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Metrics of rhamnogalacturonan I with β-(1→4)-linked galactan side chains and structural basis for its self-aggregation

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ABSTRACT

Within the family of plant cell wall polysaccharides rhamnogalacturonans I are the most diverse and structurally complex members. In present study we characterize the 3-dimensional structures and dynamic features of the constituents of RG-I along MD trajectories. It is demonstrated that extended threefold helical structure of the rhamnogalacturonan linear backbone is the most energetically favorable motif. Branching helps to stabilize a conformer of the backbone twisted along 1→2 glycosidic linkage triggering the orientation of long side chains without altering the extended overall backbone chain conformation. Formation of anti-parallel pairing of the β-galactan side chains allows us to suggest a novel mode of non-covalent cross-linking in pectins. Studied structural elements are organized to report the first attempt to characterize 3D structure of RG-I focusing on the special case of flax tertiary cell wall and elucidate the structural basis underlying the formation of RG-I self-associates and functional role of RG-I *in planta*.

1. Introduction

Cell walls of growing plants are extremely complex and sophisticated composite materials incorporating a dynamic assembly of polysaccharides, proteins, and phenolics. Among the polysaccharides, the pectins encompass a group of acidic polysaccharides, containing α-(1→4)-linked galacturonic acid residues, with distinct structural and functional domains. They are subjected to both biosynthetic and cell wall-based modifications. Despite the fact that the chemical structure of pectins has been a subject of many scientific investigations for decades, still uncertainties persist. Indeed, pectins are polymolecular and polydisperse exhibiting significant heterogeneity with respect to both chemical structure and molecular weight. The composition of plant cell wall polysaccharides varies with source and conditions of extraction, location, and many other environmental factors. Even though pectins offer a repertoire of structural complexity, they can nevertheless be described in terms of canonical structures (Voragen, Coenen, Verhoef, & Schols, 2009) enlighting the occurrence of distinct repeating specific domains. A pattern of «smooth» homogalacturonic regions alternates with ramified «hairy» regions, in which most of the neutral sugars are located. These domains have been named after their major monosaccharide constituents: rhamnogalacturonan I, rhamnogalacturonan II, arabinan, galactan, arabinogalactan I, arabinogalactan II and xylogalacturonan.

The elucidation of the spatial organization of pectin polysaccharides is a result of many investigations. These encompass theoretical and computational studies (Perez, Rodriguez-Carvajal, & Doco, 2003; Zykwinska, Thibault, & Ralet, 2008) as well as experimental approaches including X-ray diffraction (Walkinshaw & Aknott, 1981), FTIR-spectroscopy (Pose, Kirby, Mercado, Morris, & Quesada, 2012; Szymanska-Chargot, Chylinska, Kruk, & Zdunek, 2015), self-diffusion NMR (Mikshina et al., 2015a) and atomic force microscopy (Pose et al., 2012; Cybulska, Zdunek, & Koziol, 2015). The latter is a powerful tool to provide nanoscale information on size and shape of macromolecules. On AFM images the pectin fractions of primary cell wall revealed a mixture of individual molecules and micelle-like aggregates (Pose et al., 2012). As regard to individual pectin molecules, a pattern of extended chains was

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