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

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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. For this propose, in this study the behavior of hydroxyzable tannins in a wine spirit aged was examined in 250 L chestnut barrel, and in 50 L demijohns with chestnut wood staves with three levels of micro-oxygenation or nitrogen. Ellagitannins and correlated species in samples collected over different ageing times were identified using liquid chromatography coupled with quadrupole time-of-flight high resolution tandem mass spectrometry (LC-QTOF-HRMS/MS). 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] The isolation of the fragment ion at m/z 300.9979, from the tandem mass chromatogram, 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, and showing the additional expected fragmentation pattern (Figure 1). 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[4], respectively. These derivatives not only displayed a m/z compatible with the deprotonated molecules of ethanol-promoted degradation products reported by Fujieda *et al*.[5], but also displayed the three diagnostic ions 300.9979/275.0186/249.0394, which are characteristic of ellagitannins, in the tandem mass spectra. The goal of this study was to obtain a greater comprehension of ellagitannin derivatives and determine their presence in aged WSs, which are associated to an increase in gallic and ellagic acids concentrations with ageing.

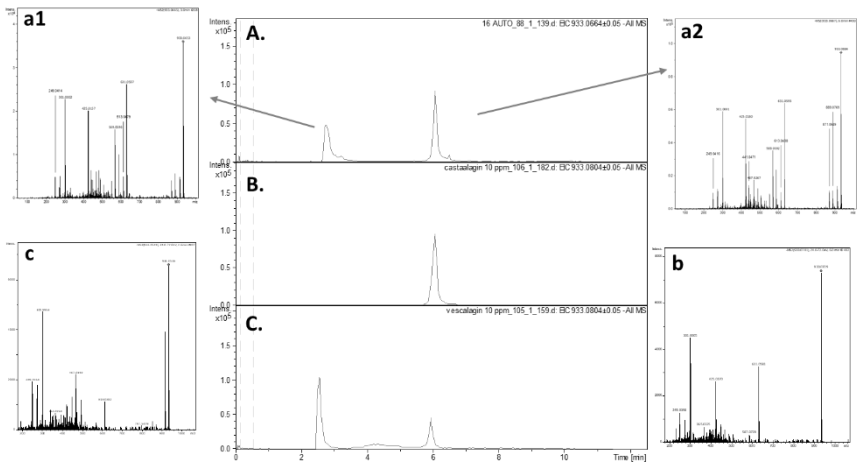

Figure 1: Extracted ion chromatogram of ion m/z 933.0649 of: A. sample CO30-180d; B. Castalagin standard; and C. Vescalagin standard. Also shown are the tandem mass spectra of vescalagin and castalagin found in WS samples (a1 and a2, respectively) and of castalagin standard (b) and of vescalagin standard (c).

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