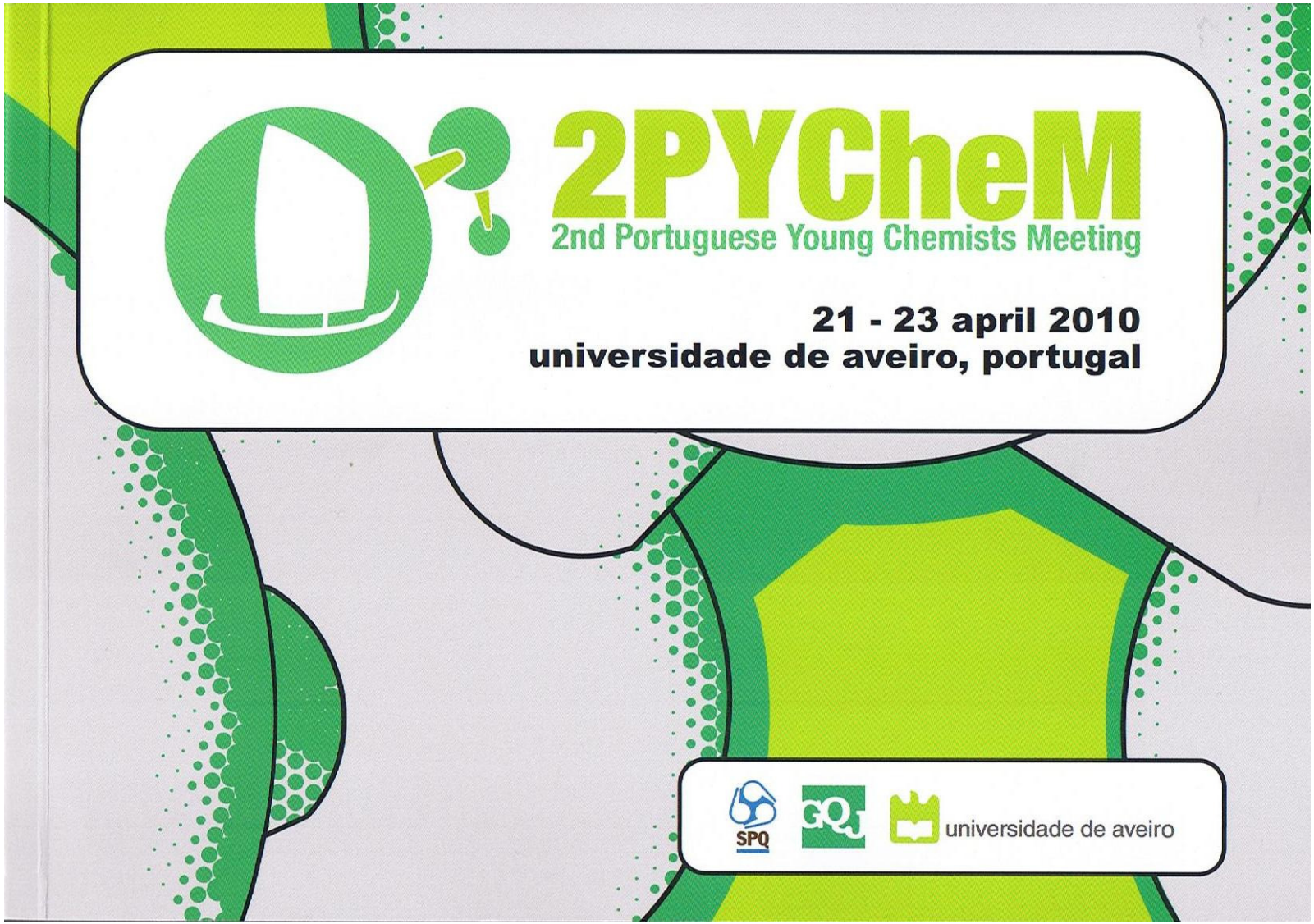
2PYCheM
2nd Portuguese Young Chemists Meeting
21 - 23 april 2010
universidade de aveiro, portugal
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Structural characterization of pectic polysaccharides by ESI-MS. Occurrence of hexoses directly linked to the galacturonic acid backbone

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Pectic polysaccharides include a large family of related polysaccharides based on a galacturonan-rich backbone. These polysaccharides are key components of the primary cell walls of fruits and vegetables, being important in determining tissues strength and flexibility. They can be viewed as multiblock components composed by four structural domains: homogalacturonan (HG), rhamnogalacturonan I (RG-I), which includes the arabinogalactan and arabinan side chains, the complex RG-II domain, and the xylogalacturonan (XGA). HG is a linear and partially 6-*O* methylated polymer constituted only by α-(1→4)-D-galacturonic acid residues [→4)-α-D-Gal*p*A-(1→]$_n$, which can be 2-*O* and 3-*O* acetylated. The repeating units of the disaccharide [→4)-α-D-Gal*p*A-(1→2)-α-L-Rha*p*-(1→] form the backbone of RG-I that comprises also branched at *O*-4 of Rha residues with Gal and/or Ara side chains. RG-II is described as a very complex heteropolysaccharide with a galacturonan backbone of around 30 residues substituted by side chains containing sugars such as 2-*O*-methyl-L-fucose and D-keto-3-deoxy-D-*manno*-2-octulosonic acid (KDO). In XGA, a HG chain is substituted on C-3 with D-Xyl.

The high sensitivity and capacity for the analysis of mixtures provided by mass spectrometry led to a re-emergence for oligosaccharides structural characterization in recent years.

In this study, we revisited the structures of pectic polysaccharides from commercial sources of citrus, as well as from plum and pear. The oligosaccharides from these pectic polysaccharide sources were generated by the selective hydrolysis of the GalA backbone with *endo*-polygalacturonase, followed by its partial separation on a Biogel size exclusion chromatography. The resultant fractions with lower molecular weight were analyzed by ESI-MS. Beyond uronic acid monomers (attributed to GalA) and the oligosaccharides characteristic of degraded HG such as GalA$_n$dHex$_q$ n=1,3; q= 1,3 (GalA-Rha series) and XGA, namely, GalA$_n$Pent$_p$ n= 2,3; p=1, it was also observed oligosaccharides bearing hexose residues linked to uronic acids (GalA$_n$Hex$_m$ n= 2,3 m= 1,2). The direct linkage of hexoses to the main galacturonan backbone is a structural feature of plant pectic polysaccharides that, until now, has been neglected but that should be included in the future structural models.

Acknowledgments

We thank the FCT for financial support through project PTDC/AGR-ALI/74587/2006.