

The Light Struck Taste of Wines

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Abstract

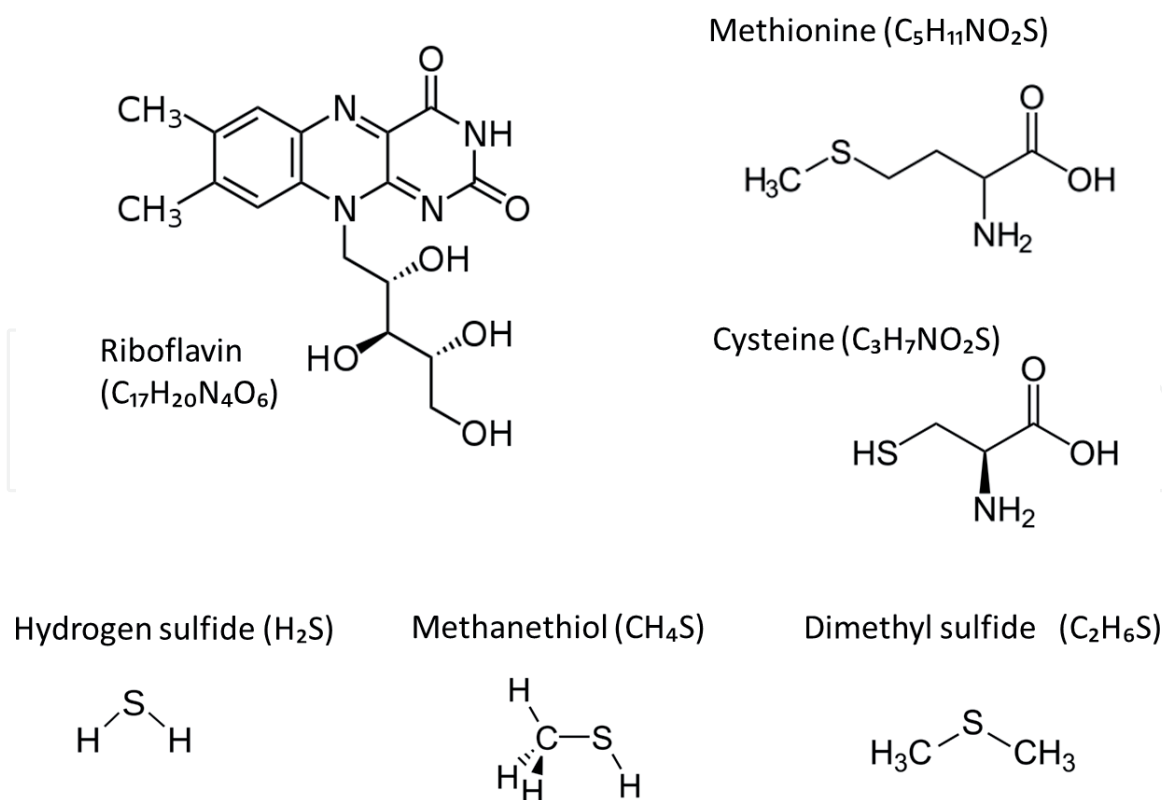
The light-struck taste (LST) of wine is a defect that mainly occurs in bottled wines exposed to light. Factors that influence the onset of the LST in wines were reported. The effect of grapes and wine composition, the alcoholic fermentation process, the yeast strains used and the conditions of yeast nutrition were included. The external factors, such as bottle color, time and nature to light exposure and type of closure were considered. Finally, the analysis of the main molecules related to this defect (sulfur volatile compounds and their amino acids and riboflavin precursors) and possible prevention measurements were also exposed.

Keywords: amino acids, wine, riboflavin, aroma, LEDs, stoppers, sensory analysis

1. Introduction

The light-struck taste (LST) of wine is a defect that mainly occurs in white and rosé bottled wines exposed to light for a considerable period of time. The light-induced changes in wines are mainly due to photochemical reactions but several factors can influence it. The most important are related to the wine composition, the spectrum of the light source, the intensity of the radiation, the optical properties of the glass bottle and the irradiation time. The wine composition alterations caused by these factors lead to detrimental effects on the sensory attributes. In bottled wine, the exposure to light can cause a significant browning effect and bring about unpleasant smells [1–5]. These bad effects were due to the photochemical oxidation involved in this deterioration which can affect phenolic substances, acids, alcohols and other wine compounds [6, 7].

In particular, riboflavin (RF) or vitamin B2 is one of the most important precursors in the generation of aromas related to the LST. This is a highly photosensitive molecule, which can undergo photochemical degradation through different ways. In addition, sulfur amino acids are involved in the photo-reduction of riboflavin being also important precursors in the appearance of sulfur volatiles. That is why, both methionine and cysteine (the sulfur amino acids of wine) in the presence of riboflavin (**Figure 1**) can suffer photo-oxidative degradation giving raise to unpleasant aromatic volatile sulfur compounds (VSCs), such as hydrogen sulfide, methanethiol, dimethyl sulfide and dimethyl disulfide (**Figure 1**). The combination of these aromatic sulfur compounds leads to the defect called 'light struck taste', 'taste of light' or in French 'goût de lumière'. Wines with this default presents unpleasant aromas described as rotten egg, garlic, onion, boiled cabbage and sometimes also provides a metallic taste perception. Given the importance of this defect and the economic losses that it may entail, both oenological and photovoltaic strategies are

**Figure 1.**

Molecular structures of precursors and aromatic compounds related to the LST default.

currently being sought to prevent the appearance of this default in bottled wines stored in wineries, supermarkets or wine bars, in order to offer consumers an optimal wine quality.

2. Influencing factors of the light-struck taste

2.1 Grape and juice composition

The grape is made up of a large amount of nutrients which will pass into the must once it is crushed which will be able to participate in the formation of the LST of wine. The major components of the grape are sugars, mainly glucose and fructose, which will be transformed into alcohol during fermentation. Nitrogen is an abundant component in grape juice with content around 200–300 mg/L. It appears in two differentiated chemical forms: inorganic (basically as ammonium form) and organic (made up of amino acids, peptides and proteins). The nature and concentrations of amino acids in grapes depend on a wide range of factors, such as fertilization, climatic conditions, and grape variety [8, 9]. They are consumed by yeasts during alcoholic fermentation and can produce some positive volatile compounds, such as esters, or negative ones, such as sulfur volatile compounds, which will influence the final aroma of the wine [10]. Amino acids represent up to 40% of the total nitrogen in wines, and yeasts release some amino acids at the end of fermentation. They act as aromatic precursors through different chemical reactions and to form aromatic compounds. On the other hand, among the minority compounds in wine related to LST, riboflavin should be highlighted. This component is found at very low concentrations (between 3 to 60 µg/L) in grape must [11]. The formation of this compound is related to the *Saccharomyces* metabolism that will play a very important role in the formation of reduction aromas of wine. Finally, sulfur aromatic compounds occur more frequently in wines from vineyards

planted in alkaline soils. This is because high pH of soil makes difficult to absorb copper which, normally used as fungicide treatment, helps to eliminate the sulfur compounds produced during winemaking. However, the current trend to replace this metal in new fungicide formulations could lead to an increase in the content of sulfur compounds in wines and therefore the risk of LST appearance. Moreover, the use of sulfur-rich phytosanitary products used in the vineyard may lead to obtaining musts with certain risk of producing this defect.

2.2 Wine fermentation, yeast and nutrients

2.2.1 Nitrogen

Yeasts use the nutrients of the must for their growth during fermentation process. Here, nitrogen is essential to develop reactions that will derive in the formation of secondary metabolites which are very important on the quality of the wine, such as glycerol, organic acids (lactic, acetic, succinic), esters, sulfur compounds or amino acids released during this phenomenon. Usually, during the alcoholic fermentation, nitrogen is added during the exponential phase of fermentation that corresponds to the growth of the yeast (first days of fermentation). Nitrogen can be assimilated by yeasts during winemaking in two different forms, as ammonium or as amino acids. In this phase it has an effect on cell growth and on the rate of fermentation [12]. In musts with few nutrients, the amount of assimilable nitrogen drops early and induces the production of hydrogen sulfide (H_2S) due to the absence of compounds that capture sulfur.

Wine yeasts can form H_2S from inorganic sulfur compounds (sulfate or sulfite), or organic sulfur compounds (cysteine, methionine or glutathione). The production of H_2S can occur from the Sulfate Reduction Sequence (SRS) route, where sulfate is used for the biosynthesis of cysteine and methionine. Sulfate is accumulated from the medium, and then reduced to sulfite following sulfite is reduced by sulfite reductase to sulfide. Therefore, when dealing with nitrogen-deficient musts, yeast will tend to synthesize it from nitrogenous precursors *o*-acetylserina and *o*-acetylhomoserina, with which the sulfite produced will be excreted as hydrogen sulfide (H_2S) [13]. Therefore, in wines with a limited content of nitrogen the supplementation with sulfur amino acids the production of hydrogen sulfide can increase considerably. H_2S is a highly reactive compound, and it can combine with different components present in wine forming other VSCs [14]. Mercaptans, sulfides and disulfides can be also found in wines.

In many cases, H_2S production can be controlled by adding nitrogenous salts such as diammonium phosphate (DAP). Some studies suggest that a concentration of 200–250 mg/L of assimilable nitrogen is necessary to minimize the risk of H_2S production. However, not all commercial strains show the same behavior to the improvement of the must by the addition of diammonium phosphate, and usually indicates a deficiency in the juice of one or more vitamins, pantothenic acid, pyridoxine or biotin, which is involved in the metabolism of H_2S . The persistence of H_2S production problems, even with nutrient supplementation, requires the selection of yeast with low H_2S production in such musts.

It has been reported that some strains appear to produce H_2S inherently without being affected by environmental conditions, possibly indicating a metabolic defect [15, 16]. Therefore, the H_2S production capacity of a specific strain has a genetic influence, since the H_2S production of different strains varies under the same conditions [13, 16, 17]. The excessive production of hydrogen sulfide that takes place during the fermentation process is a fairly common problem in winemaking [13, 17]. As mentioned, the persistence of H_2S production problems,

even with nutrient supplementation, requires the selection of yeast strains with low H₂S production. New yeast strains have been developed to produce undetectable amounts of H₂S [18]. In summary, yeasts and nutrients, such as the nitrogen content have a manifest influence on the different metabolites produced during fermentation, many of them with a very clear impact on the wine aroma and therefore in the LST default.

2.2.2 Riboflavin

Riboflavin acts as a photosensitizer in many foods and beverages. The RF level in grapes is usually less than a few tens of micrograms per liter of must [19], but can increase during winemaking mainly due to the metabolic activity of *Saccharomyces cerevisiae* [20]. Values close to 150 µg/L or even higher can eventually occur in wine depending on the yeast strain used for the alcoholic fermentation [21, 22]. Riboflavin-producing yeast strains have occasionally been found to be methionine-producing as well, which may increase the risk of spoilage [21]. The amount of methionine oxidized in wine exposed to light is related to several physical and chemical factors, including the concentration of riboflavin, oxygen, and other amino acids. Photosensitized RF can oxidize methionine as well as other amino acids. The reduced riboflavin can then be oxidized back to riboflavin by oxygen [23]. It is also known that the presence of riboflavin in wine is mainly due to the metabolism of the yeast *Saccharomyces cerevisiae*. Some *Saccharomyces* strains can prevent a high amount of riboflavin in wine [21]. Yeast is known to contain a gene, RIB5, which encodes the formation of the enzyme riboflavin synthase, which is involved in the last step of RF synthesis by yeast [20]. The use of yeast strains that have a lower capacity to produce riboflavin may be a potential means of minimizing its concentration in wine.

Some studies carried out at our facilities in the Wine Technology Center (VITEC) reported the importance in the use of different yeasts and nutrients to carry out the fermentation to diminish the RF content in wine (**Figure 2**). Different types of commercial *Saccharomyces cerevisiae* strains were assessed with different types of nutrition during fermentation. In this case, one of the *S. cerevisiae* strain used (yeast strain 2) produced higher RF content in three of the four studied nutrition conditions. In addition, nutrition 1 and especially nutrition 3 increased noticeably the production of RF. This could be explained by differences on the metabolism of each strain and the characteristics of the nutrients. These two conditions of nutrition were based on yeast cell walls, richer in vitamins while nutrition 4 was based in inorganic addition by DAP.

The ability of certain oenological yeast nutrients added during fermentation generally used to prevent the stop or sluggish fermentation can release RF. Yeast

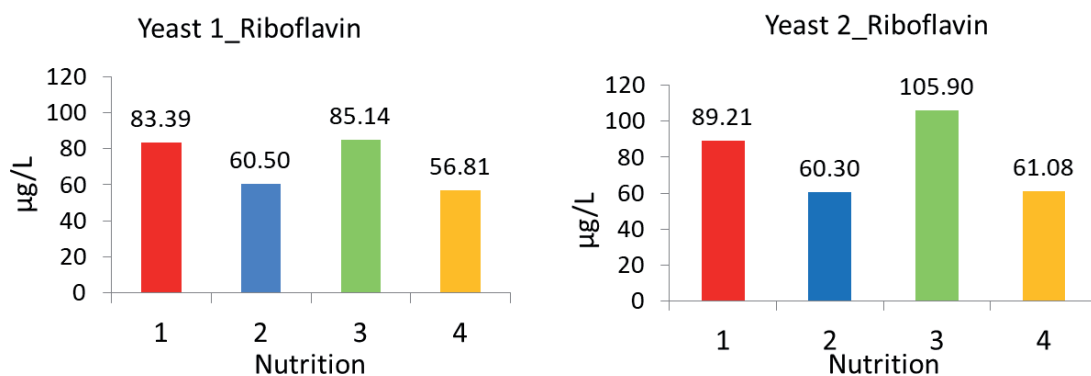


Figure 2. Production of riboflavin with two different strains of *Saccharomyces cerevisiae* through four different types of nutrition.

extract-based nutrients often contain vitamins, including RF, which can therefore increase its amount content in wine. The use of low RF products has been proposed to prevent the formation of volatile sulfur compounds. Yeast lysate can also be used as an additive to prevent the anti-fermentative activity of medium chain fatty acids [19]. The lipid fraction naturally found in yeast lysate may have affected the ability of fermenting yeast to produce purines, the precursors of riboflavin in yeast metabolism [24, 25].

2.3 Wine composition

2.3.1 The aromatic precursors

Riboflavin present in wine is likely the most important precursor of the light struck taste defect. In food and beverages, riboflavin is naturally present as flavin mononucleotide (FMN), flavin adenine dinucleotide (FAD), and riboflavin (RF). In wine only RF form has been detected [26]. In bottled wines, RF participates in light-induced reactions that affect changes in volatile compounds, color, and flavor [4, 26]. When the RF concentration in wine is greater than 100 µg/L, the wine is considered to have a high risk of presenting the LST [27]. RF is a highly photosensitive compound which can be degraded in the presence of fluorescent or phosphorescent light, with wavelengths ranging from 370 to 450 nm. Its photochemical degradation can follow several paths of which intermolecular photo-reduction is the most relevant. The first step in the degradation mechanism is the uptake of a pair of electrons from an external donor (in this case methionine) by riboflavin. By this way a reduced flavin and methional is obtained. Methional is extremely unstable and breaks down to form methanethiol and acrolein. And the reaction of two methanethiol molecules can produce dimethyl disulfide [28]. The interconversion of diethyl disulfide and ethanethiol in presence of sulfites was also reported [29]. Although the rate of reaction is slow at wine pH, model predictions indicate that the reduction of diethyl disulfide to ethanethiol over time can be of sensory importance in wine [29].

RF plays a fundamental role in the oxidation of sulfur amino acids such as methionine and cysteine. Strecker's 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 the aroma in bottled wine [30]. Glyoxal, and α -dicarbonyl compound generated during alcoholic and malolactic fermentation, reacts with methionine to form methanethiol and dimethyl disulfide, and with cysteine to form hydrogen sulfide, methanethiol, and other compounds [31, 32].

Wine is made up of a large number of different amino acids and, among them, methionine and cysteine are also important precursors for the LST appearance as these have sulfur atoms in their structure (**Figure 1**). Maujean (2001) described the thermal origin of volatile sulfur products in Champagne wines stored at 25°C in the dark could be formed by Strecker degradation of these sulfur amino acids [28]. Strecker's 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 [33]. Glyoxal (α -dicarbonyl compound generated during alcoholic and malolactic fermentation) reacts with methionine to form methanethiol and dimethyl disulfide, and also reacts with cysteine to form hydrogen sulfide, methanethiol, and other compounds [31, 32]. Methional, the initial product of Strecker's degradation of methionine, could be degraded via (retro-Michael mechanism) to form methanethiol, which is then oxidized to dimethyl disulfide [32]. Singlet oxygen, produced in photosensitized reactions, reacts with methionine resulting in the formation of dimethyl disulfide [34].

Maujean (1984) proposed that in white wine exposed to light, triplet riboflavin oxidizes methionine to methional, which then degrades to form methanethiol and dimethyl disulfide [35].

In relation to the amino acids degradation and the consequently formation of sulfur volatiles, the studies carried out in our laboratory (VITEC) confirm the data found in literature. **Figure 3** shows white wines bottled in clear glasses and exposed to three types of LED lights with different wavelength emissions. The concentrations of methionine, cysteine and the volatile sulfur compounds (as the sum of hydrogen sulfide, methanethiol, dimethyl sulfide and dimethyl disulfide), were determined after keep the wine in darkness, and after being exposed for 6 and 240 hours to different sources of light (L.1, L.2 and L.3). Results showed that the longer the light exposure time the lower the concentrations of the amino acids studied, and the higher the formation of volatile sulfur compounds. Furthermore, it should be noted that L.1 was the light that caused the greatest degradation of cysteine and methionine. As mentioned above, the nature of light is an important factor that can favor the LST default. In the next section, we can observe some examples.

2.3.2 The volatile composition

The LST is related to the formation of volatile sulfur compounds. Hydrogen sulfide, methanethiol, dimethyl sulfide, and dimethyl disulfide appear to be largely the main compounds responsible for the occurrence of this defect [28]. All these compounds are mainly responsible for the formation of “reducing” aromas after bottling [30, 33, 36]. These compounds are characterized by unpleasant aromas in wines. On the one hand, within the thiol family is found hydrogen sulfide, which is a characteristic compound for providing wines with unpleasant aromas of rotten eggs, decomposing algae or wastewater. Other characteristic thiol of this defect is the mentioned methanethiol that contributes by descriptor aromas related to putrefaction smell and cooked cabbage. It should be noted that both compounds present a very low odor threshold (OT) values, corresponding to 1.6 $\mu\text{g/L}$ and 0.3 $\mu\text{g/L}$ respectively [37, 38]. On the other hand, within the family of sulfides and disulfides are found dimethyl sulfide and dimethyl disulfide, characteristic compounds for providing aromas associated with cabbage, asparagus, corn or onion flavors when present in high concentrations. They have an odor threshold around 25 $\mu\text{g/L}$ and 29 $\mu\text{g/L}$, respectively [39–41]. The emergence of sulfur compounds related to the LST usually is also linked to a loss of fruity aromas of wines, such as ethyl and acetate esters, alcohols and fatty acids [42].

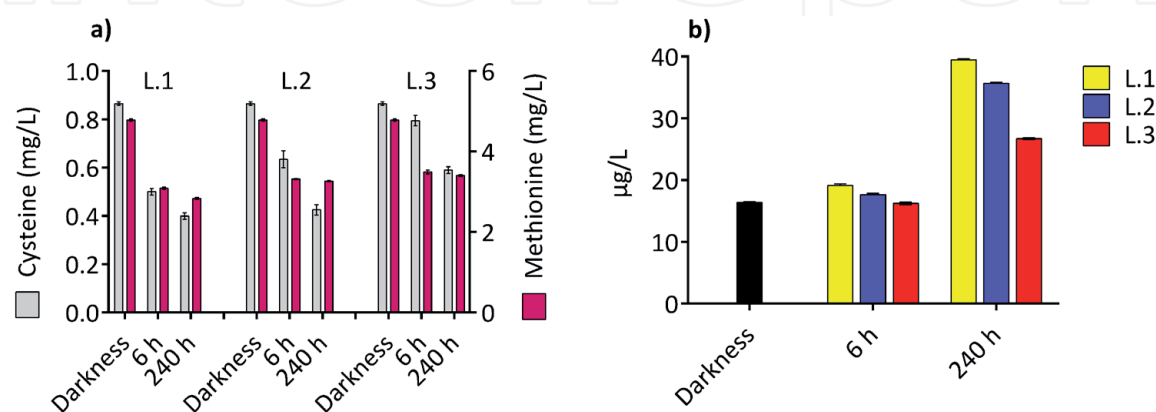


Figure 3. a) Sulfur amino acid content (cysteine and methionine) and b) volatile sulfur content, in white wines bottled in clear glass after being exposed to three types of LED lights (L.1, L.2, and L.3) during time (6 and 240 hours) compared to controls in the darkness.

Moreover, the volatile sulfur compounds related to the LST of white wines is influenced by the color of bottle. Here, some examples comparing green bottles and clear bottles are shown (Figure 4). The types of source of light were also evaluated comparing six types of LEDs (Figure 4).

As can be seen in Figure 4, the white wine bottled in clear glasses presented higher concentrations of reduction aromas after 10 days of exposure with the LA, LC and LE lights, while the wine with the green bottle presented the highest concentrations with light LA. This is consistent with the degradation of riboflavin. The greater the degradation of riboflavin, the greater the presence of aromas of sulfur compounds in the wines (see Section 2.6). All this is due to the innovation of new LEDs which minimize or eliminate the emission of the region between 370 and 442 nm of the spectrum, thus reducing the risk of wine degradation (see Section 2.5 and 2.6).

2.4 Type of closures (OTR)

The last step in winemaking process is bottling. The main aim of this is to package the wine to get the customers in a comfortable and attractive way and also to preserve the organoleptic characteristics of wines. Although it may seem the easier process step, it is critical to maintain and, sometimes, also to improve the qualities of the product over time until the consumption. On the one hand, wine should be prepared and fined to prevent chemical precipitations of salts, color matter, protein haze and microbiological alterations as well, always respecting the nature of the wine and their characteristics. On the other hand, the type of closure should be selected according to the consumption time expected. Closures should assure that the contents do not drip out of the bottle and that the contents were not altered by oxygen. Nowadays, wine producers have several options to stopper wine bottles, such as screw caps, crown corks, plastic caps of glass closures with plastic sealing.

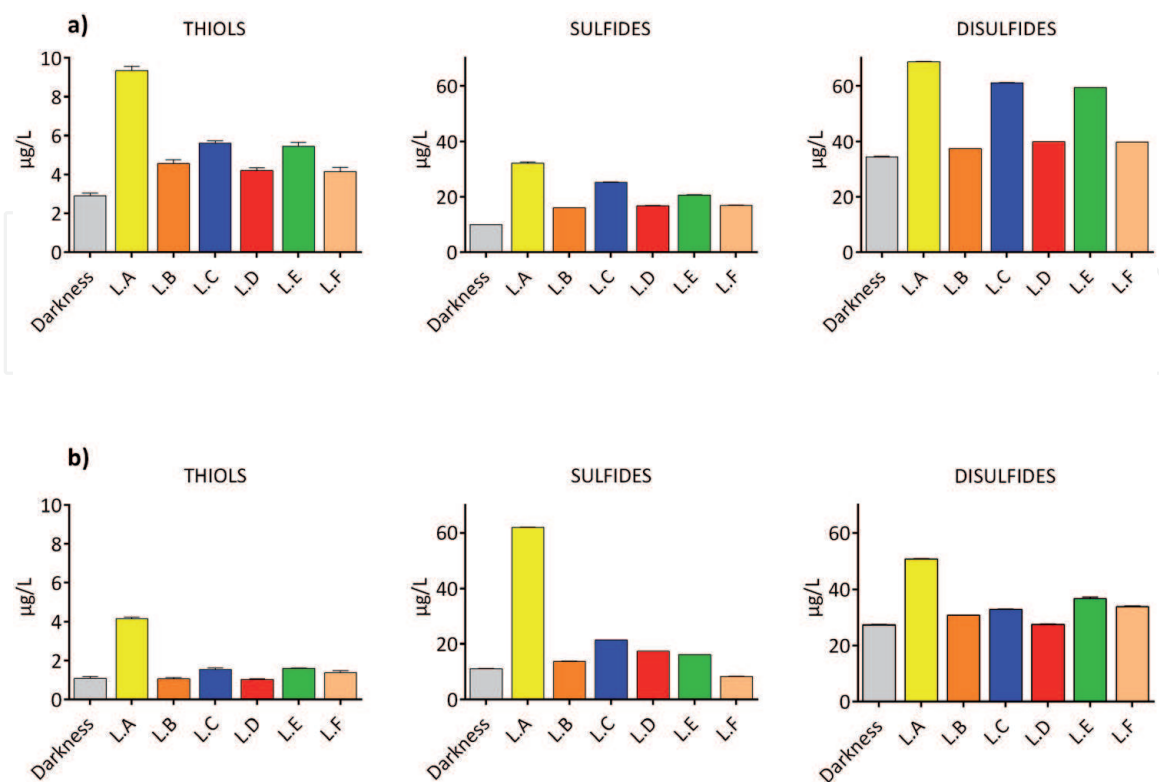


Figure 4. Production of volatile sulfur compounds in white wines bottled in different color of bottles (clear bottles; a) and green bottles; b)) after 10 days of exposure with six different types of LEDs compared with darkness condition.

Several changes can take place in wine after bottling, some of them desired and expected as increasing of complexity, roundness, pleasant and desired evolution. Anyway, also unexpected changes derived from stoppers can also occur due wine oxidation or reduction [43]. Some of these unexpected changes can modify the quality of wines and, in the worst case, these wines could be considered defective products and often undrinkable.

One of the factors with more influences in wine aging and evolution is oxygen. Oxygen is trapped in the headspace of the bottle after bottling, it is present in the wine dissolved and also permeates through the closure combined with temperature and light, modifying the oxidative status of the wine during storage [44]. So, winemakers have the option to modify and control the evolution of their wine after bottling selecting the closure type. The flow of oxygen able to pass through the closure of a wine bottle is referred to as OTR (oxygen transmission rate in 24 h). This parameter depends on the thickness of the material and the partial pressure gradient between the atmosphere of the external environment and the headspace of the bottle [45]. This oxygen ingress is typically slower than the rate of oxygen consumption of the wine, so that, after consumption of the initial excess of oxygen, dissolved and headspace concentrations of oxygen are usually very low (often micrograms per liter) [46]. Other common indicator in oenology is the total package oxygen (TPO) which can vary over a range of approximately 1 and 9 mg/L. This parameter consist of the sum of two components, wine dissolved oxygen and headspace concentration [33].

Different OTR ranges could be found in bibliography, detailing the approximately oxygen transmission rate for each type of closure. Screw cap saranex and screw cap saran tin are the closure options with lower OTR values with 0.0006 and 0.0008 mL of O₂ per day, respectively (AWRI measurements) [47]. Micro agglomerate technical corks with a very low OTR could get similar values as screw cap close to 0.0006 and 0.0007 mL of O₂ per day, natural corks increase slightly the permeability till between 0.0002 and 0.006 mL O₂ per day (Jim Peck's MOCON measurements) Finally extruded synthetic closures showed a higher permeability around 0.0019–0.0030 mL O₂ per day (Jim Peck's MOCON measurements).

In the studies carried out at VITEC, the volatile composition responsible for the reduction aromas was evaluated taking into account the use of five corks (from C1 to C5) with different OTR values (OTR values from C1 to C5 was of lower a major) in sparkling white wines throughout 3, 6 and 12 months of aging in bottle. A crown-cap (CAP) was used as control wine (**Figure 5**). As can be seen in this figure, the control samples with CAP stoppers and C1 corks with the lowest oxygen transmission (OTR), were the ones with the highest concentrations of thiols, sulfides and disulfides, mainly after 12 months (12 M) of aging in the bottle.

2.5 Type of bottles

As stated previously (**Figure 4**), another very important factor in the wine bottling step is the choice of the container in which the wine will be stored until its consumption. This container or packaging must take into account the protection and conservation of the product. In the case of wine there are different types of containers such as the tetra brick which is a cardboard for drinks made up of different layers of polyethylene, paper, and aluminum; the bag in box consisting of a polyethylene bag and a tap with a valve for dosing it; PET (polyethylene terephthalate) plastic containers; aluminum cans type; and finally, the most widely used container in the world in the case of wine, glass. Which is a mineral product obtained by fusion and that solidifies without crystallizing. It is also an inert material, and from an environmental point of view it is favorable because it is a fully recyclable material.

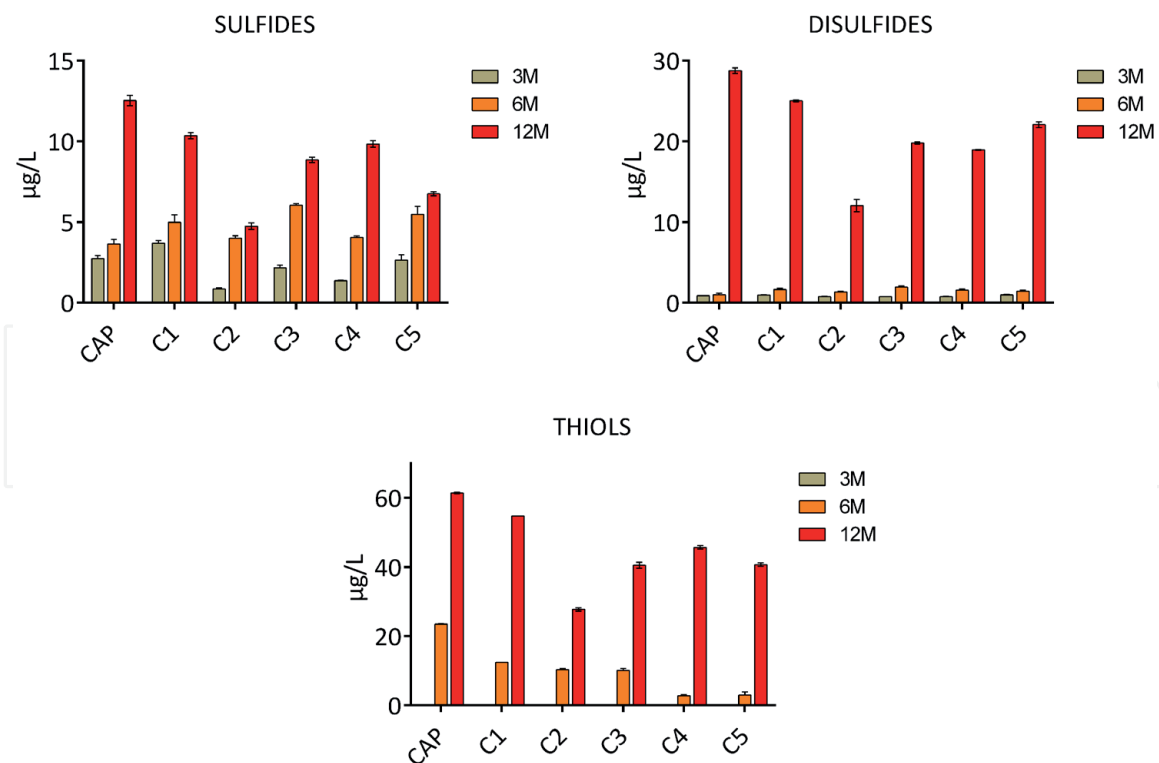


Figure 5.
 Concentrations of thiols, sulfides and disulfides in sparkling white wines stopped with 5 different types of corks and crown-CAP (CAP), over 3, 6 and 12 months of aging in the bottle.

Nowadays, different shapes of glass bottles are used (Bordeaux, Burgundy, Champagne, Rhin, Jerez, Porto) with different capacities, and of different color and shade of glass (flint, amber, green, blue, etc). The choice of the color of the glass is of great importance with regard to the preservation of wine during storage or aging. This is due to the fact that the incident light in the bottles penetrates through the glass, producing oxidation–reduction reactions in the wine and consequently affecting its organoleptic qualities. Glass wine bottles only transmit wavelengths greater than 300 nm [6]. Standard clear bottles (flint) generally transmit more than 80% of visible UV radiation above 360 nm, while clear bottles with additional UV protection, which are made by adding a UV absorbing species to glass or by coating clear bottles with a film that contains a species of this type, transmits less UV radiation [48]. Green bottles transmit considerably less light than clear ones, particularly in the region below 520 nm, while amber bottles transmit very little radiation below 520 nm. For the darker colored bottles, the heavy bottles, which have thicker glass, transmit slightly less light than the lighter counterparts.

2.6 Aging and time of light exposure

It is well known that wine is very sensible to temperature which can directly affect their global quality [49]. Temperature can play a significant role impacting directly to the color, aroma and mouthfeel accelerating their natural aging process. Ideally, wines should be stored in conditioned rooms in cellars normally with air conditioned facilities (15–20°C). However, wine could experiment changes in their temperature being exposed to less optimal conditions, especially during transport or storage distribution process [50]. Visual affectations could also be observed, being the most notable the formation of a haze resulting from the denaturing of proteins in rosé and white wines [51]. If temperatures are so high and wine it is packaged in glass bottles the temperature effects can include cork push due to the volumetric expansion of the wine impacting directly to closure seal integrity and

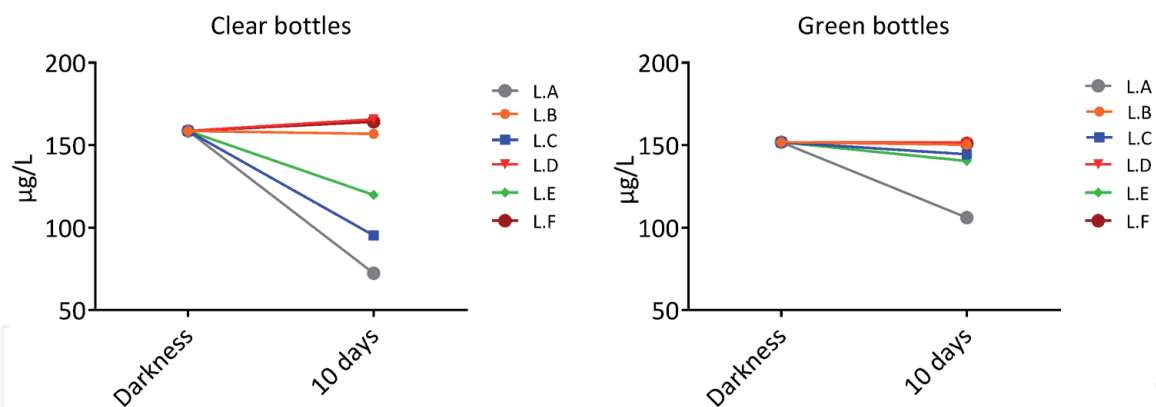


Figure 6. Degradation of riboflavin in a white wine bottled in a clear bottle and in a green bottle after 10 days of exposure to 6 different LEDs.

impacting in oxygen transmission rate (OTR) [52]. Several published studies detail the changes showed by wines when these are exposed to high temperatures, and other composition variables as pH, SO_2 concentration, alcohol content, tannins concentration or others [3, 37, 53–58].

Several authors as studied the direct effect of temperature on the volatile composition of red and white wines [59]. Over a 21-day period, the study found that a constant 40°C heat treatment had a greater impact on the aroma and volatile composition of the wines compared with that of the $20^\circ\text{C}/40^\circ\text{C}$ cycled treatment, which in turn had a greater impact on that of wines stored at a constant 20°C . These studies conclude that it is evident that as a direct result of heat, the fruity acetate compounds in the wines are disappearing and aged-like characters have developed. Temperature not only affects the volatile compounds, also non-volatile compounds as polyphenols experiment changes at high temperature. The most common effect on non-volatile in red wines is a decrease in anthocyanin concentration and a corresponding increase in tannin-bound anthocyanins.

Apart from the temperature, the light incidence is also an important factor to take into account during the aging period. As mentioned above, the susceptibility of white wines to produce the LST has been mainly associated with the photosensitizer riboflavin and the produced unpleasant odor has been attributed primarily to volatile sulfur compounds. Maujean found that hydrogen sulfide, methanethiol, and dimethyl disulfide were formed in Champagnes exposed to a solar simulation lamp in glass cuvettes, in the absence of oxygen [28]. In our study (**Figure 6**), the degradation of RF was found just after 10 days of exposure to light in white wines bottled with green and clear bottle body. As can be seen in **Figure 6**, the white wine with a clear bottle presented large decreases of RF. More than 50% of the initial content in clear bottles and more than 30% in green bottles in the case of L.A. The white wine bottled in clear glass showed a degradation of riboflavin with more types of lights.

3. Analysis of the main chemicals related to LST

To evaluate the aromatic defect that we are dealing with, it is necessary to know which compounds could be responsible but, to know the contribution of each one to wine aroma, it is also necessary to know their concentration. In addition, to have a better control of this problem, it would also be very interesting to obtain information on the concentration of the precursors since their degradation provides the unwanted volatile sulfur compounds (VSCs). However, since from a physico-chemical point of view the precursors are chemical compounds very different from

the VSCs, both the sample preparation techniques and the analytical techniques will be also different in each case.

3.1 Analysis of aromatic precursors

3.1.1 Riboflavin

Riboflavin, also known as vitamin B₂, is a dimethylated isoalloxazine linked to ribitol. In fermented beverages like wine, this heterocyclic ring is mainly found as free riboflavin although few amounts of the mononucleotide and dinucleotide forms can be also found. This is why some analytical methods propose to convert these forms to free form prior the analysis and to quantitate the total riboflavin content [26]. Traditionally, this compound has been determined by microbiological or fluorimetric methods [60]. However, when dealing with complex samples such as wine, the high performance liquid chromatography with reversed-phase column (RP-HPLC) is the most suitable technique as it separates the riboflavin from interferences. Among the different possible detectors including UV/vis, mass spectrometry and fluorescence, the latest is the most used because riboflavin naturally fluoresce. This property allows the injection of the sample directly into the HPLC although a sample filtration is recommended to avoid light scattering effect [26, 61]. Finally, it should be noted that some alternatives to these expensive and time-consuming HPLC methods have been developed. One of them is based on the fluorescence quenching effect produced by the riboflavin-binding protein what is measured by using a single diode fluorimeter [62]. According to the authors, the results obtained are comparable to those obtained by HPLC methods. The other alternative involves the use of UPLC which has become the modern HPLC showing higher sensitivity and chromatographic efficiency with a consequent run-time decrease [63].

3.1.2 Amino acids

Although the light-struck aroma precursors are only cysteine and methionine, the analysis methods found in the literature do not focus solely on these amino acids but consider as much of them as possible. Among the different techniques found in literature, the HPLC is the most frequently used for the determination of these compounds in wine or must. However, since the amino acids have no a specific chromophore group to be detected, a derivatization step is necessary. Although this derivatization can be performed before or after chromatographic separation, the pre-column option followed by HPLC or UPLC has been more widely used due to its simplicity and versatility. This derivatization reaction can be performed by using several reagents which lead to derivatives detectable by different detectors. Thus, when using ultraviolet detector, derivatising reagents such as phenylisothiocyanate, diethyl ethoxymethylenemalonate or dansyl chloride can be used. The latter reagent can also be used with fluorescence detectors in addition to other such as *o*-phthaldialdehyde, 9-fluorenylmethylchloroformate or 6-aminoquinolyl-N-hydroxysuccinimidyl carbamate. All of them present some advantages and some drawbacks but, in all cases, the main problem is that the time spent on the analysis is long [8, 64]. This is why some authors have focused on developing faster methods, such as the use of a fully automated in-loop derivatization procedure [65]. However, although these methods have been successfully applied, the way to drastically reduce the analysis time has been achieved when the derivatization step has been avoided. Today the only technique that allows a high degree of sensitivity and selectivity in the determination of amino acids without derivatization is the

so-called liquid chromatography with tandem mass spectrometry (LC–MS–MS), a mass spectrometer system highly specific for each compound structure. However, it should be pointed out that this costly technique has been applied very little to the analysis of wine components, and even less to the amino acid analysis of wine.

3.2 Analysis of volatile compounds

The volatile sulfur compounds related to LST constitutes a chemical family that includes thiols, sulfides and disulfides. This structural diversity together with the highly reactive nature of these compounds, their low volatility and their low concentration in a matrix as complex as wine, make their analysis considerably difficult.

Although the older bibliography references show methods developed as early as the 1990s which used sulfur-specific ion electrodes or the spectrophotometry with previous treatments to trap sulfur compounds but these methods have been rendered obsolete [66, 67]. In fact, nowadays, the best results are obtained when using gas chromatography coupled to specific detectors so this is the most widely used technique to analyze these compounds. Flame-photometric (FPD) [68], sulfur chemiluminescence (SCD) [69] and more recently pulsed-flame-photometric [70] are the usual required detectors. The use of the mass spectrometry (GC–MS), even being a nonspecific detection system, can be a good option mainly when working with SIM mode as it confers better sensitivity.

In any case, taking into account the usual low concentrations and the highly reactivity of VSCs, a preconcentration technique with minimal manipulation of the sample is required prior to chromatographic separation. Thus, while liquid–liquid extraction systems (either with vacuum or using reagents that selectively trap thiols such as pHMB) have not been very successful, the application of the headspace technique has given very good results. It should be noted that the concentration process required is only achieved with the dynamic modality of this technique which is also called purge and trap technique. Among the different traps, the best results are obtained when working with cold traps because, when dealing with chemical traps and complex matrices such as wine, the so-called memory effect usually occurs due to the difficulty of cleaning the traps between analyses. More recently, the technique that has emerged as the most appropriate is the so-called solid-phase microextraction (SPME) which is applied to the headspace of the sample wine. This simple and fast technique involves immersing a polymer-coated fiber into the headspace sample to extract and concentrate the analytes on the fiber. The fiber coatings that provides the best results on the sulfur compounds extraction have been Carboxen/polydimethylsiloxane or divinylbenzene/Carboxen/polydimethylsiloxane. Regarding the variables that influence the extraction process, the literature indicates that it is necessary to increase ionic strength with sodium chloride or magnesium sulfate, to agitate the sample with slow-medium speed and to use extraction temperature and time between 35 and 40°C and 20 and 40 minutes, respectively [37, 68].

4. Prevention and correction measurements

Up to now, different preventive and corrective measures have been studied to avoid the onset of the LST in both still and sparkling wines. Thus some proposed preventive measures are: avoiding grapes treated with sulfur on dates close to the harvest, avoiding excessive sulfite in grape juice, use yeast strains and nutritional conditions with low production of aromatic precursors of VSCs, racking wines

correctly, use micro-oxygenation or use preventing agents, such as polyphenols [5, 21]. Regarding to the possible corrective measures to reduce or eliminate VSCs, these could be: aerating the wine, using colloidal copper or copper sulfate or using insoluble absorbing materials such as bentonite, active carbon, or charcoal. In any case, whatever preventive or corrective measure has been chosen, it must be carefully applied as the inadequate practice of these treatments can lead to a great loss of the organoleptic characteristics of wines.

5. Conclusions

Several factors influence the formation of compounds responsible for the light struck taste (LST) in wines. As explained, the chemical composition of grapes and wines, the yeast strains used during the alcoholic fermentation process and their nutrition are decisive in the synthesis of their precursors and, subsequently to the concentration level of the VSCs. Moreover, other external factors are also crucial during the wine aging and storage period. The bottle color, the type of closure, the nature of light and the time of exposition seems to be the most important ones. As the light struck sensory perception depends on the amounts of VSCs, their quantitation becomes essential. Due to their low concentrations and the great complexity of the wine matrix, several instrumental analytical methods have been developed in recent decades to improve the analysis efficiency of these compounds. Finally, it should be noted that although the LST defect can be corrected several practices, its prevention is the best way to ensure the organoleptic quality of wine.

6. Future perspectives

The new trends in wine industry used to minimize the LST formation are related to the improvement of new LEDs technologies. These make it possible to use specific radiation sources that avoid the wavelengths most linked to the photodegradation of wine that causes this defect. Moreover, new stoppers with absorbing capacity of VSCs generated into the bottle and new materials for the packaging of wines are being developed [42, 71].

Acknowledgements

Thanks are due to the Spanish MICINN for financial support (Project ref. RTC-2017-6646-2) and Bodegas Ramón Bilbao S.A., Bodegas Martín Códax S.A.U and Grupo Prilux Iluminación S.L.U. for their support and supplying wines and lights.

Conflict of interest

The authors declare no conflict of interest.

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