Structural Diversity and Application Potential of Hemicelluloses

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Summary: Isolation and targeted modification of plant polysaccharides as well as characterization of their structural, molecular and functional properties represent an important research topic of the Institute of Chemistry, Slovak Academy of Sciences, in Bratislava. The presentation provides an overview about the occurrence, structural diversity and functional properties of hemicelluloses representing a diverse group of plant cell wall polysaccharides. They are grouped into xyloglycans, mannoglycans, xyloglucans, and mixed-linkage β-glucans. Based on own results as well as on reported data from other research groups, the structure—property relations of the hemicelluloses as well as the existing and potential applications of these polysaccharides are discussed.

Keywords: applications; biopolymers; hemicelluloses; rheology; structure-property relations

Introduction

The Institute of Chemistry was founded in 1953 by fusion of the former Research Institute for Pharmacy and Biochemistry and the Institute for Sugars and Carbohydrates, and incorporated in the newly established Slovak Academy of Sciences. Later the Institute of Wood and Cellulose Technology was incorporated. Up to 1962, basic research in the Institute of Chemistry was primarily directed to support various areas of the post-war growing economy in Czechoslovakia, such as the food, pharmaceutical, wood, pulp, paper and fiber industries. At this time started the research of plant polysaccharides, namely starch, pectin, cellulose, and hemicelluloses.

Since 1963 the research became definitely specialized on chemistry, biochemistry of carbohydrates, chemistry of the main wood components (cellulose, hemicellulose, lignin) and alkaloids with the main emphasis on basic research. New reaction pathways for the synthesis and transformation of monosaccharides as well as efficient methods for the synthesis of oligosaccharides have been developed. The oligosaccharides and their derivatives served as model compounds for structural studies of mainly xylan-type polysaccharides and for development of the advanced NMR spectroscopy, gas chromatography and mass spectrometry techniques as well as for biochemical studies. Quantum chemistry methods have been developed for conformation analysis. Except of seven scientific departments, three research supporting units also were established: department of analytical chemistry, information and library centre, and the pilot plant unit for production of rare saccharides and some plant polysaccharides (beechwood xylan, polysaccharides with covalently bound dyes for enzymology). Moreover, the Institute has been housing the Culture Collection of Yeasts (CCY), which is preserving about 3500 strains including 350 type species, and registered in the World Directory of Collections of Cultures of Microorganisms under No. 333. For industrial, research and scientific institutions, the yeast strains has been available on request up to now.

In spite of heavy emphasis on applied aspects of research during 1975–1989, the Institute maintained the dominance of

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fundamental investigations. After the political changes in 1989 and 1990, the research has been strongly directed at the relationship between structure and function of carbohydrates in biological systems, because of increasing interest in this group of compounds. This orientation still continues and concerns not only plant and microbial polysaccharides but also synthesis of biological important saccharides. Polysaccharides have been investigated in relation to their immunological and antitussive activities as well as other functional properties, to plants protection, and applicability in biotechnology and medicine.

Some projects have been focused on transformation of polysaccharides to various derivatives, applicable as additives for food, textile, pharmaceutical, and other industrial branches. Targeted modification of polysaccharides served to produce affinity carriers, applicable in clinical chemistry, biochemistry and biotechnology. Along with the variety of research activities in chemistry, physical and analytical chemistry, investigations in the field of enzymes systems degrading plant and microbial polysaccharides have lead to important results in the area of pectolytic, xylanolytic and cellulolytic enzymes, which are relevant to the development of ecologically feasible biotechnologies.

The Institute has become internationally recognized as a strong research establishment specialized in chemistry and biochemistry of carbohydrates in central Europe. It has been engaged in a broad range of international scientific cooperation and contract research with many countries from all continents. The main fields of research of the Institute are currently:

(i) Synthesis and structure of biologically significant mono- and oligosaccharides,
(ii) Plant polymers and microbial polysaccharides as biologically active substances and functionally fashionable polymers,
(iii) Glycanases - structure, function and mechanism of action,
(iv) Polysaccharides for enzyme engineering - functional properties,
(v) Structural and metabolic study of plant cells, tissues and organs.

More detailed information about the Institute of Chemistry are available on the Website: www.chem.sk.

One of the research topics of the Institute of Chemistry comprises the study of plant cell wall polysaccharides classified as hemicelluloses. Hemicelluloses, accounting for 20 to 30% of the biomass of annual and perennial plants,[1] have emerged as an immense renewable resource of biopolymers. During the last decade, an outstanding increasing interest of scientists from universities, research institutes as well as industrial companies in research of biopolymers from renewable sources can be noticed. Shortage of the natural energy sources and replacement of petroleum-based products, which is connected with the demands for solution of the worldwide environmental problems, are the main driving forces for these activities. Since usually only one fraction (mainly cellulose or starch) of the annual harvest of plant material produced by forests and agricultural lands is being utilized, conversion of the hemicelluloses to useful products may provide a fundamental solution to the problems mentioned above. However, a prerequisite is the knowledge of the hemicellulose components of plants hitherto utilised in well-established economics as well as of those traditionally used in nourishment or healing in agriculturally underdeveloped countries. Of importance are also the non-utilized agricultural plant residues, which as such represent 'secondary resources' for the production of biopolymers.

Together with cellulose and pectic polysaccharides, hemicelluloses belong to the building components of the cell walls of higher plants, where they are associated with varying levels of proteins and phenolics.[2] Depending on the plant species and the present cell walls creating according to the various functions in plants cells, tissues, and organs, the hemicellulose components might differ greatly in content and structural features.[3] In the past, the research activities in the field of hemicellulose were aimed mainly to utilize the plant biomass by conversion into sugars, chemicals, fuel and as sources of heat energy. However, hemicelluloses are also attractive as biopolymers, which can be utilized in their native or modified forms in various areas including food and non-food applications. The aim of the present article is to present an overview about the structural diversity and application possibilities of hemicelluloses.

Hemicelluloses – Classification and Structural Diversity

Hemicelluloses are usually divided into four general groups of structurally different polysaccharide types:

(i) Xyloglycans (Xylans),
(ii) Mannoglycans (Mannans),
(iii) Xyloglucans, and
(iv) Mixed-linkage β-glucans.

All of them occur in many structural variations differing in side chain types, distribution, localization and/or types and distribution of glycoside linkages in the main macromolecular chain.[4]

Xyloglycans (Xylans)

Xylans, belonging to the most abundant hemicellulose type in the plant kingdom, can be grouped in to several structural sub-classes: (i) homoxylans, (ii) glucuronoxylans, (iii) (arabino)glucuronoxylans, (iv) arabinoxylans, (v) (glucurono)arabinoxylans, and (vi) heteroxylans. The occurence and structural varieties of the sub-classes has been reported in detail in previous review papers.[4,5]

Homoxylans

Homoxylans are linear polysaccharides composed of D-xylopyranosyl (Xylp) residues linked by β-(1 → 3)-linkages (X3), β-(1 → 4)-linkages (X4) and/or mixed β-(1 → 3, 1 → 4)-linkages (Xm), as illustrated in Figure 1.

Types X3 and Xm are common in some seaweeds such as in red algaes (*Nemiales* and *Palmariales* sp.) and green algaes (*Caulerpa* and *Bryopsis* sp.), where they substitute cellulose as the skeletal polymer of the cell walls (CW). Homoxylans X4 have been rarely isolated from higher plants, such as from guar seed husks.[5] A unique heteroxylan with Xm backbone was isolated from the seeds of *Plantago* sp.[6]

Glucuronoxylans

In dicots, plants of the highest evolutionary level, the main hemicellulose component of the secondary cell walls (SCW) of woody tissues is represented by the D-glucurono-D-xylan type (Figure 2) having single side chains of α-D-glucuronic acid (GA) and/or its 4-*O*-methyl derivative (MeGA)

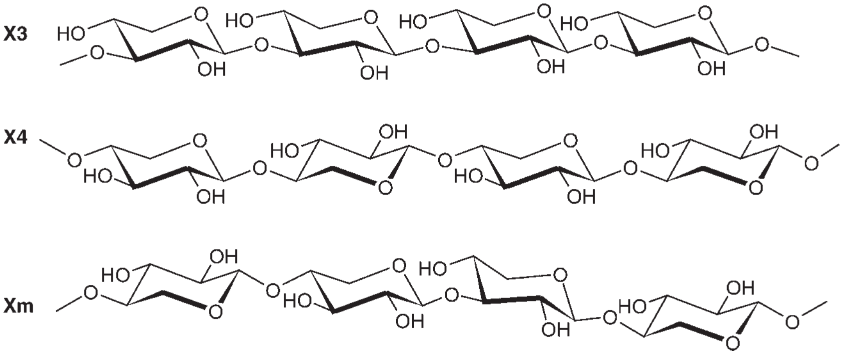

Figure 1.
Structural features of homoxylan chains with β-(1 → 3) linkages (X3), β-(1 → 4) linkages (X4), and mixed β-(1 → 3, 1 → 4) linkages (Xm).

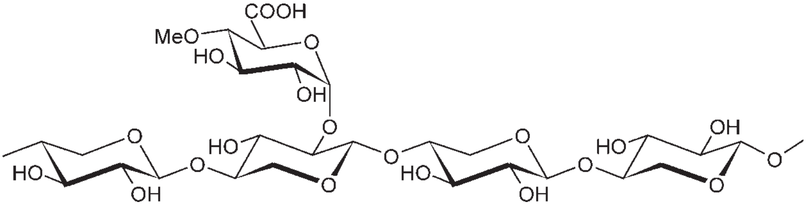

Figure 2.
Primary structure of 4-*O*-methyl-D-glucurono-D-xylan (MGX).

attached at position 2 of the Xylp monomer units. The 4-*O*-methyl-D-glucurono-D-xylan (MGX) represents more than 90% of the hemicellulose component in hardwoods and herbal plants of the temperate zone. The mole ratios of MeGA:Xyl varied between 1:4 to 1:16; on average, the ratio is about 1:10.[5] However, variations were found also within one plant (roots, stem, twigs).[7] MGX was isolated also from fruits such as from the seed pericarp of *Opuntia ficus* pear, luffa fruit fibres, date seeds, grape skin, and hulls of Jojoba beans.[4] A xylan containing only glucuronic acid side chains in various proportions (GA : Xyl = 1:6–43) was reported[5] to be present in the husks of red gram, a tropical legume of industrial importance. Recently, an unusual MGX was isolated from the wood of *Eucalyptus globulus*[8] as it contained, in addition to MeGA residues, about 30% of them substituted at position 2 with α-D-galactopyranose (Galp). The mucilaginously MGX from the seeds of quince (*Cydonia cylindrica*) is heavily branched (MeGA : Xyl ~ 1:2) and in part *O*-acetylated. *O*-Acetylated MGX have been isolated from various hardwoods, where the content of acetyl groups varied in the range 3–13%.[5]

Stepwise extraction of the beechwood Klauditz-holocellulose using dimethylsulfoxide (DMSO) gave a low amount (0.5%) of *O*-acetylated MGX with a very low MeGA content (MeGA : Xyl = 1:39), whereas MGX fractions released with 2.5% NH_4OH and 5% NaOH in the yields of 10.9% and 13.9%, respectively, showed MeGA : Xyl ratios of ~1:10.[9] Partially *O*-acetylated MGX, with MeGA: Xyl ratios of ~1:14–17 were isolated with DMSO also from the chlorite holocellulose of birch and aspen.[10] By steaming birch wood at 170–200°C, *O*-acetylated MGX with MeGA: Xyl ratios of ~1:14–91 and with degree of acetylation varying between 0.17 and 0.40 were extracted.[11]

From the above reported results it can be concluded that in hardwoods the most accessible MGX components, although they are very slightly branched with MeGA side chains, are water-soluble due to acetylation of the xylan chains. Deacetylation of the higher-branched MGX by the alkaline solvents results in partial solubility of the xylan.

(Arabino)glucuronoxylans

The structure of the (L-arabino)-D-glucurono-D-xylans (AGX) resembles that of glucuronoxylans having, in addition, single α-L-arabinofuranosyl (Araf) residues attached at position 3 of the β-(1 → 4)-xylopyranan backbone (Figure 3).

AGX occur, next to mannans, as the minor hemicellulose component in softwoods of the temperate zone and in *Ginkgo biloba*, [4] whereas, in tropical softwoods they comprise about 50% of hemicelluloses.[12] The last mentioned AGX are richer in branching by α-Araf side chains. The MeGA content of AGX is higher than in MGX of hardwoods. AGX were extracted in appreciable yields from softwoods by alkali only after a previous delignification treatment, and are contaminated with mannans.[4] In a recent paper[13] a mixture of highly degraded AGX with a degree of polymerization DP = 4–20 and free of acetyl groups, was separated from the fiber residue of spruce wood obtained by steaming or microwave treatment.[14]

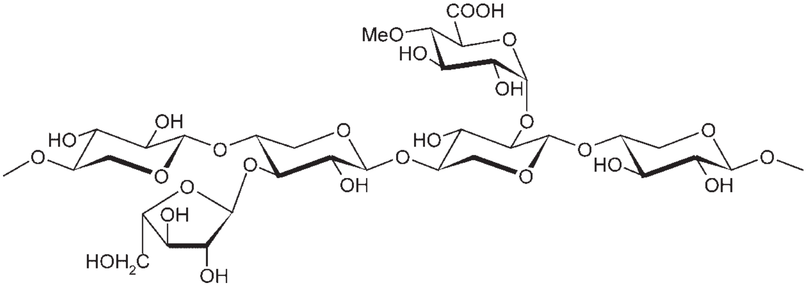

Figure 3.
Structural features of (L-arabino)-4-O-methyl-D-glucurono-D-xylan (AGX).

Arabinoxylans

L-Arabino-D-xylans (AX) are typical hemicellulose components of the CW of starchy endosperm (flour) and outer layers (bran) of cereal grains as well as seeds of other monocotyls such as rye grass, bamboo shoots, and pangola grass.[5] AX contents vary from 0.15% in rice endosperm to ~13% in whole grain flour from barley and rye, and up to 30% in wheat bran. The β-(1 → 4)-xylopyranan backbone of arabinoxylans (AX) has α-Araf residues attached at positions 2 or 3 (monosubstitution) and/or at both positions 2 and 3 of the same Xylp monomer unit (disubstitution), as shown in Figure 4.

Depending on the location of the xylan in the plant tissues and its accessibility, a part of AX can be extracted by water (WE-AX). However, the main part is extractable only by alkaline solvents (AE-AX). Both the extractibility and solubility of the isolated AX are dependent on the content and distribution of the of Araf branches.

The fine structure of AX, given by the frequency of unsubstituted, mono- and disubstituted Xylp residues in the xylan chains, are the reason of a large structural variety of AX and affects the solubility as well. For water-insoluble (wis) AX, the Ara : Xyl ratios vary in the range 1:3–5. In dependence on the extraction a separation conditions, various water-soluble (ws) AX fractions have been isolated from rye and wheat flours[5] with Ara : Xyl ratios ranging from 1:1.1–2. The water-insolubility of AX with relatively higher content of Ara, when compared to the MeGA content of the wis-GX, is due to the rather blockwise distribution of substituted Xylp residues leaving long unsubstituted regions for intermolecular H-bond formation.

A particular feature of AX is the presence of phenolic acids (mainly ferulic and *p*-coumaric acid) esterified to *O*-5 of some Araf residues. The content of ferulic acid in the water-soluble AX fractions isolated from wheat bran[15] varied from 19.9 to 32.3 mg/g. Oxidative coupling of the phenolic acids in the AX chains results in formation of cross-linked networks.[16] This reaction has been supposed of being responsible for the improved baking properties of AX-rich or AX-supplemented flours due to viscosity enhancement.[17] Such cross-linked AX from rice bran form

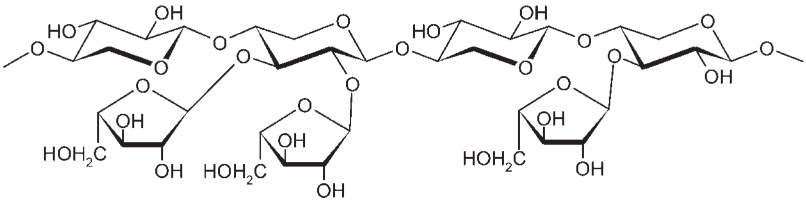

Figure 4.
Primary structure of water-soluble L-arabino-D-xylan (ws-AX).

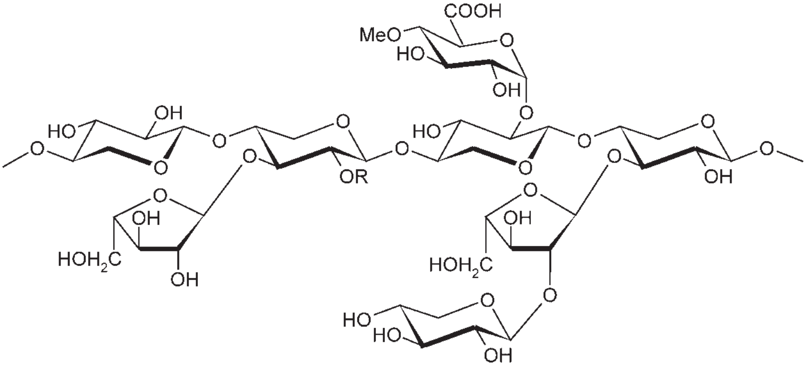

Figure 5.
Structural features of the water-soluble (D-glucurono)-L-arabino-D-xylan (ws-GAX). R: H or α-L-Araf.

water-insoluble gels marketed as 'branan ferulate' gel for wound dressing.[18] It is to be mentioned that the bound phenolic acids provide antioxidant properties to the AX, what might support the healing effect.

(Glucurono)arabinoxylans

(D-Glucurono)-L-arabino-D-xylans (GAX) are the dominant hemicelluloses in the lignified tissues of grasses and cereals (straw, stems, stalks, outer pericarp of grains). GAX isolated from various plant sources showed considerable variations of the MeGA : Xyl : Ara ratios in the range 3–9:10:1–10, and partial *O*-acetylation. In contrast to the aforementioned AGX, it contains also Xylp residues disubstitued by Araf residues.

Heteroxylans

The last xylan group (HX) includes heteroxylans of very complex structures isolated from cereal bran, seeds, gum exudates, and various mucilages.[5] They have the β-$(1 \rightarrow 4)$-xylopyranan backbone heavily substituted with a variety of single and oligosaccharide side chains and form highly viscous solutions behaving similarly as plant exudate gums.

Mannoglycans (Mannans)

The mannan-type hemicelluloses, classified in view of the backbone structure, can be divided into two groups: (i) galactomannans and (ii) glucomannans and galactoglucomannans.[4]

Galactomannans

D-Galacto-D-mannans (GaM) have the backbone made up of β–$(1 \rightarrow 4)$-linked mannopyranose (Manp) units, which is to various extent branched at position 6 by single α-Galp residues (Figure 6). They are present in the CW of storage tissues

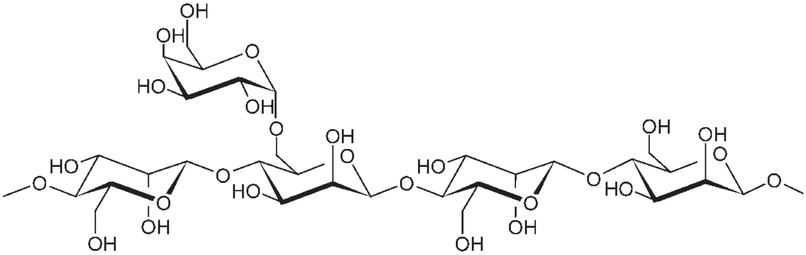

Figure 6.
Primary structure of D-galacto-D-mannan (GaM).

Table 1.
Occurence of various structural types of mannoglycans in plants.

Plant source	Mannoglycan type	Gal : Glc : Man
Hardwood, herbal plants, grasses	GaGM	0.2 : 1 : 2–3
	GM	0.1 : 1 : 1–2
Softwood	GaGM	0.3 : 1 : 4–6
	GM	0.1 : 1 : 4
Konjac mannan	GM	5 : 8
Ivory nut, date, coffee bean	wis-GaM	1 : 0 : 23–25
Legume seeds (guar, carob, cassia)	ws-GaM	1 : 0 : 1.1–5.7

(endosperm, cotyledons, perisperm) of seeds (Table 1).

Slightly branched GaM (~4% Galp) are water-insoluble, whereas the heavily branched types (30–96% Galp) are water-soluble and widely commercially used as gums (guar, tara gum, carob). The differences in the degree of branching and distribution of Galp branches along the β-$(1 \rightarrow 4)$-mannopyranan backbone (fine structure), are responsible for the structural diversity of the GaM group. The Galp residues were found to be distributed regularly (cassia GaM), blockwise (guar GaM), or randomly (carob, tara GaM). The solubility of GaM depends mainly on the Galp content, whereas the fine structure governs viscosity and molecular interactions in solution, i.e. self-association of GaM chains and co-operative association of GaM with other polymers.

Glucomannans

D-Gluco-D-mannans (GM) and (D-galacto)-D-gluco-D-mannans (GGM) possess, in contrast to GaM both β–$(1 \rightarrow 4)$-linked Manp and glucopyranose (Glcp) residues in the main chain (Figure 7). Galp residues are branching the glucomannan chain at position 6 of Manp units. The galactose content of 15% represents the limit for distinguishing GGM and GM types (Table 1). These polymers represent the main hemicellulose component of the SCW of softwoods, and the minor ones in that of hardwoods (3–5%), herbal plants and grasses. Together with xylan and xyloglucan they compose the PCW of these plants.[4]

Similarly as with the GX in hardwoods, the mannoglycans are easily extractable only by alkaline treatment from previously or simultaneously delignified materials. The most accessible is GGM, whereas GM due to its cellulose-like backbone is strongly associated to cellulose and extractable only using alkaline solvents of higher concentrations. By microwave treatment of softwoods, slightly *O*-acetylated GM of low molecular mass, composed of galactose, glucose and mannose in the mole ratio of 1:8–15: 30–60 were isolated.[20]

The structural and physicochemical properties of the storage GM, known as 'konjac mannan' in food industry, have been recently reinvestigated.[21] The results indicate that this polysaccharide, composed of glucose and mannose in the ratio 1:1.6, has the backbone slightly *O*-acetylated, and branched (about 8%) at position 6 of Glcp residues. The branches terminated by both Glcp and Manp have been suggested as a new structural feature.

The mucilaginous polysaccharide (acemannan) isolated from the parenchyma (filet) of *Aloe vera* sp. contains more than 90% of mannose and very low amounts of glucose and galactose.[4] It has the β-$(1 \rightarrow 4)$-mannopyranan backbone heavily *O*-acetylated at 2, 3 and/or 6 positions. Reports concerning the position of the hexosyl residues are still controversial and acemannan has been grouped to GM as well as to GaM.

Xyloglucans

D-Xylo-D-glucan (XG) is a hemicellulose component representing the major building material of PCW of all higher plants.[22] XG

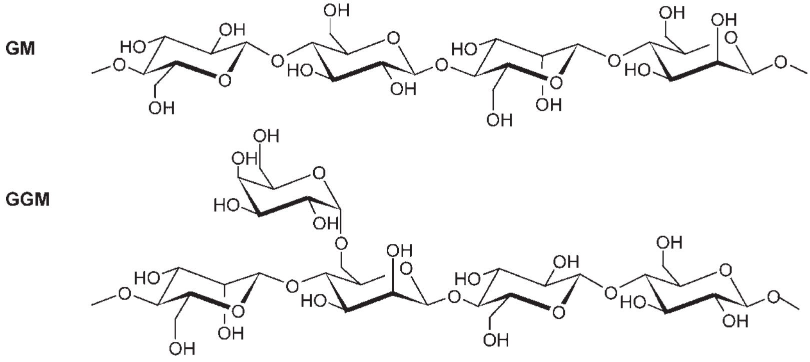

Figure 7.
Primary structure of D-gluco-D-mannan (GM) and (D-galacto)-D-gluco-D-mannan (GGM).

makes up about 20–25% of PCW in dicotyledonous angiosperms (*Sycamore*, *Arabidopsis thaliana*), somewhat less (2–5%) in grasses, and about 10% in softwoods. In tamarind seeds XG functions as a storage polysaccharide.

XG has a cellulosic β-(1 → 4)-glucopyranan backbone with α-D-Xylp residues attached at postion 6 of of Glcp residues (Figure 8). In XG of dicotyls about 60–75% of the Glc*p* units are xylosylated, in those of grasses about 30–40%.[4] The structural diversity of this hemicellulose type is created by the distribution of the Xylp branches along the main chain. Two main XG types have been distinguished:

- Type I: **-X-X-X-G-**, containing blocks composed of three xylosylated (X) units and one non-substituted (G) Glcp unit, and
- Type II: **-X-X-G-G-** with blocks of two alternating X and G units.

Type I is typical of PCW of hardwoods, herbal plants and some grasses and Typ II is present in PCW of *Solanacea* sp. (such as tomato, tobacco). Both types comprise a variety of XG structures due to the presence of additional oligomeric glycosyl side chains, composed of galactose, fucose, arabinose and/or xylose, which are attached to the backbone and/or branch the Xylp residues.[4]

The strong cellulose-XG bonding in vegetative plant CW negatively affects the extractibility of this hemicellulose component. In contrast, storage XG are

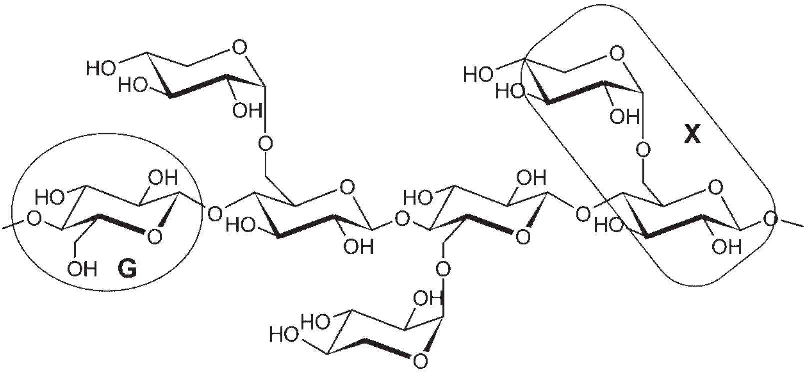

Figure 8.
Primary structure of D-xylo-D-glucan (XG).

extractible from the seeds by hot water treatments. In addition to the strong hydrogen bonds with cellulose and other CW components, covalent bonds have been considered to fix the XG in the CW, such as esters with COOH groups of pectin and/or bridging through ferulic acid esters to pectin and other hemicelluloses.[23]

Mixed-linkage β-Glucans

The mixed-linkage (1 → 3,1 → 4)-β-D-glucans (Mix-G) are unique to the Poales, the taxonomic order that includes cereal grasses. They are known as cereal β-glucans located in the subaleurone and endosperm-ic CW,[4] where they associate with cellulose microfibrils during cell growth. Oat and barley contain, depending on the cultivar, 3 to 12% and more. A structurally similar Mix-G (lichenan) is commonly found in lichen *Cetraria islandica*.

Mix-G has an unbranched backbone composed of Glcp residues linked by β-(1 → 3) and (1 → 4) linkages (Figure 9). Blocks of (1 → 4)-linkage sequences (cellotriosyl, C3 as well as cellotetraosyl, C4, and longer cellulose-like segments, C9-14) are separated by single (1 → 3)-linked Glcp residues. The mole ratios of C3/C4 segments range between 2.1–2.4 for oat, 2.8–3.3 for barley, and 4.2–4.5 for wheat, whereas in lichenan the ratio is much higher (24.49).[24] The fine structure comprising the arrangement of the blocks along the chains was suggested to be random. This explains the different extractibility of Mix-G by water and alkali due to a stronger associative behavior to the cellulose microfibrils of Mix-G chains with high C3/C4 ratios and larger amounts of contiguously (1 → 4)-linkage segments.

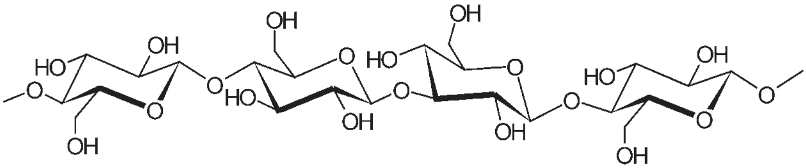

Figure 9.
Primary structure of mixed-(1 → 3,1 → 4)-linkage β-D-glucan (Mix-G).

Physicochemical and Functional Properties

The molecular mass (M_w) values reported for the various hemicelluloses show considerable variation not only between the above described structurally different groups. The values may vary depending on the estimation method even for the same sample. An essential problem in the molecular mass determination is, as usual for most plant polysaccharides, the solubility. The linear non-branched or low-branched hemicelluloses as well as irregularities in their fine structure affect the re-dissolution process of the samples. This can be explained by the aggregation tendencies of the macromolecules in solution and formation of strong intermolecular and inter-particle hydrogen bonds during the drying process. Covalent bonding of polysaccharides to lignin and other CW components by crosslinking through phenolic acids has been also assumed to contribute to aggregate formation or low solubility.[4] For the cereal xylans (AX, GAX and HX) the M_w estimates varied in the range 60–400 × 10^3 g/mol, whereas the values for the hardwood and softwood hemicelluloses (GX, AGX, GM and GaGM) were lower (<100 × 10^3 g/mol). The M_w-values reported for cereal β-glucans ranged between 0.065–3 × 10^6 g/mol for oat, 0.15–2.5 × 10^6 g/mol for barley, and 0.25–0.7 × 10^6 g/mol for wheat. Depending on the analytical method, M_w-values of 0.15 × 10^6 g/mol, 0.88 × 10^6 g/mol or even 2.5 × 10^6 g/mol were reported. The ws-GaM from seeds exhibited the highest M_w-values in the range $0.96–1.26 \times 10^6$ g/mol.

The rheological behavior of hemicelluloses is essentially affected by both the primary structure (sugar composition, type of branches) and fine structure comprising the distribution of segments or branches, shown in the previous sections. The MeGA-containing and the highly branched hemicelluloses such as GX, GAX, XG, and GaM produce solutions in water, which are shear thinning and show pseudoplastic to plastic flow behavior. Beech wood GX at concentrations >5% produce strong gels,[5] whereas ws-AX solutions have a liquid-like character also at higher concentrations. GaM from *Ipomea* seeds[25] forms reversible gels with borate ions and non-reversible gels with transition metals depending on pH, similarly as guar GaM. The GaM from *Mimosa* seeds showed a liquid-like behavior, attributed to the very high degree of galactose branches (Gal : Man $\sim$1:1).[4] Comparative studies[26] revealed that tamarind XG and apple pomace XG were shear-thinning, whereas the *Nicotiana* XG displayed near-Newtonian behavior. The molecular mass was assumed to play a major role for the XG than differences in the types of side chains, whereas the content and distribution of the galactosyl branches is essential for the solution properties of GaM.

The viscoelastic and flow behavior of Mix-G[4] indicated the formation of network-like structures even in dilute solutions in barley. In the case of Mix-G from oat, only the low molecular mass samples displayed gel-like properties owing to self-association through the cellulose-like sequences. This was supported by comparison of gels prepared from various cereal Mix-G and lichenan.[27] Lower branched hemicelluloses are partly or fully insoluble in water and produce dispersions of more or less swollen particles. However, due to the association tendencies strong gels can be produced as reported for beech wood and corn cob xylans.[5]

The rheological behavior of hemicelluloses gave information on the interactions in mixed polysaccharide systems. As has been reviewed,[4] interaction studies on xylans and storage GaMs revealed effects on starch retrogradation, pasting behavior and gel properties, depending on the structural features of the hemicelluloses. XG/gellan mixtures gave single-phase gels indicating synergistic interactions. Tamarind XG and starch did not interact synergistically, but the XG decreased the retrogradation and syneresis of starch paste.

Some of the soluble xylan-type hemicelluloses (GX, GAX, AX) were reported to exhibit tensioactive properties.[5] They produce stable foams and emulsions of the oil/water type comparable in stability to the effect of the commercial synthetic emulsifier Tween 20, and improve and/or even surpass the protein foaming before heating. The presence of small amounts of lignin and proteins acting as hydrophobic centers as well as the film-forming effect of the polysaccharide were assumed to be responsible for such effects.

Hemicelluloses from edible plants are well-known for their physiological effects as dietary fibres.[5] Investigations of the last decade revealed that some of the discussed hemicellulose types exhibit various biological activities, previously reported for fungal $(1 \rightarrow 3)$-β-glucans and pectic arabinogalactans from medicinal herbal plants. Xylans GX and Xm isolated from medicinal herbal plants, ws-GAX from corn cobs, GaM from *Aloe vera*, and tamarind XG displayed immunostimulating and anti-tumor activities. [4]

Application Potential of Hemicelluloses

Due to the above summarized functional properties of the various hemicelluloses, the application potential of these plant polysaccharides is immense and widespread over various technical and non-technical fields. The most important applications are shown in Table 2. Hemicelluloses are applicable as gels, films, coatings,

Table 2.
Application potential of commercial and non-commercial hemicelluloses.

Type	Plant source	Application fields
MGX	Beech Buckwheat hulls Birch	Drug carrier[1] Dietary fiber and food additive [29] Wheat-gluten films[4]
GAX	Rice bran, Corn bran	Super gels from branan ferulate for wound dressing[18]; branan/alginate fibers as drug carrier[4]
GAX	Corn cobs	Additive in papermaking;[1] micro- and nanoparticles as carriers of drugs and other compounds[30]
GaGM	Spruce	Wet-end additive in papermaking[4]
GM	*Amorphophallus konjac*	Hard-boiled and frozen confectionary products – replacement of gelatin[4]
GaM	Seed: *Dimophandra Cassia*, *Ipomea*	Wet-end additive in papermaking[31]; food gums[4]
XG	Seeds: *tamarind*, jatoba, copaiba, nasturtium	Textil industry; cosmetics; Wet-end additiva in papermaking[31]; in situ-gelling preparations[4]
Mix-G	Oat Barley	Fat-substitute in cheese and antidiabetic dietary fibre;[4] new biomaterials (Glucagel)[4]

adhesives, and gelling, stabilizing and viscosity-enhancing additives in food and pharmacy as well as in other industrial branches.[4] Some of them were shown to serve as biodegradable components in composites with synthetics or as pre-polymers for production of new functionalized polymeric materials, particularly the oligomeric hemicelluloses.[28]

Many of the mentioned hemicelluloses, such as the GaM from guar, carob and tara, konjac GM, ivory nut mannan, and the tamarind XG became commercially important long years ago.

However, during the past decade considerable attention has been paid to polysaccharides of hitherto non-investigated plant sources, mainly to those used in traditional food and other applications of less developed countries. In well-developed economics, particularly in agricultural based ones, research has been focused on the utilization of the polysaccharide components of secondary plant sources (by-products and wastes). The usefulness of hemicellulose-based or derived products in an industrial and biomedical context is beyond dispute and will stimulate further activities in basic and applied research.

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