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Study of the effect of H_2S, MeSH and DMS on the sensory profile of wine model solutions by Rate-All-That-Apply (RATA)

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ABSTRACT

The effect of hydrogen sulfide (H_2S), methanethiol (MeSH) and dimethyl sulfide (DMS) on the odor properties of three wine models-WM- (young white, young red and oaked red wines) was studied. Wine models were built by mixing a pool of common wine volatile and non-volatile compounds and further spiked with eight different combinations of the three sulfur compounds present at two levels (*level 0*: 0 μg L^{-1} and *level 1*: 40 μg L^{-1} of H_2S, 12 μg L^{-1} of MeSH; 55 μg L^{-1} of DMS). For each wine matrix eight WMs were produced and further submitted to sensory description by Rate-All-That-Apply (RATA) method.

Hydrogen sulfide and methanethiol were clearly involved in the formation of reductive aromas and shared the ability to act as strong suppressors of *fruity* and *floral* attributes. Specifically, hydrogen sulfide generated aromas of *rotten eggs*, while methanethiol generated significant increases in *camembert* and decreases in *citrus*, *smoky/roasted* and *oxidation* aromas. The simultaneous presence of hydrogen sulfide and methanethiol enhanced the intensity of the unspecific term *reduction*, while the specific nuances individually imparted by each of the two compounds could not be further identified. DMS did not exert any outstanding effect on the reductive character of wines and its sensory effect was matrix-dependent. It was involved in the formation of fruity notes such as *cooked/candied* and *red/black fruits* in young wines, and vegetal notes (*canned vegetables*) in oaked red WMs.

1. Introduction

Wines can develop some sensory problems that depreciate their quality and may even cause consumers' rejection (Ribéreau-Gayon, Glories, Maujean, & Dubourdieu, 2000). Olfactory defects (or off-odors) are particularly important as they might prevent tasting the wine. Wine off-odors can have different origins; they may be due to problems and diseases of the grape, they may originate in fermentation, they can appear during bottle storage and/or they may be due to the action of microorganisms such as fungi, yeasts or bacteria.

Reduction is one of the off-odors most commonly found in wines. This defect is caused by Volatile Sulfur Compounds (VSCs). Hydrogen sulfide (H_2S), described with terms such as rotten eggs, decaying seaweed or reduced taste (Mestres, Busto, & Guasch, 2000), and methanethiol (MeSH) characterized by attributes such as putrefaction, cooked cabbage or reduced taste (Mestres et al., 2000) are the most habitual VSCs responsible for the reduction off-odor.

H_2S and MeSH are formed during fermentation. The formation of small amounts of H_2S are inherent to fermentation (Schutz & Kunkee, 1977) and are related to multiple factors such as the amount of assimilable nitrogen, (Bell & Henschke, 2005; Giudici & Kunkee, 1994; Jiranek, Langridge, & Henschke, 1995; Wang, Bohlscheid, & Edwards, 2003), the redox state of the must and wine, the concentration of ethanol and the yeast strain (Jiranek et al., 1995; Rankine, 1963). The formation of MeSH has been related to yeast catabolism of methionine and cysteine (Spinnler, Berger, Lapadatescu, & Bonnarme, 2001) although it could also be related to amino acid synthesis (Landaud, Helinck, & Bonnarme, 2008). Both H_2S and MeSH partly disappear by evaporation and partly by oxidation during racking and pumping-over operations. The levels of these compounds can be controlled by winemaking processes such as copper fining, aeration and/or addition of lees (Ugliano et al., 2009; Viviers, Smith, Wilkes, & Smith, 2013). However, it is not infrequent that VSCs appear during bottle aging most likely if the closure is quite hermetic (Franco-Luesma & Ferreira, 2016; Ugliano et al., 2012).

Regarding dimethylsulfide (DMS), several precursors have been proposed for its formation in wine. One of them is cysteine that can produce DMS during fermentation (De Mora, Eschenbruch, Knowles, &

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Spedding, 1986). Dimethyl sulfoxide is another possible precursor of DMS in wine (De Mora, Lee, Shooter, & Eschenbruch, 1993). Finally, S-Methylmethionine (SMM) has been found to be the major source of DMS in beer (Anness & Bamforth, 1982; Dickenson, 1983; White & Wainwright, 1976) and more recent works have demonstrated that grapes also contain SMM ranging from few μg L^{-1} to 5 mg L^{-1} (Loscos et al., 2008; Segurel, Razungles, Riou, Salles, & Baumes, 2004; Segurel, Razungles, Riou, Trigueiro, & Baumes, 2005). As in the case of H_2S and MeSH, DMS is a highly volatile compound that is mainly lost by CO_2 entrainment during fermentation, but its levels increase during wine aging in the bottle due to the hydrolysis of SMM (Segurel et al., 2005). Winemakers tend to think that DMS, being a VSC, is one of the sources of reductive off-odors. However, its sensory role is completely different, and it has been reported to be responsible for increases in the complexity of wine aroma and enhancement of the black fruit character (Escudero, Campo, Farina, Cacho, & Ferreira, 2007; Lytra et al., 2014; Segurel et al., 2004; Spedding & Raut, 1982).

The main sensory attributes linked to these three compounds are well established, but their exact role played on wine aroma is not well known. In fact, the strong interactions that H_2S and MeSH can exert to wine components, most notably to wine metals (Franco-Luesma & Ferreira, 2014), and the high volatility of these compounds, may explain the strong disagreements between the odor thresholds reported for these compounds (Mestres et al., 2000). Furthermore, the sensory interactions between these compounds and other wine aroma compounds, which are ultimately responsible for wine aroma (Francis & Newton, 2005), are still unknown. Those interactions are best studied through the use of complex wine models displaying aroma nuances closely resembling those of real wines. Wine models ensure a perfect knowledge of aroma composition and rule out any interaction with the matrix which could affect the volatility of the aroma compounds.

Quantitative Descriptive Analysis (QDA) (Stone, Sidel, Oliver, Woolsey, & Singleton, 1974) is a powerful tool which has been widely used over the years to provide sensory descriptions of a variety of food products. However, according to Lawless (Lawless, 1999), while QDA is well adapted to describe simple products it might be less suited to profile complex products composed of hundreds of odorant compounds such as wine. In agreement with this statement, Campo et al. (Campo, Ballester, Langlois, Dacremont, & Valentin, 2010) showed that an alternative method based on citation frequency may lead to more nuanced wine descriptions than QDA. Citation frequency or pick-K methods have been mostly applied to wine (H.T. Lawless & Heymann, 2010). A wide list of descriptors is provided to trained panelists who have to choose the most pertinent ones to describe each given wine.

The citation frequency or pick-K method is a variant of the Check-All-That-Apply (CATA) method that has been recently added to the sensory evaluation toolbox (Dooley, Lee, & Meullenet, 2010). The main difference between the two methods resides in the number of terms panelists can pick to describe the products. In CATA, panelists are asked to check all the terms that describe the product and in Pick-K methods they have to choose the K attributes that are dominant in the product. So when K is small the pick-K method highlights the main characteristics of the product whereas CATA provides a more complete description. While in the literature the Pick-K method has been mostly used with trained panelists and CATA with consumers, both can be used with either type of panelists depending on the objective of the study. If the objective is to understand consumer perception of the products then both methods should be used with consumers but if the objective is to obtain a description of the products, experts or trained panelists may be better suited.

The advantage of CATA or Pick-K method over other new alternative methods such as flash profile is to make use of a pre-defined unique list of terms that is much easier to interpret in terms of product sensory profile. Its main limitation however is that it produces counts rather than rankings or intensities. To alleviate this drawback some authors (Ares et al., 2014; Reinbach, Giacalone, Ribeiro, Bredie, & Frost, 2014) proposed an intensity-based variant of CATA Analysis named Rate-All-That-Apply (RATA). In this variant, panelists are asked to rate the intensity of the terms they ticked. RATA was shown to yield superior accuracy and sample discrimination than CATA and to limit satisficing response strategies (checking attributes without thinking) by participants (Ares et al., 2014). Another advantage with RATA is that because it produces intensities rather than counts it requires a smaller number of panelists than CATA especially if the panelists are experts or trained (Giacalone & Hedelund, 2016).

A last issue with Pick-K, CATA or RATA methods is the choice of the list and the number of terms in the list. Ares and Jaeger (2015) recommend to use from 10 to 40 terms. Sensory terms can be taken from the literature or from trained panelists lexicon. If no preexisting vocabulary exist the sensory terms can be obtained via any rapid method generating vocabulary (repertory grid, sorting task, projective mapping, free descriptions…) or via focus groups or qualitative studies. The only constrain is to ensure that the terms generated are understandable by the panelists (Ares & Jaeger, 2015).

In this context and with the aim of increasing the knowledge about the impact of VSCs on wine sensory properties, the goal of this study was to test the sensory effects of H_2S, MeSH and DMS on three complex wine models reproducing aroma nuances of young whites, young reds and oaked red wines. For this purpose, we used a variant of the RATA method for characterizing wine samples with different combinations of H_2S, MeSH and DMS.

2. Materials and methods

2.1. Products

2.1.1. Chemicals and standards

Ethanol was purchased from Merck (Darmstadt, Germany). H_2S was produced by addition of an Ar-bubbled water solution of Na_2S (supplied by Sigma–Aldrich, St. Louis, MO, USA) at pH 9.6. Methanethiol was from Fluka (Steinheim, Germany) and dimethylsufide from Merck

Table 1
Composition of the three wine models (WM) employed in the study.

	White wine	Young red wine	Oaked red wine	Fraction
pH	3.2	3.5	3.5	Non volatile
Tartaric acid (g L^{-1})	5	5	4	
Glycerin (g L^{-1})	5	10	10	
Tanic acid (mg L^{-1})	15	50	100	
Commerical tannins (mg L^{-1})	–	–	10	
Quinine (mg L^{-1})	3	7	7	
Arabic gum (mg L^{-1})	15	75	75	
Ethyl alcohol (% *v/v*)	10	12	12	Volatile
Isoamyl alcohol (mg L^{-1})	120	180	180	
β-Phenylethanol (mg L^{-1})	20	30	30	
Acetic acid (mg L^{-1})	100	150	150	
Hexanoic acid (mg L^{-1})	5	2	2	
Ethyl hexanoate (mg L^{-1})	5	1	1	
Isoamyl acetate (mg L^{-1})	1,5	1	1	
Linalool (μg L^{-1})	5	–	–	
Ethyl cinnamate (μg L^{-1})	0,5	–	–	
β-Damascenone (μg L^{-1})	3	4	4	
ethyl acetate (mg L^{-1})	–	50	50	
Isovaleric acid (mg L^{-1})	–	0.3	0.3	
Diacetyl (mg L^{-1})	–	0.4	0.4	
Ethyl 2-methylbutyrate (μg L^{-1})	–	120	120	
Ethyl vanillate (mg L^{-1})	–	0.25	0.55	
Vainillin (μg L^{-1})	–	70	170	
g-Nonalactone (μg L^{-1})	–	20	20	
Guaiacol (μg L^{-1})	–	10	30	
β-Ionone (μg L^{-1})	–	0.3	0.3	
Whiskylactone (μg L^{-1})	–	–	200	
Eugenol (μg L^{-1})	–	–	20	
Furaneol (μg L^{-1})	–	–	100	
Acetovanillone (μg L^{-1})	–	–	200	