THIOL STABILITY DURING PROCESSING

The fermentation thiols 3MH and 3MHA are important flavor compounds in certain styles of white wines and are responsible for much of the tropical and citrus fruit aromas in Sauvignon blanc and Chenin blanc. They also form part of the fruit aromas in Cabernet Sauvignon, Merlot, Shiraz and Grenache, as well as other white varieties such as Riesling, Pinot gris and Gewurztraminer.

The main thiols are 3-mercaptohexan-1-ol (3MH) and 3-mercaptohexylacetate (3MHA):

<table>
<thead>
<tr>
<th></th>
<th>Aroma</th>
<th>Sensory Threshold</th>
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<tbody>
<tr>
<td>3MH</td>
<td>Passionfruit, grapefruit</td>
<td>60ng/L</td>
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<tr>
<td>3MHA</td>
<td>Passionfruit</td>
<td>4ng/L</td>
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<tr>
<td></td>
<td>Cat urine/sweaty at higher levels</td>
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The thiols are released during fermentation by yeast from their non-odorous precursors which are found in the grape. The manner in which grapes and juice are handled in the vineyard and the winery, yeast strain selection, and fermentation temperature will all contribute to the levels of thiols released into the wine during fermentation.

The thiols are highly susceptible to oxidation reactions. These reactions result in a loss in thiol aroma and flavour both during non-reductive winemaking processes and over time during normal maturation. The decrease in thiol levels is due to polyphenol oxidation, catalyzed by metals, a process that can be inhibited by reductive winemaking and the use of antioxidants such as sulfur dioxide (SO₂), ascorbic acid, and glutathione.

Research from New Zealand has shown that 3MHA is the least stable of the thiols. Levels of 3MHA were shown to have decreased in commercial wines by 20-45% three months after bottling. After one year in the bottle, levels of 3MHA were largely negligible.

3MH was found to be more stable, with levels decreasing by up to 10% three months after bottling, and up to 40% one year after bottling.
3MHA may also be converted into 3MH by hydrolysis, resulting in decreases in 3MHA and corresponding increases in 3MH.

In our small trial during the 2016 harvest, we attempted to measure the decrease in thiol levels at each critical winemaking point i.e. after fermentation, after SO2 additions, after racking, after stabilisation and after bottling.

Our results:

- Significant decreases in thiol levels were observed from the end of fermentation till after bottling.
- Thiol levels at the end of fermentation were between 600-1400mg/L for 3MH and between 500-1600 mg/L for 3MHA.
- Thiol levels after bottling were between 400-1100mg/L for 3MH and between 200-600 mg/L for 3MHA.
- From the end of fermentation till after bottling:
  - 3MH levels decreased by between 20-35%
  - 3MHA levels decreased by between 50-65%
- The largest decreases occurred during protein and cold stabilisation:
  - 3MH decreased by between 15-30%
  - 3MHA decreased by between 15-35%
- Smaller decreases were observed during bottling:
  - 3MH decreased by between 0-20%
  - 3MHA decreased by between 10-40%.
  - Oxygen management practices during bottling vary widely between wineries and thus these lower decreases at bottling may not be representative of the wider wine industry.
- An addition of just 1mg/L CuSO4 to one of the samples post bottling saw a decrease of 40% in 3MH and of 50% in 3MHA.
Some things to note:

- Sampling wines-in-production to exclude all oxygen and preserve the integrity of the sample can be difficult. Extreme caution in taking samples is required in order to obtain meaningful results.

- Attempting to get relevant thiol results before SO2 additions, i.e. directly after fermentation, is nearly impossible. In all our results, the thiols had been significantly oxidised in these pre-SO2 samples.

Conclusions:

- There is a much larger pool of thiols in wine directly after fermentation than what we find post bottling.

- The use of SO2, ascorbic acid and glutathione-containing products and working reductively, especially during wine stabilisation and at bottling will help preserve more of the thiols.

References:

