Technical note

How much do potential precursor compounds contribute to 'reductive' aromas in wines post-bottling?

Introduction

The formation of unpleasant reductive aromas in wines is an issue of concern to many winemakers. While the compounds responsible for reductive aromas are well known, and the understanding of their formation from precursors during fermentation is improving, how they form in wine post-bottling remains to be determined. A recent study evaluated a number of potential precursor compounds, including sulfur-containing amino acids, glutathione, thioacetates and disulfides, to assess their role in the formation of two key reductive aroma compounds (hydrogen sulfide (H_2S) and methanethiol (MeSH)) in white and red wines post-bottling (Bekker et al. 2017).

Evaluating precursor contributions to H_2S and MeSH concentrations post-bottling

The potential precursors chosen for evaluation were cysteine (Cys) and glutathione (GSH), which are known to release H_2S during fermentation (due to yeast activity), and methionine (Met), methylthioacetate (MeSAc), and dimethyldisulfide (DMDS), which have been suggested as precursors to MeSH. Commercially bottled red (Shiraz 2010, Cabernet Merlot 2014) and white wines (Verdelho 2012, dry white wine 2014) were obtained from local wineries. The concentrations of Cys, GSH, Met, MeSAc, and DMDS were measured in the base wines. Additions of the precursors were then made (as separate treatments) to the wines giving concentrations considered above average or high (Cys 8 mg/L, GSH 18 mg/L, Met 8 mg/L, MeSAc 50 µg/L, DMDS 50 µg/L, respectively). The role of copper in the release of reductive aroma compounds was also assessed, with additions made to the base wines and the wines with added precursor compounds at levels giving final concentrations of 1.0 mg/L (Cys and GSH experiments to release H_2S) and 0.5 mg/L (Met, MeSAc and DMDS experiments to release MeSH).

The concentrations of H_2S and MeSH in the wines were monitored over a 12-month storage period. The molar % yield of H_2S and MeSH from each of their respective precursors was also calculated.

Production of H_2S from cysteine and glutathione

The amount of H_2S produced post-bottling in the wines to which Cys or GSH had been added was low relative to the amount added (Figures 1a, 1c), as well as compared to the amount

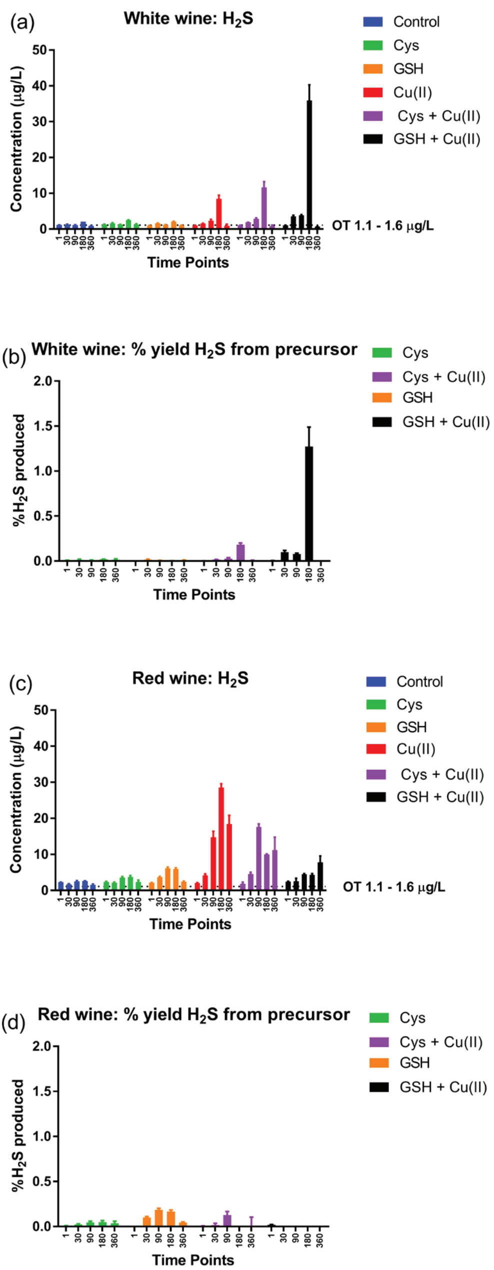

Figure 1. Concentration and percentage yield of hydrogen sulfide (H_2S) produced post-bottling from cysteine (Cys) and glutathione (GSH), with and without the addition of copper, in white and red wines. Odour threshold (OT) of H_2S is indicated on Figure 1a and 1c.

of H_2S often produced from Cys and GSH due to yeast activity during fermentation. Elevated Cys and GSH concentrations in bottled white or red wines did not produce substantially higher concentrations of H_2S than the control wines with no added Cys or GSH (Figures 1a, 1c). The % molar yield of H_2S from Cys and GSH in the red wines was relatively low, with a maximum % H_2S yield of 0.05% and 0.18%, respectively, produced in the red wines (Figures 1b, 1d).

When copper was added to the base wines (without any additional potential precursors), the formation of H_2S was increased (Figures 1a, 1c), which suggests that a pool of yet to be identified precursor compounds may also be involved in determining final H_2S concentrations in wine, through copper-assisted reactions. However, only for the white wines did the combination of GSH and copper produce substantially greater concentrations of H_2S than copper alone (Figure 1a). This was also reflected in the % molar yield of H_2S from GSH when GSH was added to white wine in combination with copper (Figure 1b), in which case the combined GSH + copper treatment yielded a maximum of 1.3% H_2S.

There were significant differences in H_2S accumulation between the white and red winest. Interestingly,

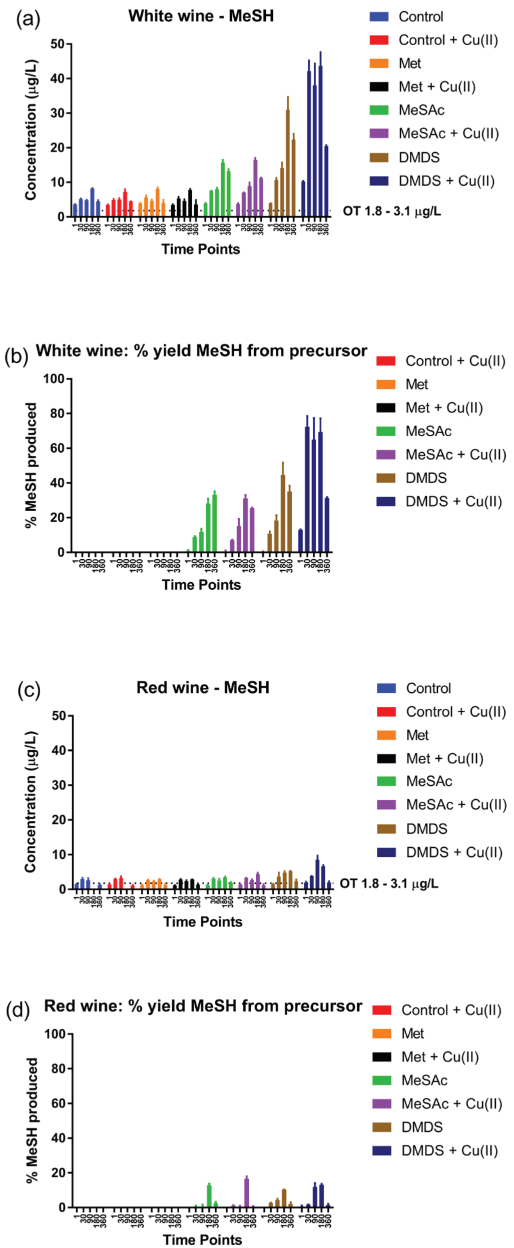

Figure 2. Concentration and percentage yield of methanethiol (MeSH) produced from methylthioacetate (MeSAc), methionine (Met), and dimethyldisulfide (DMDS), with and without the addition of copper, in white and red wines. Odour threshold (OT) of MeSH is indicated on Figure 2a and 2c.

lower H_2S concentrations were seen in red wines when Cys or GSH was present in combination with copper compared to wines with only added copper. This could be the result of interactions between copper, H_2S, Cys, GSH, and other wine compounds, such as polyphenols, quinones, and tannins. The decrease in H_2S concentrations in the red wines may also be the result of the formation of asymmetrical disulfides or polysulfanes produced from Cys/GSH reacting with H_2S, which effectively form a 'sink' for H_2S. A role of polysulfanes in modulating the concentrations of certain volatile sulfur compounds post-bottling has recently been proposed by Kreitman et al. (2017). The observed increases in H_2S concentrations from added GSH, albeit small in some instances, may still have important impacts on wine aroma, considering that H_2S has a low aroma threshold and small increases in H_2S may have large impacts on wine aroma and quality.

Production of MeSH from methylthioacetate and dimethyldisulfide

Of the three potential precursors to MeSH that were evaluated (DMDS, MeSAc, and Met), only additions of DMDS and MeSAc were found to contribute significantly to free MeSH concentrations in the wines post-bottling (Figures 2a to 2d).

MeSAc gave a maximum MeSH yield of 33% (13 µg/L) in the white wines and 13% (3.4 µg/L) in the red wines (Figures 2a to 2d). DMDS gave a maximum MeSH yield of 44% (30 µg/L) in the white wines, and a maximum MeSH yield of 10% (5.3 µg/L) in the red wines (Figures 2a to 2d). It is important to note that the amount of MeSH produced was approximately 17 times greater than its aroma threshold in the white wines, and approximately 3 times greater than its aroma threshold in the red wines (1.8 – 3.1 µg/L, Siebert et al. 2010).

The presence of copper did not increase MeSH formation from MeSAc; however, it significantly increased the formation of MeSH from DMDS, particularly in white wines. The combination of copper with DMDS gave a maximum MeSH yield of 72% (44 µg/L) in the white wines, and a maximum MeSH yield of 13% (8.5 µg/L) in the red wines (Figures 2a to 2d).

The accumulation of MeSH was remarkably different between white and red wines, with greater concentrations of MeSH measured in the white wines than in the red wines (Figures 2a, 2c). This difference in MeSH accumulation may also reflect interactions between copper, MeSH, and other red wine compounds, such as polyphenols, quinones, and tannins, as was suggested for H_2S.

These results showed that thioacetates, such as MeSAc, and disulfides, such as DMDS, have the potential to significantly affect wine aroma when present in wines post-bottling, either through their direct impacts on wine aroma when present above their aroma thresholds, or through their potential to convert to MeSH in yields up to 33% in the case of MeSAc, and up to 70% for DMDS in the presence of copper (Figure 2b).

Conclusions

This study indicated that elevated post-bottling concentrations of Cys and Met did not pose a risk for the development of high concentrations of H_2S or MeSH. Results supported previous work (Ugliano et al. 2011), which showed that elevated levels of GSH, especially when in the presence of copper, posed a slight risk for H_2S formation in wines post-bottling. Both MeSAc and DMDS were found to play important roles in MeSH formation, with up to 20% conversion of MeSAc to MeSH and up to 70% conversion of DMDS to MeSH. Furthermore, the presence of copper significantly affected the abilities of GSH and DMDS to release H_2S and MeSH.

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