The effect of transition metals on coniferaldehyde oxidation in wine spirits model solutions

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Wood is known to be a complex biological system composed mainly of cellulose, hemicelluloses and lignin. Cellulose is commonly degraded by the thermal treatment of wood during coopering giving rise to HMF and 5-methylfurfural, while hemicellulose can generate pentose by hydrolysis, and posteriorly, furfural and its derivatives. Lignin transformations during ageing process of distillates are among the most important factors that may influence the quality of aged wine spirit (WS). Lignin generates two distinct groups of the phenolic aldehydes, one consisting of syringyl-type compounds (sinapaldehyde (sipde), and syringaldehyde), and the other composed of guaiacyl-type compounds (coniferaldehyde (cofde), and vanillin, vanil).[1] The oxidation of sipde gives rise to syringaldehyde, which is oxidized to syringic acid, similarly, cofde converted to vanillin and, in turn, oxidized to vanillic acid.[1,2] It is widely assumed that the aldehydes phenolics contribute to the aroma and colour of aged wine spirits, which are determinates of consumer choice. However, few is known about the oxidation reactions that occur during the WS ageing and the involvement of phenolic aldehydes in these reactions. This work aimed to evaluate the behaviour of target phenolic aldehydes (cofde and sipde), that are among the major components of WSs, and to understand their oxidation pathway, using an oxidative catalysis approach in synthetic medium (MOS) and considering some variables, such as the presence of transition metals (copper (Cu) and iron (Fe)) and the presence of an oxidizing agent. The transition metals, Cu and Fe, are extracted from wood and are present in the wine distillate as well, may play an important role on oxidation reactions of phenolics.[3]

The combinatory reactions were performed with a model solution (EtOH/H_2O, 75:25 v/v); target phenolic aldehyde (cofde), which was selected according to its relevant behaviour during technological assay[3]; metals (Cu^{2+}, Fe^{3+}); oxidant (H_2O_2) and temperature (40 ± 1 °C). MOS was conducted as follows: five glass tubes containing 2 mg/mL of cofde in each were coded as Control$^-$ (without metals or oxidant); Control* (only oxidant); CM* (Cu^{2+}/Fe^{3+} and oxidant); CF* ($Fe^{3+}$and oxidant) and CC* (Cu^{2+} and oxidant). The reaction vessels were placed in a heating magnetic stirrer for 45 days. Substrate consumption was determined by HPLC-DAD and the chromatic properties during kinetic analysis were examined (7, 14, 30 and 45 days). The kinetic analyses showed that the system with the presence of Cu^{2+}/Fe^{3+} consumes the cofde quickly, i.e. approximately 82% of the initial concentration of cofde was consumed after 7 days (Figure 1A). In contrast, a system containing only Fe^{3+} or the oxidizing agent (H_2O_2) consumed only nearly 18% of the initial cofde. After 45 days, all systems containing the oxidizing agent had completed the conversion of cofde. The oxidation products were identified by ESI-MS, and the most relevant were: ferulic acid, vanillin, ethyl ferulate, and the ferulic acid phenoxyl radical dimer product which is stabilized by a keto-enol tautomerism. In addition, the chromatic characteristics of the samples were determined (in duplicate) using the CIELab/CIELCh method. The results for chromatic characteristics of the samples (Control$^-$, Control*, CM*, CF*, CC*) during kinetic are shown in Figure 1B-D. In general terms, the samples containing oxidant and metals (Control*, CM*, CF*, CC*) showed a continuous evolution of lightness (L*), chroma (C), green-red hue (a*), yellow hue (b*) in relation to the sample Control$^-$ during the MOS. After 30 days, CM* increased significantly the +a* values (red hue) and +b* values (yellow hue). Chroma was significantly lower in the Control-, while the samples (Control*, CM*, CF*, CC*) displayed a gradual increase during kinetics, being significantly greater in CM* than CF* and CC*. In summary, there is a greater evolution of the chromatic characteristics in the sample with metals (Cu^{2+}, Fe^{3+}) and oxidant than samples containing the metals added separately with oxidant. Cofde, their metabolites, and interaction with Cu or Fe, in catalytic percentages (5-10 mol/%), seem to be correlated with increased of the red and yellow hues, which are characteristics of aging process of WS. Therefore, this study provides information on role of these metals in phenolic aldehyde oxidation processes and their contributions to the colour development of aged WS.

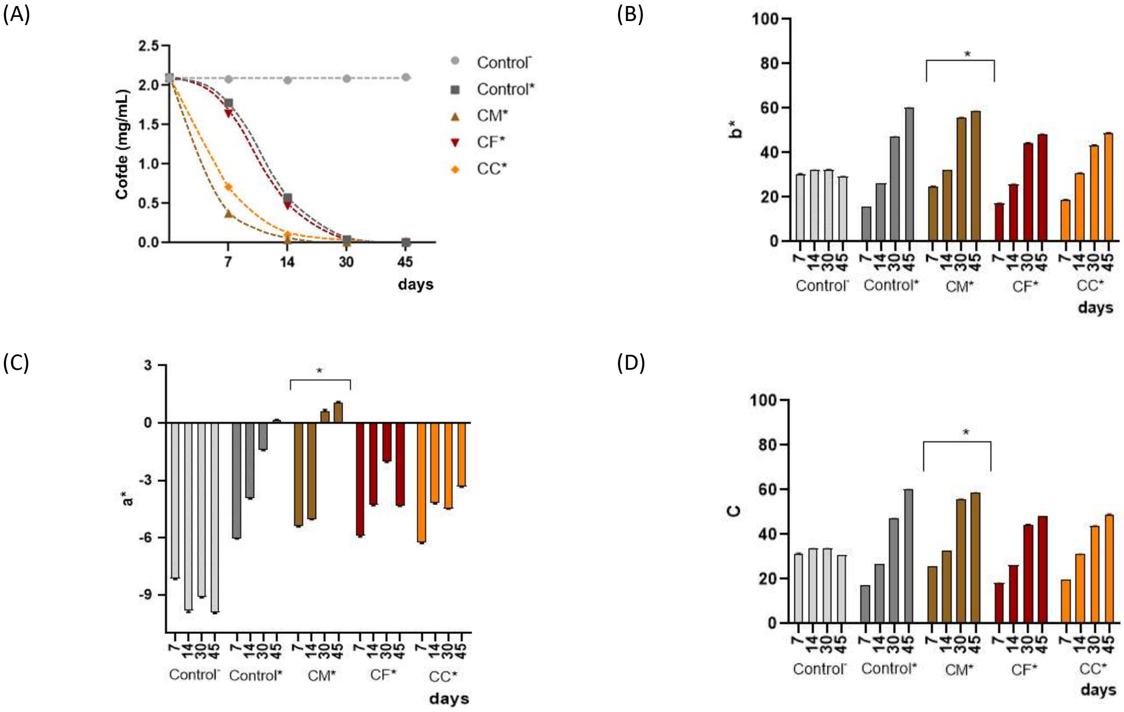

Figure 1: Kinetics curve and chromatic characteristics of samples (Control-, Control*, CM*, CF*, CC*) at 7, 14, 30 and 45 days using a modelling oxidation reaction in synthetic medium (MOS). (A) kinetics curve of consumption of cofde; (B) chromaticity coordinate b*; (C) chromaticity coordinate a*; (D) chroma. *Significance of means comparison (ANOVA, Tukey's test; $p < 0.05$) of samples is shown in each above graphics.

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