

[P1.2.07]

**Untargeted tannins glycosylated simple phenol profile by high resolution mass (Q-Orbitrap)**

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Tannins are polyphenolic compounds present in plants and used by food industries as processing aids. For the heterogeneity of plant sources, action performed in food-processing and tannin commercial cost could be different.

Free simple phenols, both as aglycones and glycosides are ubiquitous in natural kingdom, and contribute to the antioxidant intake of many plant foods, but there is little information about the glycosidically bound simple phenols of tannins. This work aimed to define the phenols precursors profile of 73 monovarietal commercial tannins of 14 different botanical origin, using a high resolution mass untargeted approach.

Combining an on-line SPE-UHPLC method with high resolution mass spectrometry (Q-Orbitrap), a new untargeted approach was developed. Identification and quantification of glycosylated phenolic compounds were performed acquiring mass spectra in full MS-data dependent MS/MS analysis at mass resolving power of 140.000, in negative ion mode and with a heated electrospray.

By accurate mass, isotopic pattern and MS/MS fragmentation, 169 precursors, 91 as monoglycosylated and 78 as diglycosylated derivatives, have been tentatively identified. This untargeted approach was validated using 3 custom synthesized glucosidic precursors. The proposed method provided a new approach to characterize oenological tannins on the basis of their botanical origin: oak tannins are characterized by the exclusive presence of coniferyl alcohol-pentoside (pent), isopropiovanillone-pent, orcinol-pent, phenol-pent, coniferaldehyde-hexoside (hex), vanillyl ethyl ether-hex, gallic acid-hex-pent, coniferaldehyde-hex-hex; marc tannins by scopoletin-pent, p-carboxyphenol-pent-pent, homovanillic alcohol-hex, vanillin-hex-pent; grape skin tannins by phenol-hex, 4-vinylphenol-pent-pent and isopropiosiringone-hex-hex; blueberry tannins by 4-vinylguayacol-pent, p-carboxyphenol-hex-pent and vanillic acid-pent-pent; citrus tannins by acetosyringone-hex, syringaldehyde-hex-hex and guaiacol-pent-pent; quebracho tannins by pyrocatechol-hex-hex and tyrosol-hex-hex; tea tannins by aesculatin-pent and syringol-hex; green tea tannins by isopropiosyringone-pent and salicylic acid-hex; chestnut tannins by eugenol-hex; tara tannins by gentisic acid-pent-pent; acacia tannins by catechin-pent; gambier acacia tannins by caffeic acid-hex-pent; brazilian acacia tannins by aesculatin-hex-pent; mimosa tannins by homovanillic alcohol-hex-hex.

Keywords: LC-HRMS, glycosilphenol, bound simple phenols