although their influences on some volatile compounds such as oak lactones, volatile phenols and furanic compounds have been reported frequently (Garde-Cerdan & Ancin-Azpilicueta, 2006; Jackson, 2008; Ortega-Heras et al., 2007; Ribéreau-Gayon et al., 2006), there is very limited data on VSCs. Due to the different changes of oxygen permeability with time between these two kinds of grain (Del Alamo-Sanza & Nevares, 2014), and the discrepant reactivities of wood with the surrounding environment in different wine matrices, it’s easy to understand that the effects of those factors on each compound of different wine types were not consistent at different timing. And it also partly reflected the importance of the compatibility of wine and oak barrel. Regardless, we could attain the intuitional results affected by those combinations in each wine through the present work.

To understand overall similarities and differences in the variation of VSCs during maturation among the wines with the five types of aging containers, hierarchical cluster analysis was performed by using these identified VSCs as variables (Fig. 4). Samples from the same base wine were obviously clustered together within a short distance, further demonstrating that the original wine matrix does have the most significant influence on its profile of VSCs. And in each wine type, samples with the same aging time generally showed the shortest distance, regardless of the aging containers used. These observations were consistent with the ANOVA results that wine type and aging time were the most important factors influencing the evolution of VSCs. Observing from the farthest hierarchical distance, nine types of wines could be divided into two major clusters according to VSCs accumulation pattern. Cluster 1 was composed mainly by 10HXC, 10CL, 11DQ, 11YQ and 11HLS, which presented the similar profiles with more abundant such sulfur compounds. In this group, wines from 11YQ and 11HLS were closely clustered with richer contents of most compounds. Wine types in cluster 2 were wines from 10SC, 11MNS, 11HXC and 10MNS, with relatively lower levels of VSCs, in particular, the concentrations of MTP, EMTP and 2MTHF were lowest. The formations of these three compounds were associated with the methionine metabolism of microorganism during winemaking (Landaud et al., 2008; Lopez Del Castillo-Lozano, Delile, Spinnler, Bonmarre, & Landaud, 2007). This suggested that the methionine metabolism routes in wines from those regions were not so active, especially in the wines from Manasi County, which was consistent in two vintages. It’s observed that the content of MMTP in wines from 10SC was the highest among all wines, this was why samples of 10SC showed more far distance compared with other wines in this group.

4. Conclusion

This work provided detailed information on the volatile sulfur compounds profiles of Cabernet Sauvignon wines produced from seven distinctive wine regions in China during oak barrel matura-
tion and revealed the effect of different containers on the volatiles evolution during one year aging. Seven compounds (DMS, MTA, MMTP, MTE, 2MTHF, EMT, MTP) were commonly found in Chinese wines and discriminated the wines from different regions in two vintages according to hierarchical cluster analysis. It indicated that the wine matrix significantly affected the evolution of VSCs during aging. During the aging process, DMS was found to increase, in contrast with other sulfur volatiles. VSCs were greatly influenced by aging containers, and most compounds were harder to be kept in oak barrel than in stainless steel tank during the one year aging. The wood grain and toasting level of oak barrel significantly affected the concentration of MTA and 2MTHF. The results of this work would improve the understanding of volatile sulfur compounds of wines aged in oak barrels and provide winemakers with references in making the proposals about oak barrel aging of red wines as well.

Acknowledgments

This work was financially supported by the National Natural Science Fund of China (Grant No. 31271917) and the China Agriculture Research System (CARS-30-jq-03). The authors thank Dr. Zhi-mun Xi of Louisiana State University for the English proofreading of this manuscript.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.foodchem.2016.01.139.

References


