Occurrence of cellobiose residues directly linked to galacturonic and in pectic acid in pectic polysaccharides

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Pectic polysaccharides are present in all plant cell walls. These polymers are constituted by different associated polysaccharides, such as homogalacturonan, xylogalacturonan, rhamnogalacturonan type I, rhamnogalacturonan type II, arabinan, and arabinogalactan [1]. This work describes the structural features of pectic polysaccharides extracted from plum (*Prunus domestica* L.) and pear (*Pyrus communis* L.) cell walls and commercial pectin, obtained from Citrus. The alfa-(1,4)-D-galacturonic acid backbone was submitted to a selective hydrolysis with endo-polygalacturonase (EPG) and the fractions with low molecular weight (< 1000 kDa) obtained by size-exclusion chromatography were analysed by mass spectrometry using electrospray ionisation (ESI-MS and ESI-MSn) and by methylation analysis The ESI-MS spectra obtained revealed the presence, in all samples, of several [M+Na]+ ions of pectic oligosaccharides identified as belonging to different series, including oligosaccharides constituted only by galacturonic acid residues (GalAn, n=1-5) and galacturonic acid residues substituted by pentose residues (GalA3Pentn, n=1-2). Surprisingly, it was also observed the occurrence of galacturonic acid residues substituted by hexose residues (GalAnHexm, n=2-5, m=1-2). The fragmentation of the observed [M+Na]+ ions, obtained under ESI-MS/MS and MSn allowed to confirm the proposed structures constituent of these pectic oligosaccharides. Furthermore, the ESI-MSn spectra of the ions that could be identified as GalAnHexm (n=2-5, m=1-2) confirmed the presence of Hex or Hex2 residues linked to a GalA residue. Methylation analysis showed the presence, in all EPG treated samples, of terminally- and 4-linked glucose. These results show that pectic polysaccharides from different origins (plum, pear, and citrus) and structural features (different proportions of branching residues) have Glc residues directly linked to GalA as single residues or as cellobiose residues. The occurrence of GalA substituted by Glc, and Glc-beta-(1,4)-Glc are structural features that, as far as we know, have never been reported to occur in pectic polysaccharides.

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