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Light-induced changes in bottled white wine and underlying photochemical mechanisms

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Abstract

Bottled white wine may be exposed to UV-visible light for considerable periods of time before it is consumed. Light exposure may induce an off-flavor known as "sunlight" flavor, bleach the color of the wine and/or increase browning and deplete sulfur dioxide. The changes that occur in bottled white wine exposed to light depend on the wine composition, the irradiation conditions and the light exposure time. The light-induced changes in the aroma, volatile composition, color and concentrations of oxygen and sulfur dioxide in bottled white wine are reviewed. In addition, the photochemical reactions thought to have a role in these changes are described. These include the riboflavin-sensitized oxidation of methionine, resulting in the formation of methanethiol and

dimethyl disulfide, and the photodegradation of iron(III) tartrate, which gives rise to glyoxylic acid, an aldehyde known to react with flavan-3-ols to form yellow xanthylium cation pigments.

Keywords

UV-visible, bottle color, riboflavin, volatile sulfur compounds, oxidation, iron(III) tartrate

1. Introduction

Bottled white wine can be exposed to UV-visible light for relatively long periods of time in retail stores, restaurants, domestic settings and elsewhere. Light exposure can induce the production of off-aromas (Dozon and Noble, 1989), color changes (Benítez et al., 2006, Dias et al., 2012) and the depletion of sulfur dioxide (Blake et al., 2010) and therefore lower the quality and reduce the shelf life of bottled white wine. These changes depend on the irradiation conditions (i.e. the spectrum of the light source, the light intensity, the optical properties of the bottle) and the duration of light exposure. Bottles may be exposed to light in different conditions and for different periods of time, and this may contribute to variation in sensory attributes and shelf life between bottles. Dark colored bottles such as green and amber bottles provide greater protection from light than clear and light colored bottles, however the latter are sometimes preferred for marketing reasons. In recent years, prompted by a desire to make wine bottling practices more sustainable, bottle producers have extended their range of lightweight bottles, and these bottles have been widely adopted by winemakers (WRAP, 2010). Although bottle color is known to have an important role in the preservation of bottled white wine that may be exposed to light, the contribution of bottle weight and other factors such as the degree of UV protection of clear bottles are not as well understood.

This review describes the major light-induced changes in bottled white wine and the photochemical mechanisms that may have a role in these changes. The pathways involved in the oxidation of bottled white wine under typical conditions (i.e. in darkness) are briefly outlined and compared with those involved in photochemical oxidation. The main factors related to the

irradiation conditions that contribute to the light-induced changes in bottled white wine are discussed. The light-induced changes in the aroma, volatile composition, color and the concentrations of oxygen and sulfur dioxide in white wine are described. Finally, the contribution of the riboflavin-sensitized oxidation of wine components and the photodegradation of iron(III) carboxylate complexes to these changes is examined.

2. Wine oxidation

Oxidation processes that occur in certain red wines under controlled conditions may be beneficial (Schmidtke et al., 2011), however those that occur in white wines generally do not offer any improvement (Singleton, 1987). The total amount of oxygen in a bottle of wine (i.e. the sum of the oxygen in the wine and in the headspace) is initially between around 1 and 9 mg/L, depending on the bottling process and the bottle closure (Ugliano et al., 2013). Oxygen is consumed by the wine during aging and more oxygen may enter the bottle through the closure (Ugliano, 2013). Oxygen has a triplet ground state in which it does not readily react with singlet species in wine, since this is spin-forbidden. In order to react with singlet species, triplet oxygen must be activated and this may be achieved through excitation to a singlet state or single electron reduction (Aust et al., 1985, Korycka-Dahl et al., 1978). Triplet oxygen may be excited to a singlet state in wine exposed to light (see Section 7), however there is no evidence that singlet oxygen is formed in wine stored in darkness, and under the latter conditions, it appears that the main means of triplet oxygen activation is single electron reduction (Danilewicz, 2003, Singleton, 1987).

Transition metals in wine such as iron and copper, typically present at around 5.5 and 0.2 mg/L respectively (Danilewicz, 2007), catalyze oxidation. For example, iron(II) can reduce oxygen to a radical species and then iron(III) can oxidize certain wine components to regenerate iron(II), completing the catalytic cycle. There is evidence that wine components that bind iron(III) more strongly than iron(II) have a critical role in facilitating iron(III)/iron(II) cycling (Danilewicz, 2013, Kreitman et al., 2013). According to the hard and soft Lewis acids and bases theory, iron(III) is a harder Lewis acid than iron(II) and consequently will form stronger complexes with hard Lewis bases abundant in wine, which include oxygen donor species such as carboxylate anions (Pearson, 1968a, Pearson, 1968b). The main carboxylic acids in wine, tartaric acid and malic acid, are typically present at 1.63 and 1.64 g/L respectively, and others include succinic acid and citric acid (Fowles, 1992). The pK_{a1} values of these acids are between 3.0 and 4.2, while the pK_{a2} values are between 4.1 and 5.2 (Ribéreau-Gayon et al., 2006), hence in wine, a considerable proportion of these acids exist as monocarboxylate and dicarboxylate anions. The formation of iron(III) carboxylate complexes in wine shifts the iron(III)/iron(II) equilibrium to favor the iron(III) form, and therefore lowers the reduction potential of the iron(III)/iron(II) couple (Danilewicz, 2003, Danilewicz, 2013). This in turn makes iron(II) a stronger reducing agent, hence the reduction of oxygen by iron(II) more favorable (Danilewicz, 2003, Danilewicz, 2013). There is evidence that in model wine solutions, iron(III) tartrate degrades upon exposure to light, and this may have important implications for iron(III)/iron(II) cycling under these conditions (see Section 9) (Clark et al., 2011, Clark et al., 2007, Clark and Scollary, 2003).

Oxygen in wine may be reduced to water through a series of four single electron reduction reactions, giving rise to the superoxide radical, the peroxide anion and the hydroxyl radical, the former two species existing predominantly as the hydroperoxyl radical and hydrogen peroxide at wine pH (Figure 1) (Danilewicz, 2003). A recent study has provided evidence that the hydroperoxyl radical may not be formed in wine and it was proposed that the intermediates in the reduction of oxygen to hydrogen peroxide might include iron oxygen complexes (Danilewicz, 2013). The Fenton reaction, whereby hydrogen peroxide is reduced by iron(II) to form a hydroxyl radical, has an important role in wine oxidation. The hydroxyl radical is a very strong oxidizing agent and will react with organic compounds in wine at near diffusion-controlled rates (Danilewicz, 2003). It oxidizes ethanol to the 1-hydroxyethyl radical, which is in turn oxidized to acetaldehyde (Figure 1) (Elias et al., 2009). The hydroxyl radical is thought to oxidize other abundant wine components such as organic acids (Danilewicz, 2003, Waterhouse and Laurie, 2006). There is evidence that tartaric acid is degraded to glyoxylic acid in model wine solutions containing iron (Es-Safi et al., 2000, Fulcrand et al., 1997). It has been proposed that in these solutions, tartaric acid is oxidized by hydroxyl radicals generated by the Fenton reaction, resulting in the initial formation of dihydroxyfumaric acid, which then degrades through decarboxylation and oxidation reactions to form glyoxylic acid and other compounds (Clark et al., 2007, Danilewicz, 2003).

Phenolic compounds are the main oxidation substrates in wine and those that have an *o*-diphenol structure are readily oxidized to semiquinone radicals, which are in turn oxidized to *o*-quinone compounds (Figure 1) (Singleton, 1987, Waterhouse and Laurie, 2006). Phenolic compounds

and their oxidation products react to form larger compounds and these reactions are responsible for wine browning (Boulton et al., 1996, Li et al., 2008). For example, flavan-3-ols such as (+)-catechin and (6)-epicatechin are nucleophilic and react with *o*-quinones to form addition products and with certain aldehydes including glyoxylic acid and glyoxal to form yellow xanthylum cations (Es-Safi et al., 2003, Es-Safi et al., 2000). In white wine, the concentrations of flavan-3-ols have been positively correlated with browning potential (Simpson, 1982, Sioumis et al., 2006).

The Strecker degradation of amino acids such as methionine and cysteine to aldehydes by α -dicarbonyl compounds formed during fermentation or oxidation contributes to the evolution of aroma in bottled wine (Ugliano, 2013). In model wine solutions, glyoxal, an α -dicarbonyl compound generated during alcoholic and malolactic fermentation, reacts with methionine to form methional, methanethiol and dimethyl disulfide (DMDS), and with cysteine to form hydrogen sulfide, methanethiol and other compounds (Marchand et al., 2000, Pripis-Nicolau et al., 2000). It has been proposed that methional, the initial product of the Strecker degradation of methionine, degrades via a retro-Michael mechanism to form methanethiol, which is then oxidized to DMDS (Pripis-Nicolau et al., 2000). More recently, it was found that the addition of ascorbic acid to a model wine solution containing methionine, iron and other wine components increased the production of methional under conditions that favored oxidation (Grant-Preece et al., 2013). In wine conditions, ascorbic acid is degraded to form α -dicarbonyl compounds including dehydroascorbic acid and xylosone (Bradshaw et al., 2011), and this may account for the greater degradation of methionine to methional in the presence of ascorbic acid (Schonberg

and Moubacher, 1952). Hydrogen sulfide, methanethiol and DMDS are among the main volatile sulfur compounds responsible for reduced off-aromas in bottled wine (Ugliano, 2013), while methional is an important aroma compound in wines spoiled by oxidation (Escudero et al., 2000), and these compounds have also been implicated in the light-induced off-aroma of bottled white wine (see Table 1 and Sections 4 and 8).

Sulfur dioxide is the main preservative in wine and is thought to perform this role primarily by reacting with hydrogen peroxide to form sulfuric acid (Figure 1) (Boulton et al., 1996). It also reacts with *o*-quinones and aldehydes to form addition products and is able to reduce *o*-quinones to the original phenolic compounds (Figure 1) (Danilewicz et al., 2008). Ascorbic acid may also be added to white wines, and there is evidence that initially, when present at high concentrations, it acts as an antioxidant, however when it has been depleted to a certain extent, it begins to have a pro-oxidant effect, and this is most evident in the absence of sulfur dioxide (Bradshaw et al., 2011). Studies in model wine solutions have shown that the degradation products of ascorbic acid can induce the polymerization of flavan-3-ols, resulting in the formation of yellow xanthylium cations (Barril et al., 2009, Barril et al., 2008, Clark et al., 2009).

3. Light source, bottle properties and other factors

Light-induced changes in white wine are due to photochemical reactions and the secondary reactions of the products. The latter may include both thermal and photochemical reactions. Photochemical reactions involve the absorption of specific wavelengths of ultraviolet (UV 200 ó 400 nm) and/or visible (400 ó 760 nm) light by a reactant, which is thereby promoted to an

excited electronic state (Wardle, 2009). The energy of the photon absorbed is equal to $h\nu$, where h is the Planck constant and ν is the frequency of the light. It should be noted that a species is more reactive in an excited electronic state than in the ground state, since the former has a less stable electron distribution, which makes the bonds weaker and increases the ability of the species to donate and accept electrons (Wardle, 2009). The light-induced changes in bottled white wine therefore depend on the light-absorbing species in the wine and the wine composition in general, the spectrum of the light source, the light intensity, the optical properties of the bottle and the irradiation time. In general, the wavelengths that cause the most damage to foods and beverages are those with the highest energy (i.e. shortest wavelength) (Bekbölet, 1990). Studies on the photochemical reactions that contribute to the light-induced changes in bottled white wine suggest that in this case, the most damaging wavelengths are below 520 nm (Clark et al., 2011, Maujean et al., 1978, Maujean and Seguin, 1983a). The temperature of the wine will also influence the observed light-induced changes, since it will affect the rates of thermal reactions and photochemical reactions, although it should be noted that photoexcitation can occur at low temperatures (Wardle, 2009).

Bottled white wine sold in retail stores is often displayed under light from artificial sources such as fluorescent lamps for relatively long periods of time. The spectrum of a typical 'cool white' fluorescent lamp consists of the mercury emission bands, with maxima at around 313, 365, 405, 436, 546 and 578 nm, as well as phosphor emission peaks with maxima at around 480 and 580 nm (Spikes, 1981). In domestic settings and restaurants, bottled white wine may also be exposed to sunlight. At sea level, the solar spectrum consists of a broad irregular peak, with a maximum

in the visible region, tailing into the UV and infrared (IR 780 nm ó 1 mm) regions, and reaching negligible values around 300 nm, since the shorter wavelengths are absorbed by ozone in the atmosphere (Spikes, 1981). Light sources with spectra similar to that of sunlight, such as xenon lamps and solar simulator lamps, were used in several studies described in this review.

Glass wine bottles only transmit wavelengths above around 300 nm (Figure 2). Standard clear (flint) bottles typically transmit more than 80% of UV-visible radiation above 360 nm (Figure 2), while clear bottles with additional UV protection, which are made by adding a UV-absorbing species to the glass or coating clear bottles in a film containing such a species, transmit less UV radiation (Hartley, 2008). Green bottles transmit considerably less light than clear bottles, particularly in the region below 520 nm (Figure 2), while amber bottles transmit very little radiation below 520 nm (Hartley, 2008). For the darker colored bottles, heavy weight bottles, which have thicker glass, transmit slightly less light than the lightweight equivalents (Figure 2). Other factors that affect the quantity and quality of the light that reaches wine in a bottle include the bottle shape, the size and position of the label, the position of the light source relative to the bottle and the use of protective sleeves (Dias et al., 2010, Hartley, 2008).

The studies reviewed here used a variety of different irradiation conditions, including different light sources, sample volumes, storage containers and storage temperatures, as well as different irradiation times. It should be noted that some of these studies did not include dark controls (i.e. samples treated in the same manner but without exposure to light). As described above, there are many changes that occur in bottled wine in darkness, and therefore, in order to demonstrate conclusively that a change observed in samples exposed to light is in fact induced by light, it is

necessary to show that the change either does not occur or occurs to a lesser extent in samples stored in darkness. Also, in some studies the sample temperature varied across the different treatments. Moreover, in some studies, samples were stored in the absence of oxygen or had a certain initial oxygen concentration, while in others the samples were frequently or continuously exposed to air. Hence, in the future, greater attention should be given to the importance of dark controls and to other variables that may influence the observed changes, such as temperature and the oxygen concentration.

4. Light-induced changes in wine aroma

Light exposure may induce an off-flavor in bottled white wine known as "sunlight" flavor or "goût de lumière". Dozon and Nobel (1989) described the sensory changes that occurred in a sparkling white wine and the corresponding original still wine, during exposure to two 40 W fluorescent bulbs in clear bottles (35 cm away from the light source for 72 hours) as a decrease in the "citrus" aroma, and an increase in the "cooked cabbage", "corn nuts", "wet dog/wet wool" and "soy/marmite" aromas. Significant changes in the aroma of the still and sparkling wines were observed after only 3.3 to 3.4 hours in clear bottles, and after 18 and 31 hours respectively in green bottles (Dozon and Noble, 1989), consistent with the greater transmission of UV-visible light by the clear bottles (Figure 2). It appears that most white wines have the potential to develop "sunlight" flavor (Mattivi et al., 2000, Pichler, 1996). A study on 85 white wines, including Chardonnay and Pinot Gris, in which samples were exposed to a tungsten bulb in glass columns for 48 hours, found that 31% of the wines exhibited an intense off-aroma, 40%

exhibited a perceptible off-aroma and the remaining 29% did not develop an off-aroma under these conditions (Mattivi et al., 2000). The susceptibility of white wines to γ -sunlight \emptyset flavor has been associated with the photosensitizer riboflavin, however other wine components are also thought to contribute (see Section 8) (Mattivi et al., 2000). There is evidence that aging Chardonnay wine on yeast lees increases its susceptibility to γ -sunlight \emptyset flavor (La Follette et al., 1993).

The light-induced off-aroma of white wine has been mainly attributed to volatile sulfur compounds (Haye et al., 1977, Maujean and Seguin, 1983a). Maujean and Seguin (1983a) found that hydrogen sulfide, methanethiol and DMDS were formed in Champagne exposed to a solar simulator lamp in glass cuvettes, in the absence of oxygen (see Section 8). In another study, methanethiol and DMDS were not detected in bottled Riesling wine exposed to light, however it was noted that the wine exhibited off-aromas similar to those associated with volatile sulfur compounds (Jung et al., 2007). Methanethiol and DMDS appear to be largely responsible for the γ -cooked cabbage \emptyset aroma of white wine affected by exposure to light (Table 1).

Light exposure can also influence the production of other undesirable aroma compounds. Jung et al. (2007) observed that the concentration of furfural increased in bottled Riesling wine exposed to light and this was more rapid in clear bottles than in amber bottles. Furfural has been positively correlated with the γ -cooked vegetable \emptyset aroma of white wines stored under conditions that favor oxidation (Escudero et al., 2002). In addition, Chardonnay wine exposed to light exhibited an acetaldehyde aroma (Dias et al., 2013) and studies in model wine solutions suggest

that exposure to light may increase the rate at which ethanol is oxidized to acetaldehyde (see Section 9) (Clark et al., 2007).

The concentrations of desirable aroma compounds in white wine, including acetate esters, alcohols, fatty acids and notably ethyl esters such as ethyl hexanoate and ethyl octanoate, may decrease upon exposure to light (Benítez et al., 2003, Benítez et al., 2006, Blake et al., 2010, Cellamare et al., 2009, D'Auria et al., 2003, Jung et al., 2007), in agreement with the perceived loss of fruity aromas under these conditions. However, only a few of these compounds were affected by both light exposure and bottle color (Benítez et al., 2006, Blake et al., 2010, Jung et al., 2007). The concentrations of esters may decrease during aging and at high temperatures due to hydrolysis (Ramey and Ough, 1980). These compounds have also been shown to degrade in model wine solutions containing riboflavin exposed to light, suggesting that under these conditions, riboflavin may have a role in their degradation (Cellamare et al., 2009, D'Auria et al., 2003). Finally, studies other alcoholic beverages and lemon oil have shown that exposure to light induces the degradation of certain terpenes (Iwanami et al., 1997, Neumann and Garcia, 1992, Refsgaard et al., 1996, Refsgaard et al., 1995, Schieberle and Grosch, 1989), a class of compounds that have a significant contribution to the aroma of certain white wines (Marais, 1983).

5. Light-induced changes in wine color

An early study found that exposure to sunlight decreased the color of white wine, while prolonged exposure increased the color of a Semillon wine, and color development in the latter

was inhibited by purging the headspace of the irradiation container with nitrogen gas (Sato et al., 1970). In most of the other studies described in this section, samples were either frequently or continuously exposed to air during irradiation. Hence, further research is needed to investigate the light-induced changes in the color of bottled white wine with a typical oxygen concentration (see Section 2). It should be noted that in addition to changes in wine color, exposure to light may also accelerate the production of copper haze (Amerine and Joslyn, 1970, Ribéreau-Gayon et al., 2006).

At a controlled, relatively high temperature (e.g. 45 °C), exposure to light accelerates the browning of bottled white wine, and more so in clear and light colored bottles than in dark colored bottles (Dias et al., 2013, Dias et al., 2012). However, if the temperature is not controlled, browning may occur more rapidly in dark colored bottles than in clear and light colored bottles (Dias et al., 2013, Maury et al., 2010). This may be partly related to the greater absorption of IR radiation by the darker colored bottles (compare transmittance at 800 nm of clear and antique green bottles in Figure 2); hence the higher temperature of the wine in these bottles (Dias et al., 2013, Maury et al., 2010). Studies on *fino* sherry, which did not report the actual temperature of the samples, showed that in a chamber maintained at 45 °C, exposure to a xenon lamp enhanced browning, and to a greater extent in clear bottles than in topaz bottles (Benítez et al., 2006), in agreement with the observed impact of bottle color on color development at a constant elevated temperature. While, in a chamber maintained at 25 °C, exposure to a xenon lamp resulted in greater browning in topaz bottles than in clear bottles (Benítez et al., 2003). Considering that xenon lamps generally radiate large amounts of heat, it is

possible that in the chamber maintained at 25 °C, the sherry in the topaz bottles was held at a higher temperature as a result of the greater absorption of IR radiation by the topaz glass, whereas in the chamber maintained at 45 °C, the heat emitted by the lamp had a less pronounced effect on the temperature of the samples. These studies have shown that in experiments on the effect of light exposure and bottle color on bottled white wine, it is necessary to monitor the actual sample temperature in addition to the temperature of the surroundings. Further studies are needed to assess the effect of exposure to light and bottle color on color development in bottled white wine maintained at a temperature more relevant to wine storage (i.e. ambient or cold storage temperature) and also to investigate the interactions between light exposure, bottle color and sample temperature.

Benítez et al. (2006) showed that in bottled *fino* sherry, the concentrations of several monomeric phenolic compounds, including (ó)-epicatechin, as well as certain benzoic acids and hydroxycinnamic acids, decreased at greater rates when exposed to a xenon lamp than when stored in darkness. Similar observations, albeit for fewer phenolic compounds, were made in a study on the impact of variable light exposure on a white wine stored in green bottles (Recamales et al., 2006). Furthermore, in *fino* sherry and model wine solutions of phenolic compounds at similar concentrations, many of these compounds were degraded at greater rates in clear bottles than in topaz bottles (Benítez et al., 2003, Benítez et al., 2006). It is likely that the photochemical oxidation mechanisms described in this review contribute to the degradation of phenolic compounds under these conditions (see Sections 7 ó 9).

The light-induced changes in the color of white wine appear to be the net result of the photodegradation and formation of various pigments. Riboflavin is a yellow pigment that is relatively stable in white wine stored in darkness and at elevated temperatures, however it degrades rapidly in white wine exposed to light (Dias et al., 2012, Perlman and Morgan, 1945). Similarly, it has been reported that while xanthylum cations derived from (+)-catechin and glyoxylic acid were stable in model wine solutions stored in darkness, these pigments were degraded in samples exposed to sunlight (George et al., 2006). On the other hand, there is evidence that the photodegradation of iron(III) tartrate gives rise to glyoxylic acid (see Section 9) (Clark et al., 2011, Clark et al., 2007, Clark and Scollary, 2003) and this may increase the production of xanthylum cations. Maury et al. (2010) identified xanthylum cations as one of the main species responsible for the increase in the absorbance at 440 nm of Sauvignon Blanc wine enriched with (+)-catechin or (ó)-epicatechin (100 mg/L) stored in bottles exposed to sunlight. The concentrations of xanthylum cations were much higher in classic green bottles than in clear bottles. This was partly attributed to the higher average temperature of the wine in the darker colored bottles, hence the greater rate of xanthylum cation production (Es-Safi et al., 2003), as well as the lower transmission of UV-visible light by these bottles (Figure 2), and therefore the slower rate of the photodegradation of these pigments (George et al., 2006, Maury et al., 2010).

6. Light-induced changes in the concentrations of oxygen and sulfur dioxide

Light exposure accelerates oxygen consumption (Rossi and Singleton, 1966, Singleton, 1987) and also affects the reduction potential of bottled wine (Maujean et al., 1978, Tomlinson and

Kilmartin, 1997). The reduction potential of bottled wine decreases during aging in typical conditions and this has been associated with the consumption of oxygen (Danilewicz, 2012, Kilmartin and Zou, 2001). Maujean et al. (1978) showed that the reduction potential of Champagne in glass cuvettes decreased during exposure to light emitted by a solar simulator lamp, filtered through glass with a maximum transmittance at 340 or 441 nm, however it barely changed when exposed to light filtered through glass with a maximum transmittance at 523 nm. Moreover, in Champagne exposed to light in cuvettes made from different types of glass, the rate at which the reduction potential decreased was found to increase as the transmittance of the glass at 360 nm increased. The addition of riboflavin also accelerated the decrease in the reduction potential of Champagne during irradiation (Maujean and Seguin, 1983a). A more recent study on bottled soy milk showed that supplementation with riboflavin increased the consumption of headspace oxygen during exposure to a fluorescent lamp (Huang et al., 2006).

Blake et al. (2010) found that the free sulfur dioxide concentration was lower in Riesling wine stored in clear bottles under 15 W fluorescent bulbs (one bulb per 10 bottles) than in samples stored in darkness after three months and also after 12 months. The same trend was also apparent for both free and bound sulfur dioxide in Cabernet Franc wine stored under the same conditions. At the end of the irradiation time, the average proportion of free sulfur dioxide retained in the Riesling and Cabernet Franc wines in clear, green and amber bottles was 33.8, 42.5 and 55.5% respectively (Blake et al., 2010).

7. Riboflavin-sensitized oxidation

Photosensitizers are species that absorb light to induce a physical or chemical change in a substrate. In foods and beverages, these include pigments such as flavins (Bekbölet, 1990). Flavins are yellow compounds that have a common isoalloxazine structure and include riboflavin (vitamin B₂) and its derivatives, flavin mononucleotide (FMN) and flavin adenine dinucleotide (FAD), which are cofactors of enzymes that catalyze electron transfer reactions in cells (Heelis, 1982, Müller, 1983). Mattivi et al. (2000) reported that in 85 white wines the average concentration of riboflavin was about 100 µg/L, while the levels of FMN and FAD were negligible. Similar values have been reported in other studies (Andrés-Lacueva et al., 1998, Cataldi et al., 2002). The total concentration of riboflavin, FMN and FAD in free-run and macerated Terret Blanc musts was 55 µg/L riboflavin equivalents (Ournac, 1968). The concentration increased during fermentation to 110 and 170 µg/L in the wines made from the free-run and macerated musts, and continued to increase in the wines left on the yeast lees, reaching 160 and 215 µg/L respectively, four days after fermentation (Ournac, 1968). Pichler (1996) suggested that the use of yeast strains that have a lower ability to produce riboflavin may be a potential means of minimizing its concentration in wine, and showed that fining with bentonite can be used to lower the riboflavin concentration of white wines.

In a model wine solution, riboflavin absorbs wavelengths below around 510 nm, with maxima in the region above 300 nm at 370 and 442 nm (Maujean and Seguin, 1983a). Riboflavin absorbs light to generate the lowest excited singlet state, which may undergo intersystem crossing to form the lowest excited triplet state (Figure 3). While the transition from the lowest excited

singlet state to the ground state is spin-allowed, the transition from the lowest excited triplet state to the ground state is spin-forbidden, thus the triplet state has a longer lifetime and is thought to be the main excited species involved in photosensitized reactions (Foote, 1976). The quantum yield of a photochemical reaction or a photophysical change is the number of moles of product formed per mole of photons (einstein) absorbed. For flavins, the quantum yield of the triplet state in neutral aqueous solutions exposed to 347 nm light is around 0.7, indicating that this process is highly efficient (Grodowski et al., 1977). The efficiency decreases as pH decreases, primarily due to the quenching of the excited states by hydrogen ions (Grodowski et al., 1977). For riboflavin in aqueous solutions at pH 2.2, the quantum yield of the triplet state is 0.4 (Grodowski et al., 1977). Hence, it is expected that at wine pH, the quantum yield for this processes would be between 0.4 and 0.7.

Photosensitized oxidation can occur through two pathways (Foote, 1976). In the type I pathway, the triplet sensitizer reacts directly with a species to form radicals, which may reduce oxygen, and in the type II pathway, the triplet sensitizer transfers its excess energy to triplet oxygen, which is thereby excited to a singlet state, and may then react with other singlet species (Figure 4). Evidently, in the absence of oxygen, only type I processes would occur, whereas in the presence of oxygen, both type I and type II processes would occur to some extent. In general, species that are readily oxidized or reduced, such as certain phenolic compounds and *o*-quinones, favor the type I pathway, whereas species that are not readily oxidized or reduced, such as alkenes and aromatic compounds, favor the type II pathway (Foote, 1976). However, some species that are predominantly degraded via the type I pathway at low oxygen concentrations

may be degraded via the type II pathway at high oxygen concentrations (Foote, 1976). Triplet riboflavin is reactive towards triplet oxygen and a range of different compounds including ascorbic acid, phenolic compounds and amino acids (Cardoso et al., 2012, Choe et al., 2005). The riboflavin-sensitized oxidation of sulfur-containing amino acids in white wine is described in the following section.

The photosensitized production of singlet oxygen may contribute to the increased rate of oxygen consumption in wine exposed to light (Figure 4) (Singleton, 1987). There is evidence that singlet oxygen is formed in skim milk and model solutions containing riboflavin exposed to fluorescent light (Bradley et al., 2003). Singlet oxygen is electrophilic and reactive towards alkenes, amines, sulfides and anions (DeRosa and Crutchley, 2002, Foote, 1976). It has been proposed that in milk, singlet oxygen reacts with methionine resulting in the formation of DMDS (Jung et al., 1998, Min and Boff, 2002). Singlet oxygen also reacts with terpenes to form hydroperoxides (Chiron et al., 1997) and this is thought to contribute to the light-induced sensory changes in lemon oil (Neumann and Garcia, 1992). Interestingly, the health benefits of resveratrol appear to be related to its ability to quench singlet oxygen (Jiang et al., 2010), hence exposure to light may lower the quantity of this compound in wine.

8. Riboflavin-sensitized production of volatile sulfur compounds

Mattivi et al. (2000) demonstrated that in 85 white wines, there was a positive correlation between the initial riboflavin concentration and the intensity of the light-induced off-aroma. Moreover, the addition of riboflavin (1 mg/L) increased the percentage of the wines that

developed an off-aroma during irradiation from 71 to 98%. An earlier study also showed that in general the susceptibility of white wines to 3-sunlightøflavor increases as the riboflavin concentration increases (Pichler, 1996). However, Mattivi et al. (2000) noted that the strength of the correlation varied for different groups of wines, and interestingly there was no correlation in the Chardonnay wines, which comprised the largest group. Mattivi et al. (2000) suggested that other wine components such as sulfur-containing amino acids, phenolic compounds and transition metal ions, might also have a role in the development of 3-sunlightøflavor in white wines, and particularly in Chardonnay. However, when a group of Chardonnay wines with a low initial riboflavin concentration and a pronounced 3-sunlightøflavor were compared to a group with a high initial riboflavin concentration and a weak 3-sunlightøflavor, it was found that the average concentrations of iron, copper, total polyphenols and hydroxycinnamic acids in the two groups of wines were not significantly different.

Maujean and Seguin (1983a) showed that the addition of riboflavin, methionine and cysteine to Champagne increased the production of methanethiol and DMDS during exposure to light in glass cuvettes, in the absence of oxygen. The presence of riboflavin was necessary for the production of hydrogen sulfide, methanethiol and DMDS in model wine solutions containing methionine and cysteine under the same conditions. UV-visible absorption spectroscopy was used to provide evidence that riboflavin was reduced in model wine solutions containing methionine during irradiation, and then recovered upon exposure to air, while it was degraded in the absence of methionine (Maujean and Seguin, 1983a, Maujean and Seguin, 1983b). Maujean and Seguin (1983a) proposed that in white wine exposed to light, triplet riboflavin oxidizes

methionine to methional, which then degrades to form methanethiol and DMDS (Figure 5).

However, methional was not detected in the irradiated wine or model wine samples. There is evidence that the riboflavin-sensitized oxidation of methionine to methional also contributes to the light-induced changes in the aroma of milk (Patton, 1954, Patton and Josephson, 1953).

Methional has been identified in skim milk exposed to sunlight and it was observed that samples of skim milk and a model solution containing riboflavin and methionine exposed to light initially developed a methional aroma, which subsequently evolved into a strong methanethiol aroma (Allen and Parks, 1975).

Maujean and Seguin (1983b) assessed the use of chemical means to inhibit the riboflavin-sensitized production of volatile sulfur off-aroma compounds in white wine. The addition of copper(II) to Champagne prevented the production of methanethiol and DMDS during exposure to light, however DMDS was detected in the irradiated samples the following day (Maujean and Seguin, 1983b). It is possible that copper(II) formed complexes with methanethiol, which eventually degraded to form DMDS (Maujean and Seguin, 1983b, Smith et al., 1994). However, the addition of a mixture of (+)-catechin and (ó)-epicatechin monomers and dimers to a model wine solution containing riboflavin and methionine slowed the production of the volatile sulfur compounds during exposure to light (Maujean and Seguin, 1983b). (+)-Catechin, ascorbic acid and tryptophan (Goldsmith et al., 2005), as well as a range of other phenolic compounds (Cardoso et al., 2006), have been shown to quench triplet riboflavin in model beer solutions. There is evidence that the light-induced off-aroma of beer arises through the direct oxidation of iso- -acids by triplet riboflavin in the presence of sulfur-containing amino acids, resulting in the

formation of 3-methyl-2-butene-1-thiol, a very potent compound with a "skunky" aroma (Goldsmith et al., 2005, Huvaere et al., 2004, Kuroiwa et al., 1963). The addition of ascorbic acid or tryptophan to beer, and either of these compounds or (+)-catechin to model beer solutions containing riboflavin, iso- α -acids and cysteine, delayed the production of "sunlight" flavor (Goldsmith et al., 2005). Similarly, the addition of ascorbic acid to skim milk decreased the production of DMDS during irradiation and lowered the intensity of the light-induced off-aroma (Jung et al., 1998). In model beer solutions, triplet riboflavin is also efficiently quenched by triplet oxygen (Goldsmith et al., 2005), and it is known that as the amount of air in bottled beer increases, the intensity of the characteristic light-induced off-aroma decreases (Gray et al., 1941, Kuroiwa et al., 1963). Therefore, it appears that in addition to the concentration of riboflavin, the concentrations of sulfur-containing amino acids and other triplet riboflavin quenchers, including phenolic compounds, ascorbic acid and oxygen, would also influence the development of "sunlight" flavor in white wine.

9. Iron(III) tartrate photodegradation and the photo-Fenton process

Many iron(III) carboxylate complexes have an absorption maxima around the near UV (300 ó 400 nm)/visible region which is usually assigned to the ligand-to-metal charge-transfer (LMCT) transition (Balzani and Carassiti, 1970). At wavelengths above 300 nm, a model wine solution containing tartaric acid and iron(II) (5 mg/L) had an absorption maximum at around 340 nm, tailing into the visible region and reaching negligible values around 500 nm (Clark et al., 2011). This peak was attributed to iron(III) tartrate formed following the oxidation of iron(II) in the

solution (Figure 1) (Clark et al., 2011). When a metal complex absorbs wavelengths within its LMCT band, an electron is partially transferred from the ligand to the metal. In this excited state, the complex can degrade, providing it has sufficient energy, to form the reduced metal ion and an oxidized ligand-derived radical (Balzani and Carassiti, 1970, Tama and Makarová, 1997). There is evidence that the photodegradation of iron(III) carboxylate complexes such as iron(III) tartrate involves the formation of a long-lived iron(II) carboxylate radical complex intermediate (Glebov et al., 2011, Pozdnyakov et al., 2012). Interestingly, the photochemical reduction of iron(III) in the presence of organic acids has been used to quantify these acids in wine and other beverages (Luque-Pérez et al., 1998, Pérez-Ruiz et al., 2004). The efficiency of the photochemical reduction of iron(III) in the presence of an organic acid depends on pH, since this affects iron(III) speciation (Abrahamson et al., 1994). Studies on the photochemical reduction of iron(III) in anaerobic solutions containing a large excess amount of a carboxylic acid exposed to near UV radiation have shown that the maximum iron(II) quantum yield occurs at pH values between 2.5 and 4 (Abrahamson et al., 1994, Baxendale and Bridge, 1955, Duka et al., 1990).

The proposed mechanism for the photochemical oxidation of α -hydroxy carboxylic acids such as tartaric acid in the presence of iron(III) involves the photodegradation of the iron(III) carboxylate complex to form an oxidized α -hydroxy carboxylate radical, which degrades through oxidation and decarboxylation to form an aldehyde or a ketone (Abrahamson et al., 1994, Balzani and Carassiti, 1970). Hence, it appears that under these conditions, tartaric acid is oxidized to 2-hydroxy-3-oxo-propanoic acid (Clark et al., 2007), which then degrades to form the observed

products, which may include glyoxylic acid, glyoxal, formic acid and formaldehyde (Balzani and Carassiti, 1970).

In acidic aqueous solutions containing hydrogen peroxide and iron(II), organic compounds are degraded to form low molecular mass compounds including carboxylic acids. Light exposure increases the rate at which the compound is degraded and possibly also the extent to which it is degraded. This is predominantly due to the photodegradation of iron(III) complexes, such as iron(III) carboxylate and hydroxy complexes (Kavitha and Palanivelu, 2004, Pignatello et al., 2006). The major monomeric iron(III) hydroxy complex in aqueous solutions at around pH 2.5 is the iron(III) monohydroxy complex, which has an absorption maximum around 300 nm and may degrade following LMCT to form iron(II) and a hydroxyl radical (Faust and Hoigné, 1990, Feng and Nansheng, 2000). Iron(II) formed through the photochemical reduction of iron(III) may then reduce oxygen or hydrogen peroxide to regenerate iron(III) (Figure 4). The degradation of a substrate under these conditions is said to occur through the photo-Fenton process (Kavitha and Palanivelu, 2004, Pignatello et al., 2006). This process is a well-known technique for the treatment of wastewater and has been applied to the treatment of winery wastewater (Monteagudo et al., 2012, Mosteo et al., 2006, Mosteo et al., 2008). Moreover, in natural acidic water systems containing iron and carboxylic acids exposed to solar radiation, this process has an important role in iron(III)/iron(II) cycling, the consumption of oxygen, the production of hydrogen peroxide and hydroxyl radicals and the degradation of sulfur dioxide and organic compounds (Faust and Zepp, 1993, Miles and Brezonik, 1981, Zuo and Hoigné, 1992, Zuo and Hoigné, 1993).

Clark et al. (2007) found that in samples of a model wine solution containing tartaric acid and a trace amount of iron (10 ± 5 g/L) exposed to sunlight, tartaric acid was degraded while glyoxylic acid, formic acid and hydrogen peroxide were formed. However, in samples stored in darkness at 45 °C, tartaric acid was stable and either no hydrogen peroxide or only a trace amount of this species was detected (Clark et al., 2007, Clark and Scollary, 2003). Hydrogen peroxide was suggested to arise through the reduction of oxygen and to accumulate in the samples exposed to light due to the photochemical reduction of iron(III) (Clark et al., 2007). The low iron concentration, in addition to the competition of other species such as oxygen with hydrogen peroxide for iron(II), were also thought to favor the accumulation of hydrogen peroxide (Clark et al., 2007). Moreover, it was noted that acetaldehyde was formed in the samples exposed to light, however it was not detected in the samples stored in darkness (Clark et al., 2007). This suggests that within the time considered, the Fenton oxidation of ethanol to acetaldehyde required the photochemical reduction of iron(III). Clark et al. (2007) proposed that tartaric acid was degraded through the photo-Fenton process to form glyoxylic acid and formic acid (Figure 6). A decrease in the oxygen concentration slowed the production of glyoxylic acid in model wine solutions exposed to light (Clark et al., 2011, Clark et al., 2007). Oxygen may limit the production of glyoxylic acid under these conditions by simultaneously limiting the rate at which iron(II) is oxidized and the production of hydrogen peroxide. Clark et al. (2011) demonstrated that in samples of the model wine solution exposed to a xenon lamp in quartz cuvettes, the presence of iron(II) (5 mg/L) and exposure to wavelengths below 520 nm were necessary for the production of glyoxylic acid. Furthermore, glyoxylic acid production was

higher in samples exposed to light filtered through sections of glass from flint and lightweight antique green bottles than in samples protected from light using heavy weight antique green glass (Figure 2) (Clark et al., 2011). These observations provide evidence that glyoxylic acid may be formed in bottled white wine exposed to light as a result of the photodegradation of iron(III) tartrate. The photochemical oxidation of tartaric acid may also generate glyoxal (Balzani and Carassiti, 1970) and both glyoxylic acid and glyoxal could contribute to the light-induced sensory deterioration of white wine (Figure 4).

10. Conclusion

UV-visible light exposure can induce negative changes in the sensory attributes and reduce the shelf life of bottled white wine. These changes depend on the wine composition, the irradiation conditions and the duration of light exposure. Further studies on the effect of exposure to light on bottled white wine in conditions similar to those encountered in the wine industry, such as in retail stores, are needed to estimate the relative importance of light exposure as a factor contributing to the spoilage of bottled white wine. The studies on the photochemical mechanisms that may contribute to the light-induced changes in bottled white wine have highlighted the important role of riboflavin in the production of γ -sunlight flavor, and have provided evidence for the photodegradation of iron(III) tartrate and the role this may have in the light-induced changes in wine color. Further studies are required to better understand the contribution of riboflavin-sensitized oxidation, the photodegradation of iron(III) carboxylate complexes and

other photochemical reactions to the light-induced changes in white wine, and to assess the effect of factors related to the wine composition and the irradiation conditions on these processes.

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References

- Abrahamson, H. B., Rezvani, A. B., and Brushmiller, J. G. (1994). Photochemical and spectroscopic studies of complexes of iron(III) with citric acid and other carboxylic acids. *Inorganica Chimica Acta*, 226: 117-127.
- Allen, C. and Parks, O. W. (1975). Evidence for methional in skim milk exposed to sunlight. *Journal of Dairy Science*, 58: 1609-1611.
- Amerine, M. A. and Joslyn, M. A., (1970). Table wines. The technology of their production 2nd ed. University of California Press, Berkeley and Los Angeles.
- Andrés-Lacueva, C., Mattivi, F., and Tonon, D. (1998). Determination of riboflavin, flavin mononucleotide and flavin-adenine dinucleotide in wine and other beverages by high-performance liquid chromatography with fluorescence detection. *Journal of Chromatography A*, 823: 355-363.
- Aust, S. D., Morehouse, L. A., and Thomas, C. E. (1985). Role of metals in oxygen radical reactions. *Journal of Free Radicals in Biology and Medicine* 1: 3-25.
- Balzani, V. and Carassiti, V., (1970). In: Photochemistry of coordination compounds. pp. 172-174, Academic Press, New York.

Barril, C., Clark, A. C., Prenzler, P. D., Karuso, P., and Scollary, G. R. (2009). Formation of pigment precursor (+)-1"-methylene-6"-hydroxy-2*H*-furan-5"-one-catechin isomers from (+)-catechin and a degradation product of ascorbic acid in a model wine system. *Journal of Agricultural and Food Chemistry*, 57: 9539-9546.

Barril, C., Clark, A. C., and Scollary, G. R. (2008). Understanding the contribution of ascorbic acid to the pigment development in model white wine systems using liquid chromatography with diode array and mass spectrometry detection techniques. *Analytica Chimica Acta*, 621: 44-51.

Baxendale, J. H. and Bridge, N. K. (1955). Photoreduction of ferric compounds in aqueous solution. *The Journal of Physical Chemistry*, 59: 783-788.

Bekbölet, M. (1990). Light effects on food. *Journal of Food Protection*, 53: 430-440.

Benítez, P., Castro, R., and García Barroso, C. (2003). Changes in the polyphenolic and volatile contents of "Fino" sherry wine exposed to ultraviolet and visible radiation during storage. *Journal of Agricultural and Food Chemistry*, 51: 6482-6487.

Benítez, P., Castro, R., Natera, R., and García Barroso, C. (2006). Changes in the polyphenolic and volatile content of "Fino" sherry wine exposed to high temperature and ultraviolet and visible radiation. *European Food Research and Technology*, 222: 302-309.

Blake, A., Kotseridis, Y., Brindle, I. D., Inglis, D., and 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: 935-944.

Boulton, R. B., Singleton, V. L., Bisson, L. F., and Kunkee, R. E., (1996). Principles and practices of winemaking. Chapman & Hall, New York.

Bradley, D. G., Lee, H. O., and Min, D. B. (2003). Singlet oxygen detection in skim milk by electron spin resonance spectroscopy. *Journal of Food Science*, 68: 491-494.

Bradshaw, M. P., Barril, C., Clark, A. C., Prenzler, P. D., and Scollary, G. R. (2011). Ascorbic acid: A review of its chemistry and reactivity in relation to a wine environment. *Critical Reviews in Food Science and Nutrition*, 51: 479-498.

Cardoso, D. R., Libardi, S. H., and Skibsted, L. H. (2012). Riboflavin as a photosensitizer. Effects on human health and food quality. *Food & Function*, 3: 487-502.

Cardoso, D. R., Olsen, K., Møller, J. K. S., and Skibsted, L. H. (2006). Phenol and terpene quenching of singlet- and triplet-excited states of riboflavin in relation to light-struck flavor formation in beer. *Journal of Agricultural and Food Chemistry*, 54: 5630-5636.

Cataldi, T. R. I., Nardiello, D., Scrano, L., and Scopa, A. (2002). Assay of riboflavin in sample wines by capillary zone electrophoresis and laser-induced fluorescence detection. *Journal of Agricultural and Food Chemistry*, 50: 6643-6647.

Cellamare, L., DøAuria, M., Emanuele, L., and Racioppi, R. (2009). The effect of light on the composition of some volatile compounds in wine: An HS-SPME-GC-MS study.

International Journal of Food Science & Technology, 44: 2377-2384.

Chiron, F., Chalchat, J. C., Garry, R. P., Pilichowski, J. F., and Lacoste, J. (1997).

Photochemical hydroperoxidation of terpenes I. Synthesis and characterization of -pinene, -pinene and limonene hydroperoxides. *Journal of Photochemistry and Photobiology A: Chemistry*, 111: 75-86.

Choe, E., Huang, R., and Min, D. B. (2005). Chemical reactions and stability of riboflavin in foods. *Journal of Food Science*, 70: R28-R36.

Clark, A. C., Dias, D. A., Smith, T. A., Ghiggino, K. P., and 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: 3575-3581.

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

Clark, A. C. and Scollary, G. R. (2003). Influence of light exposure, ethanol and copper (II) on the formation of a precursor for xanthylum cations from tartaric acid. *Australian Journal of Grape and Wine Research*, 9: 64-71.

Clark, A. C., Vestner, J., Barril, C., Maury, C., Prenzler, P. D., and Scollary, G. R. (2009). The influence of stereochemistry of antioxidants and flavanols on oxidation processes in a model wine system: ascorbic acid, erythorbic acid, (+)-catechin and (-)-epicatechin. *Journal of Agricultural and Food Chemistry*, 58: 1004-1011.

D'Auria, M., Emanuele, L., Mauriello, G., and Racioppi, R. (2003). On the origin of *brûlé* in Champagne. *Journal of Photochemistry and Photobiology A: Chemistry*, 158: 21-26.

Danilewicz, J. C. (2007). Interaction of sulfur dioxide, polyphenols, and oxygen in a wine-model system: Central role of iron and copper. *American Journal of Enology and Viticulture*, 58: 53-60.

Danilewicz, J. C. (2013). Reactions involving iron in mediating catechol oxidation in model wine. *American Journal of Enology and Viticulture*, 64: 316-324.

Danilewicz, J. C. (2012). Review of oxidative processes in wine and value of reduction potentials in enology. *American Journal of Enology and Viticulture*, 63: 1-10.

Danilewicz, J. C. (2003). Review of reaction mechanisms of oxygen and proposed intermediate reduction products in wine: Central role of iron and copper. *American Journal of Enology and Viticulture*, 54: 73-85.

- Danilewicz, J. C., Seccombe, J. T., and Whelan, J. (2008). Mechanism of interaction of polyphenols, oxygen and sulfur dioxide in model wine and wine. *American Journal of Enology and Viticulture*, 59: 128-136.
- DeRosa, M. C. and Crutchley, R. J. (2002). Photosensitized singlet oxygen and its applications. *Coordination Chemistry Reviews*, 233-234: 351-371.
- Dias, D. A., Clark, A. C., Smith, T. A., Ghiggino, K. P., and Scollary, G. R. (2013). Wine bottle colour and oxidative spoilage: Whole bottle light exposure experiments under controlled and uncontrolled temperature conditions. *Food Chemistry*, 138: 2451-2459.
- Dias, D. A., Ghiggino, K. P., Smith, T. A., and Scollary, G. R., (2010). Wine bottle colour and oxidative spoilage. The University of Melbourne, Melbourne.
- Dias, D. A., Smith, T. A., Ghiggino, K. P., and Scollary, G. R. (2012). The role of light, temperature and wine bottle colour on pigment enhancement in white wine. *Food Chemistry*, 135: 2934-2941.
- Dozon, N. M. and 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: 265-271.
- Duka, G. G., Batyr, D. G., Romanchuk, L. S., and Sychev, A. Y. (1990). Photochemical transformation of hydroxy acids in the presence of iron(III) ions. *Soviet Journal of Coordination Chemistry*, 16: 54-65.

- Elias, R. J., Andersen, M. L., Skibsted, L. H., and Waterhouse, A. L. (2009). Identification of free radical intermediates in oxidized wine using electron paramagnetic resonance spin trapping. *Journal of Agricultural and Food Chemistry*, 57: 4359-4365.
- Es-Safi, N. E., Cheynier, V., and Moutounet, M. (2003). Effect of copper on oxidation of (+)-catechin in a model solution system. *International Journal of Food Science & Technology*, 38: 153-163.
- Es-Safi, N. E., Guernevé, C., Fulcrand, H., Cheynier, V., and Moutounet, M. (2000). Xanthylum salts formation involved in wine colour changes. *International Journal of Food Science & Technology*, 35: 63-74.
- Escudero, A., Asensio, E., Cacho, J., and Ferreira, V. (2002). Sensory and chemical changes of young white wines stored under oxygen. An assessment of the role played by aldehydes and some other important odorants. *Food Chemistry*, 77: 325-331.
- Escudero, A., Hernández-Orte, P., Cacho, J., and Ferreira, V. (2000). Clues about the role of methional as character impact odorant of some oxidized wines. *Journal of Agricultural and Food Chemistry*, 48: 4268-4272.
- Faust, B. C. and Hoigné, J. (1990). Photolysis of Fe(III)-hydroxy complexes as sources of OH radicals in clouds, fog and rain. *Atmospheric Environment. Part A. General Topics*, 24: 79-89.

- Faust, B. C. and Zepp, R. G. (1993). Photochemistry of aqueous iron(III)-polycarboxylate complexes: Roles in the chemistry of atmospheric and surface waters. *Environmental Science & Technology*, 27: 2517-2522.
- Feng, W. and Nansheng, D. (2000). Photochemistry of hydrolytic iron(III) species and photoinduced degradation of organic compounds. A minireview. *Chemosphere*, 41: 1137-1147.
- Foot, C. S., (1976). Photosensitized oxidation and singlet oxygen: Consequences in biological systems. In: Free radicals in biology. Vol. 2, pp. 85-133. Pryor, W. A., Ed., Academic Press, New York.
- Fowles, G. W. A. (1992). Acids in grapes and wines: A review. *Journal of Wine Research*, 3: 25-41.
- Fulcrand, H., Cheynier, V., Oszmianski, J., and Moutounet, M. (1997). An oxidized tartaric acid residue as a new bridge potentially competing with acetaldehyde in flavan-3-ol condensation. *Phytochemistry*, 46: 223-227.
- George, N., Clark, A. C., Prenzl, P. D., and Scollary, G. R. (2006). Factors influencing the production and stability of xanthylum cation pigments in a model white wine system. *Australian Journal of Grape and Wine Research*, 12: 57-68.

- Glebov, E. M., Pozdnyakov, I. P., Grivin, V. P., Plyusnin, V. F., Zhang, X., Wu, F., and Deng, N. (2011). Intermediates in photochemistry of Fe(III) complexes with carboxylic acids in aqueous solutions. *Photochemical & Photobiological Sciences*, 10: 425-430.
- Goldsmith, M. R., Rogers, P. J., Cabral, N. M., Ghiggino, K. P., and Roddick, F. A. (2005). Riboflavin triplet quenchers inhibit lightstruck flavor formation in beer. *Journal of the American Society of Brewing Chemists*, 63: 177-184.
- Goniak, O. J. and Noble, A. C. (1987). Sensory study of selected volatile sulfur compounds in white wine. *American Journal of Enology and Viticulture*, 38: 223-227.
- Grant-Preece, P., Fang, H., Schmidtke, L. M., and Clark, A. C. (2013). Sensorially important aldehyde production from amino acids in model wine systems: Impact of ascorbic acid, erythorbic acid, glutathione and sulphur dioxide. *Food Chemistry*, 141: 304-312.
- Gray, P., Stone, I., and Rothschild, H. (1941). The action of sunlight on beer. *Wallerstein Laboratories Communications*, 4: 29-40.
- Grodowski, M. S., Veyret, B., and Weiss, K. (1977). Photochemistry of flavins II. Photophysical properties of alloxazines and isoalloxazines. *Photochemistry and Photobiology*, 26: 341-352.
- Hartley, A., (2008). The effect of ultraviolet light on wine quality. Waste and Resources Action Program, Oxon.

Haye, B., Maujean, A., Jacquemin, C., and Feuillat, M. (1977). Contribution a l'étude des "goûts de lumière" dans le vin de Champagne I. Aspects analytiques. Dosage des mercaptans et des thiols dans les vins. *Connaissance de la Vigne et du Vin*, 11: 243-254.

Heelis, P. F. (1982). The photophysical and photochemical properties of flavins (isoalloxazines). *Chemical Society Reviews*, 11: 15-39.

Huang, R., Kim, H. J., and Min, D. B. (2006). Photosensitizing effect of riboflavin, lumiflavin and lumichrome on the generation of volatiles in soy milk. *Journal of Agricultural and Food Chemistry*, 54: 2359-2364.

Huvaere, K., Olsen, K., Andersen, M. L., Skibsted, L. H., Heyerick, A., and De Keukeleire, D. (2004). Riboflavin-sensitized photooxidation of isohumulones and derivatives. *Photochemical & Photobiological Sciences*, 3: 337-340.

Iwanami, Y., Tateba, H., Kodama, N., and Kishino, K. (1997). Changes of lemon flavor components in an aqueous solution during UV irradiation. *Journal of Agricultural and Food Chemistry*, 45: 463-466.

Jiang, L. Y., He, S., Jiang, K. Z., Sun, C. R., and Pan, Y. J. (2010). Resveratrol and its oligomers from wine grapes are selective $^1\text{O}_2$ quenchers: Mechanistic implication by high-performance liquid chromatography-electrospray ionization-tandem mass spectrometry and theoretical calculation. *Journal of Agricultural and Food Chemistry*, 58: 9020-9027.

Jung, M. Y., Yoon, S. H., Lee, H. O., and Min, D. B. (1998). Singlet oxygen and ascorbic acid effects on dimethyl disulfide and off-flavor in skim milk exposed to light. *Journal of Food Science*, 63: 408-412.

Jung, R., Hey, M., Hoffmann, D., Leiner, T., Patz, C. D., Rauhut, D., Schüssler, C., and Wirsching, M. (2007). Lichteinfluss bei der Lagerung von Wein. *Mitteilungen Klosterneuburg*, 57: 224-231.

Kavitha, V. and Palanivelu, K. (2004). The role of ferrous ion in Fenton and photo-Fenton processes for the degradation of phenol. *Chemosphere*, 55: 1235-1243.

Kilmartin, P. A. and Zou, H. (2001). The effect of electrode material on the measured redox potential of red and white wines. *Electroanalysis*, 13: 1347-1350.

Korycka-Dahl, M. B., Richardson, T., and Foote, C. S. (1978). Activated oxygen species and oxidation of food constituents. *Critical Reviews in Food Science and Nutrition*, 10: 209-241.

Kreitman, G. Y., Cantu, A., Waterhouse, A. L., and Elias, R. J. (2013). Effect of metal chelators on the oxidative stability of model wine. *Journal of Agricultural and Food Chemistry*, 61: 9480-9487.

Kuroiwa, Y., Hashimoto, N., Hashimoto, H., Kokubo, E., and Nakagawa, K. (1963). Factors essential for the evolution of sunstruck flavour. *Journal of the American Society of Brewing Chemists*: 181-193.

- La Follette, G., Stambor, J., and Aiken, J. (1993). Chemical and sensory considerations in *sur lies* production of Chardonnay wines. III. Occurrence of sunstruck flavor. *Wein-Wissenschaft*, 48: 208-210.
- Li, H., Guo, A., and Wang, H. (2008). Mechanisms of oxidative browning of wine. *Food Chemistry*, 108: 1-13.
- Luque-Pérez, E., Ríos, A., and Valcárcel, M. (1998). Flow-injection spectrophotometric determination of citric acid in beverages based on a photochemical reaction. *Analytica Chimica Acta*, 366: 231-240.
- Maraís, J. (1983). Terpenes in the aroma of grapes and wines: A review. *South African Journal for Enology and Viticulture*, 4: 49-58.
- Marchand, S., de Revel, G., and Bertrand, A. (2000). Approaches to wine aroma: Release of aroma compounds from reactions between cysteine and carbonyl compounds in wine. *Journal of Agricultural and Food Chemistry*, 48: 4890-4895.
- Mattivi, F., Monetti, A., Vrhovšek, U., Tonon, D., and 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: 121-127.
- Maujean, A., Haye, M., and Feuillat, M. (1978). Contribution à l'étude des "goûts de lumière" dans le vin de Champagne II. Influence de la lumière sur le potentiel d'oxydoreduction.

Correlation avec la teneur en thiols du vin. *Connaissance de la Vigne et du Vin*, 12: 277-290.

Maujean, A. and Seguin, N. (1983a). Contribution a 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.

Maujean, A. and Seguin, N. (1983b). Contribution a l'étude des goûts de lumière dans les vins de Champagne 4 Approches a une solution à nologique des moyens de prévention des goûts de lumière. *Sciences des Aliments*, 3: 603-613.

Maury, C., Clark, A. C., and 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: 81-86.

Miles, C. J. and Brezonik, P. L. (1981). Oxygen consumption in humic-colored waters by a photochemical ferrous-ferric catalytic cycle. *Environmental Science & Technology*, 15: 1089-1095.

Min, D. B. and Boff, J. M. (2002). Chemistry and reaction of singlet oxygen in foods. *Comprehensive Reviews in Food Science and Food Safety*, 1: 58-72.

Monteagudo, J. M., Durán, A., Corral, J. M., Carnicer, A., Frades, J. M., and Alonso, M. A. (2012). Ferrioxalate-induced solar photo-Fenton system for the treatment of winery wastewaters. *Chemical Engineering Journal*, 181-182: 281-288.

- Mosteo, R., Ormad, P., Mozas, E., Sarasa, J., and Ovelleiro, J. L. (2006). Factorial experimental design of winery wastewaters treatment by heterogeneous photo-Fenton process. *Water Research*, 40: 1561-1568.
- Mosteo, R., Sarasa, J., Ormad, M. P., and Ovelleiro, J. L. (2008). Sequential solar photo-Fenton-biological system for the treatment of winery wastewaters. *Journal of Agricultural and Food Chemistry*, 56: 7333-7338.
- Müller, F., (1983). The flavin redox-system and its biological function. In: Radicals in Biochemistry. Vol. 108, pp. 71-107, Springer, Berlin and Heidelberg.
- Neumann, M. and Garcia, N. A. (1992). Kinetics and mechanism of the light-induced deterioration of lemon oil. *Journal of Agricultural and Food Chemistry*, 40: 957-960.
- Ournac, A. (1968). Riboflavine pendant la fermentation du jus de raisin et la conservation du vin sur lies. *Annales de Technologie Agricole*, 17: 67-75.
- Patton, S. (1954). The mechanism of sunlight flavor formation in milk with special reference to methionine and riboflavin. *Journal of Dairy Science*, 37: 446-452.
- Patton, S. and Josephson, D. V. (1953). Methionine-origin of sunlight flavor in milk. *Science*, 118: 211.
- Pearson, R. G. (1968a). Hard and soft acids and bases, HSAB, part I Fundamental principles. *Journal of Chemical Education*, 45: 581-587.

Pearson, R. G. (1968b). Hard and soft acids and bases, HSAB, part II Underlying theories.

Journal of Chemical Education, 45: 643-648.

Pérez-Ruiz, T., Martínez-Lozano, C., Tomás, V., and Martín, J. (2004). High-performance liquid chromatographic separation and quantification of citric, lactic, malic, oxalic and tartaric acids using a post-column photochemical reaction and chemiluminescence detection. *Journal of Chromatography A*, 1026: 57-64.

Perlman, L. and Morgan, A. F. (1945). Stability of B vitamins in grape juices and wines.

Journal of Food Science, 10: 334-341.

Pichler, U. (1996). Analisi della riboflavina nei vini bianchi e influenza della sua concentrazione. *Enotecnico*, 32: 57-62.

Pignatello, J. J., Oliveros, E., and MacKay, A. (2006). Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry. *Critical Reviews in Environmental Science and Technology*, 36: 1-84.

Pozdnyakov, I. P., Kolomeets, A. V., Plyusnin, V. F., Melnikov, A. A., Kompanets, V. O., Chekalin, S. V., Tkachenko, N., and Lemmetyinen, H. (2012). Photophysics of Fe(III)-tartrate and Fe(III)-citrate complexes in aqueous solutions. *Chemical Physics Letters*, 530: 45-48.

- Pripis-Nicolau, L., de Revel, G., Bertrand, A., and Maujean, A. (2000). Formation of flavor components by the reaction of amino acid and carbonyl compounds in mild conditions. *Journal of Agricultural and Food Chemistry*, 48: 3761-3766.
- Ramey, D. D. and Ough, C. S. (1980). Volatile ester hydrolysis or formation during storage of model solutions and wines. *Journal of Agricultural and Food Chemistry*, 28: 928-934.
- Recamales, Á. F., Sayago, A., González-Miret, M. L., and Hernanz, D. (2006). The effect of time and storage conditions on the phenolic composition and colour of white wine. *Food Research International*, 39: 220-229.
- Refsgaard, H. H. F., Brockhoff, P. M., Meilgaard, M. C., Laursen, P. F., and Skibsted, L. H. (1996). Light-induced sensory and chemical changes in aromatic bitters. *Zeitschrift für Lebensmittel-Untersuchung und-Forschung*, 203: 47-55.
- Refsgaard, H. H. F., Brockhoff, P. M., Poll, L., Olsen, C. E., Rasmussen, M., and Skibsted, L. H. (1995). Light-induced sensory and chemical changes in aquavit. *LWT - Food Science and Technology*, 28: 425-435.
- Ribéreau-Gayon, P., Glories, Y., Maujean, A., and Dubourdieu, D., (2006). Handbook of enology. Volume 2. The chemistry of wine stabilization and treatments. 2nd ed. John Wiley & Sons, Ltd, Chichester.
- Rossi, J. A. and Singleton, V. L. (1966). Contributions of grape phenols to oxygen absorption and browning of wines. *American Journal of Enology and Viticulture*, 17: 231-239.

Sato, S., Nakamura, K., Tadenuma, M., and Motegi, K. (1970). Effects of light rays on the colour of alcoholic beverages. *Nihon Jozo Kyokai Zasshi*, 65: 433-438.

Schieberle, P. and Grosch, W. (1989). Potent odorants resulting from the peroxidation of lemon oil. *Zeitschrift für Lebensmittel-Untersuchung und-Forschung*, 189: 26-31.

Schmidtke, L. M., Clark, A. C., and Scollary, G. R. (2011). Micro-oxygenation of red wine: Techniques, applications, and outcomes. *Critical Reviews in Food Science and Nutrition*, 51: 115-131.

Schonberg, A. and Moubacher, R. (1952). The Strecker degradation of α -amino acids. *Chemical Reviews*, 50: 261-277.

Siebert, T., Bramley, B., and Solomon, M. (2009). Hydrogen sulfide: Aroma detection threshold study in white and red wine. *The Australian Wine Research Institute Technical Review*, No. 183: 14-16.

Silva Ferreira, A. C., Guedes de Pinho, P., Rodrigues, P., and Hogg, T. (2002). Kinetics of oxidative degradation of white wines and how they are affected by selected technological parameters. *Journal of Agricultural and Food Chemistry*, 50: 5919-5924.

Tyima, J. and Makálová, J. (1997). Photochemistry of iron(III) complexes. *Coordination Chemistry Reviews*, 160: 161-189.

Simpson, R. F. (1982). Factors affecting oxidative browning of white wine. *Vitis*, 21: 233-239.

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: 69-77.

Sioumis, N., Kallithraka, S., Makris, D. P., and Kefalas, P. (2006). Kinetics of browning onset in white wines: Influence of principal redox-active polyphenols and impact on the reducing capacity. *Food Chemistry*, 94: 98-104.

Smith, R. C., Reed, V. D., and Hill, W. E. (1994). Oxidation of thiols by copper(II). *Phosphorus, Sulfur and Silicon and the Related Elements*, 90: 147-154.

Solomon, M., Geue, J., Osidacz, P., and Siebert, T. (2010). Aroma detection threshold study of methanethiol in white and red wine. *The Australian Wine Research Institute Technical Review*, No. 186: 8-10.

Spikes, J. D., (1981). Photodegradation of foods and beverages. In: Photochemical and photobiological reviews. Vol. 6, pp. 39-85. Smith, K. C., Ed., Springer, New York.

Tomlinson, J. W. and Kilmartin, P. A. (1997). Measurement of the redox potential of wine. *Journal of Applied Electrochemistry*, 27: 1125-1134.

Ugliano, M. (2013). Oxygen contribution to wine aroma evolution during bottle aging. *Journal of Agricultural and Food Chemistry*, 61: 6125-6136.

Ugliano, M., Dieval, J. B., Dimkou, E., Wirth, J., Cheynier, V., Jung, R., and Vidal, S. (2013).

Controlling oxygen at bottling to optimize post-bottling development of wine. *Practical Winery & Vineyard*, 34: 44–50.

Wardle, B., (2009). Principles and applications of photochemistry. John Wiley & Sons, Ltd, Chichester.

Waterhouse, A. L. and Laurie, V. F. (2006). Oxidation of wine phenolics: A critical evaluation and hypotheses. *American Journal of Enology and Viticulture*, 57: 306–313.

WRAP. (2010). Waste & Resources Action Program, Oxon.

[http://www.wrap.org.uk/sites/files/wrap/Newsletter for website.pdf](http://www.wrap.org.uk/sites/files/wrap/Newsletter%20for%20website.pdf) (24 December, 2013).

Zuo, Y. and Hoigné, J. (1993). Evidence for photochemical formation of H₂O₂ and oxidation of SO₂ in authentic fog water. *Science*, 260: 71–73.

Zuo, Y. and Hoigné, J. (1992). Formation of hydrogen peroxide and depletion of oxalic acid in atmospheric water by photolysis of iron(III)-oxalato complexes. *Environmental Science & Technology*, 26: 1014–1022.

Table 1 Aroma and threshold values of volatile sulfur compounds implicated in the light-induced off-aroma of white wine.

Compound	Aroma	Aroma threshold
Hydrogen	Rotten egg, sewage (1, 2)	1.6 µg/L in white wine (1)
Methanethiol	Cooked cabbage, putrefaction (2,	4.8 g/L in white wine (3)
Dimethyl	Cabbage, cooked cabbage, onion	29 µg/L in white wine (4)
Methional	Boiled potatoes, cooked	0.5 µg/L in 11% ethanol model

(1) Siebert et al. (2009), (2) Mestres et al. (2000), (3) Solomon et al. (2010), (4) Goniak and Noble (1987), (5) Escudero et al. (2000), (6) Silva Ferreira et al. (2002).

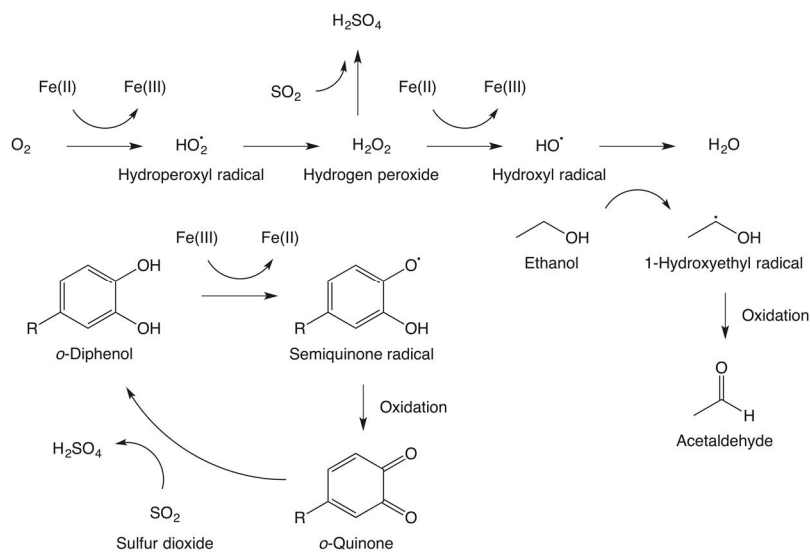


Figure 1. Iron-catalyzed oxidation of wine components.

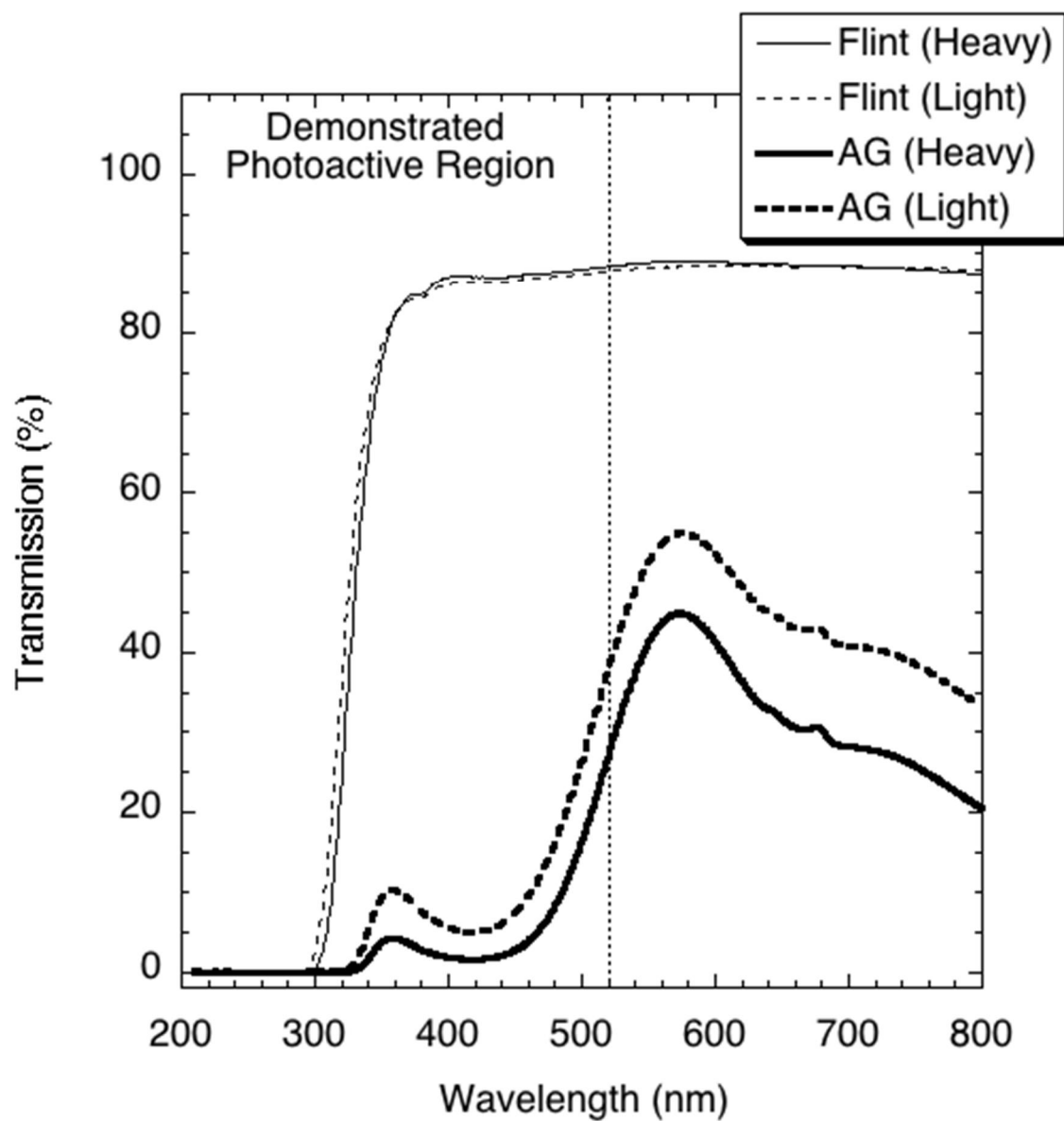


Figure 2. UV-visible transmission spectra of flint and antique green (AG) lightweight and heavy weight bottles. Reprinted with permission from Clark et al. (2011). Copyright (2011) American Chemical Society.

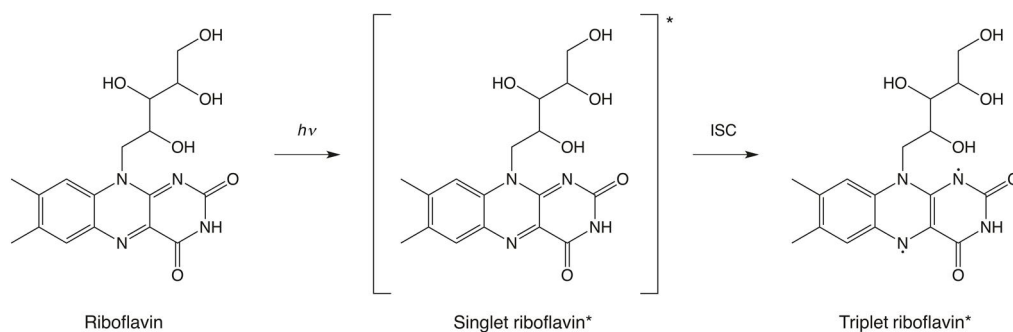


Figure 3. Excitation of ground state riboflavin to the lowest excited singlet state, followed by intersystem crossing (ISC) to the lowest excited triplet state.

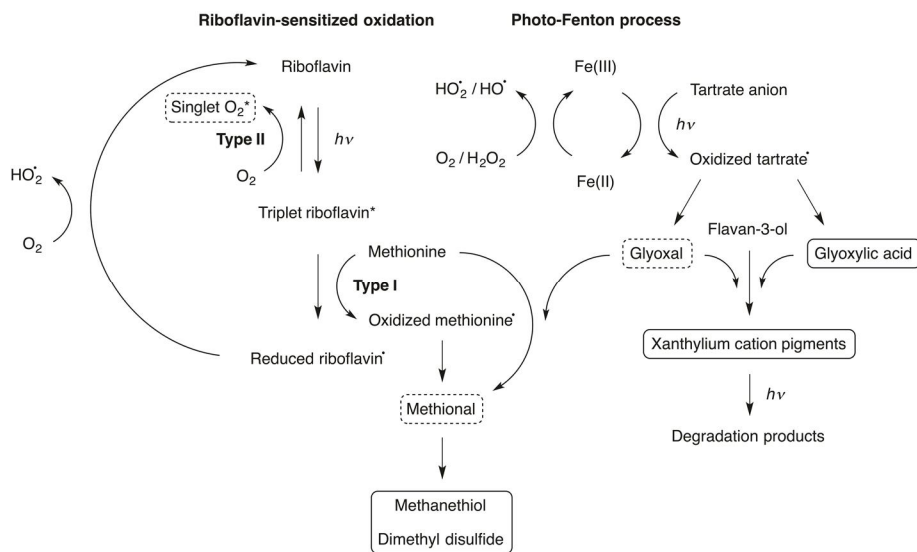


Figure 4. Riboflavin-sensitized oxidation of wine components and the photo-Fenton process in bottled white wine exposed to light. Species that have been identified in white wine and/or model wine solutions exposed to light are in bold boxes, while species that have not been identified are in dashed boxes.

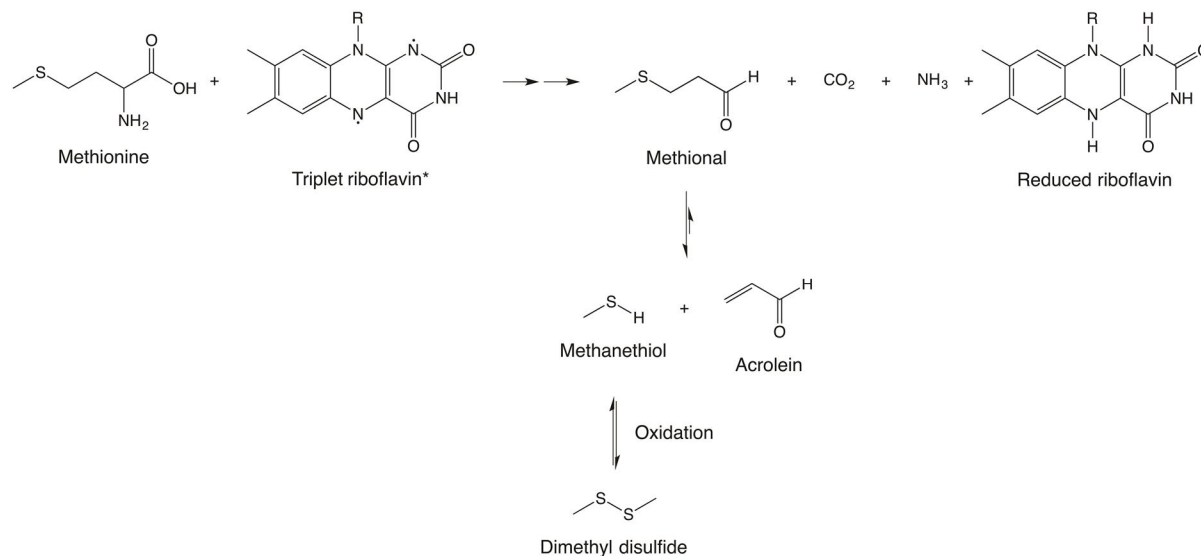


Figure 5. Pathway for the riboflavin-sensitized oxidation of methionine in bottled white wine exposed to light proposed by Maujean and Seguin (1983a).

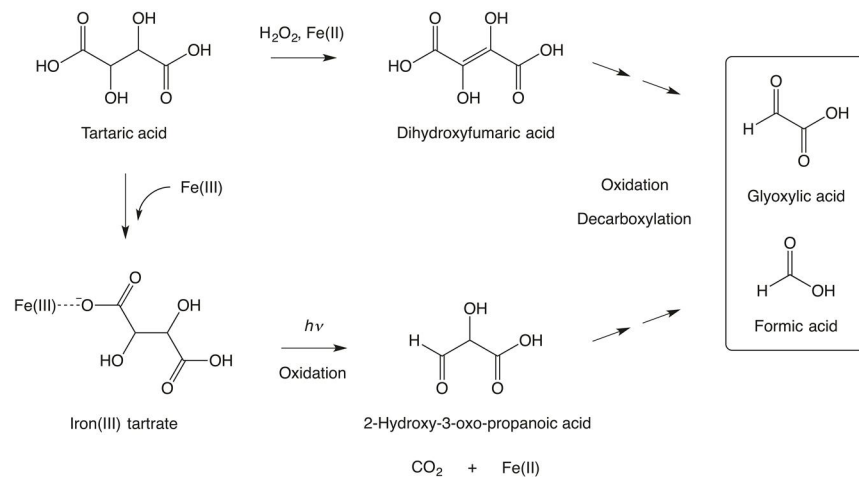


Figure 6. Pathways for the photochemical oxidation of tartaric acid in a model wine solution containing iron proposed by Clark et al. (2007).