The impact of acetaldehyde on phenolic evolution of free-SO2 wines.

Coppola Francesca, Picariello Luigi, Forino Martino, Moio Luigi, Gambuti Angelita*

Department of Agricultural Sciences, Section of Vine and Wine Sciences, University of Naples 'Federico II', Viale Italia, 83100 Avellino, Italy.

Objective

The present study aims at the investigation of acetaldehyde reactivity with low molecular weight phenols in both white and red wines. The outcome of this research is expected to provide further insights into the colour evolution of wines.

State of the Art

Acetaldehyde is the most abundant volatile aldehyde in wines. Concerning the possible impact on wine aroma, acetaldehyde can react with other wine compounds such as glycerol, leading to the formation the dioxolane and dioxane acetals, responsible for wine oxidative spoilage [1]. Typical adducts formed by the reaction of acetaldehyde with phenols consist of ethylidene-bridged compounds. Flavan-3-ols, including catechin, epicatechin, proanthocyanidins, and anthocyanins, are among the major wine polyphenols reactive with acetaldehyde [2-4].

Several studies [4-6] were conducted on the reactivity of acetaldehyde with selected wine phenols in model solutions, but the reports on such reactions in real wines are very few. Although the role of anthocyanins has been extensively investigated, to the best of our knowledge no studies focused on possible differences between the behaviour of white and red wines when added with the same amount of acetaldehyde.

Materials and Methods

Experimental Design

Four batches of red (Aglianico) and white (Falanghina) wines were prepared without acetaldehyde addition (control) and with 190 mg/L of pure acetaldehyde. Aglianico base parameters were: ethanol 13.37%, pH 3.69, titratable acidity 5.4 g/l, volatile acidity 0.54 g/l. Falanghina base parameters were: ethanol 13.12%, pH 3.42, titratable acidity 6.6 g/l, volatile acidity 0.34 g/l. Treated, and untreated (control) wines were stored in 5 L glass flasks hermetically closed and stored in the dark at 20°C for one year.

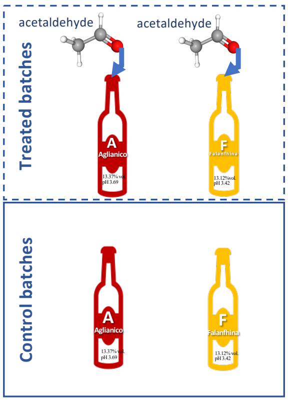

Figure 1. Batches of red (Aglianico) and white (Falanghina) wines prepared with an excess (190 mg/L) of pure acetaldehyde (Treated batches) or without (Control batches) acetaldehyde addition.

Analysis of red and white wines

Red and white wines exposed to an excess of acetaldehyde were analyzed by means of UV/Vis HPLC and Electrospray Ionization Mass Spectrometry (LC-HR ESI-MS) for the detection of low molecular weight phenols. LC-HR ESIMS experiments were performed on an Agilent 1260 Infinity II HPLC quaternary system coupled with a linear ion trap LTQ Orbitrap XL hybrid Fourier transform MS (FTMS) instrument equipped with an ESI ION MAX source (Thermo-Fisher). The chromatographic separation for red and white wines is reported in Figure 2.

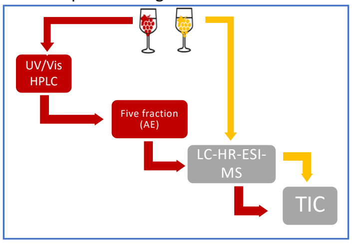

Figure 2. Red wines were preliminary subjected to HPLC-separation. From chromatographic separation, five fractions were collected and analysed by LC-HR ESIMS and total ion chromatograms (TIC) were defined. **Withe wines** were directly separated by LC-HR ESIMS defining total ion chromatograms (TIC) as reported above.

CIELAB parameters (L*. a*. b*) were determined and colour differences (DE⁄ab) were calculated as the Euclidean distance between two points in the 3D space defined by L*, a*, and b*.

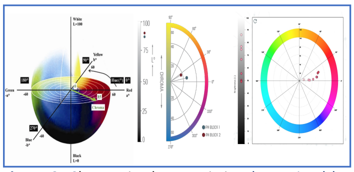

Figure 3. Chromatic characteristics determined by using the software Panorama

Results and Discussion

The chemical behaviour of acetaldehyde appeared different in white and red wines. Specifically, a dramatic loss of monomeric anthocyanins and a simultaneous massive formation of polymeric compounds (Figure 4) was detected in red wine.

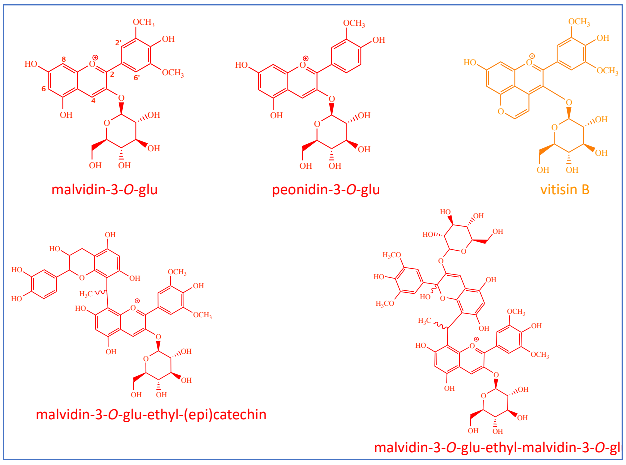

Figure 4. Stereostructures of pigments detected by LC-HR ESIMS in red wines. In the untreated wine, a number of anthocyanins was identified and quantified, Conversely, in the wine fortified with acetaldehyde only malvidin-3-O-glucoside could be detected.

The results regarding red wines highlighted that the anthocyanin moiety is not preferentially attacked by the protonated acetaldehyde, which seems to react first and preferentially with flavanols due to their better nucleophilicity when compared to anthocyanins. Subsequently, after the loss of a water molecule, the acetaldehyde-flavanol adduct attacks either another flavanol or an anthocyanin unit. In our studies conducted on real wines (pH =3.69), we only detected polymers containing just one anthocyanin unit, even if molecules of unreacted malvidin-3-O-glucoside were still present in the analyzed samples.

Instead, in white wines the formation of vinyl-flavan-3-ol derivatives was mainly detected. Infact, the comparison of the total ion chromatograms (TIC) of the untreated and treated white wines brought to light a significant decrease of the relative abundance of some chromatographic peaks along with a concomitant increase of others (Figure 5). The two peaks eluting at 11.15 and 13.51 min (m/z 289) were attributed to catechin and epicatechin, respectively. On account of previous reports, the peaks eluting at 9.65 min (m/z 577) and 14.50 (m/z 865) were assigned to a procyanidin dimer and trimer, respectively (Figure 6).

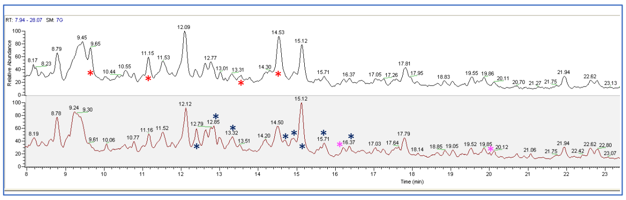

Figure 5. Total ion current chromatograms of untreated white wine (above) and of white wine treated with acetaldehyde.

Red and blue asterisks indicate ion peaks that decreased or increased, respectively, after the addition of acetaldehyde; magenta asterisks indicate peaks that seem to have been not affected by the addition of acetaldehyde.

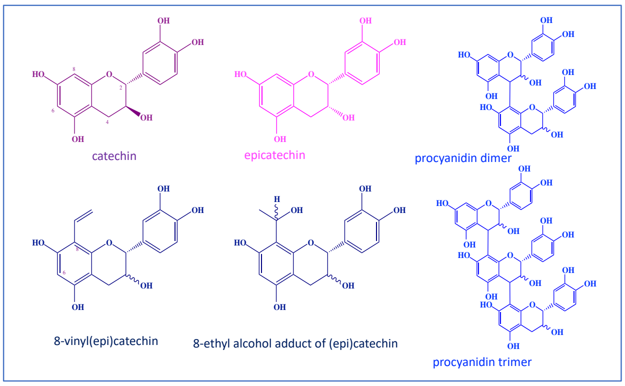

Figure 6. Stereostructures of compounds detected by LC-HR ESIMS in white wines.

On the basis of the results, it can be assumed that flavanols in white wine are helpful to quench acetaldehyde reactivity by affording more stable compounds. Therefore, on one hand the "catechol" B-ring of flavonoids can be oxidized by quinones through electron transfer reactions leading to flavanoid quinones, precursors of browning products, but on the other hand they can prevent the negative off-flavors deriving from acetaldehyde produced during oxidation [8]. In addition, in red wines the acetaldehyde led to the formation of ethylidene bridged red pigments. These latter positively enhanced the colour properties of red wines (CIELAB parameters, data not shown). Conversely, in white wines the formation of compounds, such as xanthylium ions, causing the undesired browning effects were not detected.

References

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