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Carbohydrates

Carbohydrates are biomolecules consisting of carbon, hydrogen and oxygen with a hydrogen-oxygen atom ratio of 2:1. In biochemistry carbohydrates are seen as synonymous with saccharides, which include sugars, starch and cellulose, however in the context of lignocellulosic biomass the term carbohydrate refers primarily to cellulose and hemicellulose.

CELLULOSE

Cellulose is the main constituent of organic biomass, including lignocellulosics (making up 40-50% of it) and is the most abundant and important biopolymer on Earth. In industrial use cellulose is mainly used for paper making but different kinds of modified cellulose such as cellulose ethers and esters can also be prepared for various applications, such as films, gels, or food additives.

BASIC STRUCTURE

The linear cellulose polysaccharide is formed as hundreds to thousands of individual D-glucose units interlink via β(1 -> 4) glycosidic bonds as illustrated in Figure 1. The only difference between starch and cellulose is the type of linkage between the glucose units with starch being α-linked. Unlike cows, humans lack the enzymes required to degrade cellulose but they can degrade starch.

All plants use cellulose in their cell walls. An example of this can be seen in the morphology of cellulose in fibre cells as illustrated in Figure 2. Cellulose molecules readily interact with each other, primarily with hydrogen bonding, and bundle together in groups. The term micelle has sometimes been used to describe a cellulose unit, which corresponds more accurately to the native state of cellulose, rather than individual cellulose strands or glucose molecules. As the cellulose molecules bundle together they eventually form microfibrils, which, because of the strong intermolecular hydrogen bonding between the cellulose molecules, are stiff and can be considered al- most crystalline in structure. Interlocked microfibrils form macrofibrils in similar fashion. Finally, lignin, pectin and hemicellulose fill in what voids are left in between the micro- and macrofibrils thus, establishing a solid, supportive structure for the fibre cell.[1]

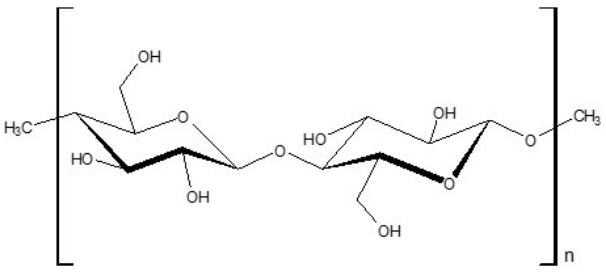

Figure 1. The repeating disaccharide unit in cellulose polymer.

HEMICELLULOSE

Hemicelluloses makes up 15-20 % of the dry wood material. Hemicelluloses are mostly different kinds of heteropolysaccharides and their native structure is less well defined and understood than cellulose.

The building blocks of hemicelluloses, as depicted in Figure 3, may include hexoses (D-glucose, D-mannose

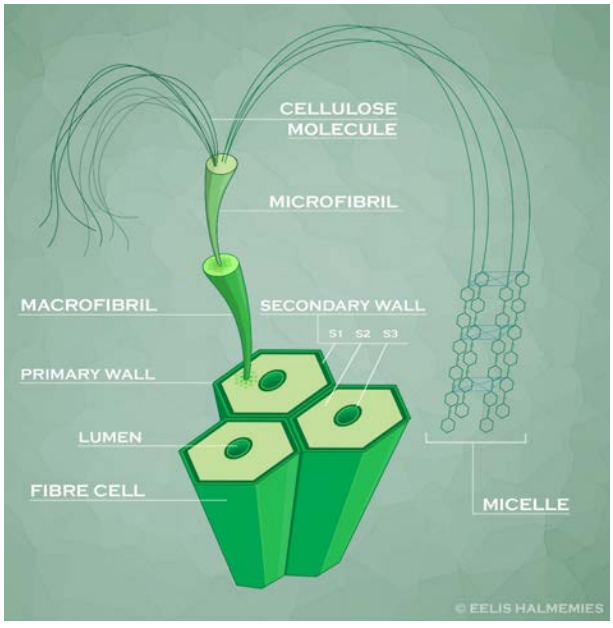

Figure 2. The morphology of cellulose in fibre / sclerenchyma cells.

and D-galactose), pentoses (D-xylose, L-arabinose, and D-arabinose) or deoxyhexoses (L-rhamnose, 6-deoxy-L-mannose, and rare L-fucose or 6-deoxy-L-galactose). Certain uronic acids (4-O-methyl-D-glucuronic acid, D-galacturonic acid, and D-glucuronic acid) have also been identified with hemicelluloses.

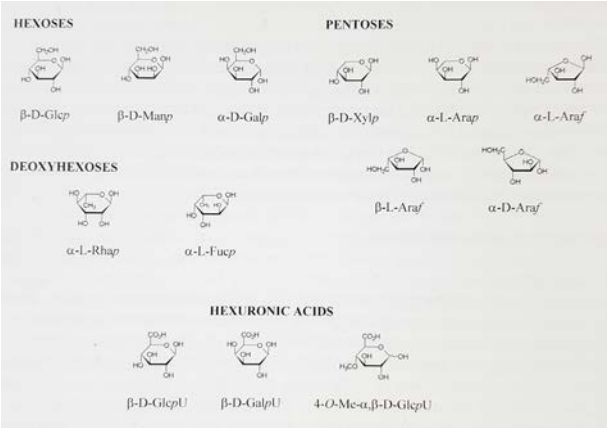

Figure 3. The sugar moieties of wood hemicelluloses.[2]

There are also differences in the hemicelluloses between softwoods and hardwoods regarding the frequency and composition of the sugar units. For example, softwood hemicelluloses, in general, contain more mannose and galactose units than the hemicelluloses of hardwoods. On the other hand, hemicelluloses of hardwoods contain more xylose units and acetylated hydroxyl groups than those of softwoods. The primary hemicelluloses in softwoods are glucomannan(s) or (galactoglucomannan(s)) as shown in Figure 4. and xylan (arabinoglucuronoxylan) shown in Figure 5.

In comparison to cellulose, hemicelluloses are thermally more unstable because of their lack of crystallinity and low degree of polymerisation. Hemicelluloses are also less soluble in alkali than cellulose. Some hemicelluloses (mainly mono- and disaccharides) are are totally soluble in water which makes the differentiation between extractives and hemicelluloses sometimes difficult.

It is probable that in their native form, the hemicelluloses also have linkages with at least part of the lignin in the wood. The nature and amount of these linkages apart from hydrogen bonding is however yet uncertain. The most frequently suggested linkages between lignin and carbohydrates are summarized in Figure 6.

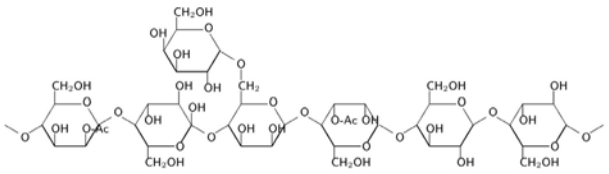

Figure 4[3]*. Galactoglucomannan consisting of interlinked galactose, glucose, and mannose units in the ratio of: Gal : Glu : Man 0.5 : 1 : 3.5. Some of the monosaccharides may be acetylated.*[2]

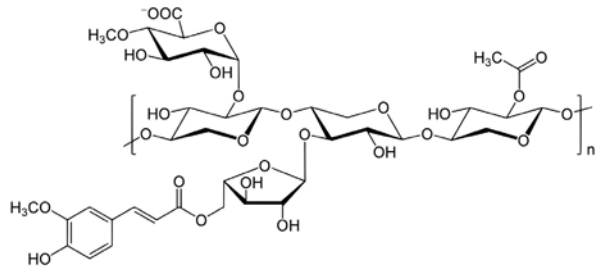

Figure 5[4]*. Xylose mainly constisting of interlinked arabinose, glucuronoic acid, and xylan units in the ratio of: Ara : GlcU : Xyl 1 : 2 : 82. The xylan in the figure has also ferulic acid attached to it.*

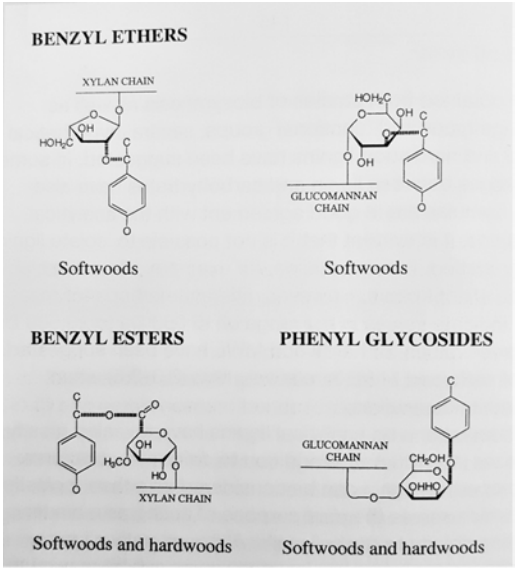

Figure 6[2]*. The most commonly suggested types of linkages between hemicelluloses and lingin.*

AUTHOR
Eelis Halmemies
Natural Resources Institute Finland (LUKE)
eelis.halmemies@luke.fi
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[1] Lynne, T. Structure of Cellulose Microfibrils in Primary Cell Walls from Collenchyma, Biochemistry and Metabolism, 2013.

[2] Alén, R. Structure and chemical composition of wood, in Forest Products Chemistry, Book 3, P. Stenius (Ed.), Fapet Oy, Helsinki, Finland, 2000, pp. 11-57.

[3] Picture from: https://upload.wikimedia.org/wikipedia/commons/2/2a/Structure_of_galactoglucomannan.svg (13.9.2018)

[4] Picture from: https://upload.wikimedia.org/wikipedia/commons/4/46/Xylan.svg (13.9.2018)

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