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Abstract

Volatile thiols are very strong-smelling molecules that can impact the aroma of numerous foods, such as fruit and beverages. Several thiols and thiol precursors have already been reported in different plants used as raw material for beverage production, either fermented or not. We focus on those thiols in beverages and their release mechanisms from precursors during the different biotechnological steps of their processes. Volatile thiols in food can be classified in two different groups: low-molecular-weight volatile thiols, which impact the smell negatively, and volatile thiols with higher boiling points, which contribute positively to the aroma profile. The first part is devoted to volatile thiols without taking into account the highly malodorous small molecules as H_2S, methanethiol, etc. The second part deals with precursors and the different release mechanisms induced by various processes such as extraction, roasting or fermentation, and the culture method that can influence the amount of thiol and their precursors.

Keywords: thiols, precursors, beverages, release mechanisms

1. Volatile thiols in beverages

1.1. Non-alcoholic beverages

1.1.1. Tropical fruit juices

Tropical fruits are significant sources of volatile thiol compounds (Table 1) as recently reviewed by Cannon and Ho (Robert J. Cannon & Ho, 2018). The different tropical fruits containing thiol are listed by alphabetical order in the following paragraphs. By extrapolation, it is possible to deduce their presence in the corresponding fruit juices, although oxidation reaction during extraction could decrease their levels.

Table 1

Durian

Durian is a tropical fruit with strong sulfur aroma not very known in the western countries but is one of the most popular fruits for Asian peoples. The first thiol identified in durian was the propane-1-thiol, as well as other low molecular weight thiols in the early 1970s, by distillation of the pulp (Baldry, Dougan, & Howard, 1972). Another volatile thiol was discovered thirteen years later in Malaysian fruits, also by distillation of the pulp: the 1-(ethylthio)-ethanethiol (Wong & Tie, 1995). More than five years later, 5-methyl-4-mercapto-2-hexanone was identified in a dichloromethane-pentane extract of three Indonesian durian fruits (Weenen, Koolhaas, & Apriyantono, 1996). The other thiols mentioned in the Table 1 were identified more recently by Li *et al.* (Li, Schieberle, & Steinhaus, 2012) including 3MB present in wine and 3MBT present in beer and coffee.

Grapefruit

Grapefruit is a citrus fruit that contains a large number of volatile sulfur compounds. Among the various compounds identified, 1-*p*-menthene-8-thiol is one of the major contributors to the grapefruit juice aroma, present in other fruits as guava, orange and pomelo. In fact, this thiol has a very low odor threshold (0.1 ng/L) and a 200-fold higher concentration in the juice (Demole, Enggist, & Ohloff, 1982). The 4MMP, also found in different fruits (guava, mango and orange) and beverages (beer, tea and wine), was identified as a volatile compound in grapefruit juice using HRGC/MS (Andrea Buettner & Schieberle, 1999). Some results showed that 4MMP provides a more authentic aroma compared to 1-*p*-menthene-8-thiol (Andrea Buettner & Schieberle, 2001). The grapefruit peel also contains thiols in their oil with 4MMPOH, present in guava, beer and wine, but does not contain any trace of 1-*p*-menthene-8-thiol or 4MMP (Lin & Rouseff, 2001). The same team identified 3MH and 3MHA in grapefruit (Lin, Jella, & Rouseff, 2002), also reported in guava, passion fruit, beer and wine. Finally, Lin *et al.* elucidated the presence of 2MFT. This compound was also found in guava, orange, cashew apple, coffee and wine. Two different behaviours were highlighted during the evaporation process: decrease of all volatile thiols (except for 1-*p*-menthene-8-thiol), which suggests that there were evaporated; presence of 1-*p*-menthene-8-thiol, which can be explained through the reaction of increased concentrations of limonene and hydrogen sulfide (Lin, Rouseff, Barros, & Naim, 2002).

Guava

Guava has many thiols in common with grapefruit. The first thiol identified in white and pink guava was 6-mercaptohexanol by direct extraction of flesh juices with dichloromethane and analyzed by GC-MS (Shibamoto, Nishimura, Yamaguchi, & Mihara, 1989). It was present at higher proportion in fresh white guava (GC area peak: 3.1%) than in fresh pink guava (0.6%) and the authors hypothesized that the difference of flavor between these two types of guava might be partially due to the presence of this compound. Sixteen years later, Mahattanatawee *et al.* and Clery *et al.* identified three important thiols: 3MH, 3MHA and 4MMPOH, using headspace and solvent extraction techniques (Clery & Hammond, 2007; Mahattanatawee, Goodner, & Baldwin, 2005). More recently, three other thiols were identified (4MMP) or confirmed (1-*p*-menthene-8-thiol and 2MFT) in guava puree using GC-pulsed flame photometric detector (GC-PFPD, sulfur mode) (Plaza, Marshall, & Rouseff, 2015).

Passion fruit

With grapefruit, yellow passion fruit is one of the most studied tropical fruits, likely due to its very intense aroma. One of the chemical classes standing out in the yellow passion fruit is sulfur-containing compound and especially thiol. Four volatile thiols were firstly identified in the passion fruit and among them, 3MH and 3MHA highly contribute to passion fruit aroma (Engel & Tressl, 1991). Oenologists and winemakers compare the aromas of certain grape varieties, particularly Sauvignon Blanc to that of passion fruit due to the presence of the 3MH and 3MHA in these grape varieties (Tominaga & Dubourdieu, 2000). Lund *et al.* confirmed the characteristic notes of tropical fruits from 3MH and 3MHA by sensory approach (Lund, et al., 2009). Werkhoff *et al.* identified one more thiol with 3-mercaptohexylpentanoate (Werkhoff, Güntert, Krammer, Sommer, & Kaulen, 1998). Finally, 3MMB and 3MMBA, found also in beer, coffee and/or wine, were also identified in passion fruit (Tominaga & Dubourdieu, 2000).

Other fruits

Many authors reported thiols in other fruits than those presented above, for example in lemon (Robert J. Cannon, et al., 2015), mango (Munafo, Didzbalis, Schnell, Schieberle, & Steinhaus, 2014), orange (Schieberle, Fischer, & Grab, 2008) and papaya (Schreier, Idstein, & Keller, 1985). There is no doubt that there are volatile thiols in other fruits than those listed above, and maybe in all vegetables at trace levels, still not highlighted.

1.1.2. Coffee

Roasted and brewed coffee

Coffee is an extensively consumed beverage in the world. The acceptability of coffee is due to many factors and one of the most contributory factors is aroma composition (Kumazawa & Masuda, 2003). In coffee, sulfur compounds such as thiols are among the most important contributors to its aroma despite their presence at relatively low concentration (Sunarharum, Williams, & Smyth, 2014). The major thiols present in coffee reported in the literature are shown in Figure 1-coffee, as well as their characteristic odor (Dulsat-Serra, Quintanilla-Casas, & Vichi, 2016; Vichi, Jerí, Cortés-Francisco, Palacios, & Caixach, 2014). Dulsat-Serra *et al* also referenced the concentration of thiols in roasted and brewed coffee. Among them, five are present in wine or/and beer. 2-furanmethanethiol (2FMT) is reported as a key odorant compound responsible for the "coffee" odor with notes of roast and fresh coffee (Mayer, Czerny, & Grosch, 2000). Several factors (degree of roasting or coffee species for example) can impact the thiol content of coffee (Dulsat-Serra, Quintanilla-Casas, & Vichi, 2016). We can notice that there is a diminution of thiol concentration when passing from roasted to brewed coffee due to the low extraction rate of brewed coffee (Mayer, Czerny, & Grosch, 2000; Semmelroch & Grosch, 1996). For example, the concentration for 2FMT is up to 5080 µg/kg in roasted coffee and only up to 39 µg/L in brewed coffee (Cheong, Tong, Ong, Liu, Curran, & Yu, 2013; Semmelroch & Grosch, 1996).

Figure 1

Variety and geographical influence on thiol contents in coffee

The variety and the geographical provenance have been shown to impact the thiol content in the coffee bean. In fact, 2FMT was reported at higher amounts and with a greater sensory impact in robusta (*Coffea canephora var. robusta*) than arabica (*Coffea arabica*), with a similar degree of roasting (Holscher & Steinhart, 1992; Semmelroch & Grosch, 1995; Semmelroch, Laskawy, Blank, & Grosch, 1995; Tressl & Silwar, 1981). This situation is not general to other thiols, since the 3MBT and 3MMBF levels were comparable in robusta and arabica (Semmelroch & Grosch, 1995; Semmelroch, Laskawy, Blank, & Grosch, 1995; Semmelroch & Grosch, 1996). However, the analysis of 2MFT by GC-O showed that the sensory impact seems to be higher in robusta than arabica coffee (Semmelroch & Grosch, 1995).

1.1.3. Tea

Tea aroma is an important factor affecting the character and quality of the product. There are many kinds of tea but only a very small number is known and consumed. Tea can be divided into three categories: green tea (unfermented), oolong tea (semi-fermented) and black tea (fermented). Traces of thiols were detected in Japanese green tea (Sen-cha) only, with 4MMP and 4-methoxy-2-methyl-2-butanethiol (4MMBT) exhibiting meaty notes (Kumazawa & Masuda, 1999). The authors suggested that these thiols were involved as key odorants of the Japanese green tea. However, 4MMP and 4MMBT have not been identified as volatile component of other kinds of tea (oolong and black tea).

1.2. Alcoholic beverages

1.2.1. Wine

Several studies highlighted the importance of varietal thiols in wine aroma and these sulfur-containing volatile compounds are considered for years now as key compounds (Roland, Schneider, & Cavelier, 2011). Among these compounds, the most studied are 4MMP responsible for box tree and blackcurrant buds notes (Darriet, Tominaga, Lavigne, Boidron, & Dubourdieu, 1995), the 3MH and its corresponding acetate (3MHA) reminiscent of grapefruit and passion fruit respectively (Tominaga, Furrer, Henry, & Dubourdieu, 1998). They contribute to the typical aroma of wines, such as Sauvignon Blanc, Petite Arvine, Petit and Gros Manseng, Melon Blanc, Bacchus, Sémillon, Verdajo, Scheurebe, Maccabeo, Gewürztraminer, Riesling, Muscat, Colombard and Tokay in white wine, Provence in rosé wine, Grenache, Cabernet Sauvignon and Merlot in red or rosé wines. Very recently, Capone *et al.* found varietal thiols in Chardonnay wine at high concentration (Capone, Barker, Williamson, & Francis, 2017). Interactions between these thiols lead to different aroma profiles depending on the amount of each thiol (Lund, et al., 2009) and the level of other

molecules. Other non-varietal sulfur compounds can positively contribute to the wine aroma through coffee and meaty notes (Figure 1-Wine).

Roland *et al.* summarized numerous data on thiols reported in the literature in terms of concentration in wine, aroma descriptors and sensory threshold in model solution. Since this review, new data were published concerning other wines (Benkwitz, Tominaga, Wohlers, Lund, Kilmartin, & Nicolau, 2012; Lv, et al., 2017), but the concentrations reported were included in the concentration range already determined by Roland *et al.* (Roland, Schneider, & Cavelier, 2011).

Beyond the varietal effect on thiol amounts in wine, the vine production area seems to have an impact on thiols concentration. A study comparing the amount of varietal thiols (3MH, 3MHA and 4MMP) in Sauvignon Blanc in different regions of New Zealand and countries (Australia, South Africa, France and USA) was published one year later (Benkwitz, Tominaga, Wohlers, Lund, Kilmartin, & Nicolau, 2012). Concerning 3MHA and 3MH, the concentrations were much higher in Marlborough than in all the other regions (Hawkes Bay and Wairarapa) and countries studied in 2003 and 2004 vintages. The amount of 4MMP was found higher in the Wairarapa region. Wines of New Zealand seems to be much concentrated in these three thiols than those of other countries studied for these vintages. Viticultural and oenological practices influence the thiols concentration in wine and will be developed in the second part of this review.

1.2.2. Beer

The importance of sulfur compounds as thiols in brewing has been pointed out more than a century ago (Garza-Ulloa, 1980). Forty-one thiols were evidenced in hops (mainly *β*-sulfanylalkyl acetates, alcohols and carbonyls) and most of them were found in beer (Figure 1-Hops) (Gros, Peeters, & Collin, 2012). Among them, 3-mercapto-4-methylpentan-1-ol was identified as a key contributor to the "Sauvignon-like" notes in beer produced with the Nelson Sauvin (NS) hop variety (Takoi, et al., 2009). Gros et *al.* studied five hop cultivars (Tomahawk, NS, Nugget, Cascade and Saaz). Tomahawk appeared particularly rich in 3-mercapto-2-ethylpropanal. Tomahawk and NS seems were found to contain higher levels of 3-mercapto-2-ethylpropyl acetate and 3-mercaptooctanal. NS proved to contain higher amounts of β-sulfanylalkyl alcohols. Finally, 3MH was found in all cultivars, with high values for Cascade (Gros, Nizet, & Collin, 2011).

3MBT was usually described as an unpleasant flavor, the so-called skunky aroma. This flavor is caused by ultraviolet light (Hill & Smith, 2000). In fact, the transmission of light to the beer through the bottle increases 3MBT formation and using green or dark bottle is advisable to limit this phenomenon (Sakuma, Rikimaru, Kobayashi, & Kowaka, 1991).

A recent study highlights the content of 3MH, 3MHA and 4MMP in different categories of beer (Pale ale, Belgium origin, Pils and experimental beers). According to the data, there is no obvious link between the category of beer and the concentration of these three thiols, with an important variability in the same category: up to 1200 $ng.L^{-1}$ for 3MH; up to 100 $ng.L^{-1}$ for

3MHA; up to 300 ng.L^{-1} for 4MMP. 3MHA was present only in experimental beers and one Pale ale and the levels were higher than those of 3MH, which is very different to the reported concentrations often close to 10% of free 3MH in wine (Roland, et al., 2016).

1.2.3. Sake

4MMP is also present in Sake, the traditional Japanese alcoholic beverage brewed by fermenting rice that has been polished to remove the bran. In fact, steamed rice is saccharified by glucoamylase of koji mold (a filamentous fungus) and the glucose formed from starch is then fermented into ethanol using a specific strain of *Saccharomyces cerevisiae* (Furukawa, Tanaka, Masumura, Kiyokawa, & Wakai, 2006). The typically pleasant smelling grassy notes has been very recently attributed to 4MMP in different Sake (Iizuka-Furukawa, Isogai, Kusaka, Fujii, & Wakai, 2017). The authors reported that this thiol is the characteristic aroma of sake made from low-glutelin rice. In the same way as in wine, 4MMP is released during AF from precursors. Iizuka-Furukawa *et al.* determined the perception threshold of 4MMP in sake at 1.2 ng/L, similar range as reported in wine and beer (Darriet, Tominaga, Lavigne, Boidron, & Dubourdieu, 1995; Toru Kishimoto, Kobayashi, Yako, Iida, & Wanikawa, 2008). There is no data on the plant variety, the rice production area or the fermentation conditions on 4MMP concentration.

In conclusion, for this part, it is interesting to highlight the frequency of appearance of thiols in beverages reviewed here. Eight thiols appear in at least 4 different beverages (Figure 2). It is interesting to notice that among these eight thiols, six of them have been identified in wine and beer, which are the most extensively studied beverages. The correlation between the number of thiol occurrence and the beverage studied seems to show that the research on thiols doesn't reach the same development level between the different beverages.

Figure 2

2. Release mechanisms from thiol precursors

The mechanisms of thiols release from their precursors are complex and depend on:

- the plant variety (already discuss in the first part)
- the growing method
- the process (roasting for coffee, fermentation for beer, sake or wine and more simply the extraction by pressing or grinding)

2.1. Formation of thiols in coffee

2.1.1. Roasting

Roasting coffee impacts the chemical and physical properties of the initial green coffee beans. Roasting consists in rapidly brought the green beans to very high temperature (approximately 200 to 250°C), which is then quickly lowered to stop the process. The formation of thiols during this process is not completely elucidated. However, it is admitted that *S*-containing amino acids are important precursors and sulfur source for reactions with other compounds (for example sugar) that occur during coffee bean roasting (Dulsat-Serra, Quintanilla-Casas, & Vichi, 2016).

The Maillard-type reaction plays a key role in the thiol formation in roasted coffee. Indeed, many authors reported the formation of 2FMT and 2MFT from the reaction between aldose and cysteine in a model system (Cerny, 2008; Dulsat-Serra, Quintanilla-Casas, & Vichi, 2016; Hofmann & Schieberle, 1997). However, this Maillard-type reaction was dismissed by Poisson *et al.* by biomimetic in-bean experiments (Poisson, Schmalzried, Davidek, Blank, & Kerler, 2009). Another important pathway involves H_2S liberated from cysteine or methionine may react with prenyl alcohol (3-methyl-2-buten-1-ol) to obtain 3MMB (Holscher, Vitzthum, & Steinhart, 1992). Holscher *et al.* published that prenyl alcohol was also identified as precursor of 3MBT.

The general observation is that not only roasty, but sulfury, earthy and smoky notes improved during roasting (Grosch, 1998). Mayer *et al.* proved that 2FMT and 3MBT increased more and more with the roasting time (Mayer, Czerny, & Grosch, 1999). Roasting temperature also influences the volatile thiols formation (Baggenstoss, Poisson, Kaegi, Perren, & Escher, 2008). Different kinetics have been reported in the literature, by comparing the evolution of 3MMB and the two corresponding esters during roasting: 3MMB and 3MMBF increase linearly with the temperature of roasting, whereas 3MMBA increases only at higher degrees (Kumazawa & Masuda, 2003). Thus, 2FMT and 3MBT/3MMBF have different behaviour: 2FMT is favoured by a long-time process at low-temperature in contrast to 3MBT and 3MMBF (Baggenstoss, Poisson, Kaegi, Perren, & Escher, 2008; Schenker, Heinemann, Huber, Pompizzi, Perren, & Escher, 2002).

2.1.2. Brewing

Once the coffee has been roasted, the amount of thiols in the brewed coffee is not proportional to the initial level in roasted coffee. In fact, the efficiency of the extraction (solid-liquid) during the brewing process is impacted by physical parameters (water temperature, pressure, time of extraction and water/coffee ratio) (Mayer, Czerny, & Grosch, 2000; Semmelroch & Grosch, 1996). However, data on the content of thiols under different coffee brewing conditions are extremely scarce and only methanethiol evolution is documented (Andueza, Maetzu, Pascual, Ibañez, de la Peña, & Cid, 2003). Methanethiol is more abundant in expresso coffee than in other types of brewed coffee, due to the extraction pressure and the higher ratio between coffee and water. In this type of brewed coffee, the water temperature is important for the extraction efficiency of methanethiol (Andueza, Maetzu, Pascual, Ibañez, de la Peña, & Cid, 2003). Although it might be possible to extrapolate methanethiol tendency on

other thiols, supplementary data are needed to highlight the impact parameters of brewing process without going beyond assumptions.

2.2. Formation of thiols by microorganism during fermentation processes: Focus on 3MH and 4MMP

Prefermentative steps can influence the thiol levels. As an example, prefermentative operations in grapes as skin maceration could lead to an increase of 3MH and 4MMP in white wine. Must conservation on lees, another prefermentative process, increases the amount of 3MH and 3MHA in wine, without increasing the amount of precursors during this process (Roland, Schneider, Charrier, Cavelier, Rossignol, & Razungles, 2011).

During winemaking or beer brewing, AF is an essential step for the sugar conversion into alcohol by yeast, but it also impacts other compounds at lower concentration such as polyphenols and aromas such as varietal thiols. 3MH and 4MMP are produced during AF by the yeast (*Saccharomyces cerevisiae*) using a β-lyase activity (Cordente, Capone, & Curtin, 2015; Tominaga, Peyrot des Gachons, & Dubourdieu, 1998) from odorless *S*-conjugate precursors.

2.2.1. Grapes and wines

Precursors and mechanisms of transformation

Several precursor families have been identified in grapes and musts and have been widely studied. They are listed below by chronological order of identification:

- cysteine *S*-conjugates to 3MH and 4MMP (Cys-3MH and Cys-4MMP) (Tominaga, Peyrot des Gachons, & Dubourdieu, 1998);
- glutathione *S*-conjugates to 3MH and 4MMP (G-3MH and G-4MMP) (Fedrizzi, Pardon, Sefton, Elsey, & Jeffery, 2009; Peyrot des Gachons, Tominaga, & Dubourdieu, 2002a);
- cysteinyl-glycine *S*-conjugates to 3MH (CysGly-3MH) (Bonnaffoux, Delpech, Rémond, Schneider, Roland, & Cavelier, 2018; Capone, Pardon, Cordente, & Jeffery, 2011);
- *S*-(3-hexan-1-al)-glutathione (G-3MHAl) and its bisulfite adduct (Thibon, Böcker, Shinkaruk, Moine, Darriet, & Dubourdieu, 2016);
- γ-glutamyl-cysteine *S*-conjugate to 3MH (γGluCys-3MH) (Bonnaffoux, Roland, Rémond, Delpech, Schneider, & Cavelier, 2017; Bonnaffoux, Delpech, Rémond, Schneider, Roland, & Cavelier, 2018).

Another pathway was also evidenced: 3MH can result of the addition of a sulfhydryl donor group to the (*E*)-2-hexenal during alcoholic fermentation (AF) (Schneider, Charrier, Razungles, & Baumes, 2006). It has been suggested that H_2S could be one of the sulfur donor

(Harsch, Benkwitz, Frost, Colonna-Ceccaldi, Gardner, & Salmon, 2013). Then, sulfonic acids were hypothesized on structural basis but not identified yet (Duhamel, Piano, Davidson, Larcher, Fedrizzi, & Barker, 2015). Finally, cysteinyl-glycine *S*-conjugates to 4MMP (CysGly-4MMP) and γ-glutamyl-cysteine *S*-conjugate to 4MMP (γGluCys-4MMP) were not identified yet. A signal by UPLC-MS/MS using stable isotope dilution assay confirmed the presence of CysGly-4MMP and γGluCys-4MMP but the intensity of the signal was below the recommended values for formal identification (Bonnaffoux, Roland, Rémond, Delpech, Schneider, & Cavelier, 2017). Cys-3MH, G-3MH, CysGly-3MH, γGluCys-3MH, Cys-4MMP and G-4MMP were quantified in different varieties of grape (Table 2) and Sauvignon Blanc presented the higher concentration of 3MH precursors (Peña-Gallego, Hernández-Orte, Cacho, & Ferreira, 2012).

Interconversions between *S*-conjugates under defined oenological conditions were highlighted. Firstly, all precursors were partially metabolised during AF (Bonnaffoux, Delpech, Rémond, Schneider, Roland, & Cavelier, 2018; Concejero, Hernandez-Orte, Astrain, Lacau, Baron, & Ferreira, 2016), whereas it was commonly accepted by scientific community that conversion was complete. During fermentation, monitoring of thiol precursor levels in the fermentation medium showed that G-3MH could be partially cleaved (7%) in γGluCys-3MH, contrarily to G-4MMP which was practically not metabolised. Regarding dipeptides, 54% of CysGly-3MH (respectively 6% of CysGly-4MMP) was cleaved into cysteinyl *S*-conjugates, while γGluCys *S*-conjugates were not metabolised (Figure 3) (Bonnaffoux, Delpech, Rémond, Schneider, Roland, & Cavelier, 2018). For precursors metabolised by the yeast, only a little part are cleaved by the yeast to give varietal thiols. Indeed, conversion yields of all cysteinyl *S*-conjugates precursors into their respective varietal thiols (3MH or 4MMP) were found to be between 0.17 and 1%(Bonnaffoux, Delpech, Rémond, Schneider, Roland, & Cavelier, 2018; Jeffery, 2016). The other part of metabolised precursors is still unknown. Different cleavages could generate some amino acids or sulfur peptides. Finally, the conversion of precursors to thiols is an epiphenomenon in quantitative terms, but still important to give the aromatic notes to wine.

Table 2

Figure 3

Another study found different conversion yields, especially for G-3MH. For example, Roland *et al.* calculated a conversion yield for G-3MH of 3% (Roland, Schneider, Le Guernevé, Razungles, & Cavelier, 2010). Therefore, this difference could be attributable to the assimilable nitrogen, which might be different from one must to another. Although numerous precursors of varietal thiols have been elucidated, the correlation between the concentration of thiols in wines and the amount of precursors found in musts is not verified (Pinu, Jouanneau, Nicolau, Gardner, & Villas-Boas, 2012). That means, other parameters drive thiol release from precursors. Furthermore, the low conversion yields remain problematic.

Influence of viticultural and oenological processes on thiol contents

The evolution of the aromatic potential, responsible for the release of varietal thiols, was studied in order to better understand the biogenesis of these precursors in berries during maturation. A study on the evolution of cysteinyl precursors in bunches of Sauvignon Blanc one month before the grape harvest showed a great variability in the precursor content, which would probably depend on the chemical composition of the berry (assimilable nitrogen for example) (Peyrot des Gachons, Tominaga, & Dubourdieu, 2000). The combination of sulfur and nitrogen foliar supply in Sauvignon Blanc vines increases the varietal thiol contents in the resulting wines, but the authors didn't report an enhance of precursors (Lacroux, et al., 2008). However, ammonium fertilization increases cysteine *S*-conjugates to 3MH, 4MMP and 4MMPOH. The maturation directly affects the concentration of certain precursors in Sauvignon Blanc (Cys-3MH, G-3MH and G-4MMP) by increasing their initial amount in berries (Roland, Vialaret, Razungles, Rigou, & Schneider, 2010). The water deficit impacts the concentration of cysteinyl precursors in Sauvignon Blanc grapes. The amount of Cys-3MH increase with a moderate water deficit, in contrary to Cys-4MMP (cases in Bordeaux conditions with a moderate water deficit) (Choné, 2001).

Cysteinylated and glutathionylated precursors of 3MH and 4MMP are mainly located in the skin (Sauvignon Blanc and Melon B.) (Peyrot des Gachons, Tominaga, & Dubourdieu, 2002b). Recently, Jeffery reports data on 3MH precursor concentration for Sauvignon Blanc grapes undergoing different treatments (Jeffery, 2016). It appears that hand-harvesting yielded lower precursor concentrations than machine harvest due to the limiting berry damage, precursor extraction and the enzymatic mechanisms generated. Similarly, precursors increased during transport or storage of grapes, for the same reason as previously. The precursors of thiols subjected to increasing doses of SO_2 added at harvest decreases proportionally, maybe due to an inhibition of enzymatic reactions (Capone & Jeffery, 2011). Some studies showed that Cys-3MH increases in rosé musts of Merlot and Cabernet Sauvignon as a result of prolonged skin maceration (Murat, Tominaga, & Dubourdieu, 2001). A prefermentative pressing cycle in the wine cellar increased varietal thiol precursors. Prefermentative cold storage of the must on their lees did not influence the concentration of Cys-3MH and G-3MH in Sauvignon Blanc must. However, the content of 3MH and 3MHA in resulting wines increased significantly and proportionally to the duration of on-lees must cold storage. This increase could be due to the formation of other thiol precursors, during prefermentative operations (Roland, Schneider, Charrier, Cavelier, Rossignol, & Razungles, 2011).

During AF, varietal thiols are released by *Saccharomyces Cerevisiae* yeast through its beta-lyase activity. Some of them have demonstrated their ability to release varietal thiols under oenological conditions (Dubourdieu, Tominaga, Masneuf, Peyrot des Gachons, & Murat, 2006; Howell, et al., 2004; Murat, Masneuf, Darriet, Lavigne, Tominaga, & Dubourdieu, 2001; Swiegers, Francis, Herderich, & Pretorius, 2006). Furthermore, a cofermentation with a non *S. cerevisiae* yeast (*Pichia kluyveri*) can generates more 3MH and 3MHA in Sauvignon Blanc wine (Anfang, Brajkovich, & Goddard, 2009) and similarly, an interspecific hybrid (*S. cerevisiae* X *S. bayanus*) was found to enhance the 4MMP concentration compared to its parent *S. cerevisiae*. Other parameters can influence the release of varietal thiols, especially the fermentation temperature. Indeed, AF conducted at 20°C instead of 13°C was found to increase 3MH, 3MHA and 4MMP concentrations in wine (Masneuf-Pomarède, Mansour, Murat, Tominaga, & Dubourdieu, 2006) and warmer conditions (around 28°C) result in larger content of 4MMP. In this latter case, the results seem to be dependent on the yeast strain used (Howell, et al., 2004). A few studies highlight precursors transport in the yeast cell required for their cleavage. In *S. cerevisiae*, the main transporter of G-3MH and G-4MMP inside the cell is *OPT1*, while *GEX1* expels these precursors out of the cell (Cordente, Capone, & Curtin, 2015; Dhaouia, et al., 2011). In the same way, only *YBT1* seems to play a role in the transport of G-3MH into the vacuole. Different degradations of glutathione *S*-conjugates involved into the vacuole or the cytosol through aminopeptidase to obtain γGluCys, CysGly and cysteine *S*-conjugates (Cordente, Capone, & Curtin, 2015). Finally, release of 3MH and 4MMP from their corresponding cysteine precursors is mediated by *STR3* and *IRC7* (Roncoroni, et al., 2011; Thibon, Marullo, Claisse, Cullin, Dubourdieu, & Tominaga, 2008).

Very recently, Takase *et al.* study the bioconversion of 3MH precursors into 3MH by lactic acid bacteria. Among species tested, *Lactobacillus plantarum* is able to metabolised Cys-3MH and CysGly-3MH to produce 3MH (Takase, Sasaki, Kiyomichi, Kobayashi, Matsuo, & Takata, 2018). However, those results were obtained either in culture medium or on a must, without the interference of AF. Thus oenological conditions need to be tested to confirm this observation since few lactic acid bacteria (except *Oenococcus oeni*) are resistant to these particular conditions.

During aging, the wine will undergo structural and aromatic modifications, while some wines increase their value and quality as they age, others might deteriorate over time, especially wines susceptible to oxidation. Thiols are chemically unstable because they are easily oxidable in disulfide, even under mild oxidative conditions (Roland, Delpech, Dagan, Ducasse, Cavelier, & Schneider, 2016; Sarrazin, Shinkaruk, Pons, Thibon, Bennetau, & Darriet, 2010). Possible mechanisms of thiol trapping were involved in the presence of oxygen (Nikolantonaki, Chichuc, Teissedre, & Darriet, 2010). The oxygen transfer rate during the storage is dependent of the type of stopper (synthetic, cork). In fact, synthetic stoppers are known for their oxygen barrier properties (Lopes, Saucier, Teissedre, & Glories, 2006). Nevertheless, the use of cork could cause an absorption of certain volatile compounds into the stopper that is called scalping. This phenomenon could be responsible for the loss of aroma in Sauvignon Blanc by trapping 3MH and 3MHA (Brajkovich, et al., 2005). However, it must be kept in mind that the total absence of oxygen, especially in white wines, results in the production of reduced dominant odors. A compromise must be made to protect the aromas of white wines from oxidation without the formation of reduced compounds. The aging on lees

before bottling could be a solution, similarly as natural glutathione or SO_2 adding which have a protecting effect against the loss of fruity notes in wines (Blanchard & 2004, 2004; Brajkovich, et al., 2005).

Oenological tannins

Oenological tannin formulations are used in winemaking for the different contribution they can give to the wine (colour stability for example).

Cys-3MH and G-3MH were identified for the first time in these formulations, from different biological sources (Grapes, tea, trees, etc …). Very high contents were found in grape skin tannins (Larcher, Tonidandel, Nicolini, & Fedrizzi, 2013), that could be considered as residue from tannins extraction:

- Cys-3MH (between around 0.3 and 200 $mg.kg^{-1}$, median = 9.1 $mg.kg^{-1}$)
- G-3MH (between around 0.2 and 138 $mg.kg^{-1}$, median = 10.1 $mg.kg^{-1}$)

These technological processing aids or additives can be used as a potential aroma of passion fruit and grape fruit for wine. Oenological tannins could be added before or during AF to allow the yeast to release 3MH in wine. However, oenological tannin addition must be carry on carefully since they can negatively impact on wine sensory character even if those authors didn't observe detrimental effect at the dosage used (Larcher, Tonidandel, Nicolini, & Fedrizzi, 2013).

2.2.2. Hops and malts: mechanisms and precursors

Occurrence of thiol precursors in both malts and hops was firstly hypothesized in 2008 (Toru Kishimoto, Morimoto, Kobayashi, Yako, & Wanikawa, 2008) and few years later, Cys-3MH was identified in hop (Gros, Peeters, & Collin, 2012). Cys-3MH was considered as precursor of 3MH thanks to an enzymatic degradation promoted by the yeast during bottle re-fermentation or during Belgian beer ageing (Nizet, Gros, Peeters, Chaumont, Robiette, & Collin, 2013; Tran, Cibaka, & Collin, 2015). The first quantification of Cys-3MH revealed that Cys-3MH might be present until 1641 ppb as 3MH equivalent in Cascade hop variety (Gros, Tran, & Collin, 2013). In addition to Cys-3MH, three others precursors of 3MH and 4MMP were identified and quantified into several hop varieties (Chinook, Saaz, Barbe Rouge, Cascade, Mistral, Aramis Alsace, Strisselspat and Mandarina) using direct LC-MS/MS analysis and SIDA (Stable isotope dilution assay) (Roland, et al., 2016):

- Cys-3MH: between around 0.130 (Mandarina) and 1.1 $mg.kg^{-1}$ (Barbe Rouge)
- G-3MH: between around 1.3 (Barbe Rouge) and 19 $mg.kg^{-1}$ (Cascade)
- Cys-4MMP: between around 0.005 (Saaz) and 0.04 $mg.kg^{-1}$ (Strisselspat)
- G-4MMP: quantified only in Chinook at 0.01 $mg.kg^{-1}$

In this study, the distribution of thiol precursors in different hop varieties seems to be very different. Thiol precursors in those variety are mainly 3MH precursors and G-3MH represented more than 80 % of the total amount of thiol precursors, except for Barbe Rouge

hops where the levels of Cys-3MH and G3MH are quite similar. Furthermore, the total amount of thiol precursors is highly dependent of the hop varieties.

We have to point out that, contrary to grapes, hops are also rich in free thiols. The proportion of free/bounded thiols (i.e. as thiol precursor) depends on the thiols considered (3MH or 4MMP and in a lesser extent on the hop variety): less than 1% for 3MH free/bounded fraction in Chinook and Barbe Rouge; up to 23% or 95% for 4MMP free/bounded fraction of Chinook or Saaz hops respectively (Roland, et al., 2016). Similar experiments on 3MH revealed that free/bounded fraction ratios are closed to 2% for Citra, 4% for Tomahawk and 7% for Cascade (Cibaka, Gros, Nizet, & Collin, 2015). Roland *et al.* also tried to build some hypotheses about thiol origins from different categories of beer (Pale ale, Belgium origin, IPA, Pils and experimental beers). They observed an important variability of thiol contents in the same category of beers. The authors were surprised to observe that 3MHA occurred practically only in experimental beers with a level higher than those of 3MH. It can be explained by the specific yeasts or fermentation conditions used during the elaboration of the experimental beers. Another counter-intuitive fact is that IPA beer, with intensive hopping, contains relatively low levels of 3MH (less than 180 $ng.L^{-1}$). Thereby, hops might not be the only source of thiol and thiol precursors for beers. Malts was hypothesized as another source (T. Kishimoto, Wanikawa, Kono, & Shibata, 2006). Other precursors need to be investigated and other precursors should be identified, based on those identified in the grape must: CysGly-3MH, γGluCys-3MH, G-3MH-Al and its bisulfite.

Other mechanisms of thiol formation have been highlighted more than 60 years ago. Indeed, a formal mechanism was described for the 3MBT formation which involved isohumulones (Kuroiwa & Hashimoto, 1961). In fact, these compounds absorbed light to give a radical reaction and release a carbonyl radical. Then, a decarbonylation to a dimethyl allyl radical, followed by a reaction including a thiol radical from a sulfur source generates 3MBT. More recently, this mechanism was fully detailed and comprehensively described (De Keukeleire, Heyerick, Huvaere, Skibsted, & Andersen, 2008).

2.2.3. Rices and Sake: mechanisms and precursors

Up to now, only one publication pointed out the contribution of 4MMP to the aroma of sake and the putative mechanisms for its genesis (Iizuka-Furukawa, Isogai, Kusaka, Fujii, & Wakai, 2017). However, G-4MMP was identified in two different sake (*Mizuhonoka sake* and *Gin-ohmi sake*) and in two different rices (*Mizuhonoka rice* and *Gin-ohmi rice*) and in koji. In contrast, Cys-4MMP was not detected in sake, rice of Mizuhonoka and Gin-ohmi and koji, probably due to the limits of detection of Cys-4MMP (23 µg/L). The authors highlight the release of 4MMP during AF from a model medium with addition of synthesized Cys-4MMP and G-4MMP in the absence and presence of sake yeast. The authors concluded that 4MMP was released from both Cys-4MMP and G-4MMP by sake yeast. However, the relationship between G-4MMP or Cys-4MMP and their corresponding thiol have not been formally certified because no filiation in the sake has been made yet.

Considering the lack of data available for the sake production context, further studies have to be performed in order to investigated the rice-growing condition impact (cultivars, water status, nitrogen fertilization) or the process impact (rice drying and storage, fermentation conditions, final product bottling and storage, …) to better understand the release mechanisms during sake production.

2.3. Formation of thiols in non-fermented juice fruits

Different exotic fruit has been investigated. For durian, few references in literature discuss the precursors and mechanisms of thiols in durian. Bacteria in the arils (fleshy envelope developed around the seed) of the fruit could be part of the mechanism release of thiol (Suhandono & Utari, 2014). In fact, these bacteria could catalyse the enzymatic release of hydrogen sulphide and methanethiol from cysteine or methionine respectively (Robert J. Cannon & Ho, 2018), which can be extended to all thiols in durian presented in Table 1.

For guava, the concentrations of 3MH and 3MHA evolve differently during maturation according to the variety of the guava. Concerning pink guava, these thiols increase from green to overripe, which is the opposite for white guava (Sinuco, Steinhaus, Schieberle, & Osorio, 2010). The authors attempted to isolate and treat precursors with β-lyase, but without produce 3MH. Instead, they hypothesized that unsaturated carbonyls, especially (*E*)-2-hexenal could be the pathway to the 3MH formation.

Passion fruit is the most documented fruit concerning release mechanisms of thiols. The first 3MH precursor identified in a passion fruit juice from La Réunion was Cys-3MH. It was identified using trimethylsilylation and then GC-MS analysis (Tominaga & Dubourdieu, 2000). More recently, three other *S*-conjugates precursors (G-3MH, CysGly-3MH and γGluCys-3MH) were identified (Fedrizzi, et al., 2012).

These precursors were identified by LC-MS comparing the retention time of the compounds naturally present in the passion fruit and those synthesized.

With the identification of these compounds, the authors proposed a hypothetical pathway for the biogenesis of 3MH (Figure 3; *in planta* and without yeast). Indeed, G-3MH could be degraded with the cleavage either of the glutamate moiety by a γ-glutamyl transferase (Grzam, Martin, Hell, & Meyer, 2007) or with the removal of the glycine residue by a carboxypeptidase (Wolf, Dietz, & Schröder, 1996) to give the CysGly-3MH and γGluCys-3MH respectively. Then, CysGly-3MH (or γGluCys-3MH) could be degraded by a carboxypeptidase (or γglutamyl transferase) to obtain the Cys-3MH.

Others hypotheses were discussed for the formation of 3MHA through the esterification of 3MH with the corresponding acid (Tressl & Albrecht, 1986). More recently, it was discovered

enzymes in the passionfruit located in the mesocarp, that could hydrolyse thioesters to their respective thiols (Edwards, Tapp, Cummins, & Brassington, 2008). This could also explain the formation of 3MH and 3MHA.

3. Conclusion

Thiols and their precursors are widely studied in beverages and food industry and a lot of release mechanisms were elucidated. It is interesting to note that several precursors, especially glutathione *S*-conjugate derivatives were identified in different plant raw materials, such as grape (and must), tannin, fruits, hop, malt and rice. Except for the passion fruit, all these plants after AF of must, rice or hop and malt can release varietal thiols according to the same mechanism: a β-lyase induced by a fermentative yeast. However, and except for grape and wine, there is a lack of knowledge about the hypothetical interconversion between these glutathione *S*-conjugates derivatives. In grape and wine, release mechanisms are widely studied, contrary in rice and sake.

Concerning thiols, several compounds, such as 3MMB, are present in different beverages (wine, beer and coffee). The mechanisms during roasting coffee such as the genesis of 3MMB and 3MBT from prenyl alcohol, could be extended to beer and red wine during high temperatures process (such as thermovinification heats process for example). However, it is important to notice that the roasting process is done by dry way while the vinification by wet way, which involved different mechanisms. Maillard reaction formations exist in wine (Marchand, de Revel, Vercauteren, & Bertrand, 2002), but they occurred mainly during storage over a very long period.

603 **References**
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