PROGRAM & BOOK OF ABSTRACTS

Assuring the integrity of the food chain: FIGHTING FOOD FRAUD

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UNTARGETED GLYCOSYLATED SIMPLE PHENOL PROFILING IN OENOLOGICAL TANNINS BY HIGH RESOLUTION MASS ANALYTICAL METHOD (SPE-LC-Q-ORBITRAP)

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Oenological tannins, highly reactive phenolic compounds, are extracted from different botanical sources, including grape, quebracho, oak, chestnut, tara and galla, and are authorised by the Organisation Internationale de la Vigne et du Vin (OIV) as clarifiers of musts and wines due to their affinity to bind proteins. Tannin addition is accepted in Europe, South Africa, USA, Australia and New Zealand, even though with some differences between different countries. Phenolic compounds are ubiquitous in natural kingdom and contribute to the antioxidant intake of many plant foods. Free simple phenols, present both in free and glycosidically bound forms, have the simplest chemical structure of all phenols, but their same antioxidant and other biological properties. Despite there are a large number of commercial tannins, there is little information about their glycosidically bound simple phenolic content. Combining an on-line SPE-UHPLC method with high resolution mass spectrometry (Q-Orbitrap), a new untargeted approach for a detailed description of the bound phenol profiles in oenological tannins was developed. On-line SPE clean-up was performed on a HyperSep™ Retain PEP SPE cartridge, while the chromatographic separation on an Acquity UPLC BEH C18 analytical column. 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. The untargeted approach, validated using expressly synthetized glycosidic precursors, let to characterize 88 monoglycosides (42 hexoside precursors, 46 pentoside) and 63 diglycosides (22 hexoside-hexoside precursor, 14 hexoside-pentoside, 16 pentoside-hexoside, 11 pentoside-pentoside). The proposed method provided a new approach to characterized oenological tannins on the basis of their botanical origin: oak tannins are characterized by the exclusive presence of coniferyl alcohol-pent, isopropovanilione-pent, orcinol-pent, phenol-pent, coniferaldehyde-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 acetylsyringone-hex, syringaldehyde-hex-he x 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: solid phase extraction, LC-MS, bound phenols, glycosylphenols