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Book of Abstracts

UHPLC-HRMS analysis for the evaluation of formation and degradation of polysulfides in wine

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Summary: *In this work the effect of pre- and post-fermentative oenological treatments on the accumulation of polysulfides in wines was investigated. The work includes studying different oenological yeasts and the effect of different metals from wine adjuvants. Moreover, polysulfide degradation was investigated. For the detection of polysulfides UHPLC-HRMS (Orbitrap) was used.*

Keywords:*polysulfides,wine,UHPLC-HRMS*

1 Introduction

The contribution of sulfur compounds to wine aroma has been studied for several years, as their role can be either positive, contributing to the fruitiness and typicity of some white wines like Sauvignon blanc, or negative when related to off-flavours caused by H2S. Recently, H2S formation from degradation of polysulfides has gained interest in the wine sector as it could potentially lead to wine defects or quality reduction [1]. It has been proposed that polysulfides can be formed upon oxidation of thiol compounds (for example glutathione and cysteine) with Cu2+ or elemental sulfur and could form a reservoir for H2S release post-bottling [2,3,4]. Polysulfide formation has been demonstrated in several matrices including real wines [5,6,7], but the exact reaction mechanisms have not been proven yet. It has been suggested that both chemical and biochemical activities can play a role [8], which is a topic that is still under investigation.

In the present work we investigated the possible technological factors that could influence the formation of polysulfides during and after fermentation. Furthermore, we proposed a new automated method using both liquid chromatography with mass spectrometry in order to isolate and subsequently study the degradation of a single polysulfide during an accelerated ageing process.

2 Methods

For the study we used ultra-high-performance liquid chromatography (UHPLC) coupled to hybrid quadrupole/high-resolution mass spectrometry (HRMS, Q-Orbitrap) for the detection, characterisation and accumulation of polysulfides. For the study of polysulfide degradation UHPLC was used with an on-line fraction collector (UHPLC-FC) in order to isolate the symmetric cysteinyl pentasulfide (CS5C). After collection the sampled compound was kept in the autosampler at 30°C to promote degradation and injections were performed until complete degradation. For the study of the effect of pre-and post-fermentative oenological treatments on the accumulation of different polysulfides, two different experimental set-ups were considered. First, the effect of varying oenological yeasts was investigated. Secondly, the influence of Cu2+ and Ag+ treatments was studied in wines fortified with varietal thiols, after supplementation with CuSO4 or AgNO3 and during accelerated ageing.

3 Results

Using UHPLC-FC and subsequent UHPLC-HRMS it was possible to follow single polysulfide degradation in time. It became evident that the cysteinyl pentasulfide completely disappeared after approximately 12 hours (Figure 1a). In Figure 1b the presence of other cysteinyl polysulfides is visualized and it is evident that the disulfide increased in parallel to the degradation of CS5C. Therefore, CSSSC could possibly be a degradation product of the pentasulfide.

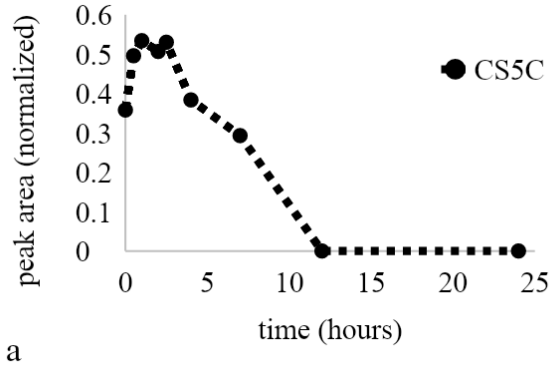
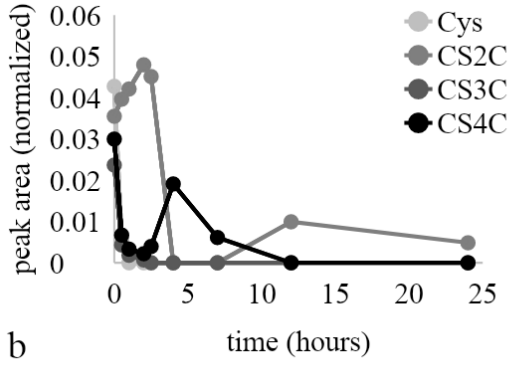


Fig 1a. Degradation of CS5C in semi-pure fraction obtained by HPLC-FC



F*ig 1b. Evolution of cysteinyl di-, tri- and tetrasulfide in semi-pure fraction obtained by HPLC-FC*

The technological studies revealed treatment effects of post-fermentation treatments with Cu2+ and Ag+. Furthermore, the utilization of different oenological yeasts resulted in different polysulfide polysulfides and significant differences in polysulfide accumulations in the final wines. The polysulfide formation of the cysteinyl and glutathionyl trisulfide are shown in Figure 2a and 2b, respectively.

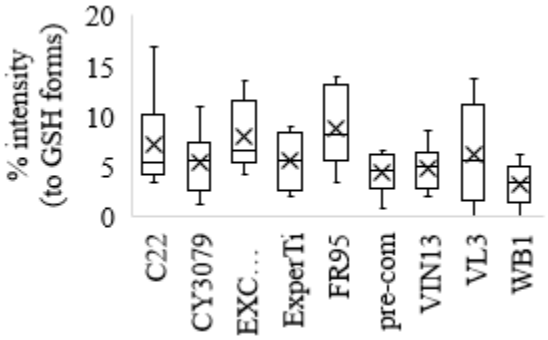


Fig 2a. GSSSG accumulation in wines fermented with different oenological yeasts, normalized as percentage intensity of sum of GSH forms

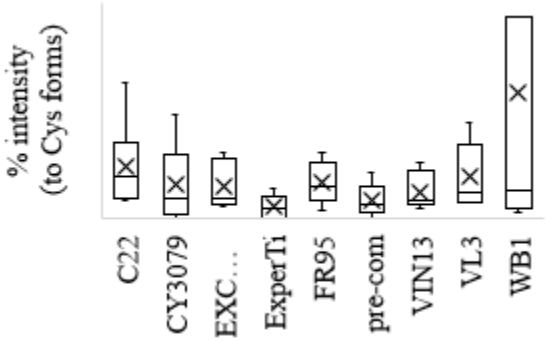


Fig 2b. CSSSC accumulation in wines fermented with different oenological yeasts, normalized as percentage intensity of sum of Cys forms

These studies gave new insides in the formation and degradation mechanisms of polysulfides, which is considered relevant with regard to potential alterations of wine quality.

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