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SCAN ME



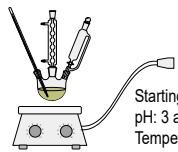
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Daniele Catorci passed away on June 27 2020

A Zoom meeting is scheduled in case you have questions and you want to meet the corresponding author\*  
Thursday June 24th 2021, from 15:00 to 16:00 (CET)  
Link: shorturl.at/IDUZ  
Meeting ID: 815 2416 2216 Passcode: macrowine

## Introduction

Flavanols have a great influence on wine ageing potential, astringency, colour stability and biological activities. In 2014<sup>a</sup>, through an untargeted approach, several sulfonated flavanols were detected in wine and it was proven that their production was favoured by the storage at high temperatures. In 2015<sup>b</sup>, through isolation and NMR structural elucidation, the presence of epicatechin 4β-sulfonated and procyanidin B2 4β-sulfonated was confirmed. In 2018<sup>c</sup> the amount of sulfonated flavanols was quantified in 200 wines, showing that their concentration can arrive at 30-40 mg/L in red aged wines. Aim of this work (published in 2020<sup>d</sup>) was to investigate the kinetics and to suggest mechanism of their formation at conditions analogous to wine.

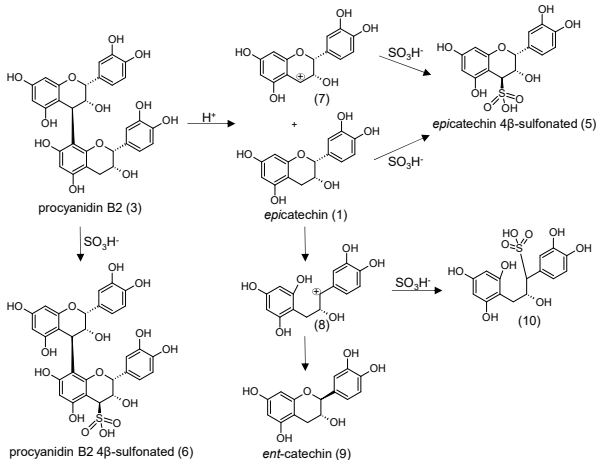
**References**  
a. Arapitsas, P.; Speri, G.; Perenzoni, D.; Angeli, A.; Mattivi, F. "The influence of storage on the "chemical age" of red wines" *Metabolomics*, 10 (2014), 816-832.  
b. Mattivi F, Arapitsas P, Perenzoni D and Guella G. "Influence of storage conditions on the composition of red wines" in *Advances in Wine Research*. ACS Books, 2015  
c. Arapitsas P, Guella G, Mattivi F. "The impact of SO<sub>2</sub> on wine flavanols and indoles in relation to wine style and age" *Scientific Reports* 8, 858 (2018)  
d. Bonaldo F, Guella G, Mattivi F, Catorci D, Arapitsas P. "Kinetic investigations of sulfite addition to flavanols" *Scientific Reports* 10, 12792 (2020).



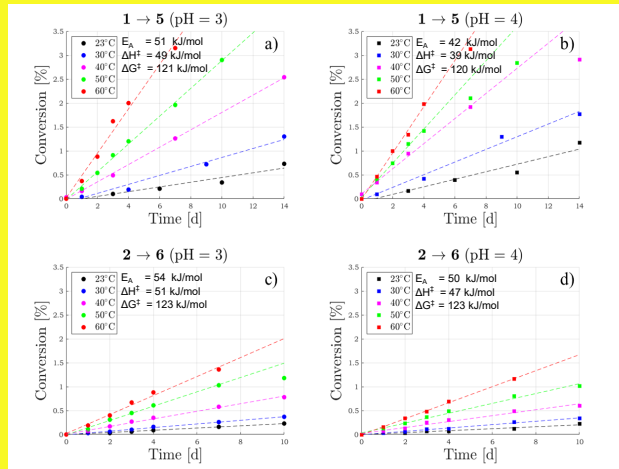
## Experimental design

Starting material: epicatechin, catechin, procyanidin B2 and procyanidin B3  
pH: 3 and 4  
Temperatures: 23, 30, 40, 50 and 60 °C

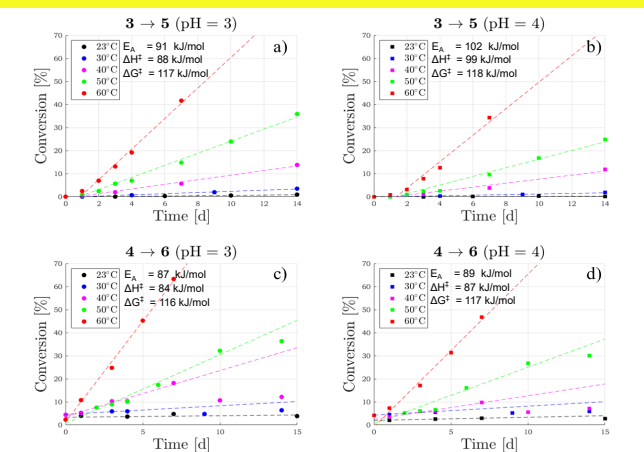
## Studied reactions



## Results

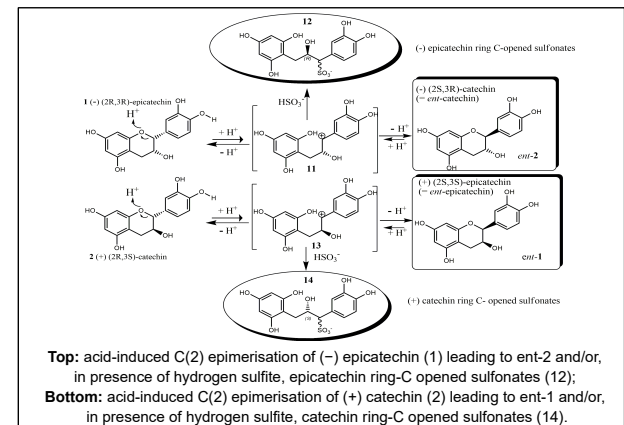
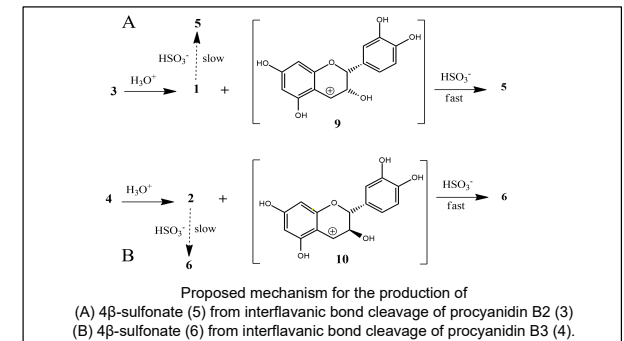


Comparison of the different temperature kinetics of epicatechin 4β-sulfonate (5) and catechin 4β-sulfonate (6) formation starting, respectively, from epicatechin (1) (a, b) and catechin (2) (c, d) at pH 3 and 4.



Comparison of the different temperature kinetics of epicatechin 4β-sulfonate (5) and catechin 4β-sulfonate (6) formation starting, respectively, from procyanidin B2 (3) (a, b) and procyanidin B3 (4) (c, d) at pH 3 and 4.

## Conclusions



## Take home messages

- The major sulfonation route that leads quickly and in good yields to monomeric 4β-sulfonated derivatives passes through the acid-catalysed depolymerisation of proanthocyanidins.
- Monomeric flavanols lead to the same 4β-sulfonated products, although in a considerably slower manner, and also to other sulfonated regioisomers.
- The kinetic data suggest the involvement of two completely different reaction mechanisms for the SO<sub>2</sub> addition: The direct sulfonation process is entropy-controlled and requires an oxidation step, while the process that passed through proanthocyanidins depolymerization is enthalpy-controlled.
- Direct sulfonation of epicatechin is slightly faster than that of catechin.

The studied reactions, starting from the flavanol *epi*-(2,3-*cis*) conformations: epicatechin and procyanidin B2  
 - The direct C4-sulfonation of epicatechin (1 → 5)  
 - The direct C4-sulfonation of procyanidin B2 (3 → 6)  
 - The acidic cleavage of procyanidin B2 (3 → 1)  
 - The indirect C4-sulfonation of epicatechin starting from procyanidin B2 (3 → [7] → 5)  
 - The isomerisation of epicatechin (1 → [8] → 9)  
 - The C2-sulfonation of epicatechin after ring opening (1 → [8] → 10)

The analogous reactions starting from the 2,3-*trans* flavanols, catechin and procyanidin B3, were also studied.

## Calculated values

E<sub>a</sub>: activation energy (Arrhenius equation)  
 ΔH<sup>‡</sup>: enthalpy of formation  
 ΔG<sup>‡</sup>: Gibbs energy  
 ΔS<sup>‡</sup>: entropy of activation