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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

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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-methyltetrahy-drothiophen-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-methyltetrahy-drothiophen-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.

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 H_2S 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,

* Corresponding author at: College of Enology, Northwest A&F University, No. 22 Xinong Road, Yangling, Shaanxi 712100, China.
E-mail address: yanlinliu@nwsuaf.edu.cn (Y.-L. Liu).

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and Kilmartin (2010) reported similar results that DMS and thioesters were not affected by oxygen when wines were aged in polyethylene tanks with micro-oxygenation 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 (Garde-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 and malolactic fermentation, those 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 SO_2 were done when the free SO_2 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 [DMS, 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-methyltetrahy-drothiophen-3-one [2MTHF, 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 [MMTP, 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, Magno, 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 $MgSO_4{\cdot}7H_2O$ 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.