Chemical and biochemical formation of polysulfides in synthetic and real wines using UHPLC-HRMS

AIM: Sulfur compounds in wine have been studied for several years due to their impact on wine flavour, but the role of polysulfides is a recent topic. Polysulfides in wine are formed when two sulfhydryl groups oxidize, especially in presence of elemental sulfur or metal catalysts from field treatment residues (Ugliano et al. 2011). These compounds are odourless, but can degrade during storage and affect the wine quality. The mechanism of their formation is still largely unknown but different chemical and biochemical pathways have been suggested. Disulfides from cysteine (Cys) and glutathione (GSH) have been revealed in model wines (Kreitman et al. 2016) and more recently also higher polymerized forms in real wines (Van Leeuwen et al. 2020). Volatile varietal thiols like 3-mercaptohexanol (3MH) and 4-mercaptopentanone (4MMP) – flavour compounds with tropical or fruity notes – could undergo similar reactions, also with Cys and GSH, subsequently losing their flavour property (fate). Even more concerning is the possible release of H2S from polysulfides during storage, leading to undesired off-flavours (Sarrazin et al. 2010). In the present work polysulfides from varietal thiols 4MMP and 3MH were identified for the first time in synthetic and real wines. Additionally, the evolution of glutathionyl and cysteinyl polysulfides was followed during fermentation. METHODS: For the study of thiolated polysulfides, synthetic standards, musts and wines and commercial SB wines were supplemented with copper sulfate and wettable sulfur to induce condensation reactions. For the evolution study, synthetic must and Chardonnay juice were supplemented with elemental sulfur, CuSO4, both, or nothing (control) and subsequently fermented until sugar dryness was reached (after 18 days). All samples were analysed using ultra-high-performance liquid chromatography (UHPLC) coupled to hybrid quadrupole/high-resolution mass spectrometry (HRMS, Q-Orbitrap). RESULTS: Thiolated polysulfides with up to 4 sulfur atoms were successfully recovered from the synthetic standards, musts and wines and characterized using Compound Discoverer. The evolution study showed different patterns of polysulfide formation for the different fermenting musts, which were assigned to the difference in matrix composition and matrix complexity. Moreover, significant differences in accumulation were revealed between the differently treated musts. CONCLUSIONS: The UHPLC/HRMS method used in both studies was successfully applied to detect polysulfides in different spiked synthetic and real wines. Differences between treatments and matrices proved the influence of known and unknown compounds playing an important role in polysulfide formation. The present method can be applied to perform ongoing polysulfide studies.

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