

Topic: Chemical and Biochemical reactions, including grape and wines microorganisms impact

### **NMR approach for monitoring the photo-degradation of riboflavin and methionine**

Daniela Fracassetti\*, Melissa Mastro, Sara Limbo, Antonio Tirelli, Enzo Ragg

Department of Food, Environmental and Nutritional Sciences (DeFENS), Università degli Studi di Milano, Milan, Italy

\*: corresponding author

The light exposure of white wine is responsible for several reactions leading to changes on colour, flavours and, consequently, affecting the sensory profile. These reactions can take place when the white wine is bottled in clear glass and their mechanisms are dependent on both light exposure and chemical composition of white wine. Particular attention has been given to the reaction involving riboflavin (RF), a photo-sensitizer compound, and methionine (Met), a sulfur-containing amino acid, that can cause the formation of volatile sulphur compounds (VSCs), namely methanethiol and dimethyl disulfide. These compounds are responsible for a defect known as light-struck taste. Previous studies showed that hydrolysable tannins, in particular those from nut galls, limited both the degradation of Met and the formation of VSCs. The effectiveness of hydrolysable tannins was also proved after light exposure and storage for 24 months.

In order to better understand the role of tannins in the photo-degradative reactions, an NMR approach was carried out. A solution containing RF (0.2 mM) and Met (2 mM) acidified at pH 3.2 was exposed to light by using fluorescence light bulbs. The solution was exposed to light up to two hours sampling it every 15 minutes. The same experimental conditions were applied in presence of gallic acid (2 mM), a constitutive unit of nut gall tannins.

The degradation of RF and Met was monitored and, as expected, their signals decreased as the light exposure increased. Results provided evidence that a new signal appeared at 2.64 ppm. This signal was assigned to the SOCH<sub>3</sub> moiety of methionine sulfoxide through the addition of the standard solution and standard 2D-NMR assignment techniques. The formation kinetic of methionine sulfoxide was measured for increased duration of light exposure and its rate resulted two-folds lower with the addition of gallic acid. This result suggests that the limited degradation of Met in presence of tannins, also observed in previous studies, is due to their action as competitor with Met in reducing RF from its excited form.

The NMR technique was suitable for monitoring the photo-degradative reaction of RF and Met. Further researches have been carried out in order to verify and prove the ability of tannins in quenching both singlet oxygen and RF.

**Keywords:** light exposure; Nuclear Magnetic Resonance; oxidation; tannins.