Chapter 4

Plant Cell Wall Polymers: Function, Structure and Biological Activity of Their Derivatives

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http://dx.doi.org/10.5772/46094

1. Introduction

Plant cell walls represent the most abundant renewable resource on this planet. They are rich in mixed complex and simple biopolymers, which has opened the door to the development of wide applications in different technologic fields. In this regard the polymerization processes that allow the synthesis of the cell wall and their components in living models are relevant, as well as the properties of the polymers and their derivatives. Therefore this chapter outlines the basis of polymerization with a biological approach in the plant cell wall, highlighting the biological effects of plant cell wall derivatives and their current applications.

Plant cell wall is a dynamic network highly organized which changes throughout the life of the cell. The new primary cell wall is born in the cell during cell division and rapidly increases in surface area during cell expansion. The middle lamella forms the interface between the primary walls of neighboring cells. Finally, at differentiation, many cells elaborate with the primary wall a secondary cell wall, building a complex structure uniquely suited to the function of the cell. The functions of the plant cell wall may be grouped by its contribution to the structural integrity supporting the cell membrane, sense extracellular information and mediate signaling processes [1]. The main components of the plant cell wall involve different polymers including polysaccharides, proteins, aromatic substances, and also water and ions. Particularly, the different biomechanical properties of the plant cell wall are mainly defined by the content of the polymers cellulose, hemicelulloses and pectins and their interactions [2].

The rapid progress on plant cell wall research has allowed the comprehension of the different structures, their biosynthesis and functions. Nevertheless, there is a new prominent and worth line of research, the biological activity of some molecules derived from the

primary cell wall polysaccharides. These active molecules named "oligosaccharins" by Albersheim in the mid 70s, include the biologically active oligosaccharides that are produced by partial hydrolysis of polymers of the cell wall. The main biologically active components of the cell wall are the pectin-derived oligosaccharides, and the hemicellulosic-derived oligosaccharides. The biological responses of plants to oligosaccharins can be divided into two broad categories: as modulators of plant defense, and plant growth and development.

This information has permitted the use of oligosaccharins as an alternative to improve different aspects such as yield and fruit quality, and may reach a higher impact in the study of the resistance of vegetable crops.

2. Plant cell wall polymers

Plant cell wall is a complex matrix of polysaccharides that provides support and strength essential for plant cell survival. Properties conferred by the cell wall are crucial to the form and function of plants. The main functions of the cell wall comprise the confer of resistance, rigidity and protection to the cell against different biotic or abiotic stresses, but still allowing nutrients, gases and various intercellular signals to reach the plasma membrane. The wall provides enough rigidity to support the heavy weight of high trees as large as 100 m height, but also is flexible and elastic allowing growth during expansion and differentiation. During growth, cell turgor pressure provides high tensile stress to the wall, enabling its enlargement due to the accumulation of polymers during a combination of stress relaxation cycles. The primary cell wall surrounds and protects the inner cell; it lies down the middle lamella during growth and expansion [2]. The primary wall is thought to contribute to the wall structural integrity, cell adhesion, and signal transduction. In this chapter we focus on the primary cell walls because it has been noted that most of their derivatives exert a biological function.

Plant cell wall is a dynamic and highly specialized network formed by a heterogeneous mixture of cellulose, hemicelluloses and pectins, and in some extent proteins and phenolic compounds. Wall composition in vascular plants is approximately 30% cellulose, 30% hemicellulose and 35% of pectin, with certain 1-5% structural proteins on dry weight basis. Cellulose and hemicelluloses polymers bring rigidity to the wall and pectin provides fluidity throw the gelatinous polysaccharides matrix. Cellulose and hemicelluloses are embedded in the amorphous pectin polymers and stabilized by proteins and phenolic compounds. Hemicelluloses bind to the surface of cellulose network preventing direct contact among microfibrils, and pectin are linked to hemicelluloses forming a gel phase.

3. Components and function of the primary constituents of plant cell wall

3.1. Cellulose

Cellulose is the main cell wall polymer that brings support to the plant. Cellulose is a linear insoluble unbranched polymer of β-(1,4)-D-Glucose residues associated with other cellulose

chains by hydrogen bonding and Van der Waals forces. Cellulose chains aggregate together to form microfibrils, which are highly crystalline and insoluble structures, each one about 3 nm in diameter, chemically stable and resistant to enzymatic attack. Cellulose microfibrils comprise the core of the plant cell wall; one third of the total mass of wall is cellulose. The variation of dry weight of cellulose in a dicot such as *Arabidopsis thaliana* ranges from 15% of leaf to 33% of stem walls. The walls of monocot grass species have approximately 6–10% cellulose in leaves and 20–40% in stems [3].

Microfibrils comprise two types of cellulose called cellulose Iα and Iβ. The Iα has a single-chain triclinic unit cell, whereas cellulose Iβ has two chain monoclinic unit cell. In both forms cellulose in parallel and the terminal glucose residues rotated 180° forming a flat ribbon in which cellobiose (two glucose molecules linked by a β-(1,4) bond) is the repeating unit [4]. Cellulose chains may align in parallel (Type I) or antiparallel (Type II) orientation to each other. Only the Type I conformation is known to naturally occur in plants; however, concentrated alkaline treatments may cause Type II cellulose to form during harsh extraction procedures. The cellulose chains may form the Type Iα or Type Iβ conformation depending on the extent of staggering of the chains in relation to each other. Probably the interaction of cellulose microfibrils with hemicelluloses may affect the ratio of Type Iα to Type Iβ cellulose [5]. The microfibrilar disposition allows the existence of micro spaces between the microfibrils that are fulfilled by matricial polysaccharides according to the age and tissue type.

3.2. Hemicelluloses

Hemicelluloses are low molecular weight polysaccharides associated in plant cell walls with lignin and cellulose. These heterogenous group of polysaccharides that have β-(1,4)-linked backbones with an equatorial configuration at C1 and C4 and hence the backbones have structural similarity [6]. Hemicelluloses in dicotyledonous plants comprise xyloglucans, xilans, mannans and glucomannans, while the β-(1,3;1,4)-glucans are restricted to Poales and a few other groups. In addition, arabinoxylans are the main hemicellulosic polisaccharides in graminaceous species such as wheat and barley, and in grasses [7].

3.2.1. Xyloglucan

Xyloglucan (XyG) is the most abundant hemicellulose in primary cell walls found in every land plant species that has been analyzed. XyG are branched with α-D-xylose linked to C-6 of the backbone. The most frequently xyloglucan structure in dicotyledonous flowering plants is the repeating heptamer integrated by four glucans residues with α-D-xylose substituents in three constitutive glucans of the backbone, followed by a single unsubstituted glucan residue (Figure 1). The presence of this repeating heptamer block is an indicator of the presence of XyG polysaccharides in dicots species [8]. Beside the XyG residues, it may contain β-D-galactose and in less proportion L-fucose-α-(1,2)-D-galactose; in all cases the galactose residues are acetylated. The fact that all the substituents of xyloglucans are conserved denotes a highly biosynthesis control. On the other hand, in

graminaceous monocots, XyG consist of 1 or 2 adjacent α-(1-6)-linked xylose residues with approximately 3 unsubstituted β-(1-4)-linked glucose backbone [9]. Despite the structural variability found in the species, the functions of the XyG in plants growth and development are hypothesized to be conserved among all species of flowering plants [10].

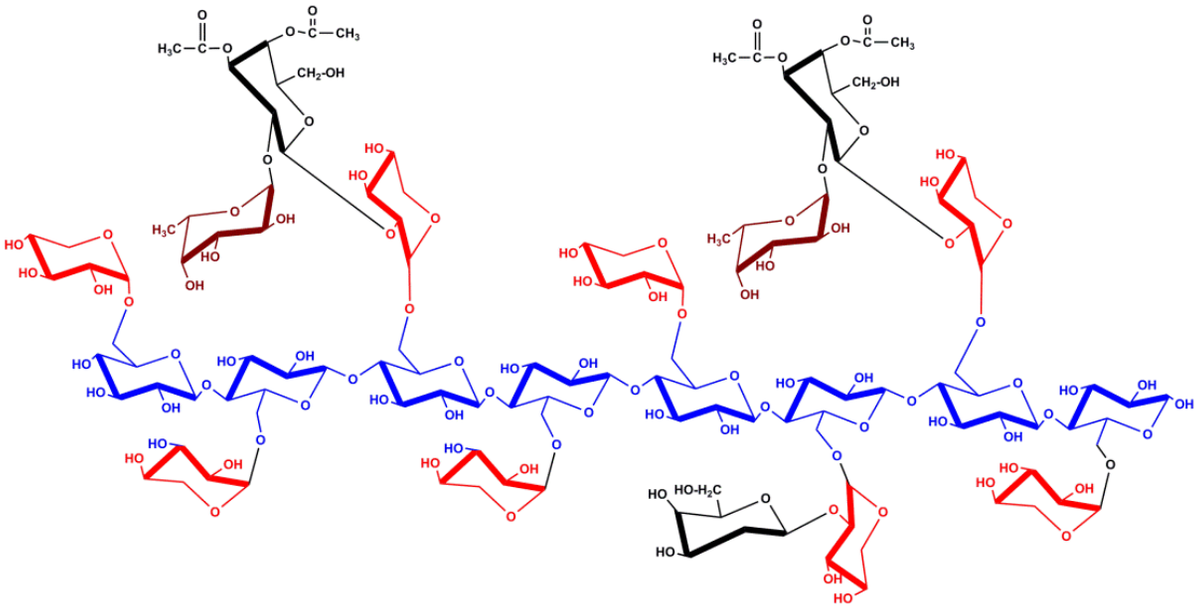

Figure 1. Structure of xyloglucan; principal component of the hemicelluloses. The heptamer block is shown (glucan$_4$-xylose$_3$). In blue backbone β-D-glucans; in red α-D-xylose; in black α-D-galactose and in brown α-L-fucose residues.

In dicotyledonous plants except for graminaceous, the cellulose and xyloglucan are in equal proportions. Some XyG chains are linked to the cellulose microfibrils supporting the important role of rigidity and maintenance of the cell, the rest XyG chains are cross-linked to cellulose microfibrils and pectic polymers, and altogether integrate the complex cell wall matrix. In addition XyG is thought to control cell wall enlargement potentially through the action of α-expansin, XyG endotransglucosylase or β-(1,4)-endoglucanases [11]. Several authors have revealed the XyG function by means of XyG-deficient mutants of *Arabidopsis thaliana*, whereas trying to elucidate the rol of xyloglucan in cell wall biomechanics and cell enlargement. More recently, mutations in two xylosyltransferase genes (*xx1*/*xx2)* involved in XyG synthesis in *Arabidopsis thaliana* resulted in a XyG-deficient mutant apparently normal but reduced in size. Hypocotyl walls were 20-50% weaker in *xx1*/*xx2* seedlings, suggesting that XyG plays a strengthening role in the cell wall [12]. It was also confirmed that when XyG is missing, pectins and xylans replace its role in cell wall biomechanics. The growth reduction in *xx1*/*xx2* plants may stem from the reduced effectiveness of α-expansin in the absence of XyG [13]. These results represent the complexity of the study of individual components in a plant cell wall matrix, it is necessary to point out the advantage of using multiple assays for a better comprehension in the wall extensibility function.

3.2.2. Xylans

Xylans are a diverse group of polysaccharides with the common backbone of β-(1,4)- linked xylose residues, with side chains of *α*-(1,2) linked glucuronic acid and 4-*O*-methyl glucuronic acid residues. Composition and distribution of the substitutions is wide variable according to the plant cell species. Xylans usually contain many arabinose residues attached to the backbone which are known as arabinoxylans and glucuronoarabinoxylans; high amounts of arabinoxylans are present in the endosperm of cereals [14]. In graminaceous species xylans may be linked to the cellulose microfibrils as the xyloglucan does in dicotyledonous plants, but the side chain branches are not attached; besides, the content of lateral substituents decrease gradually during cell growth.

3.2.3. Mannans and glucomannans

The β-(1,4)-linked polysaccharides rich in mannose or with mannose and glucose in a non-repeating pattern are the glucomannans and galactoglucomannans. Even though their presence in primary cell wall is low, mannans have been studied in their role as seed storage compounds, as evidenced by the embryo lethal phenotype in an *Arabidopsis* mutant that is lacking the major (gluco) mannan synthase in seeds [15].

3.3. Pectins

Pectins represent an outstanding family of cell wall polysaccharides with extraordinary versatile, but not yet fully known structures and functions. In plants the functions of pectins fulfills important biological functions such as: growth, development, morphogenesis, defense, cell–cell adhesion, wall structure, signaling, cell expansion, wall porosity, binding of ions, growth regulators and enzymes modulation, pollen tube growth, seed hydration, leaf abscission, and fruit development [16]. The extracted pectins of citrus peel and apples are used as a gelling and stabilizing agent in food and cosmetic industries. Pectins within the fruits and vegetables are part of the daily dietary fiber and have multiple positive effects on human health including lowering cholesterol, serum glucose levels, decrease occurrence of diabetes and cancer [17-19]. This points the relevance of pectins in diverse emerging fields of study, even in human health.

Pectins are the most wide complex family of polysaccharides in nature. They are present in primary walls of dicots and non-graminaceous monocots with approximately 35%; in grass and other commelinoid primary walls 2-10% and up to 5% in walls of woody tissues [20]. Pectins are formed with *α*-(1,4)-D-galacturonic acid residues. Galacturonic acid (GalA) comprises approximately 70% of pectin linked at the *O*-1 and the *O*-4 positions [16]. The structural classes of the pectic polysaccharides include homogalacturonan (HG), rhamnogalacturonan I (RG-I), and rhamnogalacturonan II (RG-II). Also xylogalacturonan (XGA) and apiogalacturonan (AGA) have been determined. AGA is found in the walls of aquatic plants such duckweeds (*Lemnaceae*) and marine seagrases (*Zosteraceae*) with apiose residues 2,3-linked to homogalacturonan. The XGA is more abundant, has HG substituted

by D-xylose residues which has been determined in multiple species such as marine seagrasses, pea, apple, *Arabidopsis*, soybean with *O*-3 xylose and xylose branches at *O*-2 by another xylose residue [10].

3.3.1. Homogalacturonan

Homogalacturonan (HG) is the most abundant polymer of the pectins, it comprises nearly the 60% of pectins in plant cell wall [20]. HG is formed by long chains of linear 1,4-linked α-D-galacturonic acid, some of the carboxyl groups are partially methyl-esterified at C-6 and acetyl-esterified at positions *O*-2 and/or *O*-3 (Figure 2), depending on plant species. The linear units of HG in which more than 50% of the GalA are esterified with methyl (or methoxy) groups at the C-6 position are conventionally called high methyl-esterified HGs; otherwise they are referred as to low methyl-esterified HGs. The unmethylated HG is negatively charged and may ionically interact with Ca^{2+} to form a stable gel with other pectin molecules if 10> consecutive unmethyl-esterified GalA residues are coordinated; this is called the egg box (Figure 3). The egg box model can occur upon Ca^{2+} inducing gelling approximately in 70% of the pectin in plant cell walls [21].

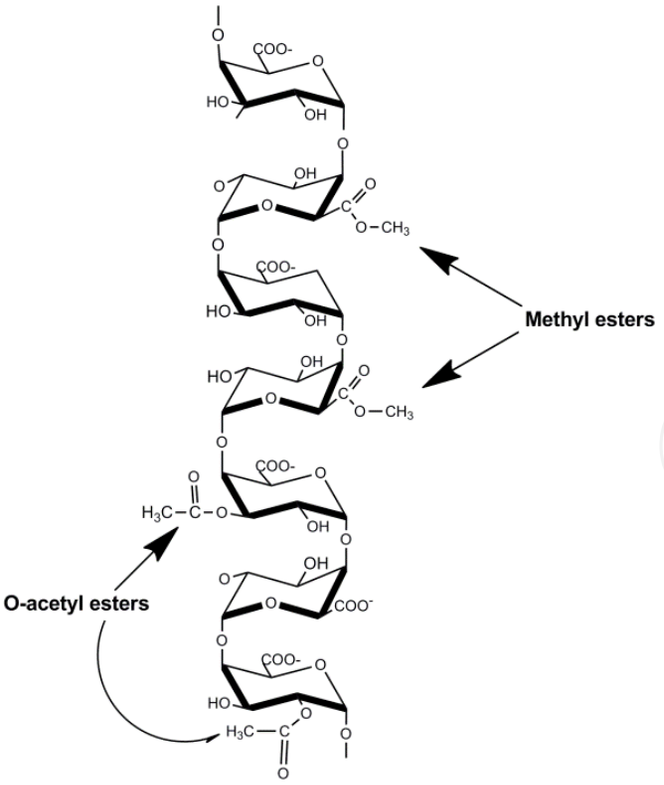

Figure 2. Homogalacturonan structure. Homogalacturonan is a linear polymer of α-(1,4)-D galacturonic acid with methyl-esterified at C-6 and acetyl-esterified at positions O-2 and/or O-3.

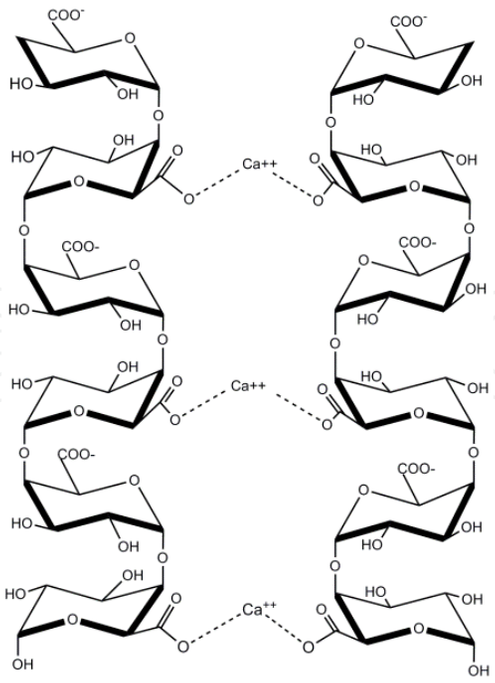

Figure 3. The egg-box model of calcium crosslinking in homogalacuronan polysaccharides.These properties favor the gellification process, therefore have been used by food technologists for the preparation of jams, candies and processed fruits products. The gels obtained using highly methyl-esterified HGs have a short and compact structure, are transparent and achieve a good preservation of original flavors; such gels are thermo-reversible. On the opposite, the low methyl-esterified HGs are thermally irreversible gels and only gell in the presence of multivalent ions (Ca^{2+}, Mg^{2+}).

3.3.2. Pectic branched polymers: Rhamnogalacturonans-I and Rhamnogalacturonans-II

Rhamnogalacturonan-I (RG-I) is a family of pectic polysaccharides that represent 20-35% of pectin. It contain a backbone of the repeating disaccharide galacturonic acid and rhamnose: [α-(1,2)-D-GalA-α-(1,4)-L-Rha]$_n$ partially substituted *O*-4 and/or *O*-3 positions of α-L rhamnose residues with single neutral glucosyl residues and with polymeric side c hains predominantly of α-(1,5)-L arabinans and β-(1,4)-D galactans, arabinogalactans-I (AG-I), arabinogalactans-II (AG-II) and possibly galacto-arabinans [22]. The backbone may be *O*-acetylated on C-2 and/or C-3 by α-L-rhamnose residues. In contrast, there is no compelling evidence that the residues are methyl-esterified, however, an enriched RG-I like wall fraction from flax has been reported to contain methyl esters [23]. The predominant side chains contain linear and branched α-L-arabinose and/or β-D-galactose residues [20] these two are linked to approximately half of the rhamnose residues of the RG-I backbone (Figure 4). The side chains showed a great heterogeneity according to the plant sources; the α-L-fucose, β-D-glucuronic acid and 4-*O*-methyl β-D-glucuronic acid, as ferulic and coumaric acid may be present [24]. The core of the polymeric side chains does not generally exceed 50 GalA residues although there are some exceptions like the galactan isolated from tobacco cell walls, with 370 units [25]. RG-I side chains are developmental and tissue-

specific differentially regulated in the type of terminal sugars and oligosaccharides attached to the backbone, it is not well understood but suggests diverse functional specialization. Besides, the rhamnose residues may range from 20 to 80% depending on the pectin, plant source and extraction method [24]. It was suggested the RG-I functions as a linkage support to other pectic polysaccharides such as HG and Rhamnogalacturonans-II (RG-II), that are covalently attached as side chains [10].

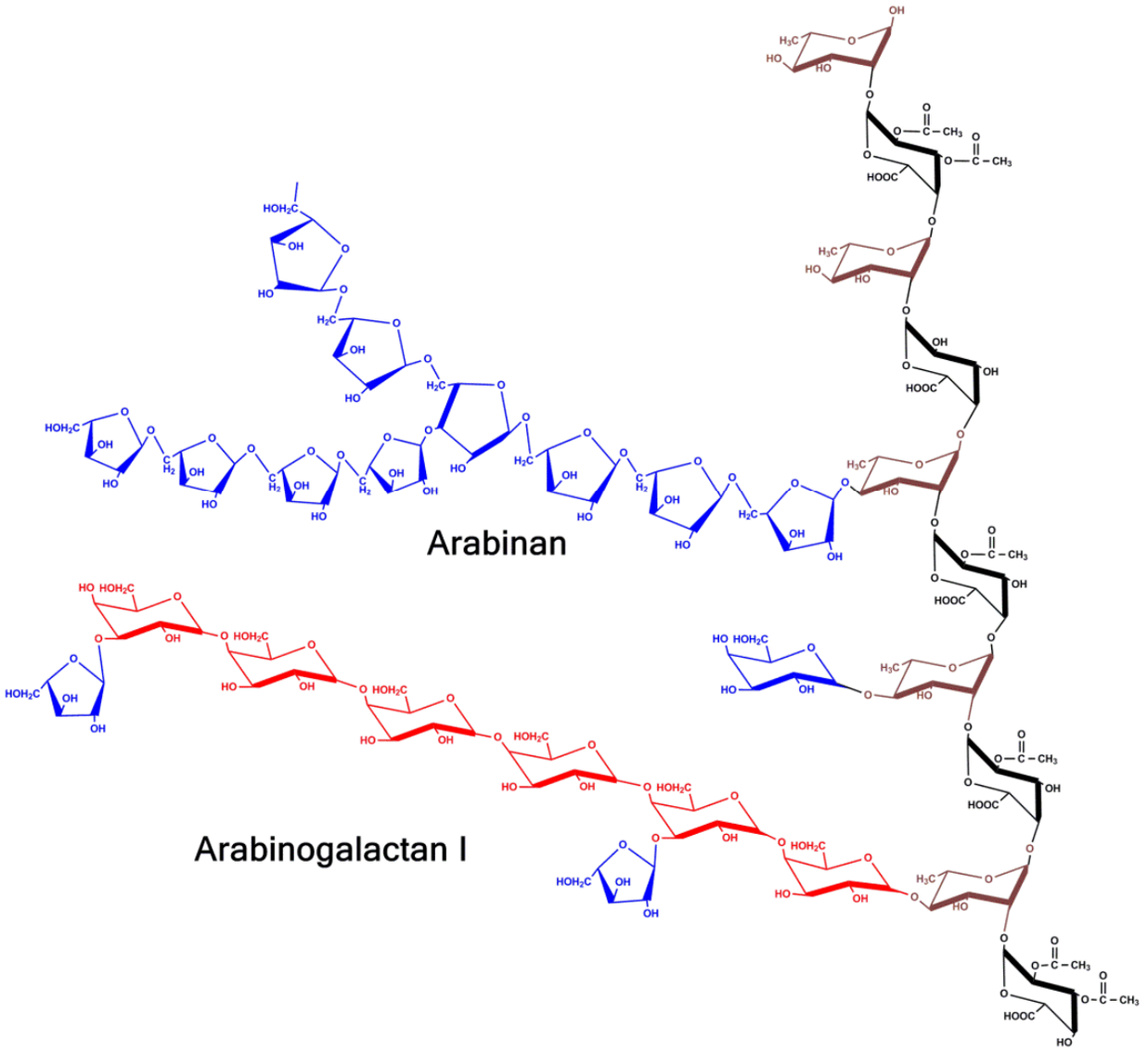

Figure 4. Major structural features of Rhamnogalacturonan I. The backbone is composed of the disaccharide repeating unit of α-(1,2)-D-Galacturonic Acid-α-(1,4)-L-Rhamnose. Branched oligosaccharides composed predominantly of α-L arabinose, in blue; and/or β-D-galactose residues, in red.

Rhamnogalacturonans-II are the most complex and branched polysaccharides of pectin. RG-II is a minor pectic component of plant cell walls with between 0.5 to 8% in dicots, non-graminaceous, monocots, and gymnosperms, and less than 0.1% in primary walls of

commelinoid monocots [26]. The RG-II has a characteristic structure of seven to nine residues of α-D-galacturonic acid backbone with four branches clearly differentiated designated A, B, C and D (Figure 5).

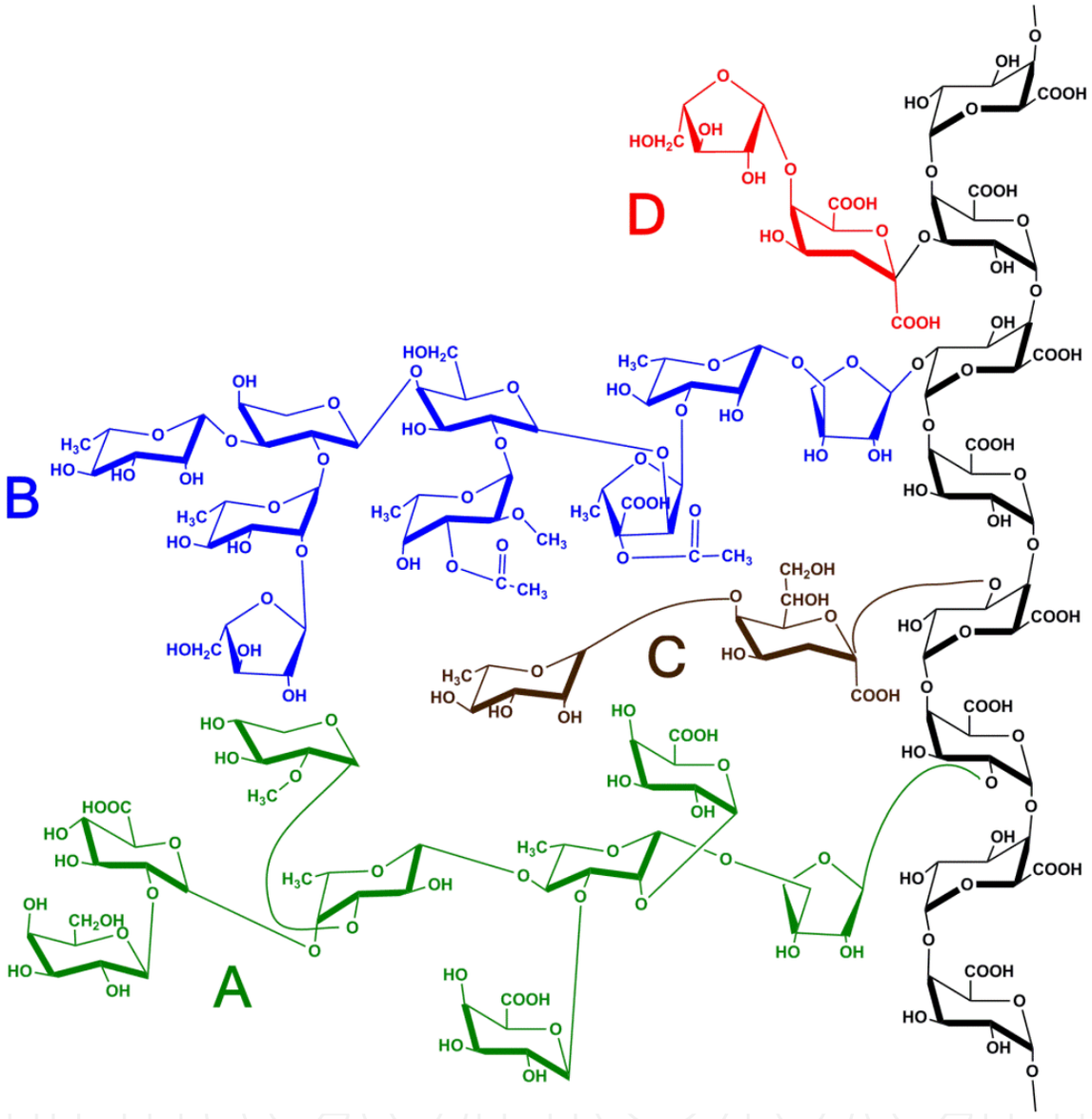

Figure 5. Structure of Rhamnogalacturonan II. The backbone of RG-II is composed of α-(1,4)-D-Galacturonic Acid residues. Four structurally different oligosaccharide side chains linked to the RG-II are represented in different colors (A-D).

RG-II has several kinds of substituents including 11 to 12 different glycosyl residues, some of them rare sugars in nature, like 2-*O*-methyl xylose, 2-*O*-methyl fucose, aceric acid, 2-keto-3-deoxy-D-lyxo heptulosaric acid (Dha) and 2-keto-3-deoxy-D-manno octulosonic acid (Kdo) [27-30]. About 28-36 individual sugars, interconnected by more than 20 different glycosidic linkages that makes a highly complex polymer with an α-D-galacturonic acid backbone partially methyl esterified at C-6 with galactosyl residues and branched with oligosaccharide chains [31]. Despite the complex structure and low amount of the RG-II, it

has been related with important and specific roles in cell walls. RG-II polymers are self-associated with borate forming borate-cross-linked RG-II dimers firstly demonstrated in complexes derived from sugar-beet [32], which contributes to the mechanical properties of the primary wall with the three-dimensional pectic network *in muro* [33]. Nearly 95% of the RG-II polymers are in the dimmer complex form (dRG-II). The combination of the covalent crosslinking among the pectic polymers HG, RG-I and RG-II sets the network of the plant cell wall, bringing together strength, flexibility and functionality to the cells.

4. Biosynthesis of the plant cell wall polymers

Cell wall biosynthesis begins during cell division in the cytokinesis phase through the formation of the cell plate in the middle of the cell. Eventually, the primary cell wall is assembled by the deposition of polymers of cellulose, hemicelluloses and pectin. The biosynthesis of wall polymers starts in the nucleus with the transcription of genes coding for wall-related proteins and enzymes. Individual elements are channeled into the endomembrane system of endoplasmic reticulum and Golgi apparatus where they are polymerized and modified. The former polymers are then transported through vesicles and secreted outside plasma membrane for subsequent assembling and linkage to the wall. This mechanism is highly regulated along the process and depends on the physiological state of the cell and the interplay of signals going in and out of the cell [34].

Specifically, the long and rigid cellulose microfibrils of plant walls are synthesized from the inner face of the plasma membrane by cellulose synthase (CESA) complexes, which comprise multiple subunits forming a rosette structure of six globular CESA-containing complexes each of which synthesizes growing cellulose chains of 6–10 cellulose molecules (For review, see [4]). Newly synthesized microfibril is propelled by the action of the CESA, which polymerize the glucan chains in the specific positions driven by cortical microtubules [35]. Afterwards, microfibril is linked with xyloglucans (XyG) and pectic polysaccharides to form the cell wall complex network. Matrix polysaccharides not only cross-link microfibrils but also prevent the self association of new microfibrils into larger aggregates. XyG interacts with the formed microfibrils in the surface and also may be trapped inside them [36]. It has been observed that in primary walls, microfibrils linked to xyloglucan are smaller in diameter (less chain per fiber) than those in secondary walls. Besides, the binding between XyG and cellulose is known to weaken cellulose networks but increase their expansibility. The XyG is bound differently to three cellulose microfibrils domains. The first is available to endoglucanases, the second has to be solubilized by concentrated alkali and a third XyG is neither enzyme accessible nor chemical [36]. According to this, the type of hydrolysis used to obtain the fractions of polysaccharides (oligosaccharides) in some assays results in products of different degree of polymerization, which is related to some specific biological functions in the cell.

In contrast to cellulose, pectic polysaccharides are synthesized in the Golgi apparatus of the plant cell, and then are secreted to the apoplastic space through vesicular compartment.

Polysaccharides are transported from cis-face to trans-face of the Golgi where they are sorted and packaged into vesicles of the trans-Golgi network for transport to the plasma membrane. The movement of the vesicles containing the polymers is presumably along actin filaments that have myosin motors. It is no clear, how the synthesis of the pectin polysaccharides is initiated or whether lipid or protein donors are involved. The possible modification of the pectic glycosyl residues may be esterification, *O*-mehtylation, acetylation and feruloylation by feruloyltransferases in some *Chemopodiaceae* species [16].

To complete the biosynthesis of polysaccharides, it is necessary the assembly of the transported elements to form the functional matrix. This event involves both enzymatic and non-enzymatic mechanisms in the apoplast [37]. The physicochemical properties existing in the wall are dependent on the hydrophobic and hydrophilic domains given by the water and solutes. The hydrophobic domain is formed by the link of cellulose microfibrils to the hydrogen bonds that lead the exclusion of water from the interacting chains. The hydrophobic interactions may also be controlled by enzymes that diminish the branching of the xyloglucan linked to cellulose microfibrils such as xylosidases and glucanases [38]. Meanwhile, the hydrophilic domain of the wall is given by pectin polymers. Together, both domains contribute to the protoplast matrix medium leading the rearrangement of some polymers as the homogalacturonan. Linear homogalacturonans are synthesized in a highly methyl-esterified form in the Golgi and transported to the wall in membrane vesicles to be desesterified by wall localized pectin methylesterases. The conversion of the HG from the methylesterified form to the negatively charged form has been associated with the decrease of growth [39].

The glycosiltransferases and hydrolases are enzymes localized in the Golgi apparatus and work together to produce the xyloglucan precursors. Some changes take place after the synthesis of hemicelulloses in the Golgi. It has been shown that a specific apoplastic glycosidases are responsible for the trimming of new xyloglycan chains and this determines the heterogeneity of the polymer in the cell wall [6]. Hydrolases are likely to play an important role in determining hemicelluloses structures in the cell wall, and are coexpressed with polysaccharide biosynthetic enzymes. For detailed information about the cell wall related enzymes see [4,6,10,16,40].

In the last decades many biochemical approaches have enabled the identification and characterization of the structure of cell wall polymers and the enzymes involved in their biosynthesis. Beside classical molecular analyses, the development of *Arabidopsis thaliana* mutants has been a breakthrough to reveal specific functions of certain components of the wall. The advances in the determination of the structures of polymers through microscopy provide one of the best views of the organization and structure allowing the development of different plant cell wall models. Immunolocalization studies also have shown the location of some polysaccharides within the cell wall and in the apoplastic region. For instance, low methyl-esterified HGs are located in the middle lamella at the cell corners and around air spaces, whereas high methyl-esterified HGs are present throughout the cell wall [20]. Therefore, non-destructive methodologies such as NMR have been key techniques for elucidating the topology, dynamic and tridimensional arrangement of some cell structures, contributing to the cell wall knowledge.

5. Biological activity of plant cell wall derivatives

Exhaustive studies on the structure and function of the plant cell wall have led to the discovery of biologically active molecules derived from its polymeric carbohydrate components. These molecules are found in nature and can be released by acid, basic or enzymatic hydrolysis of the primary cell wall polysaccharides. Due to the complex combination of carbohydrate polymers in the cell wall of plants, there are variations among the physicochemical structure of hydrolyzed fragments, which exerts striking differences on activity and specificity to regulate some physiological processes in plants. These plant oligosaccharides with regulatory properties were called oligosaccharins and have been extensively studied by the workgroup of Albersheim since the mid-70s (reviewed in [41]). Among the oligosaccharins derived from plants, the most active and therefore the most studied are those derived from pectins and hemicelluloses, whose main regulatory functions depend on the degree of polymerization, chemical composition and structure, and can be divided in two broad categories: activation of plant defense mechanisms and plant growth and development.

In order to exert their regulatory properties, oigosaccharins must be first recognized by specific plant cell receptors which may be lectin-type proteins capable of transmitting the signal into the cell [42]. Even when the complete recognition mechanisms and signaling pathway for plant-derived oligosaccharins is far from being fully understood, protein receptors that recognize these molecules have been characterized in the model plant *Arabidopsis thaliana* [43-44] and its believed the downstream processes may occur via MAP kinases activity [45] (For review about the detailed perception mechanisms of oligosaccharines by plants, see [46]).

5.1. Pectin-derived oligosaccharins

Even when the most abundant component of pectins is the galacturonic acid, partial depolymerization of the pectic polysaccharides generates fragments that may (or not) contain other residues such as rhamnose, galactose, arabinose, xylose, glucose and mannose [20]. This combination confers variability to the structure, and thereby to the biological activity of the oligosaccharins. The oligosaccharins derived from homogalacturonan are called oligogalacturonides (OGAs), which are linear oligomers of galacturonic acid, where some residues may be methyl-esterified or acetylated. OGAs are elicitors of defense responses in plants, triggering the synthesis and accumulation of phytoalexins (antimicrobial compounds) and other molecular indicators of the activation of defensive patterns, such as the induction of pathogenesis related proteins and genes related to the hypersensitive reaction [47]. OGA-induced defense response patterns are summarized in Table 1.

OGAs trigger the rapid accumulation of reactive oxygen species (ROS) in plants, which is necessary for the deposition of callose, polysaccharide produced in response to wounding and pathogen infection. Furthermore, ROS are signaling molecules of several intracellular events. Therefore it was proposed ROS were involved in the OGA-induced resistance

against fungal pathogens in three different ways: (1) directly exerting a cytotoxic effect to the invading pathogen, (2) inducing callose deposition for reinforcing the plant cell wall, and (3) mediating the signals leading to the expression of defense related genes and defensive metabolites [48]. Nevertheless, recent findings in *Arabidopsis thaliana* showed that the defensive gene activation was not directly correlated to the accumulation of hydrogen peroxide, and that OGA-induced resistance against the fungal pathogen *Botrytis cinerea* was independent of both the oxidative burst and callose deposition [49].

BIOLOGICAL ACTIVITY	PD	ORGANISM	REFERENCE
Defense Responses			
Phytoalexin synthesis	8-13	*Glycine max*	[77]
	3-12	*Glycine max*	[78]
	≥ 3	*Petroselinum sativum*	[79]
	9-15	*Phaseolus vulgaris*	[80,81]
Induction of phenylalanine ammonia-lyase	> 9	*Daucus carota*	[82]
	9-15	*Phaseolus vulgaris*	[80,81]
Induction of chalcone synthase	9-15	*Phaseolus vulgaris*	[81]
Induction of β-(1,3)-glucanase	≥ 3	*Petroselinum sativum*	[79]
Lignin synthesis	8-11	*Cucumis sativus*	[83]
	9-15	*Phaseolus vulgaris*	[81]
Protease inhibitors synthesis	2-3	*Lycopersicum esculentum*	[84]
Growth and Development			
Induction of ethylene production	5-19	*Lycopersicum esculentum*	[85]
	5-19	*Pyrus communis*	[86]
Steem growth inhibition	> 8	*Pisum sativum*	[87]
Protease inhibitors synthesis	10-14	*Nicotiana tabacum*	[88,89]
Quality Parameters			
Increase of the color and anthocyanin content	3-20	*Vitis vinifera*	[91]

Table 1. Biological activity exerted by oligogalacturonides with respect to the degree of polymerization

Plants treated with OGAs exhibit an enhanced resistance to pathogen infections. The induction of the defensive genes, peroxidase and β-(1,3)-glucanase has been related to the enhanced resistance of OGA-treated *Arabidopsis thaliana* against *Botrytis cinerea* [50-51]. Peroxidases are associated to the plant cell wall reinforcement by the synthesis of lignin, while β-(1,3)-glucanase could affect mycelium growth by hydrolyzing glucan chains from the wall of fungi [50]. In grapevine (*Vitis vinifera* L.), OGAs highly stimulated the enzymatic activity of chitinase and β-(1,3)-glucanase and induced the expression of defense related genes in different extent, which also led to a protection against *Botrytis cinerea* [47]. Some genes related to the formation of phytoalexins from the phenylpropanoid pathway were expressed rapidly and transient, various chitinase isoforms were expressed rapidly but their induction was more sustained, and some inhibitors of fungal hydrolytic enzymes were up-regulated later.

The degree of acetylation and methylation of OGAs has been less addressed but emerging research showed the influence of these functional group substituents on plant defense responses. The effect of the degree of acetylation of OGAs on the elicitation of defenses in wheat (*Triticum aestivum* L.) was studied by Randoux and coworkers [52]. It was found both acetylated and unacetylated OGAs induced accumulation of hydrogen peroxide at the site of fungal penetration, through activation of oxalate oxidase, which is also related to the enhanced peroxidase activity. Besides, the induction of lipoxigenase activity demonstrated the stimulation of the octadecanoid pathaway. Moreover, transgenic strawberries (*Fragaria vesca* L.) producing partially demethylated OGAs displayed an enhanced resistance against *Botrytis cinerea* [53].

Table 1 shows that OGAs modulate diverse growth and developmental processes in plants. Early responses related to the signaling transduction pathways comprise membrane depolarization, cytosolic acidification, apoplast alkalinization and calcium mobilization at the plasma membrane level, due to the activity of Ca^{2+} channels. Calcium ions are very important second messengers in plants and its level in intracellular compartments is determinant for the kind of physiological response. In tobacco cells OGAs induced different patterns of Ca^{2+} influx into cytosol, mitochondria and chloroplasts [54]. The increase in cytosolic free Ca^{2+} has been proposed to mediate the regulation of stomatal aperture and production of hydrogen peroxide in the guard cells of tomato (*Licopersicon esculentum* L.) and *Commelina communis* L. [55]. Calcium may also directly interact with long-sized OGAs promoting the formation of structures with an "egg-box" conformation, which may potentiate their biological activity [56]. Nevertheless the promotion of vegetative shoot formation in *Nicotiana tabacum* explants has been observed to be independent of exogenous Ca^{2+} [57].

OGAs regulate morphogenesis in plant tissues in a process associated with the action of auxins, which are growth-regulating phytohormones. Particularly, OGAs and auxins appear to play an antagonist role; since OGAs inhibit the expression of some auxin-inducible genes steps downstream of the auxin perception [58]. In this sense, root differentiation induced by OGAs was studied in *Arabidopsis thaliana* seedlings, where treatments decreased trichoblasts length but increased the number and length of root hairs [59]. Similar results were found in maize (*Zea mays* L.) seedlings where OGAs inhibited coleoptile growth and modified root architecture by inducing lateral root formation [59]. The growth inhibitory activity exerted by OGAs seems to be caused by (1) inhibition of cell elongation; since cell division in the primary root meristem is not altered [59] and (2) inactivation of a kinase enzyme implicated in the TOR signaling pathway, which integrates nutrient and growth factor signals in eukaryotic cells [60]. On the contrary OGAs induced primary root length growth in alfalfa (*Medicago sativa* L.) seedlings [61], which confirms that OGA-inducing activities are dependent on the plant species perceiving the signal.

Interestingly, the structure and stimulating activity of a rhamnogalacturonan I-derived oligosaccharide (RG-IO) isolated from flowers of *Nerium indicum* Mill. was investigated [62]. The structural features of the oligomer consisted in a rhamnogalacturonan backbone with

several branches *O*-4 linked to L-rhamnose residues. To determine the structure of the branches the oligomer was partialy hidrolized and analyzed by mass spectrometry (ESI-MS). Branches were found to be mainly composed by β-(1,4)-D-galactan, a highly branched arabino β-(1,3;1,6)-D-galactan, and α-(1,5)-L-arabinan. Furthermore, RG-IO stimulated *in vitro* the production of nitric oxide in macrophage cells. Removal of some side chains from RG-IO reduced nitric oxide production, pointing out the relevance of the branches for its biological activity.

5.2. Hemicellulose-derived oligosaccharins

Xyloglucan is the main hemicellulosic component of the plant cell wall. Biological effects of xyloglucan derivatives are related to the intrinsic physiological function of polymeric xyloglucan in plant cells, comprising the control of extensibility and mechanics of the cell wall and cell expansion. Most research in this field highlights their regulatory activity on cell growth and elongation, which relies in the molecular size, distribution, and levels of substituted xylosyl units with galactosyl and fucosyl residues [63]. It has been observed active xyloglucan oligomers (XGOs) accelerate cell elongation in peeled stem segments of *Pisum sativum* [64], and in suspension-cultured cells of *Nicotiana tabacum*, expansion led to cell division [65]. On the contrary, treatments with polymeric xyloglucan suppressed cell elongation [64-65], indicating that molecular size is a determinant factor of response specificity.

Xyloglucan-derived octasaccharides promoted growth of coleoptiles in wheat seedlings and induced a rapid increase of α-L-fucosidase activity in *Rubus fruticosus* protoplasts [63]. In wheat immature embryos a xyloglucan-derived pentasaccharide induced rhizogenesis and stimulated the formation of callus and meristematic zones [66]. A fucose-galactose-xylose trisaccharide fragment of xyloglucan inhibited ethylene biosynthesis, stimulated embryogenesis in cell cultures of cotton (*Gossypium hirsutum* L.) and formation of callus [67]. In contrast, a mixture of XGOs induced ethylene production in whole fruits of persimmon (*Diospyros kaki* L.). Interestingly, non-fucosylated XGOs augmented ethylene levels in a greater extent than fucosylated XGOs [68]. Also, XGOs lacking the fucosyl residue were inactive to modulate potato resistance to disease [69], and to inhibit gibberellic acid-induced elongation of pea (*Pisum sativum* L.) epicotyls [70], when compared to fucosylated XGOs. These observations altogether may provide a clue to a better understanding of the relationship between the presence of certain substituents and the sensitivity of the response.

On the other hand, galactoglucomannan is composed by a backbone of glucose and mannose residues with side chains of galactose. More recent research about cell wall oligosaccharides derivatives has demonstrated a growth-regulating activity of galactoglucomannan-derived oligosaccharins at very low concentrations. Galactoglucomannan oligosaccharides (GGMOs) modulate root morphology in mung bean (*Vigna radiata* L.) [71] and *Karwinskia humboldtiana* [72] by a respective induction or inhibition of adventitious root formation. More recent research found GGMOs inhibited lateral roots formation but stimulated

their elongation, without any effect on adventitious root elongation in mung bean seedlings [73].

Furthermore, GGMOs inhibited the elongation induced by exogenous phytohormones of pea stem segments [74], root and hypocotyl growth of mung bean [71, 73] and *K. humboldtiana* roots [72], indicating an antagonist activity of GGMOs against growth regulators, such as 2,4-dichlorophenoxyacetic acid, indole-3-acetic acid, indole-3-butyric acid, 1-naphthaleneacetic acid and gibberellic acid, at different extent. In addition, an increase in the activity of cell wall associated peroxidases has been reported during the GGMO-mediated inhibition of the elongation of hypocotyls in mung bean plants [73] and epicotyls in peas [75]. Which suggests the growth inhibition caused by GGMOs may be the result of processes catalyzed by plant cell wall peroxidases.

5.3. Cellulose-derived oligosaccharins

During many years it was thought that only non-cellulosic oligosaccharides derived from plant cell wall were biologically active. Surprisingly, it has been recently demonstrated that fragments of oligosaccharides released during cellulose degradation, called cellodextrins (CD), induce a variety of defense responses in grapevine cells. CD are oligomers of linear β-(1,4)-linked glucose residues. The induction of oxidative burst, transient elevation of cytosolic Ca^{2+}, expression of defense-related genes, and stimulation of chitinase and β-1,3-glucanase activities were triggered by CD in grapevine cells. Also, CD oligomers with a degree of polymerization ≥7 enhanced protection in detached leaves of grapevine against *Botrytis cinerea*, suggesting CD are important elicitors of defense reactions [76]. These results have opened the door to the study of many other biological processes where CD may be involved and to elucidate their action mechanisms in plants.

6. Current applications of plant cell wall-derived oligosaccharins

Increasing knowledge of the factors that modulate the biological activity of cell wall-derived oligosaccharides has naturally led to the development of technologies aimed to exploit the potential of these molecules in different fields. The first successful applications occurred in agriculture, where different crops can now be treated with commercially available preparations of pectin-derived-oligosaccharins in order to enhance the basal resistance of plants, and decrease the possible losses related to phytopatogenic infections. Another alternative is the use of oligosaccharins to improve the yield, as seen in tomato (*Lycopersicum esculentum* Mill.), where foliar treatments increased fruit yield by up to 40% with respect to the non-treated controls, and improved parameters of quality such as soluble solids content (SSC), acidity and firmness [90]. Encouraging results were found in *Vitis vinifera* L., since preharvest treatments of clusters with pectin-derived oligosaccharides enhanced the red color of table grapes cv. 'Flame Seedless' without affecting berry firmness neither SSC. Berry color enhancement was achieved due to a

higher anthocyanin content in berry skin, given by the stimulation of the phenylpropanoid pathway [91]. Recent findings showed an increase in the antioxidant capacity of OGA-treated table grapes cv. 'Red Globe' and 'Flame Seedless', as a consequence of the induction of anthocyanins, flavonoids and phenolic compounds (non-published data). As a result of this research it was generated a register method for controlling coloration in table grapes based on oligogalacturonide (92). On the other hand, OGAs are currently being used in the industry of cosmetics. This emerging trend is based on the ability of OGAs to stimulate adhesion of keratinocytes to proteins of the dermoepidermal junction. This biological effect is apparently exerted by OGAs with a degree of polymerization ≤ 5 as indicated in the US patent [93]. However, further research is necessary to continue with the development of reliable applications.

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Acknowledgement

The authors appreciate the support of Juan Reyes Calderón with the edition of the figures shown in this chapter.

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