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Thiols: From Harvest to Bottle

Making the most of winemaking practices that enhance fruit aromas

by Russell Moss

Research has confirmed that machine-harvested fruit has higher concentrations of thiols.

The old adage "great wines start in the vineyard" is indeed true. However, perhaps a more accurate statement would be: "Great wines start in the vineyard and end on the palate." The truly great wines of the world come from close attention to detail in both the vineyard and the winery.

I reviewed the viticultural techniques that grapegrowers can use to enhance positive tropical fruit aromas in wines from certain cultivars in the June 2015 issue of Wines & Vines. In this article, I will explore how winemakers can further enhance the positive varietal aromas coming from thiols through practices from harvest to bottle.

It’s important to point out that a “thiol” is any organic compound that contains a sulfyhydryl (-SH) group; therefore, an off-aroma such as methyl mercaptan is also considered a thiol. However, for the purposes of this article, “thiols” refers to three important compounds that confer specific, pleasant aromas to wines. The three positive thiols of most interest are shown in the table on page 123, along with abbreviations and corresponding descriptors.

KEY POINTS

- Aromatic grape varieties should be harvested at cooler times of the day ?and by machine, if possible, in order to conserve volatile thiols.
- Cold soaking must treated with SO2 and pressing in an anaerobic environment may maximize the wine's aromatic potential and minimize the negative effect of oxidation.
- Specific yeast strains have been identified that produce wines with high ?concentrations of volatile thiols. Yeast rehydration also may help to boost ?the wine's aromatics.
- Aromatic wines do well when packaged using screwcaps or synthetic corks that restrict oxygen ingress.

Thiols are an extremely important varietal aroma class (i.e., aromas arising from the grape itself) and are responsible for some of the pleasant tropical fruit aromas that are intrinsic to varieties such as Petit Manseng, Sauvignon Blanc, Cayuga White, Riesling, Sémillon and Gewürztraminer. The threshold of detection of these aromas is in the parts per trillion range. To put that in perspective, the thiol with the highest threshold of detection, 3-mercaptohexan-1-ol (3MH), could be perceived in an Olympic-sized swimming pool if you were to dose it with a mere 0.15 grams of 3MH, according to research from Carien Coetzee and W.J. du Toit.

In Petit Manseng, a grape of increasing importance in the southeastern United States, Takatoshi Tominaga found 3MH to be at a concentration that was about 75 times greater than the perception threshold of this compound. To my knowledge, the development of an analytical method and a survey of wines has been the only public research conducted upon this important aromatic class in the United States.

The exact origin of the volatile thiols in wine continues to elude the scientific community. They are present as non-volatile amino acid conjugates in the juice, and they also seem to be produced during fermentation. However, Farhana R. Pinu discovered there is no correlation between the concentration of amino acid conjugates and the volatile thiols produced in the resulting wine. The current theory from Nina Duhamel is that sulfonic acids in the must may act as precursors, which are then reduced during fermentation to form their corresponding volatile thiol. This area of wine science offers a wealth of possibilities for potential discovery.

Regardless of the origin of thiols, research and experience has elucidated vineyard and winery practices that can increase their concentrations in the resulting wine.

Harvesting methods

New Zealand Sauvignon Blanc is known to contain some of the highest concentrations of volatile thiols of any wine in the world, according to Frank Benkwitz. Most of the Sauvignon Blanc in Marlborough, N.Z., is harvested with machines out of necessity. This is fortuitous, as it has been demonstrated by several researchers that machine harvesting of fruit results in higher concentrations of volatile thiols in wines compared to wines made from hand-harvested fruit. Thomas Allen hypothesized in 2011 that an increase in enzymatic activity in “damaged” machine-harvested fruit may play a role in the formation of thiol precursors, which might explain the increase in volatile thiols in the resulting wine.

The time of day at which the fruit is harvested also may play a role in the concentration of thiols in the resulting wine. Oxidation will occur faster in warmer juice than cooler juice. This oxidation can then lead to loss of aromatic potential by the volatile thiols, as it can lead to formation of quinones, which will oxidize the volatile thiols after fermentation, Allen said. Therefore, harvest should be conducted in the cooler periods of the day in order to minimize oxidation.

Cold soak

In other growing regions, such as

11 WAYS TO MAXIMIZE

the eastern United States, machine harvesting is not commonly practiced. However, winemakers can try to mimic the effect of machine harvesting through the use of cold maceration. The only studies I know to have evaluated the impact of a traditional cold soak on thiol concentrations have simply measured the amino acid-conjugated thiols in the must. The conjugated thiols tend to increase in must that has had a cold soak. However, because the conjugated thiols in juice represent less than 10% of the final volatile thiol concentration in wine, the results from these studies can't be extrapolated to final wine.

For a study using a novel cryogenic maceration technique, Sauvignon Blanc was harvested, crushed and underwent a cold soak at -4° F (-20° C) using dry ice. Upon reaching -4° F, the must was allowed to warm over a 24-hour period to ambient temperature before it was pressed and vinified. In this study, concentrations of volatile thiols in wines made from hand-picked/cryogenically macerated fruit were greater than those measured in wines made from machine-harvested fruit. Through sensory analysis, the wines made from hand-harvested fruit were found to be less aromatic than the wines of machine-harvested fruit. However, no discernible sensorial difference was seen between the wines made from machine-harvested fruit and cold-soaked musts, according to university researcher Kenneth J. Olejar. Further research is needed to

AROMATIC THIOLS

Employing the following strategies can help winemakers maximize the aromatic potential of thiol-driven varieties from harvest to bottle. 1. Harvest during cooler hours of the day.

2. Use a brief cold soak (no more than 24 hours).

3. Add 50ppm of SO_2 to the must before cold soak and pressing.

4. Maintain a relatively reductive environment at all stages (ensure adequate O_2 in must for healthy fermentation).

5. Avoid long/high-pressure cycles.

6. Choose a yeast strain known to produce high concentrations of thiols.

7. Rehydrate yeast with a complex organic rehydration nutrient.

8. Avoid or m inimize the use of DAP.

9. Use fermentation temperatures around 18°-20° C.

10. Avoid copper fining.

11. Bottle under screwcap or technical cork.

determine the efficacy of cold soaks as a means to increase the aromas coming from thiols.

Regardless of whether or not volatile thiols increase with skin contact, they may increase reduced glutathione (GSH) concentrations in the resulting wine. GSH is a naturally occurring antioxidant in grapes and is found in especially high concentrations in Sauvignon Blanc. In wine, it can react with quinones, which can oxidize the volatile thiols, thereby depressing their aromatic impact. GSH can also preserve esters, terpenes and wine color during aging, according to multiple studies.

A recent study of Sauvignon Blanc by Alexandre Pons found that skin contact of only 18 hours increased the GSH concentration in the must up to 55% more than in the initial concentration. Results were highly variable between batches, but they always showed a higher glutathione concentration with skin contact. The same study found the GSH concentration to be highest in the cold-soaked must after only 30 minutes. After 30 minutes, the concentration of GSH decreased. This phenomenon occurs because most GSH is found in the skins of the grape. Therefore, even if cold soak doesn't increase the volatile thiol concentration in a wine, it may help to preserve their aroma through an increase in GSH. It is advisable to conduct a cold soak under CO2 and with the addition of SO2 in order to deactivate polyphenol oxidases and minimize oxidation, thereby allowing for the maximum retention of GSH, according to W.J. du Toit.

Anti-oxidant additions

The concentration of conjugated thiols is known to increase during the oxidation of juice, according to a study by Aurélie Roland. However, the volatile thiols in wine are easily oxidized. Polyphenol oxidases may cause phenols such as caftaric acid and catechins to oxidize into quinones, which can cause the rapid oxidation of thiols during fermentation. Therefore, wines made from musts that have been treated with an addition of

50ppm of SO_2 are likely to have higher concentrations of aromas arising from volatile thiols, research from Carien Coetzee reveals.

It's worth noting that adding ascorbic acid prior to fermentation may provide additional protection against oxidation, as it is a more powerful reducer of quinones than SO_2, according to a 2014 study by Maria Nikolantonaki. Ascorbic acid additions warrant further research with regard to their use in the production of high-quality, thiol-driven wines, as the study by Nikolantonaki was performed in a model wine. It should be noted that ascorbic acid is unpredictable and can lead to the formation of pigments that SO_2 can't prevent. It also has been implicated in the formation of sotolon, a compound that produces a maple syrup-like aroma in prematurely aged white wines.

Pressing

Oxygen seems to be the arch-enemy of the volatile thiols. As mentioned previously, oxygen inclusion during the juice stage will lead to a depression in the final concentration of GSH. Less GSH in the wine may leave thiols more vulnerable to oxidation by quinones. Therefore, pressing should be conducted under a reductive environment with carbon dioxide or nitrogen gas in order to preserve volatile thiols.

With increasing pressure, one can extract more conjugated thiols in the press. However, with higher pressure, one will begin to extract more phenols, which can then oxidize to form quinones. The quinones will react with glutathione, thereby leaving the thiols more vulnerable to oxidation, according to research by Manu Maggu of New Zealand. Consequently, it's worth adding SO_2 prior to pressing, as well as pressing in an anaerobic environment in order to inhibit the polyphenol oxidases and maximize aromatic potential of the volatile thiols.

Yeast strain

Various yeast strains have been demonstrated to produce wines with increased concentrations of volatile thiols. As the origin of the volatile thiols is not fully understood, it is not known entirely why some yeast strains result in wines with more volatile thiols than other strains. However, it is known that an enzyme (β-lyase) is responsible for the cleavage of the carbon-sulfur bond between the non-volatile amino acid/thiol conjugates. As the conjugated thiols can account for 10% of the volatile thiols, increased β-lyase activity can lead to higher thiol concentrations in wines.

Multiple studies report that yeast strains such as Levuline ALS, Zymaflore VL3, Anchor VIN 13 and Uvaferm SVG have demonstrated a remarkable ability to produce wines with high concentrations of volatile thiols. Interestingly, a co-fermentation of Pichia kluyveri and Saccharomyces cerevisiae was demonstrated by Nicole Anfang to significantly increase concentrations of 3MHA in the resulting wine. Currently, CHR Hansen markets a commercial P. kluyveri strain that can be directly inoculated (no rehydration needed) and followed by a S. cerevisiae strain after the consumption of about 8° Brix.

Yeast nutrition

The amino acid-conjugated thiols in the juice are metabolized by yeast, and the carbon-sulfur bond between the amino acid and the thiol is cleaved by an enzyme known as β-lyase. The addition of diammonium phosphate (DAP) can interfere with the pathway that regulates amino acid transport and, in turn, this can lead to wines with a lower volatile thiol concentration. This phenomenon is known as nitrogen catabolite repression (NCR).

The use of Laffort's Dynastart, a yeast rehydration that is made of yeast autolysates and inactivated yeast, has been shown to lead to wines with higher concentrations of volatile thiols than wines made from yeast rehydrated with DAP.

However, both the organic and inorganic rehydration regimes had greater thiol concentrations than the control, which had no nutrient additions during fermentation, according to a paper by Gal Winter.

Fermentation temperature

Higher fermentation temperatures have been demonstrated to increase volatile thiols in wine. However, important aromas that are intrinsic to many white wine styles are lost at higher fermentation temperatures.

Therefore, a fermentation temperature of 18°-20° C (64°-68° F) is recommended in order to obtain the greatest concentration of volatile thiols while still retaining some of the pleasant aromas produced during wine fermentation.

Fining

Thiols contain a –SH group. As such, when a winemaker adds copper to a final wine to remove sulfides, he or she will also be removing the volatile thiols. This loss occurs because the copper can bind with the sulfhydryl group of thiols and form copper sulfate, which will settle out. Copper can also directly cause thiols to oxidize into disulfides, according to Maurizio Ugliano. Fungicides that contain copper can also be responsible for residual copper in the must. In order to remove any residual copper from must, winemakers can use an adsorbant copolymer known as polyvinyl imidazole-polyvinylpyrrolidone (PVI/PVP), according to research by Helena Mira. Enartis Vinquiry recently released two PVI/PVP products in the United States.

Closures

The permeability of wine packaging to oxygen is an important factor in conserving aromas. It is well known that screwcap and technical corks are two of the most impermeable closures currently on the market. While screwcaps have been linked to reductive aromas, one can minimize the risk through encouraging a healthy fermentation and making sure the pre-bottle SO2 addition is not in excess of what is needed.

Paulo Lopes found that the Saranex liner, which consists of layers of low-density polyethylene and Saran, has been found to minimize the reductive aromas and preserve wine aroma. A crucial component of the Saranex liner is low-density polyethylene, which may play a direct role in minimizing the reductive aromas by scalping the unpleasant volatile sulfur compounds, according to research by Maria Silva. The potential for reductive aromas to arise under screwcap can be minimized by encouraging a healthy fermentation, allowing greater ullage (headspace) at bottling and by making efficient (rather than excessive) SO_2 additions, according to a doctoral paper written by Evdokia Dimkou.

Conclusion

Although the origins of volatile thiols remain elusive, there are production methods that are known to increase, preserve or decrease their aromatic impact. With the information presented here and in the previous article related to vineyard practices, the vintner can devise a “vine-to-bottle” management strategy to maximize the expression of these pleasant varietal aromas.

A graduate of Lincoln University in New Zealand, Russell Moss is pursuing a master’s degree in viticulture and a master’s degree in enology at Virginia Polytechnic Institute and State University in Winchester, Va. His major advisor is Dr. Tony Wolf, professor of viticulture. Moss is currently investigating how foliar nitrogen and sulfur sprays impact volatile thiols in Sauvignon Blanc and Petit Manseng.