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Iron(III) Tartrate as a Potential Precursor of Light-Induced Oxidative Degradation of White Wine: Studies in a Model Wine System

Andrew C. Clark,[†] Daniel A. Dias,[*,‡] Trevor A. Smith,[‡] Kenneth P. Ghiggino,[‡] and Geoffrey R. Scollary[‡]

[†]National Wine and Grape Industry Centre, School of Agricultural and Wine Sciences, Charles Sturt University, Locked Bag 588, Wagga Wagga, New South Wales 2678, Australia

[‡]School of Chemistry, The University of Melbourne, Parkville, Victoria 3010, Australia

Supporting Information

ABSTRACT: The potential for iron(III) tartrate to act as a photoactivator in light-induced oxidative degradation of white wine is described. Using a tartaric-acid-based model wine system containing 5 mg/L iron, exposure to light from a xenon arc lamp led to the oxidative degradation of tartaric acid and the production of glyoxylic acid. The critical wavelength of light for the degradation process was found to be below 520 nm. No glyoxylic acid was formed in the absence of iron and/or light. Flint glass offered little protection from the light-induced photodegradation of tartaric acid. Antique Green glass offered more protection but did not stop the photodegradation process.

KEYWORDS: Iron(III) tartrate, photoactivation, degradation of tartaric acid, glyoxylic acid production, wine bottle color, white wine oxidation

INTRODUCTION

The role of iron in wine spoilage has long been recognized, although the outcomes attributed to iron-based chemistry differ. Iron casse is a phenomenon that may occur at iron concentrations above 15−20 mg/L.[1] In white wine, the casse is commonly insoluble iron(III) phosphate, and in some cases, the precipitate can also involve soluble proteins.[1] Improvements in vineyard and winemaking technologies have resulted in considerably lower iron concentrations, and this has resulted in a reduction in the occurrence of iron casse.

The second role that can be attributed to iron is an involvement in oxidative processes, often leading to enhanced coloration or browning, as it is sometimes known.[2] Iron and copper are the two most widely studied metal ions in relation to oxidative spoilage[3,4] because they have the capacity to activate molecular oxygen as well as catalyze the degradation of hydrogen peroxide to the hydroxyl radical.[5,6] However, the activity of metal ions to act as catalysts or mediators of oxidative spoilage processes will be dependent upon the chemical form or speciation of the metal ion.

Numerous methods have been employed for the measurement of iron speciation in wine, and many are summarized within the work by Ferreira et al.[7] The techniques have allowed for the quantification of free or weak complexes of iron(II) and iron(III), as well as the measurement of strongly bound iron complexes. In general, the results show that the iron speciation can vary considerably depending upon the wine analyzed and the technique adopted. For example, Costa and Araújo[8] analyzed 10 wines (i.e., red and white varieties) and showed that iron(III) varied over 25−75% of the total iron concentration. Alternatively, Tasev et al.[9] showed that no wines exceeded 15% iron(III), iron(II) ranged from 28 to 44%, and the remaining fraction was "organically bound Fe species." Weber[10] showed that, in a white wine containing 10.9 mg/L iron, only 1.4 mg/L could be found associated with the acid fraction of the wine and the majority of this iron (i.e., 70%) was bound to tartrate rather than malate or lactate. Finally, Paleologos et al.[11] showed that a fraction of iron in wine exists as an insoluble complex with tannins and other related compounds, whereby 1−7% and 6−23% of the total iron concentration was found in these forms in white and red wines, respectively.

The role of iron in the degradation of tartaric acid was described by Fenton in 1894. The combination of iron(II) and hydrogen peroxide, now commonly referred to as Fenton chemistry, produces the hydroxyl radical as well as iron(III).[12] Various degradation products have been described.[13−15] However, the concentration of iron(II) used in these studies was around 50 mg/L (1 mM), about 10-fold higher than the upper limit of iron in wine. More recently, Elias and Waterhouse[16] have examined some of the factors that influence Fenton chemistry under wine-like conditions, although the focus was not specifically on iron chemistry.

A link between the presence of iron and enhanced coloration of model white wine systems was proposed.[17] Oxidative degradation of tartaric acid to form glyoxylic acid with a subsequent reaction of glyoxylic acid with catechin-type phenolic compounds was shown to lead to the formation of xanthylium pigments,[17,18] via a carboxymethine-linked catechin dimer intermediate.[19] In white wine and model wine systems, these glyoxylic-acid-derived pigments contribute to the brown coloration indicative of oxidative spoilage.[20,21] The presence of iron(II) in the model wine systems was observed to accelerate the formation of xanthylium pigments,[4] which led to speculation

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that iron was capable of enhancing the oxidation of tartaric acid.[22] Almost all studies have used added iron(II), and there has not been any attempt to assess the Fe^{II}/Fe^{III} redox status under the aerobic conditions of the experiments describing pigment production.[22]

Clark et al. described the sunlight-induced degradation of tartaric acid to give glyoxylic acid.[23] It was argued that trace contamination of the tartaric acid solution by iron was the basis for the initiation of the photodegradation process. A mechanism for the degradation of tartaric acid via photochemical and Fenton chemistry processes was proposed,[23] and the impact of ethanol and copper(II) ions on the production and stability of glyoxylic acid was described. However, there was no attempt to identify the critical wavelength required for the proposed light-induced photodegradation.

The photoactivity of iron(III) tartrate is well-established, with its application to photography being recognized for more than 100 years.[24] Abrahamson et al. examined the photochemistry of iron(III) carboxylate complexes in some detail.[25] While focusing on iron(III) citrate, the authors reported that iron(III) tartrate showed marked photoactivity in the pH range of 2.7−4.0. The work by Abrahamson et al. used a high Fe(III)/carboxylate ratio, the opposite to the situation in wine.[25] However, the combination of the work by Clark et al. and Abrahamson et al. suggested that the photochemistry of iron(III) tartrate would benefit from further study to determine if it was a potential means of initiating light-induced pigment formation.

This study investigates the impact of iron(III) on the generation of glyoxylic acid from tartaric acid in a model white wine system under controlled temperature and light conditions. The specific focus was the determination of the critical wavelengths for photoactivation leading to the formation of glyoxylic acid. Furthermore, the capacity of two types of glass bottles (clear and dark green) to protect or limit the photodegradation of tartaric acid to glyoxylic acid is also discussed.[23,25]

MATERIALS AND METHODS

Reagents and Apparatus. All items of glassware and plasticware were soaked for at least 16 h in 10% nitric acid (BDH, AnalaR) and then rinsed with copious amounts of grade 1 water (ISO3696). Solutions and dilutions were prepared using grade 1 water. Potassium hydrogen L-(+)-tartrate (>99%) and L-(+)-tartaric acid (>99.5%) were obtained from Sigma-Aldrich (St. Louis, MO). Iron(II) sulfate heptahydrate (>98%) and ethanol (AR grade, >99.5%) were purchased from Ajax Fine Chemicals (Australia).

Ion-exclusion chromatography (IEC) was conducted using a Waters (Milford, MA) 2690 Separation Module, run by Millennium[32] software that was connected to a Waters 2996 photodiode array (PDA) detector. The chromatography was performed on a 300 × 7.8 mm Aminex HPX-87H organic acid analysis cation-exchange column (Bio-Rad Laboratories, Australia). The IEC analyses were carried out with a sample injection of 10 μL, column temperature of 25 °C, and flow rate of 0.5 mL/min, with an isocratic elution of 19% aqueous acetonitrile with 5 mM sulfuric acid. Detection of glyoxylic acid was performed at 210 nm, and it was quantified via an external calibration graph.

IEC with both PDA and mass spectrometry (MS) detection was conducted using Agilent 1200 Series Triple Quadrapole (6410) high-performance liquid chromatography (HPLC)−MS. The column and liquid chromatography (LC) conditions were as described above, except that the isocratic solvent was 0.5% acetic acid in water. MS was operated at 350 °C, gas flow of 9 L/min, nebulizer at 40 psi, and capillary at 4 kV. MS analyses were carried out in the negative-ion mode, with the fragmentor at 80 V and scanning from m/z 60 to 300.

Glass Bottles. Wine bottles (Claret punted, 750 mL) were used in this research. The bottles are designated here by their trade names to describe their color: Flint (clear, FG) and Antique Green (dark brown/green, AG). Both traditional weight and newer lightweight bottles were used. The corresponding bottle thicknesses were used (where n = number of replicate measurements for the same glass type; numbers in parentheses are standard deviations): Flint [heavyweight, 3.18 (0.54) mm; n = 12], Flint [lightweight, 2.05 (0.44) mm; n = 9], Antique Green [heavyweight, 3.03 (0.44) mm; n = 12], and Antique Green [lightweight, 2.25 (0.33) mm; n = 9].

Model Wine Base Systems. The model wine base was prepared by the addition of 0.011 M potassium hydrogen tartrate and 0.007 M L-(+)-tartaric acid to 12% (v/v) aqueous ethanol and stirring overnight before use. The pH of these solutions was 3.2 ± 0.1.[26] Standard solutions (5 mg/L) were prepared from stock solutions of 100 mg/L iron(II) by adding iron(II) sulfate to the model wine base when required.

Small-Scale Irradiation Setup and Exposure Studies. The various wine base samples were placed in a quartz cuvette (effectively transmissive above 200 nm), sealed with a Teflon stopper, and placed in the cell holder of a Cary Bio50 UV/vis spectrophotometer. The cuvette was maintained at 45 °C using a CARY single-cell Peltier accessory during a 30 min irradiation time. This temperature was chosen because it is routinely used in wine oxidation studies for the accelerated aging of wine[23,27] and also because no increase in the sample temperature, as a result of radiant heat from the xenon lamp, occurred during the irradiation period because the temperature of the wine in the cuvette was maintained in the CARY single-cell Peltier accessory at 45 ± 1 °C.[23] A high-pressure xenon arc lamp (XBO 150 W1) installed in a Rofin fan-cooled housing fitted with a collimating lens was placed 145 mm away from the center of the cuvette, and the light was directed through a 1 × 2 cm window onto the cuvette (Figure S1 in the Supporting Information). The total light intensity reaching the cuvette was measured to be approximately 0.60 W. Short-arc, high-pressure xenon arc lamps have an emission spectrum closely approximating noon sunlight, with an equivalent flux of ∼0.6 W/m^2. Sections of glass cut from wine bottles were used as filters and were placed directly in front of the cuvette holder window as shown in Figure S2 in the Supporting Information to simulate a sample of wine in a bottle. Ultraviolet (UV) and visible light and selected visible light filters used in the light irradiation studies were placed between the xenon arc lamp and the model wine sample in the cuvette (see Figure S2 in the Supporting Information for layout). The filters used are as follows: visible radiation (λ > 400 nm) (UF 12), UV light (λ 300−400 nm) (5543a), and a yellow filter (λ > 520 nm) (3486). The production of glyoxylic acid following irradiation was monitored by IEC.

RESULTS AND DISCUSSION

Absorption Spectrum of the Model Wine Base Containing Added Iron. The iron concentration added to the model wine base in the experiments described here was 5 mg/L iron(II). This concentration of iron was chosen because it is typical of concentrations in wine.[28] The ratio of iron ions/tartaric acid was 0.005 (8.95×10^{-5} M Fe and 0.019 M tartaric acid). Upon the addition of iron(II) to the model wine base, the solution immediately exhibited a pale yellow color, indicative of iron(III) complexes with ligands containing oxygen donor atoms.[25] Although the iron was added as iron(II), its gradual conversion to iron(III) was evident in the oxidizing environment used here.[20,29]

The absorption spectrum of an iron/wine base solution is shown in Figure 1. The spectrum shows a well-defined absorbance peak

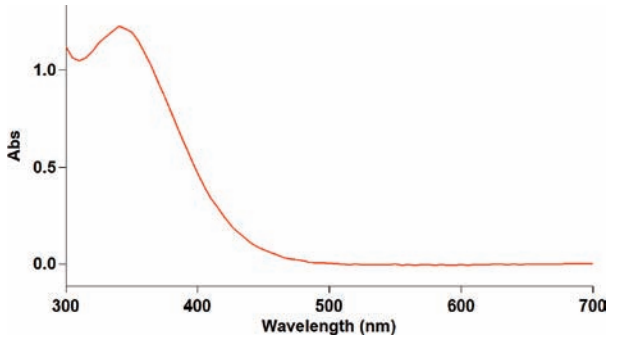

Figure 1. Absorption spectrum of the tartaric acid wine base containing added 5 mg/L iron(II).

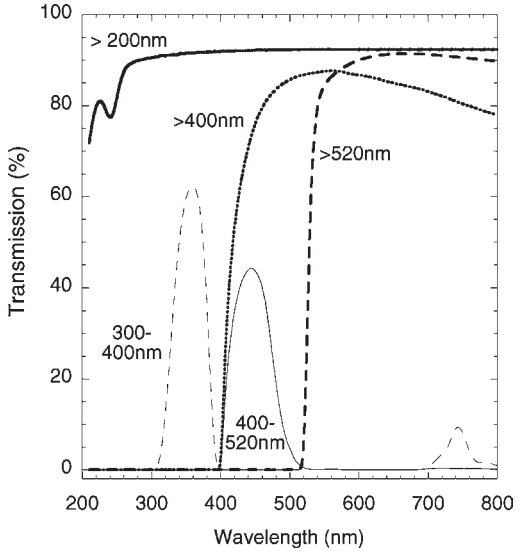

Figure 2. Transmission spectra for cutoff filters used in irradiation experiments.

centered around 350 nm tailing into the visible region, indicating the capacity to absorb radiation in the low-visible/UV region. The nature of the iron(III)/tartrate species has been the subject of considerable discussion and debate for many years. Bobtelsky and Jordan[30] argued for a structure in which the iron(III)/tartrate ratio was 2:3, noting however that other structures may also be possible, especially when the iron(III) concentration exceeds the tartrate concentration. Others have proposed iron(III)/tartrate ratios of 1:1, 1:2, and 1:3, depending upon the pH, concentration, and ratio of reactants and methodology used.[31−33]

Hanby and Johnson[34] have examined the absorption spectrum of the iron(III) tartrate system in detail, albeit in alkaline solution, and have assigned the band centered around 350 nm (Figure 1) to a charge-transfer transition. The photochemical studies of iron(III)−organic acid complexes by Abrahamson et al. were performed at 366 nm, confirming that the band around 350 nm in Figure 1 is of importance for the iron(III)-tartrate-mediated photodegradation studies performed here.[25]

Identification of the Critical Wavelength for Iron(III) Tartrate Photoactivation. To determine the critical wavelength of impact on iron(III) photoactivity, irradiation experiments were performed using the small-scale setup shown in Figure S1 in the Supporting Information. Various cutoff filters were placed between the xenon arc lamp and the spectrophotometer cell. Two broad visible region filters were used, above 520 nm and above 400 nm, as well as two narrow range filters, between 400 and 520 nm and between 300 and 400 nm. The transmission spectra of the cutoff filters are shown in Figure 2. In the absence of any filter, the quartz cell allowed for transmission of both visible and UV radiation (Figure 2).

The decision to monitor glyoxylic acid production as a measure of tartaric acid degradation was based on the mechanism for iron(III) tartrate photodegradation proposed by Clark et al.[23] Its identity was confirmed by a comparison of its UV/vis spectra and chromatographic retention time to that of a commercial standard, as well as analysis by LC−MS, whereby it was detected at m/z 73 and 91 (both negative-ion modes). The m/z 73 ion corresponds to glyoxylate, while the m/z 91 ion corresponds to the hydrated form of glyoxylate (i.e., the hemiacetal). IEC chromatograms for the samples after 30 min exposure are presented in Figure 3 and clearly identify the conditions under which glyoxylic acid is produced. Table 1 summarizes the actual concentrations of glyoxylic acid generated.

It is apparent from Figure 3 and Table 1 that exposure to light above 520 nm does not result in the production of glyoxylic acid. Rather, wavelengths between 300 and 520 nm are critical for its formation. A quantitative comparison between the amount produced and the different wavelength ranges is difficult because the intensity of light reaching the sample varies from one cutoff filter to another.

The results for the exposure studies that allow for radiation down to 200 nm to reach the sample, i.e., in the absence of an additional light filter (Table 1), are more of academic interest and not relevant to normal wine storage, because all glass bottles eliminate wavelengths below 300 nm reaching the sample. Wavelengths below 300 nm can induce different photochemical processes, such as the well-documented production of hydrogen peroxide from water.[35] This is evident in the sample irradiated at >200 nm without iron, whereby H_2O_2 accumulates (Figure 3F). The assignment of peak 1 in the IEC chromatogram (Figure 3F) as being due to hydrogen peroxide was made via the matching of the retention time and extracted UV/vis spectrum (i.e., λ_{max} = 250 nm) to a standard of hydrogen peroxide. The use of IEC for the detection and quantification of hydrogen peroxide in model wine systems has previously been described.[23]

This hydrogen peroxide can lower the yield of glyoxylic acid by oxidizing it to formic acid.[23,27] As expected, no hydrogen peroxide accumulated in the sample irradiated at >200 nm with added iron; however, an alternate product was formed that was not identified (Figure 3E).

Influence of Experimental Conditions on the Production of Glyoxylic Acid. The influence of experimental conditions on the production of glyoxylic acid was investigated. The variables examined were wine base containing 5 mg/L iron (control), wine base without added iron (no iron), lower oxygen concentration achieved by flushing the sample and headspace with nitrogen (low oxygen), no exposure to light but the same temperature as all other samples (no light), omission of ethanol and iron from the control (no EtOH and Fe), and omission of ethanol only from the control (no EtOH). All exposure experiments were performed at 45 °C using a cutoff filter that allowed only light less than 400 nm to reach the sample. The concentrations of generated glyoxylic acid formed are shown in Table 2.

It is immediately apparent from the data in Table 2 that the presence of iron is essential for the production of glyoxylic acid.

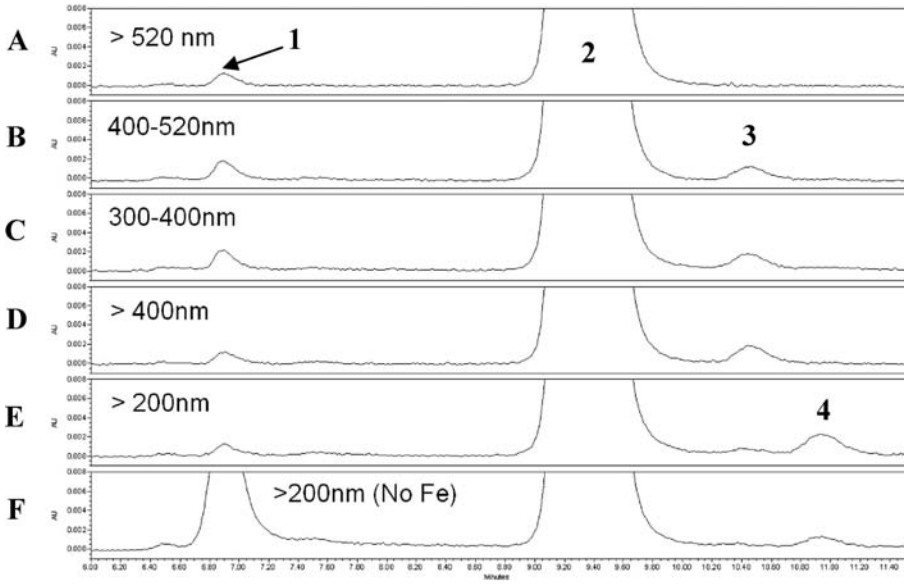

Figure 3. IEC chromatograms for wine base solutions exposed to different wavelengths: 1, hydrogen peroxide; 2, tartaric acid; 3, glyoxylic acid; and 4, unidentified.

Table 1. Concentrations of Glyoxylic Acid Generated from the Tartaric Acid Wine Base Containing 5 mg/L Iron as a Function of the Exposure Wavelength[a]

sample	glyoxylic acid concentration (mM)
WB/Fe, >520 nm	not detected
WB/Fe, 400−520 nm	0.35 ± 0.04
WB/Fe, 300−400 nm	0.354 ± 0.008
WB/Fe, >400 nm	0.43 ± 0.09
WB/Fe, >200 nm	0.11 ± 0.02
WB, >200 nm	0.03 ± 0.03

[a] WB, wine base; WB/Fe, wine base containing added 5 mg/L iron(II). Concentrations are the mean of three replicates, with 95% confidence limits.

Table 2. Glyoxylic Acid Concentrations Produced in Relation to Wine Base Composition and Experimental Conditions[a]

sample	glyoxylic acid concentration (mM)
control	0.43 ± 0.09
no Fe	not detected
low oxygen	0.17 ± 0.05
no light	not detected
no EtOH and Fe	not detected
no EtOH	0.29 ± 0.03

[a] See the text for an explanation of sample designations. Concentrations are the mean of three replicates, with 95% confidence limits.

Further, the presence of light (<400 nm in this experiment) is also essential. Both of these observations underscore the photochemical process involving iron and tartrate in the production of glyoxylic acid.

A reduction of the oxygen concentration in the system reduced the amount of glyoxylic acid generated (Table 2), pointing to the oxidative nature of the photochemically initiated reaction under examination here. The absence of ethanol in the "model wine" decreased the amount of glyoxylic acid produced. This observation is surprising, given that ethanol is a known radical scavenger; that is, a higher concentration of glyoxylic acid would be expected if a radical mechanism (i.e., Fenton chemistry) dominated the tartaric acid cleavage step. This observation is one that requires further investigation but supports the importance of the photochemical step in the production of glyoxylic acid in this system.

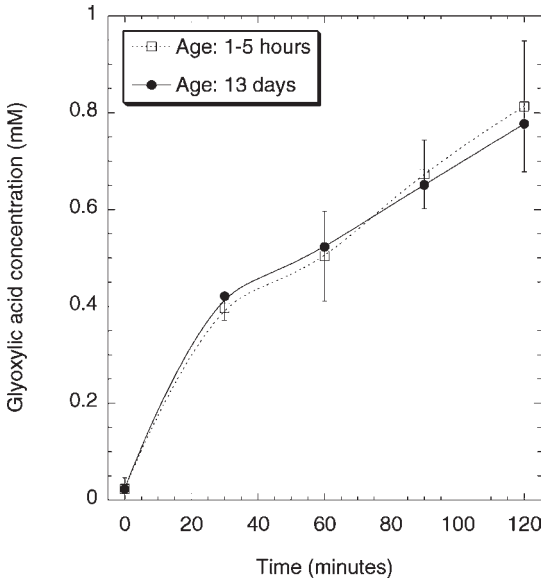

Figure 4. Impact of the age of the model wine base, with added 5 mg/L iron(II), on the production of glyoxylic acid.

During these experiments, it was observed that, for solutions of the wine base with added iron(II) (i.e., 5 mg/L), which were stored in darkness at room temperature, the intensity of the iron(III) tartrate peak around 350 nm (Figure 1) in the UV/vis spectrum increased with time. To determine if this had any impact of the production of glyoxylic acid, irradiation

experiments were performed on a freshly prepared wine base (used within 1−5 h after preparation) containing 5 mg/L iron and compared to a wine base that had been prepared 13 days before irradiation (Figure 4).

Figure 4 presents the time course for the production of glyoxylic acid over a 2 h period for these two experiments. There is no significant difference between the rate of glyoxylic acid formation or between the amount that is generated, indicating that the iron/tartrate system retains its capacity for photoactivation. The observed changes in the intensity of the UV absorbance for iron tartrate may well reflect changes in the structure of the iron/tartrate complex itself, but clearly, any structural rearrangement does not detract from the capacity of the model wine base containing iron for photoactivation.

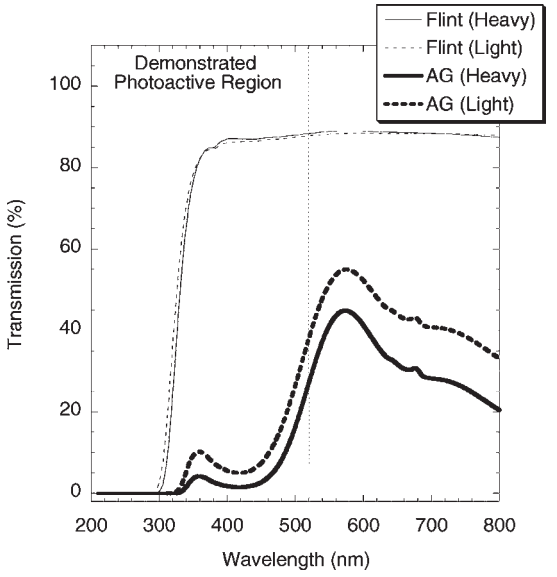

Figure 5. Bottle transmission spectra.

Effect of Bottle Color and Weight on the Production of Glyoxylic Acid. The impact of different glasses used in wine bottles on the production of glyoxylic acid was examined. Two glass types were selected: Flint (colorless) and Antique Green (dark green). In addition, the effect of bottle weight was also examined. To do this, traditional "heavyweight" (∼500 g) bottles were compared to the newer "lightweight" or "lean" (∼360 g) bottles. Sections of glass were cut from the main body of each bottle type. The sections were taken from below the bottleneck and above the punt. The glass sections were placed in front of the cell holding the model wine base to simulate wine in a bottle (see Figure S2 in the Supporting Information).

Figure 5 shows the relationship between the transmission spectra of the different glass types in relation to the photoactive region (<520 nm; see Table 1) for glyoxylic acid production. Further detail of the transmission spectra as a function of the bottle length can be found in Figures S3 and S4 in the Supporting Information.

The wine base sample containing 5 mg/L added iron(II) was exposed to light at 45 °C for 30 min using the different glass filters; the results obtained for glyoxylic acid production are shown in Table 3, with the supporting chromatograms in

Table 3. Glyoxylic Acid Concentrations Produced as a Function of the Glass Filter Color and Weight[a]

sample	glyoxylic acid concentration (mM)
Flint (heavy)	0.437 ± 0.003
Flint (light)	0.43 ± 0.03
Antique Green (heavy)	0.11 ± 0.01
Antique Green (light)	0.34 ± 0.05

[a] Concentrations are the mean of three replicates, with 95% confidence limits.

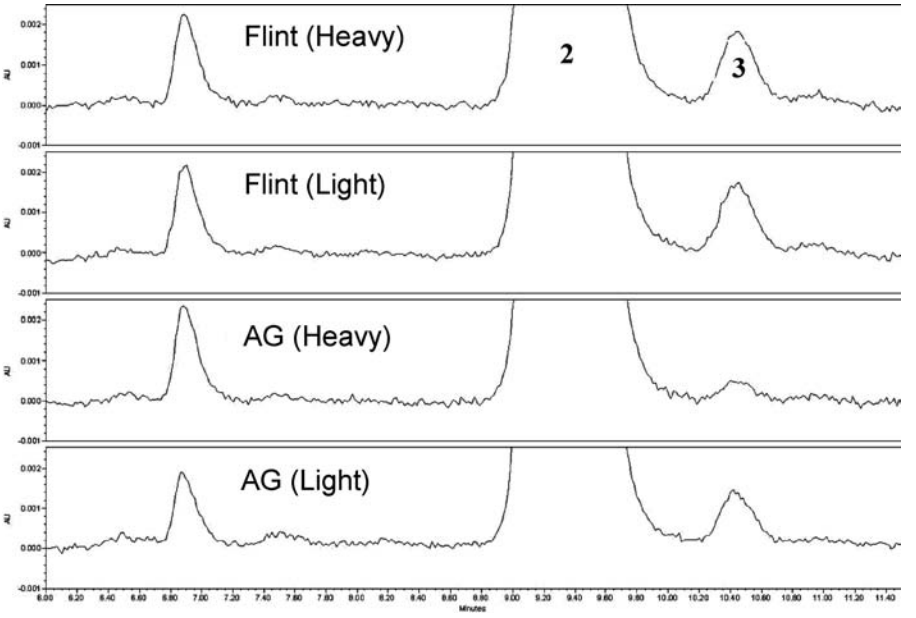

Figure 6. IEC chromatograms showing the production of glyoxylic acid in a model wine base, with added 5 mg/L iron(II), after exposure to light filtered by passage through Flint and Antique Green glass: 2, tartaric acid; 3, glyoxylic acid.

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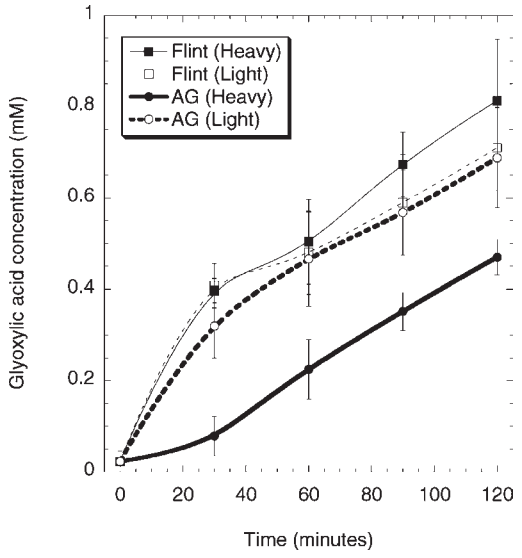

Figure 7. Impact of bottle color and bottle weight on the time course of the production of glyoxylic acid in a model wine base, with added 5 mg/L iron(II), after exposure to light filtered by passage through Flint and Antique Green glass.

Figure 6. Clearly, Flint glass results in a higher production of glyoxylic acid, and the amount produced is independent of bottle thickness. While the heavyweight Antique Green glass filter results in less glyoxylic acid being formed, it is important to note that it does not stop its production. This is in agreement with the transmission spectra/photoactive region shown in Figure 5. Flint glass, irrespective of bottle weight, is transmissive to light to 300 nm. There is a significant cutoff below 500 nm with Antique Green, although some transmission occurs between 340 and 380 nm. Higher transmissivity is observed for the light-weighted, in comparison to the heavy-weighted, Antique Green glass (Figure 5).

Figure 7 presents the time course for the production of glyoxylic acid when using Flint and Antique Green glass as filters in the irradiation experiment. The data show that there is a significant difference between the two weights for Antique Green in terms of both the rate and amount of glyoxylic acid production that is not apparent with the Flint glass. It is possible that there may be a threshold of light that is required to generate a high yield of glyoxylic acid. This threshold is exceeded with Flint (both weights) but, for Antique Green, only with the lightweight. The data in Figure 7 also illustrate that the amount of glyoxylic acid increases throughout the exposure, in contrast to the fluctuating concentration reported for sunlight exposure by Clark et al.[23] This study, however, involved a significant concentration of iron, whereas Clark et al. had only trace levels of iron present ($\sim$10 μg/L).[23] Also, the study by Clark et al. relied upon sunlight exposure to samples that was often interrupted by intermittent cloud cover during the 10 day duration of the experiment.[23] These data again underscore the critical role that iron, as iron(III), plays in this photoactivation process.

The results of this study identify the critical role of iron(III) tartrate as a potential photoactivator in the wine matrix. While this work was performed in a model wine matrix with only a minimum number of components, there are many potential binding agents for iron(III) in a white wine matrix. Measurement of the distribution of the iron(III) species in white wine, that is, its chemical speciation, and assessing the ability of these species to participate in photochemical reactions is an essential area of further work.

■ ASSOCIATED CONTENT

Supporting Information. Small-scale wine irradiation arrangement (Figures S1 and S2), comparison of percent transmission values as a function of the bottle length for heavy- and light (lean)-weighted Flint and Antique Green bottles (Figure S3), and comparison of percent transmission versus wavelength for heavy- and light-weighted bottles (Flint and Antique Green bottles) at 15 cm from bottle opening (Figure S4). This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Address: Metabolomics Australia, School of Botany, The University of Melbourne, Parkville, Victoria 3010, Australia. Telephone: +61-3-8344-3318. E-mail: ddias@unimelb.edu.au.

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■ REFERENCES

(1) Jackson, R. S. *Wine Science: Principles and Applications*; Academic Press: Burlington, MA, 2008; pp 431−432.

(2) Li, H.; Guo, A.; Wang, H. Mechanisms of oxidative browning of wine. *Food Chem.* **2008**, *108*, 1–13.

(3) Berg, H. W.; Akiyoshi, M. Some factors involved in browning of white wines. *Am. J. Enol. Vitic.* **1956**, *7* (1), 1–7.

(4) Oszmianski, J.; Cheynier, V.; Moutounet, M. Iron-catalyzed oxidation of (+)-catechin in model systems. *J. Agric. Food Chem.* **1996**, *47* (4), 1712–1715.

(5) Danilewicz, J. C. Review of reaction mechanisms of oxygen and proposed intermediate reduction products in wine: Central role of iron and copper. *Am. J. Enol. Vitic.* **2003**, *54*, 73–85.

(6) Waterhouse, A.; Laurie, V. Oxidation of wine phenolics: A critical evaluation and hypothesis. *Am. J. Enol. Vitic.* **2006**, *57*, 306–313.

(7) Ferreira, S. L. C.; Ferreira, H. S.; de Jesus, R. M.; Santos, J. V. S.; Brandao, G. C.; Souza, A. S. Development of method for the speciation of inorganic iron in wine samples. *Anal. Chim. Acta* **2007**, *602*, 89–93.

(8) Costa, R. C. C.; Araújo, A. N. Determination of Fe(III) and total Fe in wines by sequential injection analysis and flame atomic absorption spectrometry. *Anal. Chim. Acta* **2001**, *438*, 227–233.

(9) Tasev, K.; Karadjova, I.; Arpadjan, S.; Cvetkovic, J.; Stafilov, T. Liquid/liquid extraction and column solid phase extraction procedures for iron species determination in wines. *Food Control* **2006**, *17*, 484–488.

(10) Weber, G. Speciation of iron using HPLC with electrochemical and flame-AAS detection. *Fresenius' J. Anal. Chem.* **1991**, *340*, 161–165.

(11) Paleologos, E. K.; Giokas, D. L.; Tzouwara-Karayanni, S. M.; Karayannis, M. I. Micelle mediated methodology for the determination of free and bound iron in wines by flame atomic absorption spectrometry. *Anal. Chim. Acta* **2002**, *458*, 241–248.

(12) Fenton, H. Oxidation of tartaric acid in presence of iron. *J. Chem. Soc.* **1894**, *65*, 899–910.

(13) Fenton, H.; Jackson, H. The oxidation of polyhydric alcohols in presence of iron. *J. Chem. Soc., Trans.* **1899**, *75*, 1–11.

(14) Benrath, A. Reactions photochimiques en solutions aqueous. *J. Prakt. Chem.* **1917**, *96*, 190–201.

(15) Baraud, J. E. Étude des dérivés naturels de l'acide tartrique. *Ann. Chim.* **1954**, *9*, 535–604.

(16) Elias, R. J.; Waterhouse, A. Controlling the Fenton reaction in wine. *J. Agric. Food Chem.* **2010**, *58* (3), 1699–1707.

(17) Es-Safi, N.-E.; Guernevé, C. L.; Labarbe, B.; Fulcrand, H.; Cheynier, V.; Moutounet, M. Structure of a new xanthylium salt derivative. *Tetrahedron Lett.* **1999**, *40* (32), 5869–5872.

(18) Es-Safi, N.-E.; Le Guernevé, C.; Fulcrand, H.; Cheynier, V.; Moutounet, M. Xanthylium salts formation involved in wine colour changes. *Int. J. Food Sci. Technol.* **2000**, *35* (1), 63–74.

(19) Drinkine, J.; Glories, Y.; Saucier, C. (+)-Catechin−aldehyde condensations: Competition between acetaldehyde and glyoxylic acid. *J. Agric. Food Chem.* **2005**, *53* (19), 7552–7558.

(20) George, N.; Clark, A. C.; Prenzler, P. D.; Scollary, G. R. Factors influencing the production and stability of xanthylium cation pigments in a model white wine system. *Aust. J. Grape Wine Res.* **2006**, *12* (1), 57–68.

(21) Maury, C.; Clark, A. C.; Scollary, G. R. Determination of the impact of bottle colour and phenolic concentration on pigment development in white wine stored under external conditions. *Anal. Chim. Acta* **2010**, *60* (1−2), 81–86.

(22) Fulcrand, H.; Cheynier, V.; Oszmianski, J.; Moutounet, M. An oxidized tartaric acid residue as a new bridge potentially competing with acetaldehyde in flavan-3-ol condensation. *Phytochemistry* **1997**, *46* (2), 223–227.

(23) Clark, A. C.; Prenzler, P. D.; Scollary, G. R. Impact of the condition of storage of tartaric acid solutions on the production and stability of glyoxylic acid. *Food Chem.* **2007**, *102* (3), 905–916.

(24) Ware, M. *Cyanotype*; National Museum Photography, Film and Television: West Yorkshire, U.K., 1999; p 27 and 153.

(25) Abrahamson, H. B.; Rezvani, A. B.; Brushmiller, J. G. Photochemical and spectroscopic studies of complexes, of iron(III) with citric acid and other carboxylic acids. *Inorg. Chim. Acta* **1994**, *226* (1−2), 117–127.

(26) Clark, A. C.; Pedretti, F.; Prenzler, P. D.; Scollary, G. R. Impact of ascorbic acid on the oxidative colouration and associated reactions of a model wine solution containing (+)-catechin, caffeic acid and iron. *Aust. J. Grape Wine Res.* **2008**, *14* (3), 238–249.

(27) Clark, A. C.; Scollary, G. R. Influence of light exposure, ethanol and copper(II) on the formation of a precursor for xanthylium cations from tartaric acid. *Aust. J. Grape Wine Res.* **2003**, *9* (1), 64–71.

(28) Navarre, C. *L'Oenologie*; Lavoisier Tec and Doc: Paris, France, 1991; p 322.

(29) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; John Wiley and Sons: New York, 1988; p 713 and 757.

(30) Bobtelsky, M.; Jordan, J. The structure and behaviour of ferric tartrate and citrate complexes in dilute solutions. *J. Am. Chem. Soc.* **1947**, *69* (10), 2286–2290.

(31) Green, R. W.; Parkins, G. M. Complexes of iron with D-tartaric and *meso*-tartaric acids. *J. Phys. Chem.* **1961**, *65* (9), 1658–1659.

(32) Timberlake, C. F. Iron−tartrate complexes. *J. Chem. Soc.* **1964**, 1229–1240.

(33) Gallet, J.-P.; Ďaris, R. A. Etude thermometrique de la formation des complexes du fer(III), de l'aluminium et du gallium. Tartrates et citrates. *Anal. Chim. Acta* **1967**, *39* (C), 341–348.

(34) Hanby, J. R.; Johnson, D. C. Bond structure in the alkaline ferric−tartrate system. *J. Polym. Sci., Part A-1: Polym. Chem.* **1969**, *7* (10), 2983–2994.

(35) Legrini, O.; Oliveros, E.; Braun, A. M. Photochemical processes for water treatment. *Chem. Rev.* **1993**, *93*, 671–698.