



Reactivity of volatile thiols with polyphenols in a wine-model medium: Impact of oxygen, iron, and sulfur dioxide

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ABSTRACT

As volatile thiols are nucleophiles, they are capable of additional reactions with electrophiles. In enology, this concerns reactions between volatile or non-volatile thiols and oxidized phenolic compounds. Initial studies concerning the reactivity of volatile thiols with polyphenols showed that (+)-catechin played a detrimental role in the level of 3-sulfanylhexasan-1-ol (3SH), in the absence of sulfur dioxide. Our experiment revealed that (–)-epicatechin was more reactive with volatile thiols than (+)-catechin. Furthermore, Fe (III) was shown to play a crucial role in catalyzing polyphenol oxidation reactions, by affecting the direct reaction of phenolic compounds with oxygen. It was noted that, even if the volatile thiols studied were members of the same chemical family, they exhibited a different behavior pattern under oxidation conditions. 2-furanmethanethiol (2FMT) was more reactive than 3-sulfanylhexasan-1-ol with both (+)-catechin and (–)-epicatechin. In contrast, 4-methyl-4-sulfanylpentan-2-one (4MSP) was less reactive with these phenolics. Additionally, the vital role of sulfur dioxide in protecting 3-sulfanylhexasan-1-ol, 2-furanmethanethiol, and 4-methyl-4-sulfanylpentan-2-one was demonstrated in the model medium.

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1. Introduction

Volatile thiols are very strong-smelling molecules, characterized by a very low perception threshold, on the order of a few nanograms per liter in some wines. Volatile thiols contribute to their aromatic complexity and distinctive character [1–8]. Volatile thiols may be divided into two main groups, according to their formation pathway. The first group contains volatile thiols released from cysteinylated conjugates, known as aroma precursors, during alcoholic fermentation, via the metabolic activity of *Saccharomyces cerevisiae* [9–11]. These volatile thiols contribute to varietal aroma, for example: 3-sulfanylhexasan-1-ol (3SH), which exhibits grapefruit and passion fruit nuances [4], as well as its acetate (A3SH) produced by yeast acetylase and 4-methyl-4-sulfanylpentan-2-one (4MSP), reminiscent of box tree and broom [1], all typical nuances of Sauvignon blanc wines [1,2,4]. The second main group of volatile thiols consists of molecules formed during alcoholic fermentation and (or) ageing, particularly in oak barrels. Compounds such as 2-furanmethanethiol (2FMT) and 2-methyl-3-furanthiol (MFT) contribute to the empyreumatic aroma of wines [12]. 2FMT, with its well-known roast coffee aroma [13,14], has been identified in red and white wines aged in oak barrels [15], Petit-Manseng dessert wines [15], and Champagne [16].

During the past decade, studies have clearly shown that volatile thiol levels decrease, in the presence of oxygen, during wine ageing and after bottling [17,18]. As these compounds contribute to the wine's [19] aromatic distinctiveness and complexity, it is important to understand the chemical mechanisms involved in their degradation. Thiols are highly reactive compounds which oxidize easily in the presence of trace amounts of metal ions (iron, copper) (Fig. 1; reactions 9,10) [20]. Also, these compounds can undergo nucleophilic, acid-catalyzed, substitution reactions with polymeric phenolic compounds [21]. This property was highly exploited as a laboratory method in order to estimate the degree of polymerization of proanthocyanidins [22,23]. This reaction could also explain partially the glutathione disappearance in oak-aged wines [24,25]. However, due to their chemical structure and properties, thiols degradation may also be due to chemical reactions with phenolic compound oxidation products, in the presence of metal ions.

Under wine oxidation conditions, phenolic compounds are one of the primary reactants with oxygen and more precisely with RSO (reactive species of oxygen) which are the activated oxygen species formed during O_2 reduction in the presence of metals. The formation of those species requires the addition of four electrons to O_2 and the process may be illustrated as follows: $O_2 + e^-$, $H^+ \rightarrow HO_2^* + e^-$, $H^+ \rightarrow H_2O_2 + e^-$, $H^+ \rightarrow \cdot OH (+H_2O) + e^-$, $H^+ \rightarrow (2)H_2O$. This leads to the formation of free superoxide ($O_2^{\cdot -}$) and peroxide (O_2^{2-}) radicals, which may be directly reduced by phenolic molecules and are better oxidants than O_2 (Fig. 1; reactions 1–3) [26,27]. At the pH of wine, peroxide (O_2^{2-}) radicals are

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