



Short communication

Reactivity of 3-sulfanyl-1-hexanol and catechol-containing phenolics *in vitro*V. Felipe Laurie^{a,*}, María C. Zúñiga^b, Verónica Carrasco-Sánchez^c, Leonardo S. Santos^c, Álvaro Cañete^d, Claudio Olea-Azar^e, Maurizio Ugliano^f, Eduardo Agosin^b^aSchool of Agricultural Sciences, Universidad de Talca, 2 Norte 685, Talca, Chile^bDepartment of Chemical and Bioprocess Engineering, School of Engineering, Pontificia Universidad Católica de Chile, Vicuña Mackenna 4860, Macul, Santiago, Chile^cChemistry Institute of Natural Resources, Universidad de Talca, 2 Norte 685, Talca, Chile^dSchool of Chemistry, Pontificia Universidad Católica de Chile, Vicuña Mackenna 4860, Macul, Santiago, Chile^eFaculty of Chemical and Pharmaceutical Sciences, University of Chile, Sergio Livingstone 1007, Independencia, Santiago, Chile^fNomacorc Oxygen Management Research Center, 2260 route du Grès, 84100 Orange, France

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ABSTRACT

Volatile species with thiol functions are important contributors to the flavour of a wide variety of wine types. However, in spite of their importance, their fate during winemaking has not been fully elucidated. In this work, the iron-catalysed reaction between 3-sulfanyl-1-hexanol, catechol-containing phenolics, and sulfurous acid, under *in vitro* aerobic conditions was evaluated by means of electrospray ionisation mass spectrometry (ESI-MS). The results indicate that a direct addition reaction between the thiol and some of the phenolics tested, and between sulfite and some of the phenolics may occur, thus contributing evidence of a possible route of thiol losses in wines.

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1. Introduction

Ripe grape berries contain numerous non-volatile conjugated compounds, some of which are released during winemaking, giving rise to volatiles that contribute part of the characteristic aromas of wines. Among these, thiol-containing compounds have been given a good deal of attention (Pardon et al., 2008), mainly because they contribute very powerful odorants that are present in a wide variety of wines (Bouchilloux, Darriet, Henry, Lavigne-Cruege, & Dubourdieu, 1998; Ferreira, Ortin, Escudero, Lopez, & Cacho, 2002; Fretz, Luisier, Tominaga, & Amado, 2005; Tominaga, Darriet, & Dubourdieu, 1996). 3-Sulfanyl-1-hexanol (3SH), also known as 3-mercaptohexan-1-ol, is one of the most significant thiol-containing compounds in wine, given its tropical fruit nuances and occurrence in several white, rose, and red wine products (Blanchard, Darriet, & Dubourdieu, 2004; Brajkovich et al., 2005).

Production of 3SH results from odourless (S)-cysteine and (S)-glutathionyl conjugates present in grape juices that are cleaved of their amino acid moiety during fermentation, probably by the

action of β -lyase type enzymes of the fermenting yeast, by breaking the S–C bonds of the conjugate (Murat et al., 2001; Schneider, Charrier, Razungles, & Baumes, 2006; Tominaga, Baltenweck-Guyot, Des Gachons, & Dubourdieu, 2000; Tominaga, des Gachons, & Dubourdieu, 1998). (E)-2-hexenal (Schneider et al., 2006) and (S)-3-(hexan-1-ol)-glutathione (Des Gachons, Tominaga, & Dubourdieu, 2002; Roland, Schneider, Le Guerneve, Razungles, & Cavelier, 2010) have also been proposed as potential precursors of 3SH in wines. Given the relatively low yields of 3SH obtained based on all these mechanisms, the likelihood of additional unidentified precursor(s) have also been acknowledged (Subileau, Schneider, Salmon, & Degryse, 2008). Moreover, grape variety and winemaking conditions (i.e. the type of fermenting yeast or the grape pressing cycles employed, among others) may influence the concentration of volatile thiols obtained in the finished product (Patel et al., 2010; Roland et al., 2011; Swiegers et al., 2007; Ugliano et al., 2011).

Under an oxidative environment, both wine colour and aroma changes are expected to take place during wine production and ageing (Lambropoulos & Roussis, 2007; Laurie & Clark, 2010; Singleton, 1987). These changes are mainly due to the interaction of oxygen and transition metals catalyst with oxidisable constituents,

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such as phenolic compounds and ascorbic acid. The oxidation of phenolic compounds allows a cascade of reactions that encompass the formation of reactive quinones (electrophiles) and hydrogen peroxide, leading to further reactions of addition between quinones and wine nucleophiles, and the oxidation of multiple wine species by peroxide-generated hydroxyl radicals (Danilewicz, 2003; Laurie & Clark, 2010; Laurie & Waterhouse, 2006; Singleton, 1987; Waterhouse & Laurie, 2006). The bisulfite ion, the main ionised species of sulfur dioxide present at wine pH, is responsible for the protection against chemical oxidation, owing its ability to react with peroxide and prevent the formation of hydroxyl radicals (Boulton, Singleton, Bisson, & Kunkel, 1996; Danilewicz, 2003).

Regarding 3SH, the evidence suggests that its decrease during winemaking and ageing could be due to its reactivity towards electrophilic quinones, more than as a result of direct thiol oxidation (Blanchard et al., 2004; Murat, Tominaga, Saucier, Glories, & Dubourdieu, 2003; Nikolantonaki, Chichuc, Teissedre, & Darriet, 2010). Nevertheless, the oxidative degradation of thiols has also been reported (Jocelyn, 1972; Sarrazin et al., 2010).

The aim of these trials is to present further evidence on the reactivity of 3SH with catechol-containing phenolics under *in vitro* aerobic conditions, and discuss the likelihood of the reactions suggested happening in wine.

2. Materials and methods

2.1. General

All glass and plasticware was thoroughly washed and rinsed with abundant water. Ultra-pure water was used to prepare all solutions and dilutions. Ethanol ($\geq 99.9\%$), iron(III) chloride hexahydrate ($\geq 99\%$), sulfurous acid ($\geq 6\%$ SO_2), hydrochloric acid (1 M), and 3SH were purchased from Merck or Aldrich. 4-Methylcatechol ($\geq 95\%$), (+)-catechin hydrate ($\geq 95\%$), and quercetin hydrate ($\geq 95\%$) were purchased from Sigma-Aldrich. All reagents and chemicals described were used without additional purification.

2.2. Experimental set-up

12% (v/v) aqueous ethanol solutions containing $1 \mu\text{g L}^{-1}$ of 3SH alone, or in combination with 500 mg L^{-1} of phenolics (either 4-methylcatechol, catechin, or quercetin), adjusted to pH 3.5 using hydrochloric acid, were the base solutions used to evaluate their reactivity. Each of the above solutions was treated with the following reagents, as indicated in Table 1: (a) Iron(III) chloride ($1 \mu\text{g L}^{-1}$), (b) sulfurous acid (30 mg L^{-1}), or (c) a combination of both. These amounts of reagents were chosen to avoid saturation of the spectrometric system.

The level of dissolved oxygen (DO) reached during the preparation of the solutions was approximately 5.8 mg L^{-1} . The equipment

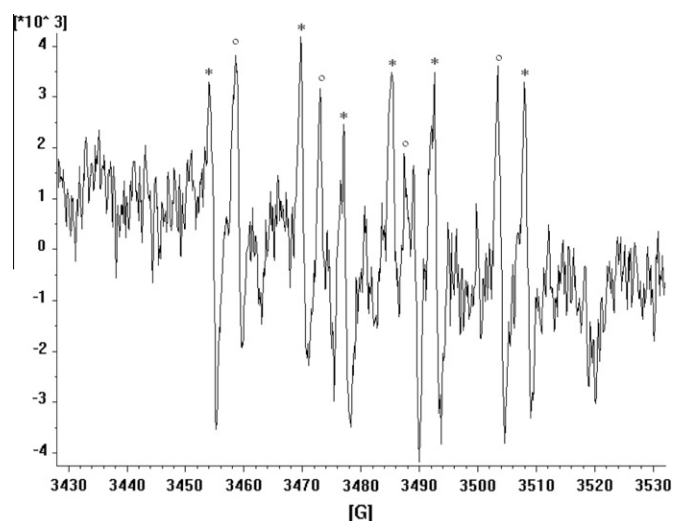


Fig. 1. EPR spectra of the DMPO spin adducts formed in Fe^{3+} ($1 \mu\text{g L}^{-1}$)/ SO_2 (30 mg L^{-1}) solutions. DMPO/OH spin adducts are denoted as (°) and DMPO/MeCH₂OH spin adducts are denoted as (*).

used for measuring DO was a NomaSense oxygen analyser set (NomaSense, Zebulon, NC). Further trials to evaluate pH changes after sulfurous acid addition showed an acidity reduction to approximately pH 3. The samples were stored at room temperature (20°C) in 1.5-mL vials and analysed by ESI-MS at 0, 5 min, 15 min, 30 min, 1 h, and 24 h after the addition of iron, sulfurous acid, or their combination. In an attempt to obtain further evidence of the oxidative conditions of the environment chosen, analyses of free radicals by ESR spectrometry were performed as explained below.

2.3. Free radical analyses

The formation of free radicals generated from the $\text{Fe(III)}/\text{SO}_2$ combination (1 and $2 \mu\text{g L}^{-1}$ of Fe(III) and 30 mg L^{-1} SO_2) present in the solutions used (12% ethanol adjusted to pH 3.5 with HCl), was evaluated by means of an ESR spectrometer using 5,5-dimethylpyrrolidine-N-oxide (DMPO 1.5 M) as spin trapping agent, as described elsewhere (Elias, Andersen, Skibsted, & Waterhouse, 2009). ESR spectra were recorded in the X band (9.7 GHz) using a rectangular-cavity spectrometer, Bruker ECS 106. The field modulation frequency was 50 kHz. The hyperfine splitting constants were estimated to be accurate within 0.05 G. The experiment was conducted at room temperature.

2.4. High-resolution mass spectrometry

ESI-MS and ESI-MS/MS analyses were conducted in a high-resolution hybrid quadrupole (Q) and orthogonal time-of-flight (TOF)

Table 1

Experimental conditions employed to evaluate the reactivity of 3-sulfanyl-1-hexanol in solutions containing phenolics, iron or/and sulfite.

Treatments	3-Sulfanyl-1-hexanol ($\mu\text{g L}^{-1}$)	Phenolics ^a (mg L^{-1})	Iron(III) chloride ($\mu\text{g L}^{-1}$)	Sulfurous acid (mg L^{-1})
a	1	–	–	–
b	1	–	1	–
c	1	–	–	30
d	1	–	1	30
e	1	500	–	–
f	1	500	1	–
g	1	500	–	30
h	1	500	1	30

^a Phenolics being either 4-methylcatechol, catechin, or quercetin.

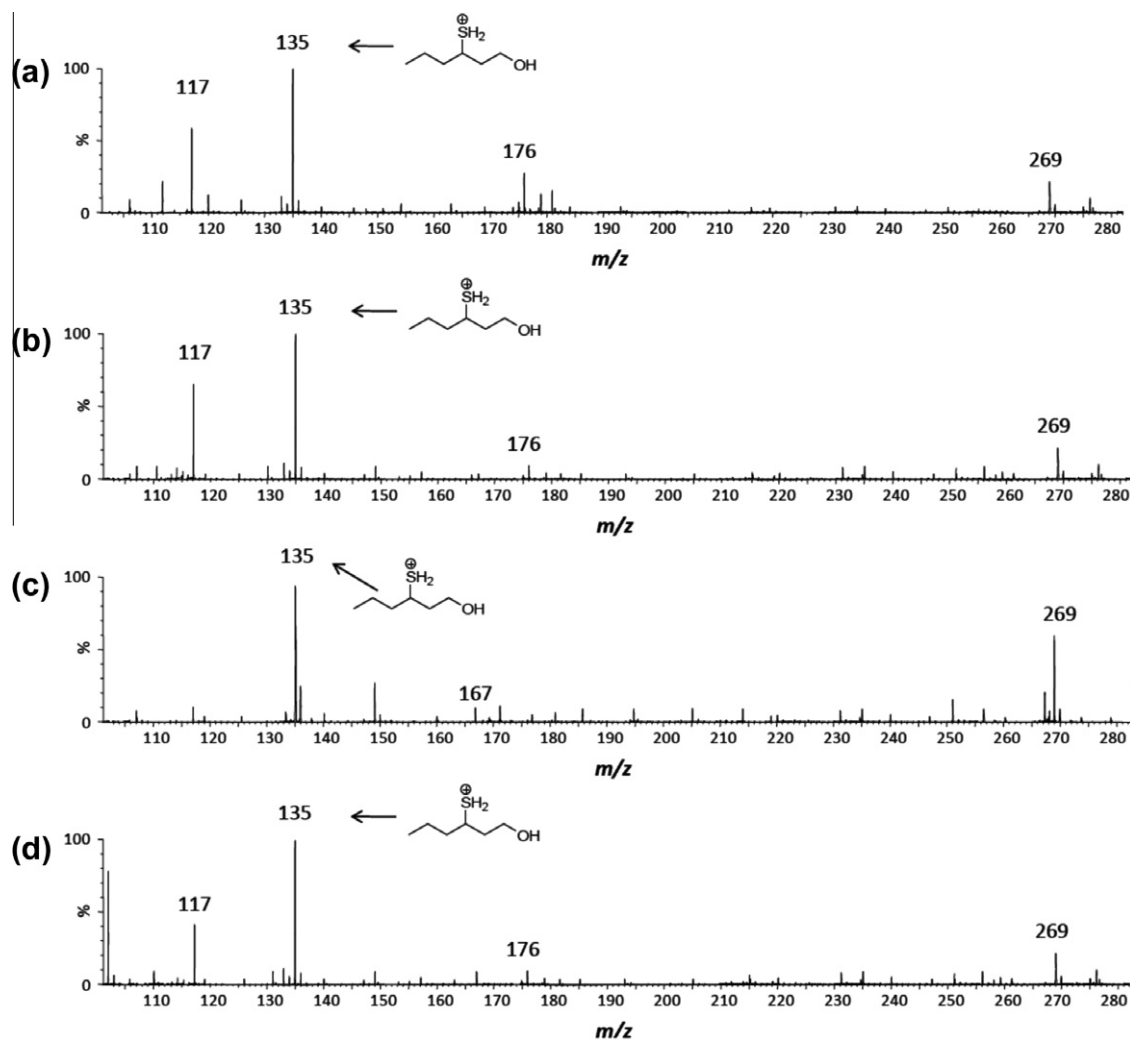


Fig. 2. ESI-MS spectrum of: (a) 3-sulfanyl-1-hexanol (3SH), (b) 3SH and sulfite, (c) 3SH and iron, and (d) 3SH, sulfite and iron *in vitro*, under aerobic conditions.

mass spectrometer (Waters/Micromass Q-TOF micro, Manchester, UK) with a constant nebuliser temperature of 100 °C. The experiments were carried out in positive ion mode, and the cone and extractor potentials were set at 10 and 3.0 V, respectively, with a scan range of m/z 100–600. MS/MS experiments were carried out by mass selection of a specific ion in Q1, which was then submitted to collision-induced dissociation (CID) with helium in the collision chamber. The product ion MS analysis was accomplished with the high-resolution orthogonal TOF analyser. The samples were directly infused into the ESI source, via a syringe pump, at flow rates of $5 \mu\text{L min}^{-1}$, via the instrument's injection valve.

3. Results and discussion

3.1. Free radical formation evidence

The formation of free radicals was tested using ESR, by means of the addition of DMPO into the Fe(III)/SO₂ solutions employed (solutions containing either iron or sulfite alone did not form any radicals). The results obtained suggest that 1-hydroxyethyl and hydroxyl radicals were being formed (Fig. 1). The coupling constants due to the DMPO/·OH adduct obtained were: $a_N = 15.6 \text{ G}$, $a_H = 15.5 \text{ G}$, whilst those due to DMPO/MeCH·OH were: $a_N = 15.6 \text{ G}$ and $a_H = 22.9 \text{ G}$, values that are similar to those

obtained elsewhere (Elias et al., 2009) ($a_N = 14.7 \text{ G}$, $a_H = 14.0 \text{ G}$ and $a_N = 15.7 \text{ G}$, $a_H = 22.4 \text{ G}$, respectively). At wine pH (*i.e.* roughly between pH 3 and 4), sulfite will be mainly in the form of the bisulfite ion (HSO₃⁻, $pK_1 = 1.81$), thus allowing the reduction of Fe(III) to Fe(II) and the radical-mediated formation of the adducts shown. Similarly, phenolic compounds have metal reducing properties that allow them to lower their oxidation states, for instance, from Cu(II) to Cu(I) or Fe(III) to Fe(II), thus increasing their ability to catalyse oxidation reactions (Waterhouse & Laurie, 2006).

3.2. Reactivity of 3-sulfanyl-1-hexanol

As expected, the ESI-MS spectrum of 3SH (m/z 135) remained stable at all reaction times analysed (0–24 h) if no other reagents were added to the solution (Fig. 2a). When 3SH and sulfite (Fig. 2b), 3SH and iron (Fig. 2c), or all three reactants were mixed (Fig. 2d), the formation of adducts at m/z of 167 (possibly an adduct with S=O (OH)) and/or m/z of 149 (possibly a cyclic adduct with S=O) were observed (Fig. 3).

When a simple phenol (*i.e.* 4-methylcatechol) was included as part of the reaction vials, the results were the following. When 3SH and 4-methylcatechol (Fig. 4a); 3SH, 4-methylcatechol, and sulfite (Fig. 4b); and 3SH, 4-methylcatechol, and iron (Fig. 4c) were mixed, the m/z signals corresponding to 3SH (m/z 135), 4-methylcatechol (m/z 125) and its quinone (m/z 123) were found.

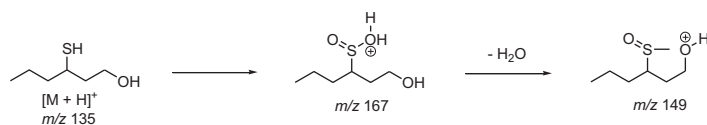


Fig. 3. Possible adducts formed due to the reaction of 3-sulfanyl-1-hexanol (3SH) and sulfite, 3SH and iron, and the combination of all three reagents.

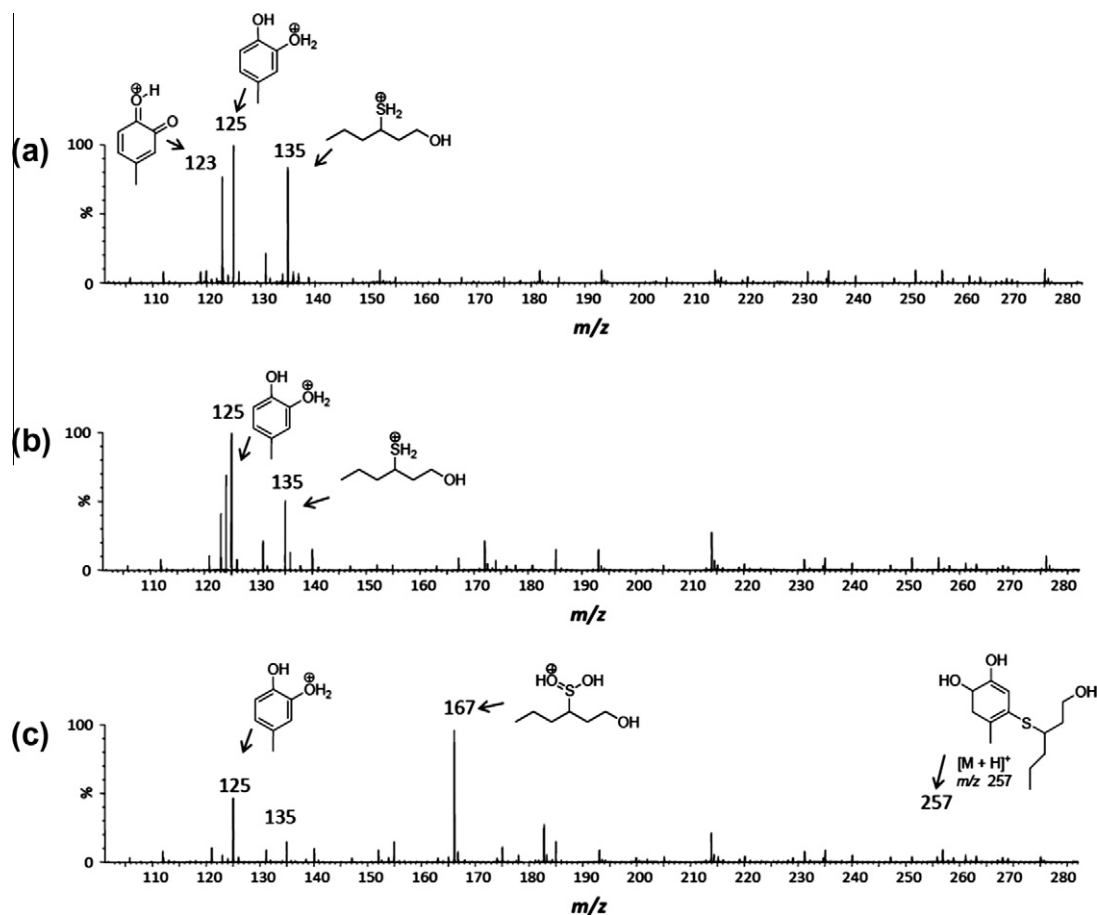


Fig. 4. ESI-MS spectrum of: (a) 3-sulfanyl-1-hexanol (3SH) and 4-methylcatechol; (b) 3SH, 4-methylcatechol and sulfite; and (c) 3SH, 4-methylcatechol and iron *in vitro*, under aerobic conditions.

Interestingly, a signal at m/z of 257 (probably an adduct between the catechol and 3SH) was observed when 3SH, the catechol and iron were mixed.

Finally, if all reagents were part of the solution (i.e. 3SH, 4-methylcatechol, iron and sulfite), the resulting ESI-MS data suggest the formation of addition products with m/z of 205 (probably a reaction product between the catechol and sulfite), and m/z of 256 and 257 (an intermediate and product of the reaction between the catechol and thiol, respectively) (Fig. 5). Spectra collected at different time points after the addition of the reagents indicate that the formation of these products was fast and that they remain relatively stable during the time of the experiment (Fig. 5).

Additionally, the results shown above suggest that although competitive reactions occur between 4-methylcatechol and 3SH, and between 4-methylcatechol and sulfite, the adduct resulting from the reaction between the phenolic and 3SH does happen (Fig. 6). In wine systems, especially reds, where longer reaction times are typical for the maturation/ageing of the product, one

could expect that the catechol-containing phenolics-3SH adducts might still be forming, in spite of the smaller concentration of 3SH compared with sulfites.

When quercetin was used instead of 4-methylcatechol, its combination with Fe(III) and sulfite produced an adduct between the flavonol and sulfite, but none was observed between the flavonol and 3SH, suggesting that longer reaction times could have been required (Fig. 7). Also, the same species previously observed at m/z 149 with cyclic S=O and m/z 167 with S=O(OH) were detected (Fig. 7). Conversely, when the former phenolic compounds were replaced by catechin, the addition reactions with sulfite or 3SH were not observed. This could be explained by the differences in structural stability between the three phenols. For instance, in a study performed in slightly acidic hydroalcoholic media, catechin was shown to be more stable than quercetin (Makris, Turan, Gulsen, & Kefalas, 2007).

Well known examples of the reactivity between quinones and thiols are that of caftaric acid-quinone and glutathione in the

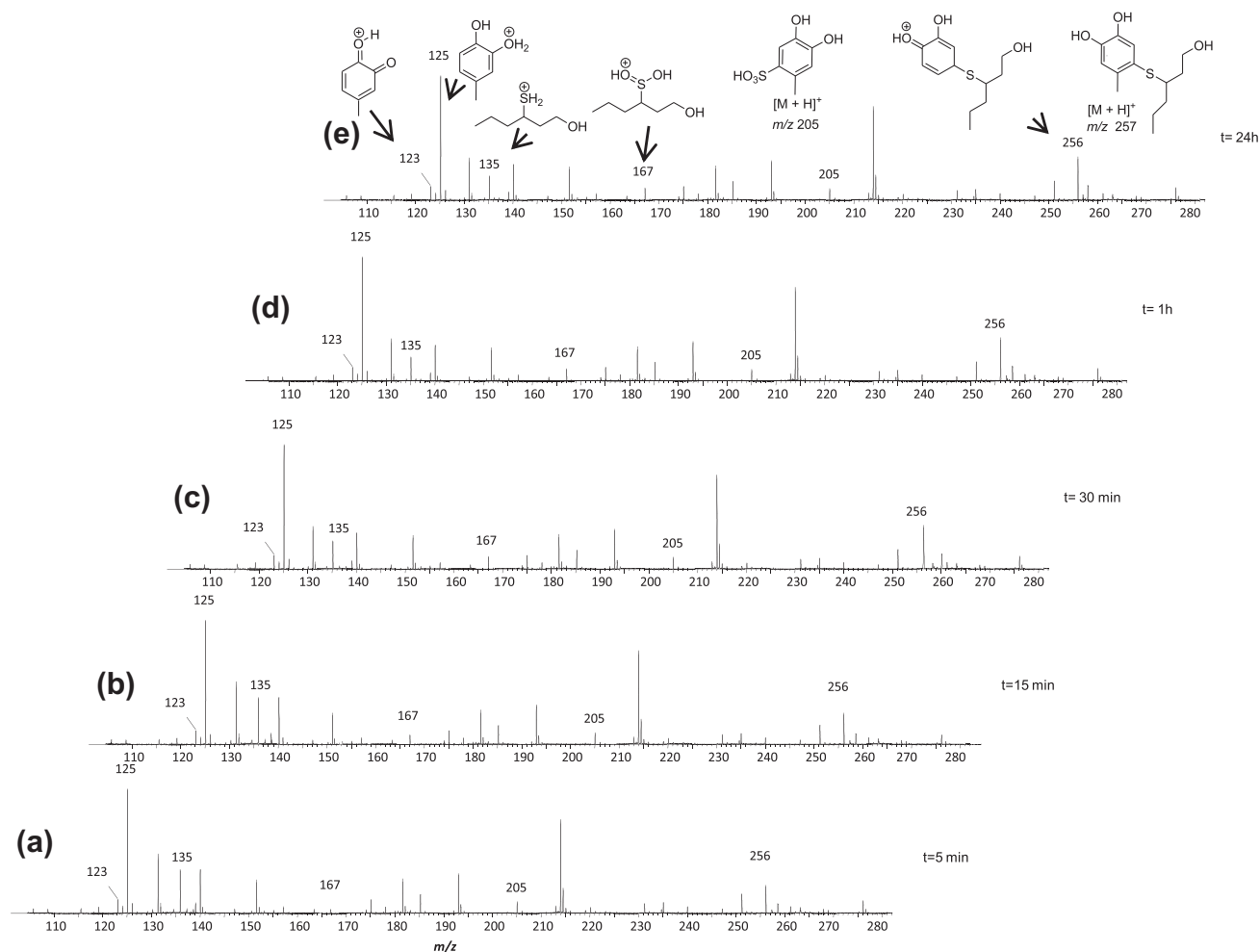


Fig. 5. ESI-MS spectrum of the reaction among 3-sulfanyl-1-hexanol, 4-methylcatechol, sulfite and iron *in vitro*, under aerobic conditions, at different time points (5, 15, 30, 60 min and 24 h).

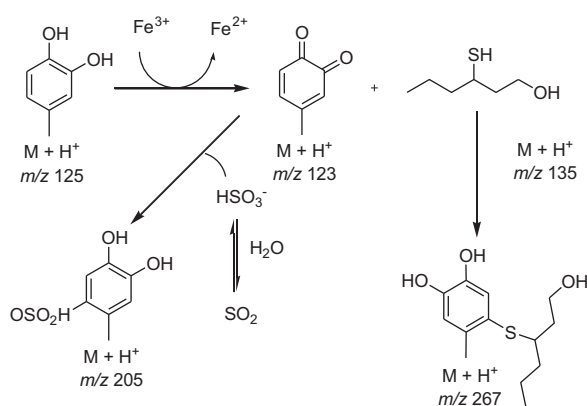


Fig. 6. Possible mechanism for the reaction of 3-sulfanyl-1-hexanol and sulfite in catechol-containing solutions, under aerobic conditions.

formation of “grape reaction product” (Singleton, 1987; Singleton, Salgues, Zaya, & Trousdale, 1985), and 3SH and quinones (Blanchard et al., 2004). In the latter, the authors showed that after the oxidation of catechin, the content of 3-sulfanyl-1-hexanol decreases, suggesting the reaction of 3SH with quinones. Moreover,

sensory studies conducted *in vitro* have also suggested an interaction between 3SH and polyphenols, based on the suppression of the thiol aroma in the presence of phenolics, such as quercetin and catechin, with the flavonol having a more powerful suppression effect (Lund, Nicolau, Gardner, & Kilmartin, 2009).

SO₂ has been shown to protect volatile compounds, such as esters and alcohols, in bottled wine (Garde-Cerdan & Ancin-Azpilicueta, 2007). Regarding bottle closure systems, there is evidence suggesting that the loss of 3SH during wine ageing could be due to adsorption by the closure or wine oxidation; the latter being triggered by high oxygen exposure during bottling or due to the use of a high oxygen transfer rate closure during ageing (Brajkovic et al., 2005; Lopes et al., 2009). Quantification of 3SH and adducts yields based on the proposed mechanism should be addressed in future experiments.

During wine ageing, the long periods of time required to achieve this process may contribute to the progress/likelihood of these reactions, in spite of the reduced molar fraction of thiols to phenolics in wine. However, considering the limitations on the design of these *in vitro* lab-scale trials, these results might be used mainly as an indication of possible reactions that will require confirmation using real wine systems. Moreover, searching for some of the adducts observed here in different wines is a goal of future investigations.

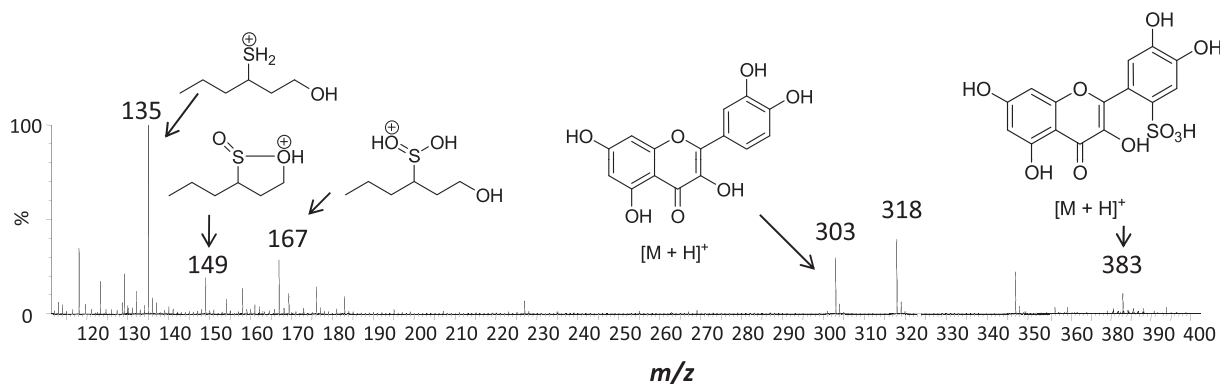


Fig. 7. ESI-MS spectrum of the reaction between 3-sulfanyl-1-hexanol (3SH), quercetin, iron and sulfite *in vitro*, under aerobic conditions.

4. Conclusions

Further evidence on the reactivity of sulphur-containing compounds, based on ESR spectroscopy and ESI-MS monitoring of the reaction of 3SH with oxidising agents was shown. Evidence of a direct addition reaction between 3SH and 4-methylcatechol, competing with that of sulfite with phenolics (4-methylcatechol and quercetin) was shown. This information reinforces the key role that iron and sulfite may play in oxidation reactions in matrices such as wine. These observations suggest the need to explore the presence of these adducts in wine, as well as performing supplementary experiments to elucidate the mechanism by which some phenolics would be less reactive or unreactive.

Acknowledgments

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