Can acetaldehyde-reactive polyphenols (ARPs) be assayed?

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Introduction

Oxygen consumption rates (OCRs) have been consistently found to be negatively correlated to the Initial content of total acetaldehyde in wine [1, 2], which suggests that directly or indirectly, this compound plays an important role in wine oxygen consumption kinetics. Interestingly, the amount of acetaldehyde accumulated during wine oxidation (0-16 mg/L) was found to depend negatively on the initial concentration of certain anthocyanins and tannins [1, 3]. This suggests that anthocyanins such as malvidin, are in fact aldehyde reactive polyphenols (ARPs) whose presence seems to be crucial not only for oxygen consumption kinetics but for determining the fate of acetaldehyde and of other relevant wine aldehydes during wine oxidation. It can be thought that the presence and amount of these compounds should be closely related to the aging potential of the wine. Although acetaldehyde is known to react with anthocyanins, flavonols and tannins, there is not a well-defined category of aldehyde-reactive polyphenols (ARPs).

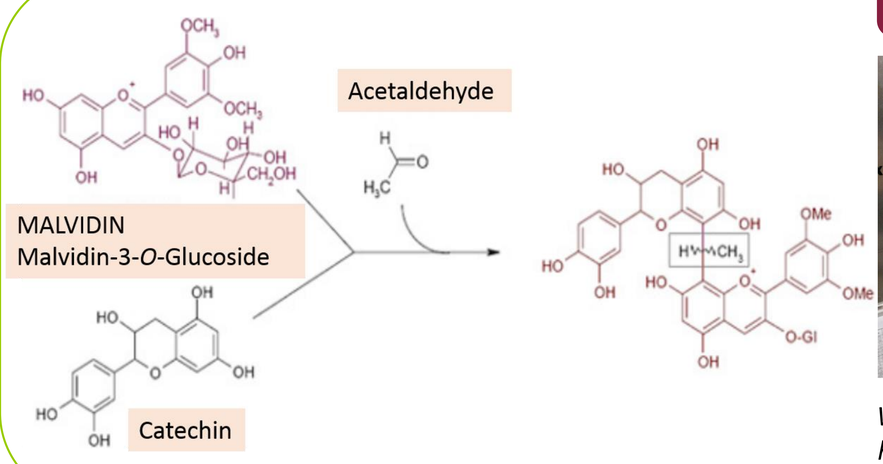
We hypothesized that these ARPs, with apparently such a large enological significance, could be measured by measuring the rate at which each wine consumes acetaldehyde and/or the maxima amounts of acetaldehyde that each wine can consume.

For testing the hypothesis we have studied the kinetics of acetaldehyde consumption of different wines or model wines containing polyphenols extracts in different temperature conditions and at different spiked levels.

OBJECTIVE

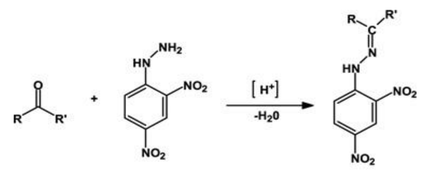
The main purpose of the present work was to assess whether the **kinetics of acetaldehyde consumption in red wines** can provide a new polyphenol index which should be linked to wine oxygen consumption kinetics and to the maximum oxygen that each wine can consume.

Material and methods



Wines and synthetic wines with polyphenol extracts have been spiked with different levels acetaldehyde inside of an oxygen-free chamber.

Temperature control

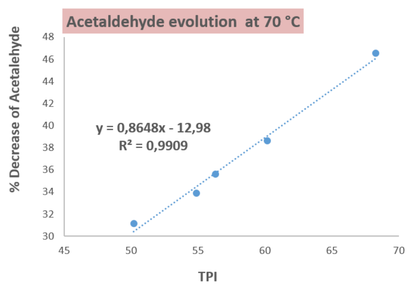


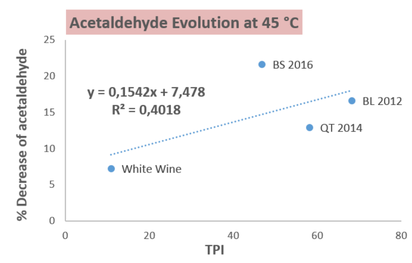
HPLC determination of acetaldehyde with previous derivatization with DNPH [4]

Results

1. 70° C

Preliminary results suggested that to have a quick measurement of ARPs, the wine should be spiked with 300 mg/L of acetaldehyde and the reaction performed at relatively large temperatures





We found that at 70° C it is possible to get precise measurements of the amount of acetaldehyde consumed by a wine during 4 days, and that different wines have large differences in this parameter. However, for out dismay, this parameter was perfectly correlated to TPI.

We tried then smaller temperatures and higher times (7days), and observed that at 45° C the amount of acetaldehyde consumed by wines was no longer correlated to TPI.

2. 25° C vs 45 °C

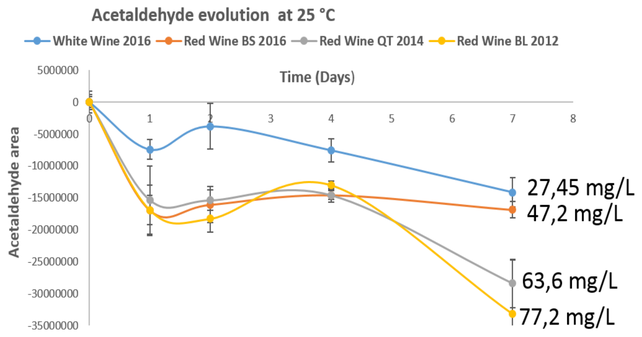
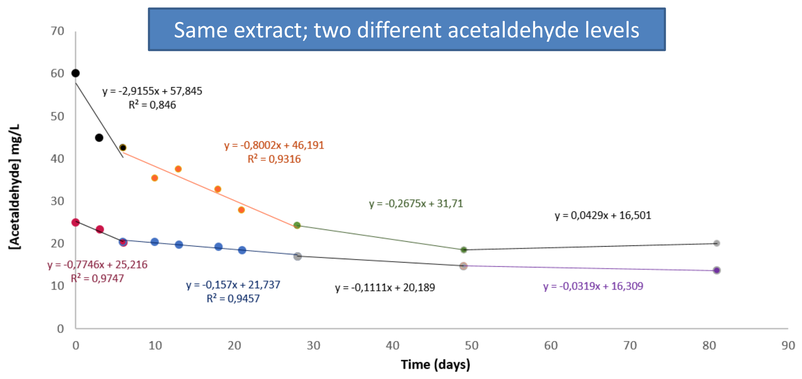


Fig 1. Consumption of acetaldehyde in 4 different commercial wines. Wines were spiked with 300 mg/L of acetaldehyde and were further incubated during 7 days at 25 and 45 °C.

The consumption of acetaldehyde by wine at 45° C seems to be quite erratic, imprecise and not very different among wines. Clearly differences were seen only between white and reds. In any case, consumption at 45°C is not correlated to consumption at 25° C, which invalidates 45° C as test temperature.

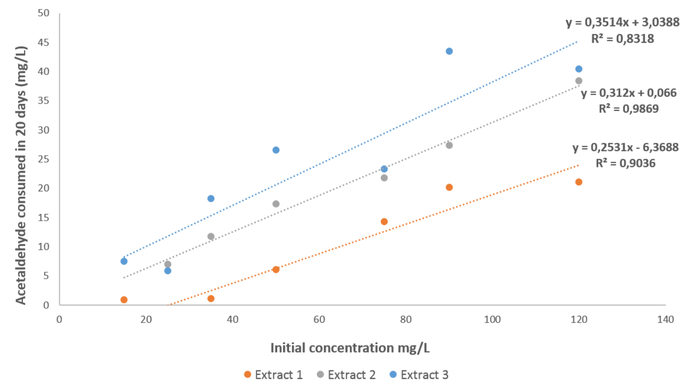
3. 35° C with polyphenolic extracts

Same extract; two different acetaldehyde levels



Acetaldehyde consumption follows a complex kinetics, with apparently a high order, and seems to reach an equilibrium point. Such equilibrium point seems to depend on the amount of acetaldehyde previously consumed by the phenolic extract.

Three extracts, different acetaldehyde levels, a single reaction time (20 days)



Acetaldehyde consumption rates depend on the polyphenolic composition, but they are too imprecise to build a reliable index. In its present form, wines could hardly be separated into four different "acetaldehyde consumption categories".

Conclusions

1- Although it is true that different wines consume acetaldehyde at different rates, acetaldehyde consumption at room or low temperatures is quite imprecise, which makes impractical the use of acetaldehyde consumption rates as index to categorize wine polyphenolic composition by defining a discrete ARP category.

2- Although acetaldehyde consumption rates become more precise at 70 degrees, it has been found that at such temperature, this parameter is essentially another measurement of the Total Polyphenol Index of the wine, having therefore nothing to do with the parameters determining oxygen consumption rates or ARPs.

3- Kinetically, acetaldehyde consumption rates are too complex, showing a high order dependence towards acetaldehyde concentration and a equilibrium concentration. Such concentrations was found to depend on the previous uptake of acetaldehyde by the polyphenolic fraction, but it was too imprecise to extract clear conclusions.

4.- In any case, measured acetaldehyde consumption rates are smaller than expected attending to known oxygen consumption kinetics and acetaldehyde accumulation rates.

5- Our results, therefore, do not completely support the existence of a well-defined category of Aldehyde Reactive Polyphenols, as previous results had suggested. This unexpected outcome could suggest that during oxidation, it is not acetaldehyde the reactive species, but one of their radical precursors. Additional research should be carried out to verify this.

[1] Carrascón, V.; Vallverdú-Queralt, A.; Meudec, E.; Sommerer, N.; Fernández-Zurbano, P.; Ferreira, V.; Food Chemistry, 2018, 241, 206-214. [2] Marrufo-Curtido, A.; Carrascón, V.; Bueno, M.,Ferreira, V.; Escudero, A. Food Chemistry, 2018, 248, 37-45.[3] Bueno, M., Marrufo-Curtido, A.; Carrascón, Fernández-Zurbano, P.; Escudero, A. V.;.Ferreira, V.; Frontiers, in press. [4] Han, G.; Wang, H.; Webb, M., Waterhouse, A *Talanta*, 2015, **134**, 596-602.

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