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Spotlight on release mechanisms of volatile thiols in beverages

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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 H₂S, 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

41 *Durian*

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

52

53 *Grapefruit*

54 Grapefruit is a citrus fruit that contains a large number of volatile sulfur compounds. Among
55 the various compounds identified, 1-*p*-menthene-8-thiol is one of the major contributors to the
56 grapefruit juice aroma, present in other fruits as guava, orange and pomelo. In fact, this thiol
57 has a very low odor threshold (0.1 ng/L) and a 200-fold higher concentration in the juice
58 (Demole, Enggist, & Ohloff, 1982). The 4MMP, also found in different fruits (guava, mango
59 and orange) and beverages (beer, tea and wine), was identified as a volatile compound in
60 grapefruit juice using HRGC/MS (Andrea Buettner & Schieberle, 1999). Some results
61 showed that 4MMP provides a more authentic aroma compared to 1-*p*-menthene-8-thiol
62 (Andrea Buettner & Schieberle, 2001). The grapefruit peel also contains thiols in their oil
63 with 4MMPOH, present in guava, beer and wine, but does not contain any trace of 1-*p*-
64 menthene-8-thiol or 4MMP (Lin & Rouseff, 2001). The same team identified 3MH and
65 3MHA in grapefruit (Lin, Jella, & Rouseff, 2002), also reported in guava, passion fruit, beer
66 and wine. Finally, Lin *et al.* elucidated the presence of 2MFT. This compound was also found
67 in guava, orange, cashew apple, coffee and wine. Two different behaviours were highlighted
68 during the evaporation process: decrease of all volatile thiols (except for 1-*p*-menthene-8-
69 thiol), which suggests that there were evaporated; presence of 1-*p*-menthene-8-thiol, which
70 can be explained through the reaction of increased concentrations of limonene and hydrogen
71 sulfide (Lin, Rouseff, Barros, & Naim, 2002).

72

73 *Guava*

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

85

86 *Passion fruit*

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

99

100 *Other fruits*

101 Many authors reported thiols in other fruits than those presented above, for example in lemon
102 (Robert J. Cannon, et al., 2015), mango (Munafo, Didzbalis, Schnell, Schieberle, & Steinhaus,
103 2014), orange (Schieberle, Fischer, & Grab, 2008) and papaya (Schreier, Idstein, & Keller,
104 1985). There is no doubt that there are volatile thiols in other fruits than those listed above,
105 and maybe in all vegetables at trace levels, still not highlighted.

106

107 *1.1.2. Coffee*

108

109 *Roasted and brewed coffee*

110 Coffee is an extensively consumed beverage in the world. The acceptability of coffee is due to
111 many factors and one of the most contributory factors is aroma composition (Kumazawa &
112 Masuda, 2003). In coffee, sulfur compounds such as thiols are among the most important
113 contributors to its aroma despite their presence at relatively low concentration (Sunarharum,
114 Williams, & Smyth, 2014). The major thiols present in coffee reported in the literature are
115 shown in Figure 1-coffee, as well as their characteristic odor (Dulsat-Serra, Quintanilla-Casas,
116 & Vichi, 2016; Vichi, Jerí, Cortés-Francisco, Palacios, & Caixach, 2014). Dulsat-Serra *et al*
117 also referenced the concentration of thiols in roasted and brewed coffee. Among them, five
118 are present in wine or/and beer. 2-furanmethanethiol (2FMT) is reported as a key odorant
119 compound responsible for the “coffee” odor with notes of roast and fresh coffee (Mayer,
120 Czerny, & Grosch, 2000). Several factors (degree of roasting or coffee species for example)
121 can impact the thiol content of coffee (Dulsat-Serra, Quintanilla-Casas, & Vichi, 2016). We
122 can notice that there is a diminution of thiol concentration when passing from roasted to
123 brewed coffee due to the low extraction rate of brewed coffee (Mayer, Czerny, & Grosch,
124 2000; Semmelroch & Grosch, 1996). For example, the concentration for 2FMT is up to 5080
125 µg/kg in roasted coffee and only up to 39 µg/L in brewed coffee (Cheong, Tong, Ong, Liu,
126 Curran, & Yu, 2013; Semmelroch & Grosch, 1996).

127

Figure 1

128

129 *Variety and geographical influence on thiol contents in coffee*

130 The variety and the geographical provenance have been shown to impact the thiol content in
131 the coffee bean. In fact, 2FMT was reported at higher amounts and with a greater sensory
132 impact in robusta (*Coffea canephora* var. *robusta*) than arabica (*Coffea arabica*), with a
133 similar degree of roasting (Holscher & Steinhart, 1992; Semmelroch & Grosch, 1995;
134 Semmelroch, Laskawy, Blank, & Grosch, 1995; Tressl & Silwar, 1981). This situation is not
135 general to other thiols, since the 3MBT and 3MMBF levels were comparable in robusta and
136 arabica (Semmelroch & Grosch, 1995; Semmelroch, Laskawy, Blank, & Grosch, 1995;
137 Semmelroch & Grosch, 1996). However, the analysis of 2MFT by GC-O showed that the
138 sensory impact seems to be higher in robusta than arabica coffee (Semmelroch & Grosch,
139 1995).

140

141 *1.1.3. Tea*

142

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

151

152 *1.2. Alcoholic beverages*

153

154 *1.2.1. Wine*

155

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

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

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

177 Beyond the varietal effect on thiol amounts in wine, the vine production area seems to have an
178 impact on thiols concentration. A study comparing the amount of varietal thiols (3MH,
179 3MHA and 4MMP) in Sauvignon Blanc in different regions of New Zealand and countries
180 (Australia, South Africa, France and USA) was published one year later (Benkwitz,
181 Tominaga, Wohlers, Lund, Kilmartin, & Nicolau, 2012). Concerning 3MHA and 3MH, the
182 concentrations were much higher in Marlborough than in all the other regions (Hawkes Bay
183 and Wairarapa) and countries studied in 2003 and 2004 vintages. The amount of 4MMP was
184 found higher in the Wairarapa region. Wines of New Zealand seems to be much concentrated
185 in these three thiols than those of other countries studied for these vintages. Viticultural and
186 oenological practices influence the thiols concentration in wine and will be developed in the
187 second part of this review.

188

189 1.2.2. Beer

190

191 The importance of sulfur compounds as thiols in brewing has been pointed out more than a
192 century ago (Garza-Ulloa, 1980). Forty-one thiols were evidenced in hops (mainly β -
193 sulfanylalkyl acetates, alcohols and carbonyls) and most of them were found in beer (Figure
194 1-Hops) (Gros, Peeters, & Collin, 2012). Among them, 3-mercapto-4-methylpentan-1-ol was
195 identified as a key contributor to the “Sauvignon-like” notes in beer produced with the Nelson
196 Sauvin (NS) hop variety (Takoi, et al., 2009). Gros *et al.* studied five hop cultivars
197 (Tomahawk, NS, Nugget, Cascade and Saaz). Tomahawk appeared particularly rich in 3-
198 mercapto-2-ethylpropanal. Tomahawk and NS seems were found to contain higher levels of
199 3-mercapto-2-ethylpropyl acetate and 3-mercaptooctanal. NS proved to contain higher
200 amounts of β -sulfanylalkyl alcohols. Finally, 3MH was found in all cultivars, with high
201 values for Cascade (Gros, Nizet, & Collin, 2011).

202 3MBT was usually described as an unpleasant flavor, the so-called skunky aroma. This flavor
203 is caused by ultraviolet light (Hill & Smith, 2000). In fact, the transmission of light to the beer
204 through the bottle increases 3MBT formation and using green or dark bottle is advisable to
205 limit this phenomenon (Sakuma, Rikimaru, Kobayashi, & Kowaka, 1991).

206

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

211 3MHA; up to 300 ng.L⁻¹ for 4MMP. 3MHA was present only in experimental beers and one
212 Pale ale and the levels were higher than those of 3MH, which is very different to the reported
213 concentrations often close to 10% of free 3MH in wine (Roland, et al., 2016).

214

215 *1.2.3. Sake*

216

217 4MMP is also present in Sake, the traditional Japanese alcoholic beverage brewed by
218 fermenting rice that has been polished to remove the bran. In fact, steamed rice is saccharified
219 by glucoamylase of koji mold (a filamentous fungus) and the glucose formed from starch is
220 then fermented into ethanol using a specific strain of *Saccharomyces cerevisiae* (Furukawa,
221 Tanaka, Masumura, Kiyokawa, & Wakai, 2006). The typically pleasant smelling grassy notes
222 has been very recently attributed to 4MMP in different Sake (Iizuka-Furukawa, Isogai,
223 Kusaka, Fujii, & Wakai, 2017). The authors reported that this thiol is the characteristic aroma
224 of sake made from low-glutelin rice. In the same way as in wine, 4MMP is released during
225 AF from precursors. Iizuka-Furukawa *et al.* determined the perception threshold of 4MMP in
226 sake at 1.2 ng/L, similar range as reported in wine and beer (Darriet, Tominaga, Lavigne,
227 Boidron, & Dubourdieu, 1995; Toru Kishimoto, Kobayashi, Yako, Iida, & Wanikawa, 2008).
228 There is no data on the plant variety, the rice production area or the fermentation conditions
229 on 4MMP concentration.

230

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

237

Figure 2

238

239 **2. Release mechanisms from thiol precursors**

240

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

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

246

247

248 *2.1. Formation of thiols in coffee*

249

250 *2.1.1. Roasting*

251

252 Roasting coffee impacts the chemical and physical properties of the initial green coffee beans.
253 Roasting consists in rapidly brought the green beans to very high temperature (approximately
254 200 to 250°C), which is then quickly lowered to stop the process. The formation of thiols
255 during this process is not completely elucidated. However, it is admitted that S-containing
256 amino acids are important precursors and sulfur source for reactions with other compounds
257 (for example sugar) that occur during coffee bean roasting (Dulsat-Serra, Quintanilla-Casas,
258 & Vichi, 2016).

259 The Maillard-type reaction plays a key role in the thiol formation in roasted coffee. Indeed,
260 many authors reported the formation of 2FMT and 2MFT from the reaction between aldose
261 and cysteine in a model system (Cerny, 2008; Dulsat-Serra, Quintanilla-Casas, & Vichi, 2016;
262 Hofmann & Schieberle, 1997). However, this Maillard-type reaction was dismissed by
263 Poisson *et al.* by biomimetic in-bean experiments (Poisson, Schmalzried, Davidek, Blank, &
264 Kerler, 2009). Another important pathway involves H₂S liberated from cysteine or methionine
265 may react with prenyl alcohol (3-methyl-2-buten-1-ol) to obtain 3MMB (Holscher, Vitzthum,
266 & Steinhart, 1992). Holscher *et al.* published that prenyl alcohol was also identified as
267 precursor of 3MBT.

268

269 The general observation is that not only roasty, but sulfury, earthy and smoky notes improved
270 during roasting (Grosch, 1998). Mayer *et al.* proved that 2FMT and 3MBT increased more
271 and more with the roasting time (Mayer, Czerny, & Grosch, 1999). Roasting temperature also
272 influences the volatile thiols formation (Baggenstoss, Poisson, Kaegi, Perren, & Escher,
273 2008). Different kinetics have been reported in the literature, by comparing the evolution of
274 3MMB and the two corresponding esters during roasting: 3MMB and 3MMBF increase
275 linearly with the temperature of roasting, whereas 3MMBA increases only at higher degrees
276 (Kumazawa & Masuda, 2003). Thus, 2FMT and 3MBT/3MMBF have different behaviour:
277 2FMT is favoured by a long-time process at low-temperature in contrast to 3MBT and
278 3MMBF (Baggenstoss, Poisson, Kaegi, Perren, & Escher, 2008; Schenker, Heinemann,
279 Huber, Pompizzi, Perren, & Escher, 2002).

280 2.1.2. Brewing

281

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

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

295

296 **2.2. Formation of thiols by microorganism during fermentation processes: Focus on** 297 **3MH and 4MMP**

298

299 Prefermentative steps can influence the thiol levels. As an example, prefermentative
300 operations in grapes as skin maceration could lead to an increase of 3MH and 4MMP in white
301 wine. Must conservation on lees, another prefermentative process, increases the amount of
302 3MH and 3MHA in wine, without increasing the amount of precursors during this process
303 (Roland, Schneider, Charrier, Cavelier, Rossignol, & Razungles, 2011).

304

305 During winemaking or beer brewing, AF is an essential step for the sugar conversion into
306 alcohol by yeast, but it also impacts other compounds at lower concentration such as
307 polyphenols and aromas such as varietal thiols. 3MH and 4MMP are produced during AF by
308 the yeast (*Saccharomyces cerevisiae*) using a β -lyase activity (Cordente, Capone, & Curtin,
309 2015; Tominaga, Peyrot des Gachons, & Dubourdieu, 1998) from odorless *S*-conjugate
310 precursors.

311

312 **2.2.1. Grapes and wines**

313

314 *Precursors and mechanisms of transformation*

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

- 317 - cysteine *S*-conjugates to 3MH and 4MMP (Cys-3MH and Cys-4MMP) (Tominaga,
318 Peyrot des Gachons, & Dubourdieu, 1998);
- 319 - glutathione *S*-conjugates to 3MH and 4MMP (G-3MH and G-4MMP) (Fedrizzi,
320 Pardon, Sefton, Elsey, & Jeffery, 2009; Peyrot des Gachons, Tominaga, &
321 Dubourdieu, 2002a);
- 322 - cysteinyl-glycine *S*-conjugates to 3MH (CysGly-3MH) (Bonnaffoux, Delpech,
323 Rémond, Schneider, Roland, & Cavelier, 2018; Capone, Pardon, Cordente, & Jeffery,
324 2011);
- 325 - *S*-(3-hexan-1-yl)-glutathione (G-3MHA1) and its bisulfite adduct (Thibon, Böcker,
326 Shinkaruk, Moine, Darriet, & Dubourdieu, 2016);
- 327 - γ -glutamyl-cysteine *S*-conjugate to 3MH (γ GluCys-3MH) (Bonnaffoux, Roland,
328 Rémond, Delpech, Schneider, & Cavelier, 2017; Bonnaffoux, Delpech, Rémond,
329 Schneider, Roland, & Cavelier, 2018).

330

331 Another pathway was also evidenced: 3MH can result of the addition of a sulfhydryl donor
332 group to the (*E*)-2-hexenal during alcoholic fermentation (AF) (Schneider, Charrier,
333 Razungles, & Baumes, 2006). It has been suggested that H₂S could be one of the sulfur donor

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

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

362

363

Table 2

364

365

Figure 3

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

375

376 *Influence of viticultural and oenological processes on thiol contents*

377 The evolution of the aromatic potential, responsible for the release of varietal thiols, was
378 studied in order to better understand the biogenesis of these precursors in berries during
379 maturation. A study on the evolution of cysteinyl precursors in bunches of Sauvignon Blanc
380 one month before the grape harvest showed a great variability in the precursor content, which
381 would probably depend on the chemical composition of the berry (assimilable nitrogen for
382 example) (Peyrot des Gachons, Tominaga, & Dubourdieu, 2000). The combination of sulfur
383 and nitrogen foliar supply in Sauvignon Blanc vines increases the varietal thiol contents in the
384 resulting wines, but the authors didn't report an enhance of precursors (Lacroux, et al., 2008).
385 However, ammonium fertilization increases cysteine S-conjugates to 3MH, 4MMP and
386 4MMPOH. The maturation directly affects the concentration of certain precursors in
387 Sauvignon Blanc (Cys-3MH, G-3MH and G-4MMP) by increasing their initial amount in
388 berries (Roland, Vialaret, Razungles, Rigou, & Schneider, 2010). The water deficit impacts
389 the concentration of cysteinyl precursors in Sauvignon Blanc grapes. The amount of Cys-
390 3MH increase with a moderate water deficit, in contrary to Cys-4MMP (cases in Bordeaux
391 conditions with a moderate water deficit) (Choné, 2001).

392 Cysteinylated and glutathionylated precursors of 3MH and 4MMP are mainly located in the
393 skin (Sauvignon Blanc and Melon B.) (Peyrot des Gachons, Tominaga, & Dubourdieu,
394 2002b). Recently, Jeffery reports data on 3MH precursor concentration for Sauvignon Blanc
395 grapes undergoing different treatments (Jeffery, 2016). It appears that hand-harvesting yielded
396 lower precursor concentrations than machine harvest due to the limiting berry damage,
397 precursor extraction and the enzymatic mechanisms generated. Similarly, precursors increased
398 during transport or storage of grapes, for the same reason as previously. The precursors of
399 thiols subjected to increasing doses of SO₂ added at harvest decreases proportionally, maybe
400 due to an inhibition of enzymatic reactions (Capone & Jeffery, 2011). Some studies showed
401 that Cys-3MH increases in rosé musts of Merlot and Cabernet Sauvignon as a result of
402 prolonged skin maceration (Murat, Tominaga, & Dubourdieu, 2001). A prefermentative
403 pressing cycle in the wine cellar increased varietal thiol precursors. Prefermentative cold
404 storage of the must on their lees did not influence the concentration of Cys-3MH and G-3MH
405 in Sauvignon Blanc must. However, the content of 3MH and 3MHA in resulting wines
406 increased significantly and proportionally to the duration of on-lees must cold storage. This
407 increase could be due to the formation of other thiol precursors, during prefermentative
408 operations (Roland, Schneider, Charrier, Cavelier, Rossignol, & Razungles, 2011).

409 During AF, varietal thiols are released by *Saccharomyces Cerevisiae* yeast through its beta-
410 lyase activity. Some of them have demonstrated their ability to release varietal thiols under
411 oenological conditions (Dubourdieu, Tominaga, Masneuf, Peyrot des Gachons, & Murat,
412 2006; Howell, et al., 2004; Murat, Masneuf, Darriet, Lavigne, Tominaga, & Dubourdieu,
413 2001; Swiegers, Francis, Herderich, & Pretorius, 2006). Furthermore, a cofermentation with a
414 non *S. cerevisiae* yeast (*Pichia kluyveri*) can generate more 3MH and 3MHA in Sauvignon
415 Blanc wine (Anfang, Brajkovich, & Goddard, 2009) and similarly, an interspecific hybrid (*S.*
416 *cerevisiae* X *S. bayanus*) was found to enhance the 4MMP concentration compared to its
417 parent *S. cerevisiae*. Other parameters can influence the release of varietal thiols, especially
418 the fermentation temperature. Indeed, AF conducted at 20°C instead of 13°C was found to
419 increase 3MH, 3MHA and 4MMP concentrations in wine (Masneuf-Pomarède, Mansour,
420 Murat, Tominaga, & Dubourdieu, 2006) and warmer conditions (around 28°C) result in larger
421 content of 4MMP. In this latter case, the results seem to be dependent on the yeast strain used
422 (Howell, et al., 2004). A few studies highlight precursors transport in the yeast cell required
423 for their cleavage. In *S. cerevisiae*, the main transporter of G-3MH and G-4MMP inside the
424 cell is *OPT1*, while *GEX1* expels these precursors out of the cell (Cordente, Capone, &
425 Curtin, 2015; Dhaouia, et al., 2011). In the same way, only *YBT1* seems to play a role in the
426 transport of G-3MH into the vacuole. Different degradations of glutathione *S*-conjugates
427 involved into the vacuole or the cytosol through aminopeptidase to obtain γ GluCys, CysGly
428 and cysteine *S*-conjugates (Cordente, Capone, & Curtin, 2015). Finally, release of 3MH and
429 4MMP from their corresponding cysteine precursors is mediated by *STR3* and *IRC7*
430 (Roncoroni, et al., 2011; Thibon, Marullo, Claisse, Cullin, Dubourdieu, & Tominaga, 2008).

431 Very recently, Takase *et al.* study the bioconversion of 3MH precursors into 3MH by lactic
432 acid bacteria. Among species tested, *Lactobacillus plantarum* is able to metabolise Cys-
433 3MH and CysGly-3MH to produce 3MH (Takase, Sasaki, Kiyomichi, Kobayashi, Matsuo, &
434 Takata, 2018). However, those results were obtained either in culture medium or on a must,
435 without the interference of AF. Thus oenological conditions need to be tested to confirm this
436 observation since few lactic acid bacteria (except *Oenococcus oeni*) are resistant to these
437 particular conditions.

438

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

454 before bottling could be a solution, similarly as natural glutathione or SO₂ adding which have
455 a protecting effect against the loss of fruity notes in wines (Blanchard & 2004, 2004;
456 Brajkovich, et al., 2005).

457

458 *Oenological tannins*

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

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

465 - Cys-3MH (between around 0.3 and 200 mg.kg⁻¹, median = 9.1 mg.kg⁻¹)

466 - G-3MH (between around 0.2 and 138 mg.kg⁻¹, median = 10.1 mg.kg⁻¹)

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

473

474 *2.2.2. Hops and malts: mechanisms and precursors*

475

476 Occurrence of thiol precursors in both malts and hops was firstly hypothesized in 2008 (Toru
477 Kishimoto, Morimoto, Kobayashi, Yako, & Wanikawa, 2008) and few years later, Cys-3MH
478 was identified in hop (Gros, Peeters, & Collin, 2012). Cys-3MH was considered as precursor
479 of 3MH thanks to an enzymatic degradation promoted by the yeast during bottle re-
480 fermentation or during Belgian beer ageing (Nizet, Gros, Peeters, Chaumont, Robiette, &
481 Collin, 2013; Tran, Cibaka, & Collin, 2015). The first quantification of Cys-3MH revealed
482 that Cys-3MH might be present until 1641 ppb as 3MH equivalent in Cascade hop variety
483 (Gros, Tran, & Collin, 2013). In addition to Cys-3MH, three others precursors of 3MH and
484 4MMP were identified and quantified into several hop varieties (Chinook, Saaz, Barbe Rouge,
485 Cascade, Mistral, Aramis Alsace, Strisselspat and Mandarina) using direct LC-MS/MS
486 analysis and SIDA (Stable isotope dilution assay) (Roland, et al., 2016):

487 - Cys-3MH: between around 0.130 (Mandarina) and 1.1 mg.kg⁻¹ (Barbe Rouge)

488 - G-3MH: between around 1.3 (Barbe Rouge) and 19 mg.kg⁻¹ (Cascade)

489 - Cys-4MMP: between around 0.005 (Saaz) and 0.04 mg.kg⁻¹ (Strisselspat)

490 - G-4MMP: quantified only in Chinook at 0.01 mg.kg⁻¹

491

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

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

497
498 We have to point out that, contrary to grapes, hops are also rich in free thiols. The proportion
499 of free/bounded thiols (i.e. as thiol precursor) depends on the thiols considered (3MH or
500 4MMP and in a lesser extent on the hop variety): less than 1% for 3MH free/bounded fraction
501 in Chinook and Barbe Rouge; up to 23% or 95% for 4MMP free/bounded fraction of Chinook
502 or Saaz hops respectively (Roland, et al., 2016). Similar experiments on 3MH revealed that
503 free/bounded fraction ratios are closed to 2% for Citra, 4% for Tomahawk and 7% for
504 Cascade (Cibaka, Gros, Nizet, & Collin, 2015). Roland *et al.* also tried to build some
505 hypotheses about thiol origins from different categories of beer (Pale ale, Belgium origin,
506 IPA, Pils and experimental beers). They observed an important variability of thiol contents in
507 the same category of beers. The authors were surprised to observe that 3MHA occurred
508 practically only in experimental beers with a level higher than those of 3MH. It can be
509 explained by the specific yeasts or fermentation conditions used during the elaboration of the
510 experimental beers. Another counter-intuitive fact is that IPA beer, with intensive hopping,
511 contains relatively low levels of 3MH (less than 180 ng.L⁻¹). Thereby, hops might not be the
512 only source of thiol and thiol precursors for beers. Malts was hypothesized as another source
513 (T. Kishimoto, Wanikawa, Kono, & Shibata, 2006). Other precursors need to be investigated
514 and other precursors should be identified, based on those identified in the grape must:
515 CysGly-3MH, γ GluCys-3MH, G-3MH-Al and its bisulfite.

516

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

524

525 2.2.3. Rices and Sake: mechanisms and precursors

526

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

538

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

544

545 **2.3. Formation of thiols in non-fermented juice fruits**

546

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

553

554 For guava, the concentrations of 3MH and 3MHA evolve differently during maturation
555 according to the variety of the guava. Concerning pink guava, these thiols increase from green
556 to overripe, which is the opposite for white guava (Sinuco, Steinhaus, Schieberle, & Osorio,
557 2010). The authors attempted to isolate and treat precursors with β -lyase, but without produce
558 3MH. Instead, they hypothesized that unsaturated carbonyls, especially (*E*)-2-hexenal could
559 be the pathway to the 3MH formation.

560

561 Passion fruit is the most documented fruit concerning release mechanisms of thiols. The first
562 3MH precursor identified in a passion fruit juice from La Réunion was Cys-3MH. It was
563 identified using trimethylsilylation and then GC-MS analysis (Tominaga & Dubourdieu,
564 2000). More recently, three other *S*-conjugates precursors (G-3MH, CysGly-3MH and
565 γ GluCys-3MH) were identified (Fedrizzi, et al., 2012).

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

568 With the identification of these compounds, the authors proposed a hypothetical pathway for
569 the biogenesis of 3MH (Figure 3; *in planta* and without yeast). Indeed, G-3MH could be
570 degraded with the cleavage either of the glutamate moiety by a γ -glutamyl transferase
571 (Grzam, Martin, Hell, & Meyer, 2007) or with the removal of the glycine residue by a
572 carboxypeptidase (Wolf, Dietz, & Schröder, 1996) to give the CysGly-3MH and γ GluCys-
573 3MH respectively. Then, CysGly-3MH (or γ GluCys-3MH) could be degraded by a
574 carboxypeptidase (or γ glutamyl transferase) to obtain the Cys-3MH.

575

576 Others hypotheses were discussed for the formation of 3MHA through the esterification of
577 3MH with the corresponding acid (Tressl & Albrecht, 1986). More recently, it was discovered

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

581

582 **3. Conclusion**

583

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

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

601

602

603 **References**
604

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