Thiol and 2-Alkenal Reactions in Grape Juice Media to Form Aroma Precursors in Wine: The Impact of pH, Temperature, and SO₂

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Introduction

The volatile polyfunctional thiol 3-sulfanylhexan-1-ol (3SH) is a key odorant for the varietal aroma of Sauvignon blanc wine, imparting desirable grapefruit and/or passionfruit skin aromas [1]. During fermentation, yeast produces 3SH from grape-derived precursors including 3-5-cysteinyl-hexanal (Cys-3MH) and 3-5-glutathionyl-hexanal (Glut-3MH). Cleavage of Cys-3MH via yeast β-lactase enzymes (step 1) release 3SH, with other enzymes responsible for converting Glut-3MH to Cys-3MH (step 5). Although the concentrations of these precursors are in ng/L amounts, less than 5% and 10% yields have been reported for Glut-3MH and Cys-3MH, respectively [2].

Trans-2-hexenal is conjugated enzymatically by glutathione in the grape berry (steps 1 and 2) but it has been proposed that Glut-3MH and Cys-3MH could also be formed chemically during grape processing via the intermediate 3-5-glutathionylhexanal (Glut-3MH) [2] and its bisulfite adduct form [3].

We aimed to determine whether the chemical reaction between glutathione and trans-2-alkenals in grape juice could occur at a significant rate in conditions relevant to grape juice processing, and to assess the impact of juice pH, temperature and sulfur dioxide on the formation rates of Glut-3MHal. Reaction products resulting from glutathione and trans-2-alkenals were also compared to those derived from cysteine and trans-2-alkenals and the presence of identified products were determined in five different white grape juices.

Methods

Additions of either glutathione or cysteine with respective trans-2-alkenals or hexanal, ascorbic acid, Cu(II), Fe(II), caffeic acid and/or SO₂

Sterile filtration and storage at 13 °C. Dilution with either water or acetaldehyde

Low resolution LC-MS/MS and high resolution LC-HRMS/MS analyses to determine reaction products

Impact of pH, temperature and other alkenals on Glut-3MHal formation and measurement of the formation of other thioester alkanals

Discussion and conclusions

The reaction between glutathione with various trans-2-alkenals produced the corresponding thioster alkenals, with the 5-glutathionyl unit of glutathione joining at the carbon-carbon double bond of the alkenals.

In the reaction between cysteine and trans-2-hexenal, a thioether is formed by the reaction of the ammonia moiety of cysteine with the aldehyde group of hexanal. This cyclizing does not occur for glutathione due to the retention of the functional aldehyde.

Appreciable amounts of Glut-3MHal (3 mg/L glutathione equivalents after 3 days of storage) was formed from the chemical reaction between glutathione and trans-2-hexenal under grape juice-like conditions, a timeframe relevant to grape processing.

Addition of SO₂ resulted in the formation of bisulfite adducts versions of the thioster alkenals, connected at the aldehyde group. Formation of the bisulfite adduct of Glut-3MHal was favoured over the free adduct form.

Glut-3MHal and its bisulfite adduct was detected in all white grape juices tested.

Addition of acetaldehyde to the juice resulted in the release of hydrogen sulfide from the bound aldehydes and an increase in free Glut-3MHal.

Methods to release the hydrogen sulfide adduct from Glut-3MHal could unlock this reservoir of bound precursor for the production of 3SH.

Acknowledgments

This research (NWG1401) was funded by a Charles Sturt University Research Fellowship Scheme through The National Wine and Grape Industry Centre (NWGIC).

References


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(Received 20 June 2016; revised 7 August 2016; accepted 9 August 2016.)