

Deciphering the structure of pectic oligosaccharides by a new tandem mass spectrometry method based on photo-activation in the Vacuum UltraViolet range

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Carbohydrates are involved in many biological functions and represent a vast reservoir of molecules of high functional interest for several industries. These functions are tightly connected to their structure, yet many of them remain incompletely resolved. The complexity and heterogeneity of natural carbohydrates has long challenged the field of analytical chemistry. Mass spectrometry, with its remarkable sensitivity, rapidity and high information content, is a forefront method for that purpose. However, classical tandem mass spectrometry based on low-energy collision-activated dissociation (LE-CAD) fails in many cases to achieve definitive structural assignments.

In this work, we explored an original instrumental setup using Vacuum UltraViolet (VUV) synchrotron radiation as an activation process for tandem mass spectrometry. A complex mixture of oligogalacturonates, released by the enzymatic degradation of highly methylated pectin and exhibiting many isomers differing by their methylation pattern was investigated. More than 35 oligogalacturonates with various degrees of polymerization and of methyl-esterification were identified. In particular, despite their lack of stability, methyl groups were unequivocally positioned. The comprehensiveness of this structural determination enabled to refine the knowledge about the mode of action of the enzyme used for degradation.

Photo-activation was also performed following a direct coupling with Ultra Performance Liquid Chromatography (UPLC). The dynamic range was improved and a tremendous amount of information was yielded, even on minor species. This illustrates the potential of this analytical workflow for the structural analysis of complex carbohydrates mixtures.