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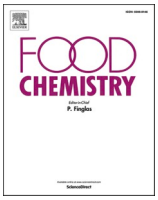

Impact of light on protective fractions of Cu in white wine: Influence of oxygen and bottle colour

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ABSTRACT

Cu(II)-organic acid (fraction I) and Cu(I)-thiol (fraction II) complexes can suppress sulfhydryl off-aromas in wine. This study investigated the impact of light exposure on the protective fractions of Cu of bottled white wine. Fluorescent light-exposed Chardonnay with two initial concentrations of dissolved oxygen (0.5 and 10 mg/L) was stored in different coloured bottles and concentrations of Cu fractions and riboflavin, a photo-initiator at 370–440 nm, were measured during 110 days storage. Light-exposed wines with lower oxygen concentrations resulted in a 100-fold decrease in the Cu fraction I half-life, and a 60-fold decrease for Cu fractions I and II combined. The half-life for Cu fraction I decay during light exposure was extended 30-fold with the use of brown compared to flint glass. Light exposure can rapidly exhaust the protective Cu fractions in wine, and bottles with less light transmission below 440 nm can slow this loss.

1. Introduction

Copper (Cu) present in wine can originate from a variety of sources, including natural metabolism of grapes, viticultural sprays, contamination and/or its use as a fining agent (Clark, Wilkes, & Scollary, 2015; Provenzano et al., 2010). The addition of Cu(II) to wine for the removal of sulfidic off-aromas associated with reductive wine attributes is a well-established process in wine production (Clark et al., 2015; Reschke, Tran, Bekker, Wilkes, & Johnson, 2015). This involves Cu(II) predominantly reacting with hydrogen sulfide and methanethiol to form non-volatile products such as Cu(II) or Cu(I) complexes and sulfhydryl oxidation products (e.g., disulfides, diorganopolysulfanes) (Kreitman, Danilewicz, Jeffery, & Elias, 2017). More recently, different measurable fractions of Cu in wine have been reported (Clark, Zhang, & Kontoudakis, 2020) and their concentrations linked to the suppression of hydrogen sulfide and methanethiol accumulation in bottle aged wine (Zhang, Blackman, Prenzler, & Clark, 2022). The protective Cu fractions include Cu fraction I, which was attributed to Cu(II) associated with organic acids (e.g., tartaric acid), and Cu fraction II, associated with Cu (I) thiol species (e.g., glutathione). An additional Cu fraction was identified (i.e., Cu fraction III) which was associated with copper sulfides. Cu fraction I concentrations above 0.035 mg/L were attributed to low methanethiol concentrations, while combined concentrations for Cu fraction I and II above 0.015 mg/L were associated with low hydrogen sulfide concentrations (Zhang et al., 2022). The protective Cu fractions gradually decreased in concentration in wines bottled with low dissolved oxygen concentrations and aged in typical cellar conditions (i.e., darkness at 14–17 °C with relative humidity 65–75%). Alternatively, wines with high oxygen concentrations had an increase in the protective Cu fractions (Kontoudakis, Guo, Scollary, & Clark, 2017). However, the influence of light exposure on protective Cu fractions has not been reported.

Riboflavin is known to be a critical initiator of the photochemical reactions that promote the emergence of undesirable volatile sulfur compounds, termed as '*light struck*' aroma (Dozon & Noble, 1989). While riboflavin can be found in grape must (typically at 0.003–0.060 mg/L), substantial concentration increases can occur during alcoholic fermentation (Mattivi, Monetti, Vrhovšek, Tonon, & Andrés-Lacueva, 2000;

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Ribéreau-Gayon, Glories, Maujean, & Dubourdieu, 2006), depending on yeast strain (Fracassetti et al., 2017), and if wine is subsequently aged on lees (Ournac, 1968). Concentrations of riboflavin in wine as high as 0.20 mg/L have been reported (Ournac, 1968), but only 0.05–0.08 mg/L of riboflavin is required to result in perceptible light struck characters (Mattivi et al., 2000). The light wavelength range from 370 to 440 nm is the most efficient for riboflavin excitation from a singlet electronic state to a triplet state, which then leads to two key pathways depending on oxygen availability. Pathway type I occurs independent of oxygen and involves the excited triplet riboflavin reacting directly with phenolic compounds and amino acids (Fracassetti, Limbo, Messina, Pellegrino, & Tirelli, 2021; Grant-Preece, Barril, Schmidtke, Scollary, & Clark, 2017). Pathway type II involves the reaction of triplet riboflavin with oxygen to produce singlet oxygen which is capable of amino acid degradation (Fracassetti et al., 2021; Min & Boff, 2002). In general, the oxygen concentration in bottled commercial wine is minimised to avoid oxidative spoilage, thereby creating conditions expected to favour a type I photodegradation pathway for riboflavin. Both pathways degrade the amino acid methionine to methanethiol (MeSH) and dimethyl disulfide (DMDS) (Maujean & Seguin, 1983). These compounds can cause sulfhydryl off-aromas in wine, most often described as *sewage* and *onion*, respectively (Smith, Bekker, Smith, & Wilkes, 2015). Due to the lower aroma threshold of MeSH (i.e., 1.8–3.1 μg/L), it is generally considered to impart the more detrimental odour (Siebert, Solomon, Pollnitz, & Jeffery, 2010; Solomon, Geue, Osidacz, & Siebert, 2010). The impact of light exposure on the sensory and chemical properties of wine has been extensively studied (Blake, Kotseridis, Brindle, Inglis, & Pickering, 2010; Cellamare, D'Auria, Emanuele, & Racioppi, 2009; D'Auria, Emanuele, Mauriello, & Racioppi, 2003; Haye, Maujean, Jacquemin, & Feuillat, 1977) but its impact on Cu fractions is unknown. Given the known ability of Cu(II) to interact with MeSH and other sulfhydryl compounds (Kreitman, Elias, Jeffery, & Sacks, 2019), it is expected that the photochemical production of sulfhydryl compounds will impact the distribution of Cu amongst its different fractions.

Bottles made from dark glass are known to limit the impact of light exposure on wine (Arapitsas et al., 2020; Cáceres-Mella et al., 2014; Carlin, Mattivi, Durantini, Dalledonne, & Arapitsas, 2022; Dias, Clark, Smith, Ghiggino, & Scollary, 2013; Guerrini et al., 2019; Lan et al., 2021). A variety of different bottle colours (e.g., transparent/flint, blue, green, brown) are available, with selection often driven by tradition, market forces and/or consumer preference (Barber & Almanza, 2007). Flint bottles are often used to allow the unfettered perception of white wine colour by the consumer, however this bottle colour also allows a high proportion of light into the wine. At the wavelengths of light that enable photochemical reactions to occur in wine (i.e., 370–440 nm), flint and arctic blue glass allow the transmission of >80% of light, while <40%, 10% and 5% of this light is transmitted through French green, antique green and amber/brown glass, respectively (Clark, Dias, Smith, Ghiggino, & Scollary, 2011; Grant-Preece et al., 2017; Hartley, 2008; Lan et al., 2021; Laposa, Vesztergom, Kocsis, & Keszei, 2023; Maury, Clark, & Scollary, 2010). The availability of rate data for the photoinduced riboflavin decay in wine is sparse, but 0.4 mg/L of riboflavin was shown to be fully depleted within a few hours (Fracassetti, Limbo, Pellegrino, & Tirelli, 2019) upon exposure to fluorescent light in transparent bottles (i.e., flint). The impact of bottle colour on the photodegradation decay rates of riboflavin, nor any subsequent impact on Cu fractions, has not been reported.

This study aimed to determine the impact of light exposure on the protective Cu fractions in wine. The concentrations of riboflavin and Cu fractions were monitored during the exposure of white wine to light over a period of days to months. The rates of any concentration changes and associated half-lives were determined for white wine with variable oxygen concentrations (i.e., high and low) and/or using different coloured bottles (i.e., flint, arctic blue, French green, antique green and brown).

2. Materials and methods

2.1. Chemicals

All glassware was soaked overnight in 10%(*v*/v) nitric acid (VWR, Radnor, PA, USA) and then rinsed with copious amounts of 18.2 MΩ water (Millipore Milli-Q Plus, Billerica, MA, USA) prior to use. Solutions and dilutions were prepared using the same 18.2 MΩ quality water. Copper(II) sulfate pentahydrate was purchased from VWR (Radnor, PA, USA). Riboflavin, 2,20-biquinoline-4,40-dicarboxylic acid dipotassium salt trihydrate (BCA), silver(I) nitrate, and TraceCERT Cu standard for ICP [1000 ± 2 mg/L in 2% (*w*/w) nitric acid] were sourced from Sigma-Aldrich (Castle Hill, NSW, Australia). Methanol (LC grade solvent, Honeywell, MI, USA), acetonitrile (LC grade solvent, Sigma-Aldrich, Castle Hill, NSW, Australia) and glacial acetic acid (Ajax Finechem, Taren Point, NSW, Australia) were used as UPLC solvents.

2.2. Wine bottles

Bordeaux-style glass wine bottles (750 mL, heavy weight) were used in this study (Fig. S1). Bottle colours comprised flint (F), arctic blue (AB), French green (FG), antique green (AG) and brown (B), which span the most common colours used for wine bottles. Flint bottles were purchased from Plasdene Glass Pak (Milperra, NSW, Australia), while arctic blue, French green and antique green bottles were donated by Visy (Southbank, Vic., Australia), and all bottles (including flint) had similar properties, including mass (i.e., 530 to 580 g) and height (i.e., 31 cm). Brown bottles were sourced from commercially available wines (i.e., emptied, cleaned and re-used) and were heavier (by 32%) and taller (i.e., by 9%) than the other bottles (Table S1). The transmission characteristics of each coloured bottle were collected over the wavelength range from 200 to 1100 nm using a UV/Vis spectrophotometer (Shimadzu, Kyoto, Japan) (Fig. S2).

2.3. Wine bottling preparation and experimental design

A commercial 2022 Chardonnay wine (13.0% (*v*/v)) was sourced from a retail outlet. The general specification of the wine is shown in Table S2. Chardonnay wine was used for all light exposure experiments with the addition of 0.5 mg/L riboflavin and 0.3 mg/L of Cu(II) immediately prior to rebottling. The final concentrations of riboflavin and total Cu were 0.62 ± 0.03 and 0.54 ± 0.02 mg/L, respectively. To achieve samples with a high oxygen concentration, an air pump (Dynapumps, Thomastown, Vic., Australia) was used to sparge the wine (for ~5 min) until the dissolved oxygen in the wine exceeded 10 mg/L. The oxygen concentration was measured with a PSt3 oxygen sensor within a PSt3-oxygen sensor dipping probe and Fibrox 3 LCD trace meter (Precision Sensing GmbH, Regensburg, Germany). Wines were then bottled (in triplicate) in 750 mL flint glass wine bottles for each treatment and sealed with tin liner screwcap closures (Orara, Hawthorn, Vic., Australia).

Wines with low oxygen concentrations were prepared in an anaerobic hood by sparging samples with nitrogen gas (99.99% purity, BOC Gas & Gear, Wagga Wagga, NSW, Australia). These wines were bottled (in triplicate) in 750 mL flint, arctic blue, French green, antique green and brown bottles and sealed with screwcap closures. The dissolved oxygen concentrations in the wine was below 0.3 mg/L immediately after bottling, which was consistent with the dissolved oxygen concentration routinely achieved in commercial wines (O'Brien 2009). All wines were stored at 20 ± 2 °C for a period of days to months (Table 1) until the near depletion of riboflavin (i.e., < 0.1 mg/L).

The irradiation of samples was conducted in a temperature-controlled incubator fitted with internal black-screen coverings to limit light reflection. Wine samples were irradiated with two 18 W florescent lights (Osram Lumilux®, Munich, Germany) that emitted cool white light (4000 K) with a luminous flux of 1300 lm. The emission

Table 1
Treatments applied to Chardonnay wines exposed to light under different storage conditions over a period of 1 to 110 days. Triplicate bottles of each treatment were prepared.

Code	Bottle colour	Light exposure conditions	Oxygen concentration conditions	Storage period (days)
F_O	Flint	Light	High	1
D_O	Control[1]	Dark	High	1
F	Flint	Light	Low	1
D	Control	Dark	Low	1
AB	Arctic Blue	Light	Low	2
FG	French Green	Light	Low	3
AG	Antique Green	Light	Low	24
B	Brown	Light	Low	110
D2	Control	Dark	Low	110

[1] 'Control' indicates that a Flint bottle was covered in aluminum foil and was non-transmissive to incident light.

spectra (supplied by Osram Lumilux®) associated with the fluorescent tube is shown in Fig. S3. Wine samples were placed 13 cm from the light source which gave an average light intensity of approximately 100 μmol/m^2/s, as determined by a LICOR Biosciences LI-185 A photometer (Lincoln, NE, USA). Control samples (i.e., samples stored without light exposure) were covered with aluminum foil before being stored in the same incubator as the light-exposed samples. The measurement of riboflavin and Cu fraction concentrations were performed at 10 time-points within the storage period for each treatment as outlined in Table 1. During sampling of the low oxygen samples, nitrogen gas was continually blown into the top of triplicate sample bottles for 10 min to minimise any increase in dissolved oxygen concentrations. Preliminary trials demonstrated this procedure maintained dissolved oxygen concentrations below 0.5 mg/L (data not shown).

2.4. Chemical analysis

Riboflavin concentrations were measured by Ultrahigh-Performance Liquid Chromatography (UPLC, Waters, Milford, USA) coupled to a photodiode array detector (PDA, Waters, Milford, USA), using a Waters Acquity BEH C18 column (2.1 mm, 50 mm, 1.7 μm, Waters, Milford, USA), and run by Empower 3 chromatography manager software (Waters, Milford, USA), as previously described (Dias, Smith, Ghiggino, and Scollary (2012). Briefly, the sample injection volume was 7.5 μL, and mobile phase A was 0.5% (*v*/v) acetic acid in water and mobile phase B was 0.5%(v/v) acetic acid in methanol. The flow rate was 0.45 mL/min and the solvent gradient conditions were identical to those reported by Dias et al. (2012). Chromatograms and UV/visible spectra were collected over the wavelength range of 200–700 nm.

The concentrations of total Cu and Cu fractions were quantified using the colorimetric techniques developed by Clark et al. (2020) and Kontoudakis, Smith, Smith, Wilkes, and Clark (2020). Wine samples were adjusted to pH 4.0 with concentrated sodium hydroxide prior to measurement with a UV/Vis spectrophotometer (ThermoFischer Scientific, Scoresby, VIC, Australia) at the wavelength of 563 nm. Cu fraction I and II concentrations were measured after incubating wine samples with bicinchoninic acid (BCA) for 1 and 30 min, respectively. Total Cu concentrations were determined after the incubation of wine samples with BCA and silver(I) for 30 min, and Cu fraction III concentration calculated as the difference between total Cu and the combined Cu fraction I and II concentrations.

The total concentration of Cu was also determined by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES, Agilent Technologies), with a high salts nebuliser/spray chamber as described by Kontoudakis et al. (2020). Free and total sulfur dioxide (SO_2) concentrations were determined using a Konelab 20XT automated analyser (Thermo Fisher Scientific, Scoresby, VIC, Australia) with analysis kits also supplied by Thermo Fisher Scientific. Total phenolic compounds (TPC) were measured by UV–Visible spectrometry at a wavelength of 280 nm according to Iland, Bruer, Edwards, Weeks, and Wilkes (2004).

2.5. Statistical analysis

Statistical analyses were conducted on IBM SPSS Statistic software (version 27, Chicago, IL, USA). Paired-sample *t*-tests were performed to compare a pair of mean values at a significance level of 95% ($p < 0.05$) before and after light exposure in each treatment. The rate constants and half-life data for riboflavin and Cu fractions were treated with log transformation in order to normalise the data prior to one-way analysis of variance (ANOVA) and post hoc multiple comparisons. At a significance level of 95% ($p < 0.05$), Tukey's test was applied where equal variances could be assumed and Dunnett's T3 test was used for unequal variances. The quoted uncertainly is the standard deviation of three replications within one treatment.

3. Results and discussion

3.1. The impact of light on Cu fractions in conditions of low and high oxygen: Flint bottles

To establish the actual oxygen availability to the different samples throughout the experiment, the dissolved oxygen concentration results will first be presented, along with the changes in oxidisable wine substrates (i.e., sulfur dioxide and phenolic compounds). This will be followed by the riboflavin and Cu fraction results.

The initial dissolved oxygen concentration measured in the high-oxygen samples was 10.8 ± 0.4 mg/L. With exposure to light, the oxygen concentration rapidly decreased to 2.9 ± 0.1 mg/L during the first 6 h (F_O, Fig. 1A), and then plateaued, whereas in the samples stored in darkness (D_O, Fig. 1A), a slower decrease in dissolved oxygen was observed. The accelerated oxygen consumption with light exposure is consistent with previous studies (Rossi & Singleton, 1966; Singleton, 1987). The dissolved oxygen concentrations of all samples with low initial oxygen levels remained constant throughout the storage period (i.e., <0.3 mg/L, sample F and D, Fig. 1A), and suggests there was no significant ingress of oxygen into the low oxygen samples arising from the sampling procedure.

The initial concentrations of free and total SO_2 were significantly lower ($p < 0.05$) in the wines with higher initial oxygen concentration (e.g., D_O versus D, Fig. 1B,C) and this was likely a consequence of the air-sparging procedure causing some volatilisation of molecular sulfur dioxide. When these high oxygen samples were exposed to light, the magnitude of the loss of free and total SO_2 was substantially greater, around 3-fold higher than samples stored in dark (i.e., F_O vs D_O, Fig. 1B,C). Light also accelerated loss of free and total SO_2 in the low oxygen samples (i.e., treatments F vs D, Fig. 1B,C), but not as markedly as in the high oxygen samples.

Light exposure did not induce a loss of total phenolic compounds (TPC) from the low oxygen samples (sample F, Fig. S4D). A significant decrease in TPC was evident in the high oxygen sample stored in darkness (sample D_O, Fig. S4D), but light exposure did not cause any further loss (F_O, Fig. S4D). The TPC decrease in the high oxygen samples was

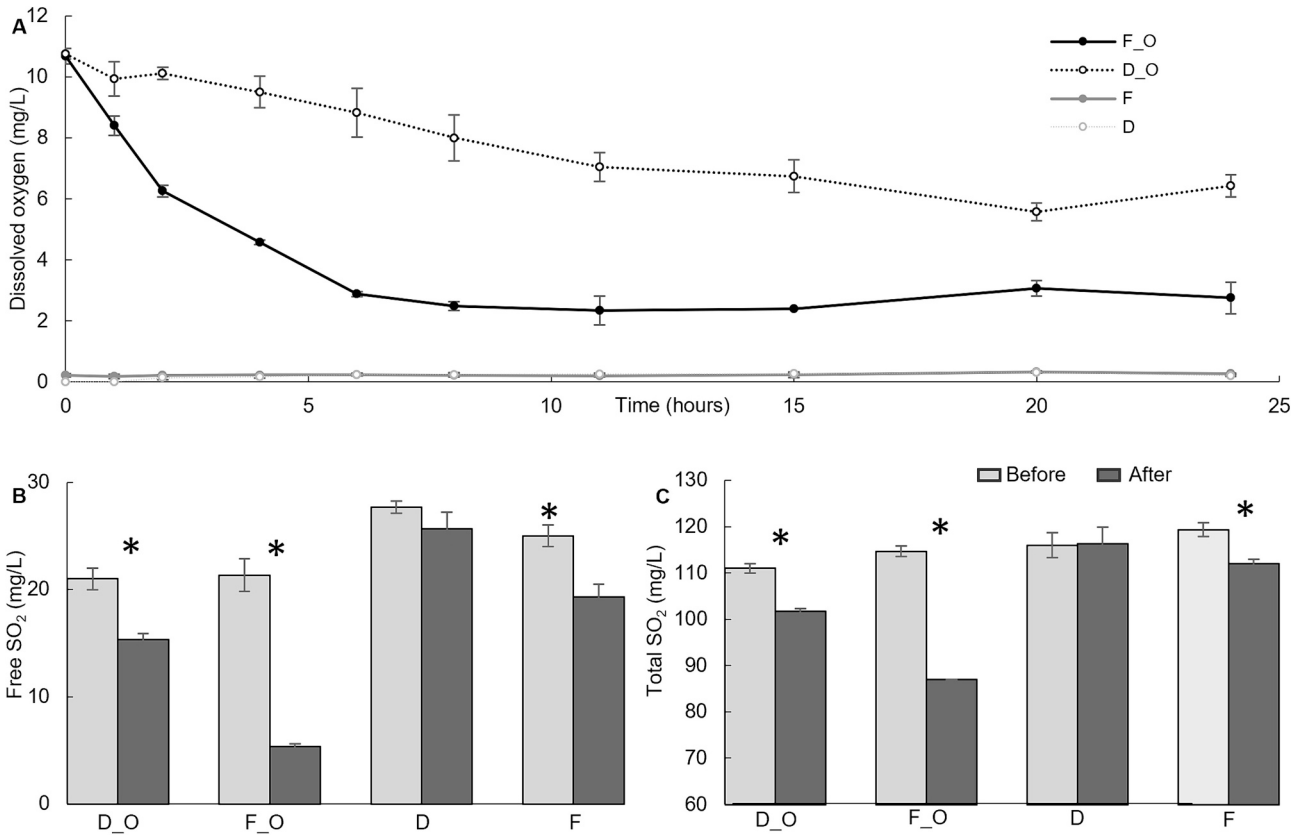

Fig. 1. The changes in concentrations (mg/L) of dissolved oxygen (A), free sulfur dioxide (B) and total sulfur dioxide (C) in Flint bottle in high (F_O) and low (F) oxygen concentration compared to control samples stored in dark (D_O and D). Error bars represent the standard deviation ($n = 3$) for the measurement of triplicate samples within each treatment. Star sign (*) means significant difference ($p < 0.05$), using the paired-samples *t*-test, between values for the start (0 day) and end (1 day) of the storage experiment.

most likely a consequence of phenolic oxidation products having lower 280 nm extinction coefficients compared to the parent phenolic compounds (Harbertson & Spayd, 2006; Singleton, 1987). It is interesting to note that the TPC change still occurred in the high oxygen samples despite the presence of appreciable free sulfur dioxide concentrations at the end of the experiment (i.e., > 10 mg/L of free sulfur dioxide in the dark control). The pH of wine samples remained at 3.45 regardless of oxygen and/or light exposure (data not shown).

With light exposure the riboflavin concentration in samples decreased as expected (samples F and F_O, Fig. 2A), while those samples stored in darkness had very stable riboflavin concentrations (i.e., ~ 0.6 mg/L,) throughout the experiment (samples D and D_O, Fig. 2A). Initially, the concentrations of riboflavin were similar between the F_O and F samples, but after several hours (~ 6 h), lower concentrations were evident in F_O compared to F (i.e., F_O vs F, Fig. 2A). In the higher oxygen environment, the riboflavin degradation mechanism is more likely to occur via pathway type II, whereby singlet oxygen may have contributed to riboflavin decay.

The concentration data for riboflavin was modelled for first and second order decay (Table 2, Fig. S5-S6, Table S3-S4) and the coefficients of determination (R^2) presented in Table 2 provide an assessment of the fit for each order of decay. The photo-degradation of riboflavin under high oxygen conditions was best modelled by a first order decay process ($R^2 = 0.998$), whereas samples with low initial oxygen concentrations were better modelled by second order decay ($R^2 = 0.978$). The half-life for riboflavin when exposed to light was 30% longer in the low oxygen concentration samples compared to the samples bottled with a high oxygen concentration.

After the addition of 0.3 mg/L of Cu(II) to the wines at bottling, differences in the measurable fractions were found, with Cu fraction I having the highest concentration, followed by fractions II and III in every treatment (see time 0 h, Fig. 2B-D). Cu fractions in samples with high initial oxygen concentrations (sample F_O and D_O, Fig. 2B-D) showed minimal change over the one day storage period, regardless of light exposure. In the treatment with low initial oxygen (sample F), a dramatic decrease in the Cu fraction I concentration was observed (i.e., a loss of 97% of the initial concentration) after one day of light exposure. In the same treatment, the Cu fraction II concentration increased during the first few hours of light exposure, but then decreased to 60% of the original concentration (sample F, Fig. 2C). The Cu fraction III concentration increased steadily for the first 15 h of light exposure and then plateaued at around 75% of the total Cu concentration (sample F, Fig. 2D). In contrast, for the sample stored in darkness (i.e., sample D), a more modest 43% decrease in Cu fraction I was observed (Fig. 2B) and only minor changes in Cu fractions II and III occurred during the same time-period (Fig. 2C,D). These results indicate that light exposure was able to efficiently transition Cu fractions I and II to Cu fraction III in low oxygen concentrations. Given that Cu fraction III is associated with copper sulfides, this suggests that light exposure is able to assist Cu(II) in procuring sulfide from some sources. The increase and subsequent decrease in Cu fraction II, the fraction associated with Cu(I)-thiol species, implies an initial increase in thiol species capable of interaction with Cu(II)-organic acids (i.e., Cu fraction I), with a further transition of this species to copper sulfides (i.e., Cu fraction III).

From Fig. 2A and B, it is evident that Cu fraction I and riboflavin were depleted within a similar time frame of approximately 20 h. However, the decay of Cu fraction I was faster than that of riboflavin with calculated half-lives of 0.06 and 0.17 days, respectively (Tables 2 and 3). Furthermore, if the rates are expressed in mmol/(L·hr) units, rather than the mg/(L·hr), then it equates to decay rates of 0.05 mmol/

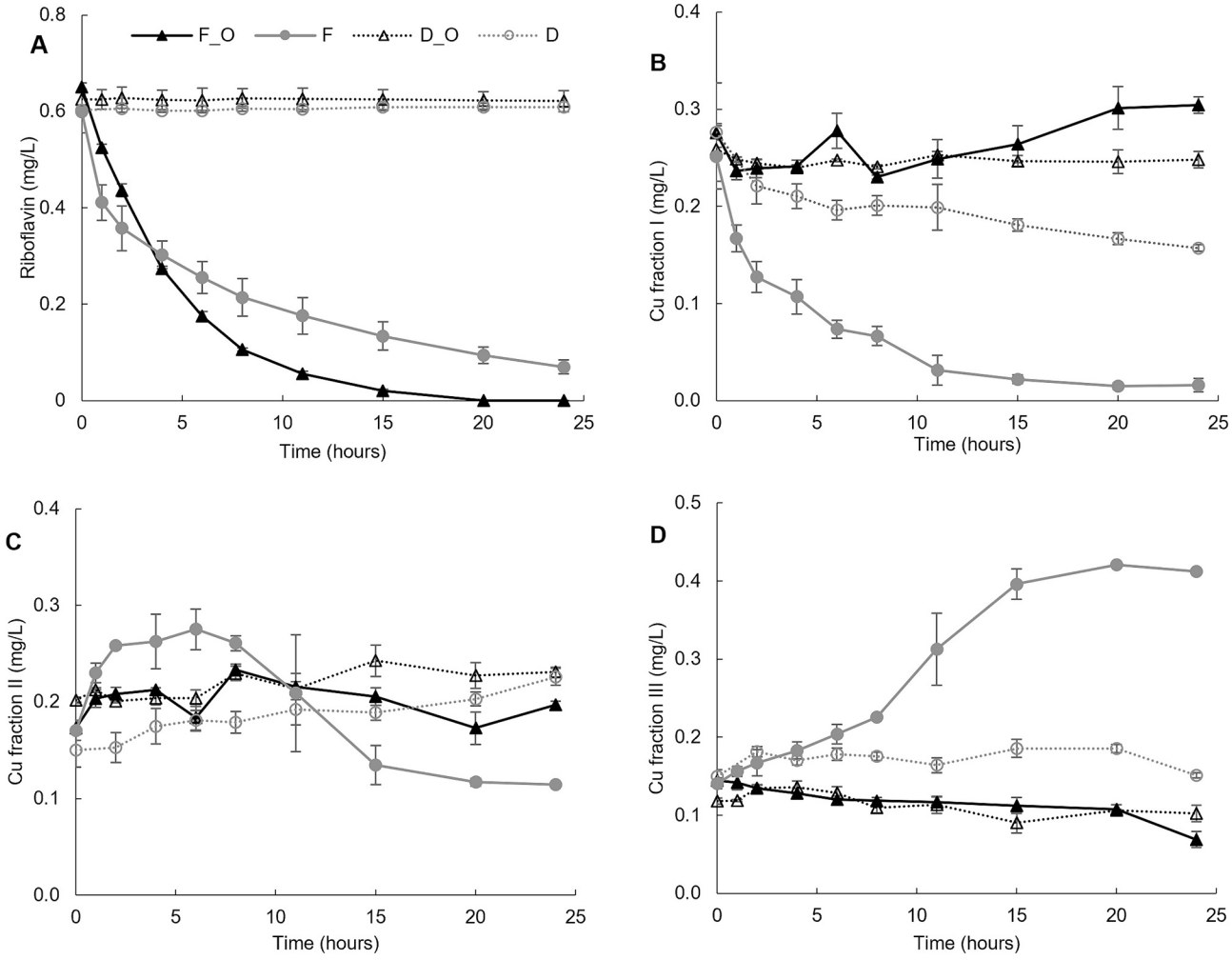

Fig. 2. The changes in concentration (mg/L) of riboflavin (A), Cu fraction I (B), fraction II (C) and fraction III (D) for Chardonnay wine in flint bottles in high and low oxygen concentrations in 24 h. Error bars represent the standard deviation (n = 3) for the measurement of triplicate samples within each treatment. F_O: flint, high oxygen; F: flint, low oxygen; D_O: dark, high oxygen; D: dark, low oxygen.

Table 2
Decay rates and half-life for riboflavin in each treatment.

Treatment	1st order			2nd order		
	Rate[a] ($hours^{-1}$)	R^2	Half-life[b] (days)	Rate[b] ($mg^{-1}{\cdot}L{\cdot}hours^{-1}$)	R^2	Half-life[b] (days)
F_O (Flint+high O_2)	0.23 ± 0.01[a]	0.998	0.130 ± 0.005[d]	2.8 ± 0.5[a]	0.796	0.020 ± 0.003
F (Flint)	0.084 ± 0.008[b]	0.957	0.35 ± 0.03	0.4 ± 0.1[b]	0.978	0.17 ± 0.03[d]
AB (Arctic blue)	0.055 ± 0.003[c]	0.955	0.53 ± 0.03	0.32 ± 0.06[b]	0.989	0.26 ± 0.02[d]
FG (French green)	0.022 ± 0.001[d]	0.958	1.29 ± 0.07	0.099 ± 0.009[c]	0.969	0.66 ± 0.09[c]
AG (Antique green)	0.00390 ± 0.00006[e]	0.942	7.5 ± 0.1	0.0152 ± 0.0003[d]	0.993	4.26 ± 0.08[b]
B (Brown)	0.00060 ± 0.00006[f]	0.923	46 ± 4	0.0027 ± 0.0003[e]	0.990	25 ± 2[a]

Values are expressed as means (n = 3) ± standard deviation. Values followed by different letters within a column, or for the underlined half-life data, indicate significant differences ($p < 0.05$) using Tukey's and Dunnett's T3 test for post hoc multiple comparison. The preferred modelling is indicated by the underlined half-life data.

[a] Tukey's test was applied for post hoc multiple comparison.

[b] Dunnett's T3 test was applied for post hoc multiple comparison.

(L·hr) compared to 0.001 mmol/(L·hr) for Cu fraction I and riboflavin, respectively. Finally, despite the molar concentration of riboflavin (0.0016 mmol/L or 0.6 mg/L) at the start of the experiment being less than half that of the molar concentration of the Cu fraction I (0.0039 mmol/L or 0.25 mg/L), the light source was still able to fully deplete Cu fraction I. Further work is required to establish if photochemical mechanisms, independent of riboflavin, can also contribute to the loss of Cu fractions I and II.

These results show that light can significantly accelerate the loss of Cu fractions I and II from white wine. Given that both these fractions of Cu are linked to the suppression of reductive aroma compounds in wine, it is possible that the exposure of bottled wine to light may have a legacy effect whereby the wine is more prone to reductive spoilage, even if later aged under ideal conditions.

Table 3
Decay rates and half-life for Cu fractions in different coloured bottles samples at lower oxygen concentrations.

Treatment	Cu fraction I			Combined Cu fraction I and II					
	2nd order rate[a] (mg^{-1}L.$hours^{-1}$)	R^2	Half-life[a] (days)	1st order rate[b] ($hours^{-1}$)	R^2	Half-life[b] (days)	2nd order rate[a] (mg^{-1}L.$hours^{-1}$)	R^2	Half-life[b] (days)
F (Flint)	3.1 ± 0.6^{a}	0.923	0.06 ± 0.02^{d}	0.062 ± 0.003^{a}	0.933	0.47 ± 0.02^{d}	0.27 ± 0.02^{a}	0.896	0.37 ± 0.02
AB (Arctic blue)	2.5 ± 0.6^{a}	0.977	0.08 ± 0.03^{d}	0.047 ± 0.001^{b}	0.980	0.62 ± 0.01^{c}	0.40 ± 0.04^{b}	0.948	0.32 ± 0.04
FG (French green)	0.54 ± 0.04^{b}	0.975	0.35 ± 0.02^{c}	0.011 ± 0.001^{c}	0.967	2.7 ± 0.3^{b}	0.055 ± 0.007^{c}	0.969	2.6 ± 0.5
AG (Antique green)	0.32 ± 0.03^{c}	0.970	0.6 ± 0.1^{c}	0.0042 ± 0.0002^{d}	0.925	6.9 ± 0.3^{b}	0.051 ± 0.004^{c}	0.969	2.6 ± 0.4
B (Brown)	0.13 ± 0.01^{d}	0.977	1.9 ± 0.4^{b}	0.0013 ± 0.0002^{e}	0.796	23 ± 3	0.022 ± 0.005^{d}	0.957	8 ± 3^{b}
D2 (Dark)	0.030 ± 0.002^{e}	0.968	6.9 ± 0.6^{a}	0.00050 ± 0.00006^{f}	0.866	63 ± 8	0.0048 ± 0.0004^{e}	0.981	32 ± 5^{a}

Results are expressed as mean ± standard deviation, different letters within a column, or for the underlined combined Cu fraction I and II half-life data, indicate significant differences ($p < 0.05$) using Tukey's and Dunnett's T3 test for post hoc multiple comparison. The preferred modelling is indicated by the underlined half-life data.

[a] Tukey's test was applied for post hoc multiple comparison.

[b] Dunnett's T3 test was applied for post hoc multiple comparison.

3.2. The impact of light on Cu fractions in low oxygen conditions: Variable bottle colours

In contrast to the flint bottle, there was no significant difference in the decrease of free or total SO_2 in the brown bottles when compared to the sample stored in the dark (i.e., sample B versus D2, Fig. S4B,C). That is, after 110 days of light exposure, samples in brown bottles (B) had free and total SO_2 concentrations similar to those of the wine stored in darkness (D2).

Upon light exposure, the riboflavin concentration decreased more slowly in the other coloured bottles compared to flint bottles (Fig. 3A, Table 2). This was consistent with the decreased transmittance % in these bottles at the 370–440 nm wavelengths (Fig. S2) which were brown < antique green < French green < arctic blue < flint. The decay rate for riboflavin in the coloured bottles was best modelled by second order decay ($R^2 = 0.969$–0.993) (Table 2) and this order of decay was similar to that observed for the flint bottle with low oxygen conditions (Table 2, Section 3.1).

The half-life for riboflavin decay was approximately 150-fold higher when wine was stored in brown (B) bottles compared to flint (F) bottles. The lower decay rate for riboflavin upon light exposure in the coloured bottles with less light transmission below 440 nm was consistent with the previously reported delayed onset of light stuck aroma in wines in more intensely coloured wine bottles. For example, Dozon and Noble (1989) reported that Chardonnay wine exposed to fluorescent light showed undesirable aromas after 3 h in flint bottles and after 18 h in green bottles. The kinetic data shown in Table 2 is the first report that models the impact of different coloured bottles for riboflavin photodegradation.

It is interesting that Cu fractions I and II decayed more quickly in the control Chardonnay than has been reported for other wines in previous studies. For example, the two white wines reported by Zhang et al. (2022) had average half-lives for Cu fraction I of 90 ± 30 days, while in the current study, a half-life of 7-days was observed (Table 3). The half-lives for the combined Cu fractions I and II decay were 95 ± 7 days in the Zhang et al. (2022) study, but only approximately 32 days in the current study (Table 3). However, the storage temperature used in this current study (20 ± 2 °C) was higher than the 14 °C used by Zhang et al. (2022), and temperature is known to accelerate the production of copper sulfides in wine (i.e., Cu fraction III) (Ferreira, Franco-Luesma, Vela, López, & Hernández-Orte, 2018).

For samples exposed to light, the bottles with less light transmission below 440 nm (i.e., brown) also slowed the observed changes for protective Cu fractions (Fig. 3B,C and Fig. S7B,C) and decreased the decay rate of both Cu fraction I and the combined Cu I and II fractions (Table 3). The decrease in Cu fraction I concentrations were best modelled by second order decay for all samples, whereas the decrease in the combined Cu fractions I and II were best modelled by first order decay in the lighter coloured bottles (i.e., flint, arctic blue, French green and antique green), and second order for the more intensely coloured bottles (i.e., brown) at 370–440 nm. That is, first order for faster decay (i.e., half-life <7 days), and second order for the slower decay (i.e., half-life >7 days). Brown bottles extended the half-life of Cu fraction I by approximately 30 times, and the combined fraction I and II by approximately 15-fold, compared with flint bottles. However, even brown bottles could not provide full protection from the effects of light, with significant differences evident between samples in brown bottles (B) compared to those stored in darkness (D2) (Table 3).

4. Conclusions

This study has established the rates of change for Cu fractions and riboflavin during light exposure to a Chardonnay wine. The influence of different initial wine dissolved oxygen concentrations and bottle colour were investigated. The half-lives for Cu fractions I and II provided some insight on the length of time that Cu(II) can offer protection from light-

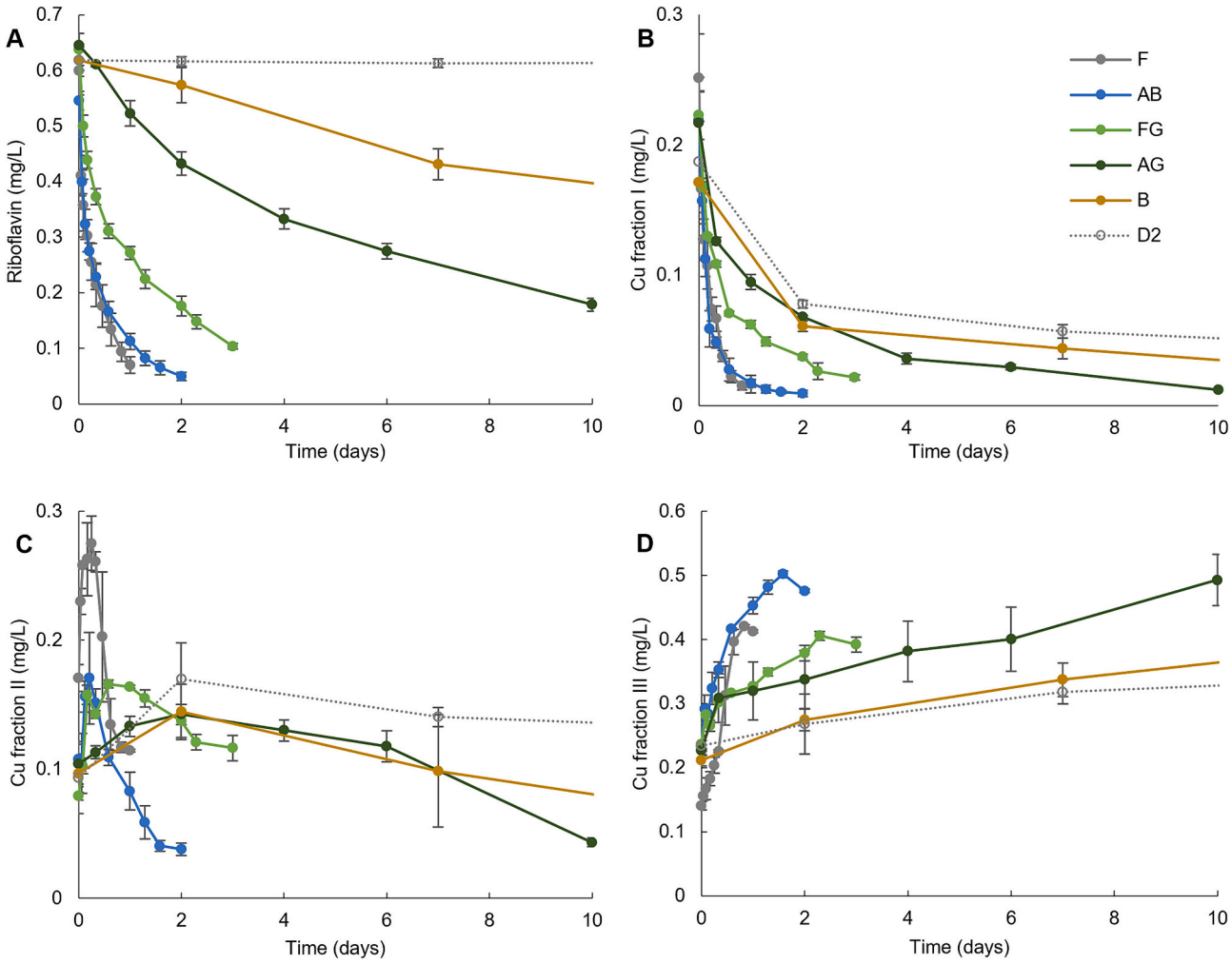

Fig. 3. The changes in concentration (mg/L) of riboflavin (A), Cu fraction I (B), fraction II (C) and fraction III (D) for Chardonnay wine in different coloured bottles in low oxygen concentrations over the first 10-days of the experiment. For the entire experimental data set, refer to Fig. S7. Error bars represent the standard deviation (n = 3) for the measurement of triplicate samples within each treatment. F: flint; AB: arctic blue; FG: French green; AG: antique green; B: brown; D2: dark.

induced spoilage in each of the different coloured wine bottles. At typical oxygen concentrations of bottled wine (i.e., at low oxygen), light exposure in the presence of riboflavin had a significant impact, accelerating the loss of the Cu I and II fractions, particularly in the flint bottle. Light exposure also increased the procurement of sulfide by Cu(II), as seen by the increase in Cu fraction III in the flint bottle within one day. As expected, coloured bottles with lower light transmission at 370–440 nm wavelengths mitigated the impact of light on the decay of both riboflavin and the protective Cu fractions, however, it could not completely prevent the effect of light exposure.

Winemakers, retailers and consumers should be aware that short-term light exposure can induce undesirable compositional changes in white wine, beyond that of light struck aroma, that may have ramifications for wine shelf-life. That is, protective Cu fractions are rapidly depleted upon light exposure thereby increasing the risk of sulfidic-off odour emergence during subsequent bottle aging. Furthermore, the inherent variability of light exposure of wines in retail settings, including the different intensities of light exposure by bottles on different shelves, may induce variability in the loss of protective Cu fractions and thus, seemingly random emergence of sulfidic-off odours. Although winemakers are often constrained by marketing considerations in their choice of bottle colour for white wine, this work demonstrates that such a choice may have significant implications for the compositional changes of wine during storage and aging. Future work could assess the extent of variation in the riboflavin and Cu fractions decay rates in different white wines exposed to light. Other valuable future work would be to investigate the impact of different Cu fractions on the occurrence of light struck aromas in bottle aged white wine with variable riboflavin concentrations.

CRediT authorship contribution statement

Isara Vongluanngam: Writing – review & editing, Writing – original draft, Visualization, Formal analysis, Data curation, Conceptualization. **Xinyi Zhang:** Writing – review & editing, Supervision, Conceptualization. **John W. Blackman:** Writing – review & editing, Supervision. **Leigh M. Schmidtke:** Writing – review & editing, Supervision. **Kerry L. Wilkinson:** Writing – review & editing, Supervision. **Andrew C. Clark:** Writing – review & editing, Writing – original draft, Supervision, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.foodchem.2024.139504.

References

Arapitsas, P., Dalledonne, S., Scholz, M., Catapano, A., Carlin, S., & Mattivi, F. (2020). White wine light-strike fault: A comparison between flint and green glass bottles under the typical supermarket conditions. *Food Packaging and Shelf Life, 24*, Article 100492. https://doi.org/10.1016/j.fpsl.2020.100492

Barber, N., & Almanza, B. A. (2007). Influence of wine packaging on consumers' decision to purchase. *Journal of Foodservice Business Research, 9*(4), 83–98. https://doi.org/10.1300/J369v09n04_06

Blake, A., Kotseridis, Y., Brindle, I. D., Inglis, D., & Pickering, G. J. (2010). Effect of light and temperature on 3-alkyl-2-methoxypyrazine concentration and other impact odourants of Riesling and cabernet franc wine during bottle ageing. *Food Chemistry, 119*(3), 935–944. https://doi.org/10.1016/j.foodchem.2009.07.052

Cáceres-Mella, A., Flores-Valdivia, D., Laurie, V. F., López-Solís, R., Peña-Neira, A., & l.. (2014). Chemical and sensory effects of storing sauvignon blanc wine in colored bottles under artificial light. *Journal of Agricultural and Food Chemistry, 62*(29), 7255–7262. https://doi.org/10.1021/jf501467f

Carlin, S., Mattivi, F., Durantini, V., Dalledonne, S., & Arapitsas, P. (2022). Flint glass bottles cause white wine aroma identity degradation. *Proceedings of the National Academy of Sciences, 119*(29). https://doi.org/10.1073/pnas.2121940119. e2121940119-e2121940119.

Cellamare, L., D'Auria, M., Emanuele, L., & Racioppi, R. (2009). Effect of light on the composition of some volatile compounds in wine: An HS-SPME-GC-MS study. *International Journal of Food Science and Technology, 44*(12), 2377–2384. https://doi.org/10.1111/j.1365-2621.2008.01723.x

Clark, A. C., Dias, D. A., Smith, T. A., Ghiggino, K. P., & Scollary, G. R. (2011). Iron(III) tartrate as a potential precursor of light-induced oxidative degradation of white wine: Studies in a model wine system. *Journal of Agricultural and Food Chemistry, 59*(8), 3575–3581. https://doi.org/10.1021/jf104897z

Clark, A. C., Wilkes, E. N., & Scollary, G. R. (2015). Chemistry of copper in white wine: A review. *Australian Journal of Grape and Wine Research, 21*(3), 339–350. https://doi.org/10.1111/ajgw.12159

Clark, A. C., Zhang, X., & Kontoudakis, N. (2020). Simplified measures of copper fractions in wine: Colorimetric and filtration-based approaches. *Australian Journal of Grape and Wine Research, 26*(4), 399–409. https://doi.org/10.1111/ajgw.12450

D'Auria, M., Emanuele, L., Mauriello, G., & Racioppi, R. (2003). On the origin of "Goût de Lumiere" in champagne. *Journal of Photochemistry and Photobiology A: Chemistry, 158*(1), 21–26. https://doi.org/10.1016/S1010-6030(03)00095-9

Dias, D. A., Clark, A. C., Smith, T. A., Ghiggino, K. P., & Scollary, G. R. (2013). Wine bottle colour and oxidative spoilage: Whole bottle light exposure experiments under controlled and uncontrolled temperature conditions. *Food Chemistry, 138*(4), 2451–2459. https://doi.org/10.1016/j.foodchem.2012.12.024

Dias, D. A., Smith, T. A., Ghiggino, K. P., & Scollary, G. R. (2012). The role of light, temperature and wine bottle colour on pigment enhancement in white wine. *Food Chemistry, 135*(4), 2934–2941. https://doi.org/10.1016/j.foodchem.2012.07.068

Dozon, N. M., & Noble, A. C. (1989). Sensory study of the effect of fluorescent light on a sparkling wine and its base wine. *American Journal of Enology and Viticulture, 40*(4), 265–271. https://doi.org/10.5344/ajev.1989.40.4.265

Ferreira, V., Franco-Luesma, E., Vela, E., López, R., & Hernández-Orte, P. N. (2018). Elusive chemistry of hydrogen sulfide and mercaptans in wine. *Journal of Agricultural and Food Chemistry, 66*(10), 2237–2246. https://doi.org/10.1021/acs.jafc.7b02427

Fracassetti, D., Gabrielli, M., Encinas, J., Manara, M., Pellegrino, I., & Tirelli, A. (2017). Approaches to prevent the light-struck taste in white wine. *Australian Journal of Grape and Wine Research, 23*(3), 329–333. https://doi.org/10.1111/ajgw.12295

Fracassetti, D., Limbo, S., Messina, N., Pellegrino, L., & Tirelli, A. (2021). Light-struck taste in white wine: Protective role of glutathione, sulfur dioxide and hydrolysable tannins. *Molecules, 26*(17), 5297. https://doi.org/10.3390/molecules26175297

Fracassetti, D., Limbo, S., Pellegrino, L., & Tirelli, A. (2019). Light-induced reactions of methionine and riboflavin in model wine: Effects of hydrolysable tannins and sulfur dioxide. *Food Chemistry, 298*, Article 124952. https://doi.org/10.1016/j.foodchem.2019.124952

Grant-Preece, P., Barril, C., Schmidtke, L. M., Scollary, G. R., & Clark, A. C. (2017). Light-induced changes in bottled white wine and underlying photochemical mechanisms. *Critical Reviews in Food Science and Nutrition, 57*(4), 743–754. https://doi.org/10.1080/10408398.2014.919246

Guerrini, L., Pantani, O. L., Politi, S., Angeloni, G., Masella, P., Calamai, L., & Parenti, A. (2019). Does bottle color protect red wine from photo-oxidation? *Packaging Technology and Science, 32*(5), 259–265. https://doi.org/10.1002/pts.2433

Harbertson, J. F., & Spayd, S. (2006). Measuring phenolics in the winery. *American Journal of Enology and Viticulture, 57*(3), 280–288. https://doi.org/10.5344/ajev.2006.57.3.280

Hartley, A. (2008). *The effect of ultraviolet light on wine quality*. Oxon: Waste and Resources Action Program.

Haye, B., Maujean, A., Jacquemin, C., & Feuillat, M. (1977). Contribution à l'étude des « goûts de lumière » dans le vin de champagne *. 1. Aspects analytiques - Dosage des mercaptans et des thiols dans les vins. *OENO one, 11*(3), 243–254. https://doi.org/10.20870/oeno-one.1977.11.3.1443

Iland, P., Bruer, N., Edwards, G., Weeks, S., & Wilkes, E. (2004). *Chemical analysis of grapes and wine: Techniques and concepts* (2 ed.). Patrick Iland Wine Promotions.

Kontoudakis, N., Guo, A., Scollary, G. R., & Clark, A. C. (2017). The impact of aging wine in high and low oxygen conditions on the fractionation of Cu and Fe in chardonnay wine. *Food Chemistry, 229*, 319–328. https://doi.org/10.1016/j.foodchem.2017.02.065

Kontoudakis, N., Smith, M., Smith, P. A., Wilkes, E. N., & Clark, A. C. (2020). The colorimetric determination of copper in wine: Total copper. *Australian Journal of Grape and Wine Research, 26*(2), 121–129. https://doi.org/10.1111/ajgw.12425

Kreitman, G. Y., Danilewicz, J. C., Jeffery, D. W., & Elias, R. J. (2017). Copper(II)-mediated hydrogen sulfide and thiol oxidation to disulfides and organic polysulfanes and their reductive cleavage in wine: Mechanistic eucidation and potential applications. *Journal of Agricultural and Food Chemistry, 65*(12), 2564–2571. https://doi.org/10.1021/acs.jafc.6b05418

Kreitman, G. Y., Elias, R. J., Jeffery, D. W., & Sacks, G. L. (2019). Loss and formation of malodorous volatile sulfhydryl compounds during wine storage. *Critical Reviews in Food Science and Nutrition, 59*(11), 1728–1752. https://doi.org/10.1080/10408398.2018.1427043

Lan, H., Li, S., Yang, J., Li, J., Yuan, C., & Guo, A. (2021). Effects of light exposure on chemical and sensory properties of storing Meili Rosé wine in colored bottles. *Food Chemistry, 345*, Article 128854. https://doi.org/10.1016/j.foodchem.2020.128854

Laposa, Z., Vesztergom, S., Kocsis, M., & Keszei, E. (2023). In situ measurement of light transmission into wine bottles and calculation of shelf life. *OENO one, 57*(1), 265–277. https://doi.org/10.20870/oeno-one.2023.57.1.7172

Mattivi, F., Monetti, A., Vrhovšek, U., Tonon, D., & Andrés-Lacueva, C. (2000). High-performance liquid chromatographic determination of the riboflavin concentration in white wines for predicting their resistance to light. *Journal of Chromatography A, 888*(1), 121–127. https://doi.org/10.1016/S0021-9673(00)00561-6

Maujean, A., & Seguin, N. (1983). Contribution à l'étude des goûts de lumière dans les vins de Champagne. 3. Les réactions photochimiques responsables des goûts de lumière dans le vin de Champagne. *Sciences des Aliments, 3*, 589–601.

Maury, C., Clark, A. C., & Scollary, G. R. (2010). Determination of the impact of bottle colour and phenolic concentration on pigment development in white wine stored under external conditions. *Analytica Chimica Acta, 660*(1), 81–86. https://doi.org/10.1016/j.aca.2009.11.048

Min, D. B., & Boff, J. M. (2002). Chemistry and reaction of singlet oxygen in foods. *Comprehensive Reviews in Food Science and Food Safety, 1*, 58–72. https://doi.org/10.1111/j.1541-4337.2002.tb00007.x

Ournac, A. (1968). Riboflavin pendant la fermentation du jus de raisin et la conservation du vin sur lies. *Annales de Technologie Agricole, 17*, 67–75.

Provenzano, M. R., El Bilali, H., Simeone, V., Baser, N., Mondelli, D., & Cesari, G. (2010). Copper contents in grapes and wines from a Mediterranean organic vineyard. *Food Chemistry, 122*(4), 1338–1343. https://doi.org/10.1016/j.foodchem.2010.03.103

Reschke, S., Tran, T., Bekker, M., Wilkes, E., & Johnson, D. (2015). AWRI: Using copper more effectively in winemaking. *Wine and Viticulture Journal, 30*(5), 35–39.

Ribéreau-Gayon, P., Glories, Y., Maujean, A., & Dubourdieu, D. (2006). Handbook of enology. In (2 ed.), *Vol. 2. The chemistry of wine stablization and treatments*. John Wiley & SonsV. https://doi.org/10.1002/0470010363.

Rossi, J. A., & Singleton, V. L. (1966). Contributions of grape phenols to oxygen absorption and browning of wines. *American Journal of Enology and Viticulture, 17*, 231–239.

Siebert, T. E., Solomon, M. R., Pollnitz, A. P., & Jeffery, D. W. (2010). Selective determination of volatile sulfur compounds in wine by gas chromatography with sulfur chemiluminescence detection. *Journal of Agricultural and Food Chemistry, 58*(17), 9454–9462. https://doi.org/10.1021/jf102008r

Singleton, V. L. (1987). Oxygen with phenols and related reactions in musts, wines, and model systems: Observations and practical implications. *American Journal of Enology and Viticulture, 38*(1), 69–77. https://doi.org/10.5344/ajev.1987.38.1.69

Smith, M. E., Bekker, M. Z., Smith, P. A., & Wilkes, E. N. (2015). Source of volatile sulfur compounds in wine. *Australian Journal of Grape and Wine Research, 21*(S1), 705–712. https://doi.org/10.1111/ajgw.12193

Solomon, M. R., Geue, J., Osidacz, P., & Siebert, T. E. (2010). Aroma detection threshold study of methanethiol in white and red wine. *AWRI Technical Review, 186*, 8–10.

Zhang, X., Blackman, J. W., Prenzler, P. D., & Clark, A. C. (2022). Suppression of reductive characters in white wine by Cu fractions: Efficiency and duration of protection during bottle aging. *Food Chemistry, 393*, Article 133305. https://doi.org/10.1016/j.foodchem.2022.133305