A new perspective on vescalagin, castalagin, and their degradation pathways in wine spirits ageing

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Introduction

Wine spirits (WS) are usually aged in wooden barrels, but using wood pieces instead of barrels, with or without micro-oxygenation, is a technological alternative that our team has been investigated.[1,2] The current research was focused on identifying ellagitannins, their derived species, and the evolution of degradation pathways. These compounds are originated from wood constituents and revealed an important sensory impact in aged wine spirits due to their association with the sensation of astringency, which have a close relationship with quality of these beverages.[3]

Results

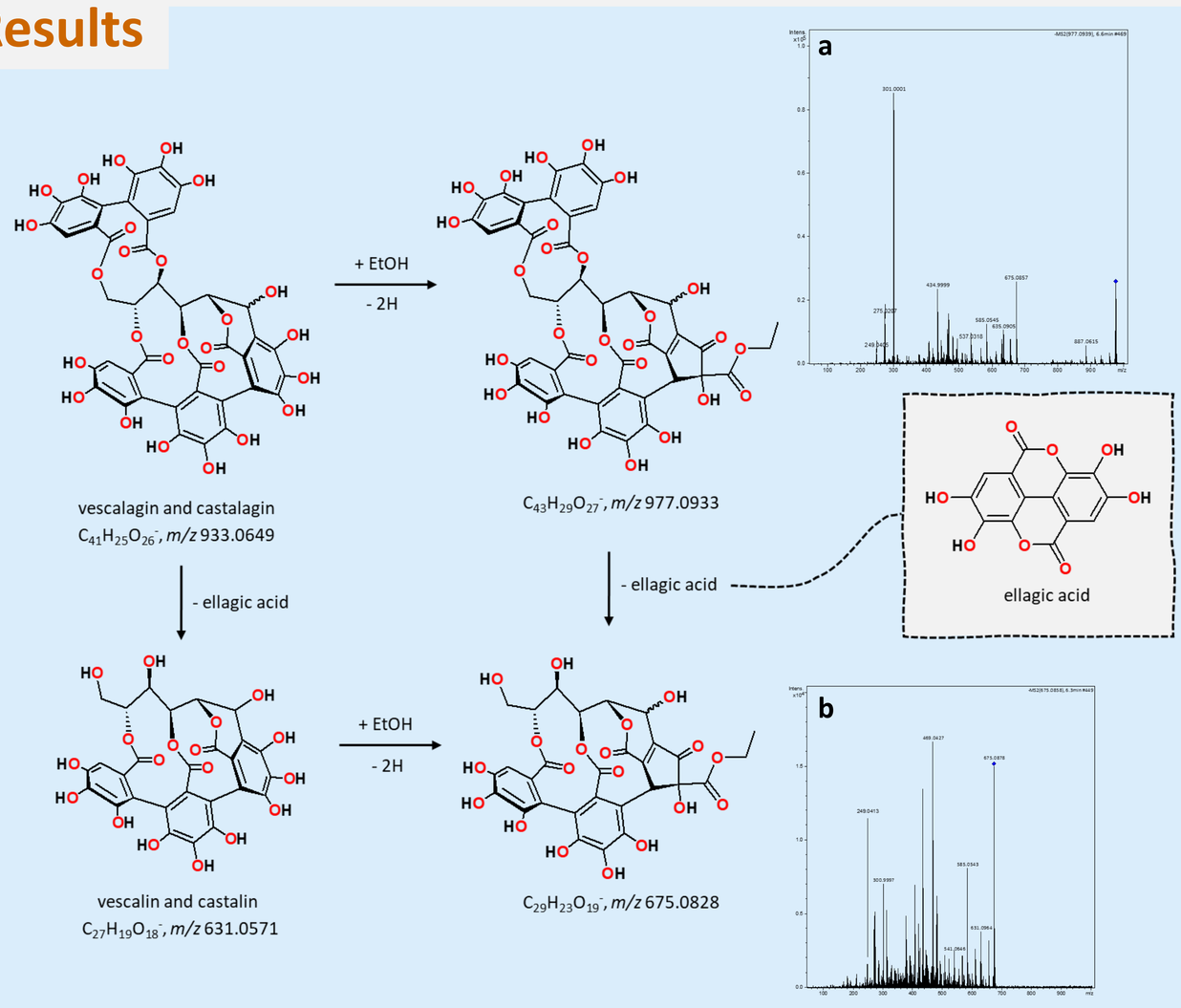

Figure 1: Structures of vescalagin/castalagin isomers and their degradation pathway for the two derivatives that were tentatively assigned to the ethanol-promoted oxidation products of vescalagin/ castalagin and vescalin/castalin**.** Tandem mass spectrum of the deprotonated molecule of a derivative tentatively assigned to the degradation product of (**a**) vescalagin/castalagin with EtOH, and (**b**) vescalin/castalin with EtOH. Derivatives displayed a m/z compatible with the deprotonated molecules of ethanol-promoted degradation products reported by Fujieda *et al.*[4], but also displayed the three diagnostic ions 300.9979/275.0186/249.0394, which are characteristic of ellagic tannins, in the tandem mass spectra.

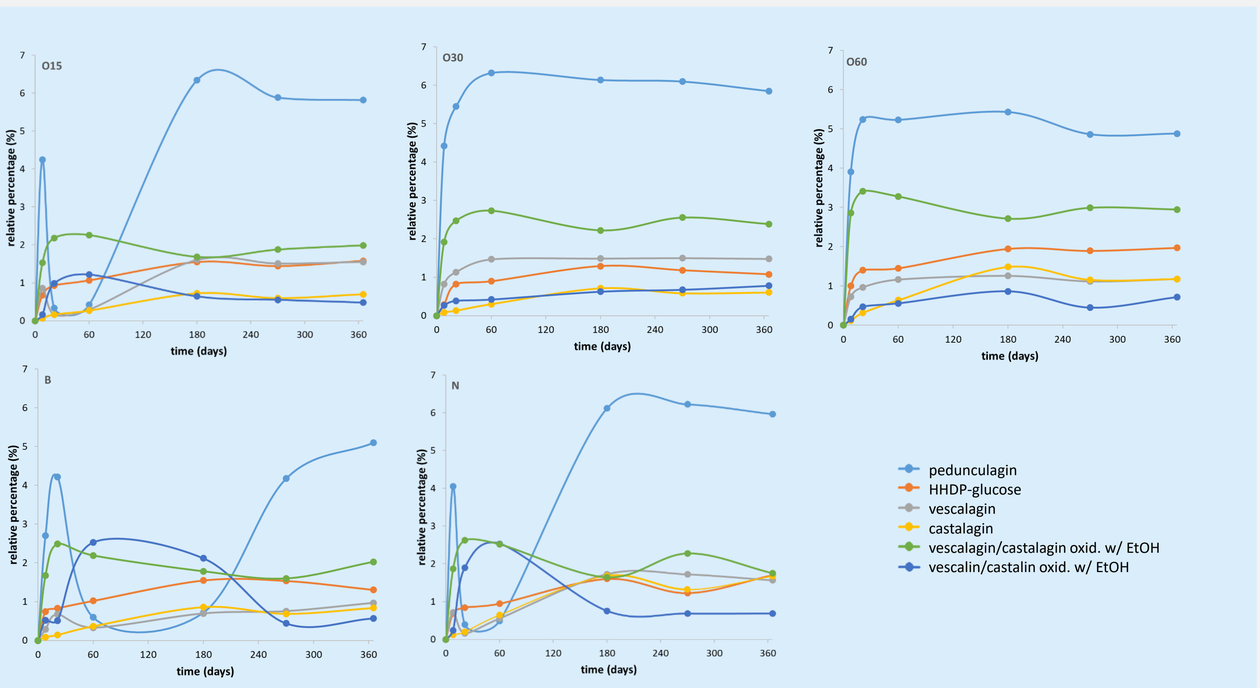

Figure 2: Contents of vescalagin, castalagin and their derivatives in the aged WSs according to the ageing modalities (**B**, **O15**, **O30**, **O60** and **N**), and the ageing time (8, 21, 60, 180, 270 and 365 days). **O15**, **O30**, **O60** – MOX modalities combined with chestnut staves, **B** – Chestnut barrel, **N** – nitrogen (control).

Materials and Methods

Research Methodology: A wine distillate produced by Adega Cooperativa da Lourinhã (Lourinhã, Portugal) was aged for 12 months in 50 L demijohns with Portuguese chestnut (*Castanea sativa* Mill.) wood staves using three levels of micro-oxygenation (**O15, O30 and O60**), nitrogen (**N, control**), and wooden barrels (**B**), in replicates. The WSs were sampled at **0, 8, 21, 60, 180, 270 and 365 days** of ageing, and ellagitannins and correlated species were identified using liquid chromatography coupled with quadrupole time-of-flight high resolution tandem mass spectrometry (LC-QTOF-HRMS/MS).

LC-QTOF-HRMS/MS Analysis: Analyses were conducted on a Bruker Impact II quadrupole time-of-flight mass spectrometer equipped with an ESI source (Bruker Daltoniks, Bremen, Germany). Chromatographic separations were performed in an Ultimate 3000 RSLCnano system (ThermoFisher Scientific) using a Luna C18 column (3.0 µm, 2.0 × 150 mm; Phenomenex) and an elution gradient of 0.1% formic acid in water (mobile phase A), and 0.1% formic acid in acetonitrile (mobile phase B) at a flow rate of 170 µL/min.

Objectives

Obtain a greater comprehension of ellagitannin derivatives and determine their presence in aged WSs, which are associated with an increase in gallic and ellagic acids concentrations with ageing.

Conclusions

- The isolation of the fragment ion at m/z 300.9979 allowed the identification of four hydroxyzable tannins of chestnut wood origin: **HHDP-glucose** (m/z 481.0648), **pedunculagin** (m/z 783.0714) and the two stereoisomers, **vescalagin** and **castalagin** (m/z 933.0649 and 933.0653), that displayed identical tandem mass spectra.
- Vescalagin and castalagin isomers showed less expression in the presence of oxygen, which highlights their prompt reactivity under these conditions.
- At m/z 977.0933 and 675.0828, two additional products were assigned to products resulting from **ethanol-promoted oxidation of castalagin/vescalagin and castalin/vescalagin**,[5] respectively.
- **Nitrogen modality** (**N**) profile evolved in a **similar manner to the traditional ageing process**, but at a faster rate (close to 100 days faster), which was also observed for the content of some volatile compounds in the same WS samples.[2]
- The presence of products stemming from their degradation (hydrolysis), which exhibit more than two-fold the relative percentage of the vescalagin and castalagin isomers, demonstrates their importance in contributing to the increased complexity of wooden-derived substrates in aged WSs.

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