



Consumption of Damascenone in Wine by SO₂

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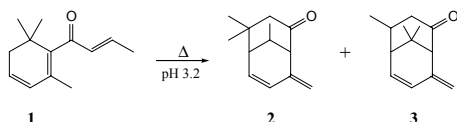
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Introduction

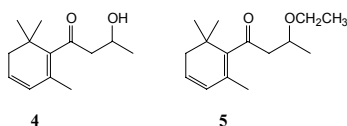
Damascenone (**1**) has been identified as one of the most important aroma compounds in wine, contributing positively to the fruity aroma of varieties such as Merlot and Cabernet Sauvignon. It is known to form in microgram per litre quantities mainly during fermentation, with the concentration then falling off by approximately 75% in only four months.¹ With an aroma threshold of 50 ng/L (model wine), losses can lead to significant changes in wine aroma and therefore quality. The interaction of damascenone with the wine matrix, including natural and added nucleophiles, was studied to try to account for the observed loss.

Loss due to wine conditions

Loss purely due to the wine matrix - an acidic, 10-15% ethanolic aqueous medium, was studied by heating damascenone (**1**) in a model wine (10% ethanol, buffered at pH 3.2). A decrease in damascenone was observed and the two major products were identified as **2** and **3**, by NMR, mass spectrometry and by X-ray crystallography of their 2,4-dinitrophenylhydrazone derivatives. Compounds **2** and **3** had previously been tentatively identified when damascenone was heated with p-TsOH.²



To determine whether these compounds also form under normal wine conditions, the experiment was repeated at room temperature. The same two products were identified by GC-MS. Damascenone was also found to react with water and ethanol to form **4** and **5**, respectively.



The combined rate of consumption of damascenone via the above two processes at room temperature was found to be too slow to account for the loss observed in young wines (Figure 1).

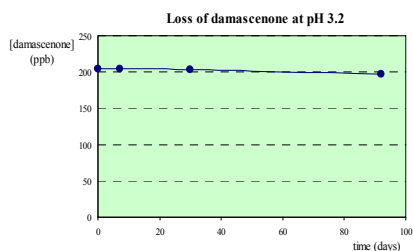


Figure 1

Loss due to reaction with nucleophiles

There are various nucleophiles present in wine - amines, thiols, alcohols, amino acids, acetate, tartrate and many more. These can theoretically react with damascenone to convert it into compounds with little or no aroma. Figure 2 shows a variety of nucleophiles and their effect on the concentration of damascenone, at 45°C, in model wine. Most nucleophiles were seen to react slowly, with the exception of SO₂, which was studied further.

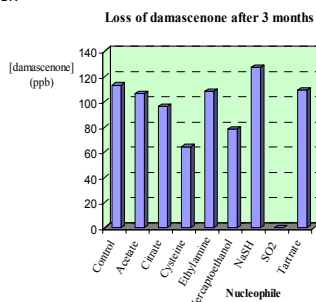


Figure 2

Consumption by SO₂

A detailed study into the consumption of damascenone by SO₂ was conducted, with emphasis on the effect of pH, SO₂ concentration and temperature. A solution of damascenone (1 mg/L) in model wine was reacted with free SO₂ (80 or 200 mg/L), at either pH 3.2 or 3.4, and at room temperature or 45°C. The rapid decrease in damascenone concentration could clearly be seen at room temperature, with the major rate-determining factor being the added SO₂ (Figure 3). The rate of consumption was independent of pH.

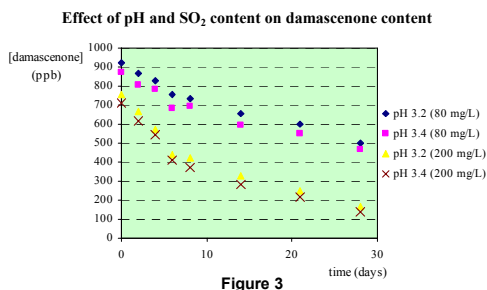
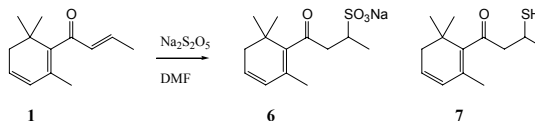


Figure 3

Based on experimental data, the structure of the damascenone-SO₂ adduct was assigned as **6**. The structure was confirmed by LC-MS and also by conversion to the known thiol **7**.



To confirm that this product **6** would form under wine-like conditions, a solution of damascenone (100 mg) in model wine (500 mL) with 100 mg SO₂ was stirred at room temperature for 4 weeks. The products were then extracted and analysed; the sulfonic acid derivative **6** was identified by NMR as the major product.

Conclusion

The loss of damascenone observed in young wines can be attributed to a variety of causes, including reaction with the wine matrix or various nucleophilic species. However, these play a minor role compared to the effect of sulfur dioxide. SO₂ was seen to decrease the concentration of damascenone in model wine rapidly by converting it to a sulfonic acid derivative. This is an unusual reaction, as SO₂ would usually react with the carbonyl group of such compounds, rather than at the alkene site. Further studies need to be undertaken to determine the rate of damascenone consumption when other compounds that also react with SO₂ are present.

References

1. Guth, H. 'The Chemistry of Wine Flavor' (ACS Symposium Series Nr. 714), Eds A.L. Waterhouse and S.E. Ebeler, ACS, Washington D.C. 1999, pp 39-54.
2. Demole, E.; Enggist, P. *Helv. Chim. Acta*, 1976, 59, 1938-1943.