Hetero-polysaccharides

Up to 1/3rd of biomass is composed of hemicelluloses

What is hemicellulose?

Originally believed to be a precursor to cellulose, denoted by “hemi”

Better referred to as hetero-polysaccharide

Hetero-polysaccharides play important function in the cell wall during lignification as well as serve in the interface between the cellulose fibrils and lignin

Hetero-polysaccharides

Hetero (meaning different) or in this context made up of more than one type of monosaccharide unit

- In contrast cellulose is only made up of glucose units

Short chains (polymer size is related to about 200 units)

Hetero-polysaccharides have a branched topology

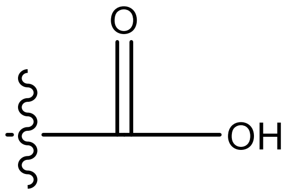
Hetero-polysaccharides have an amorphous morphology (in their native state)

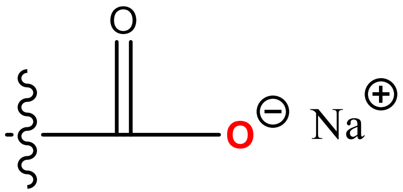
Hetero-polysaccharides have different functional groups than cellulose

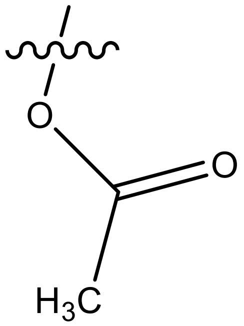
Hetero-polysaccharides have “charged” branches

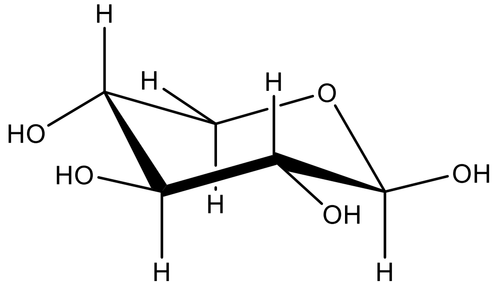
Hetero-polysaccharides can be partially acetylated and partially methoxylated

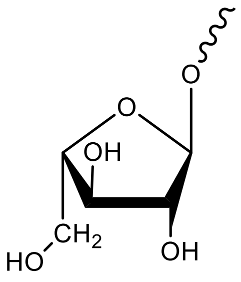
Some polysaccharides contain 5-carbon sugars in a pyranose ring (6-member) and some contain a 5- carbon sugar in a furanose ring (5-member)





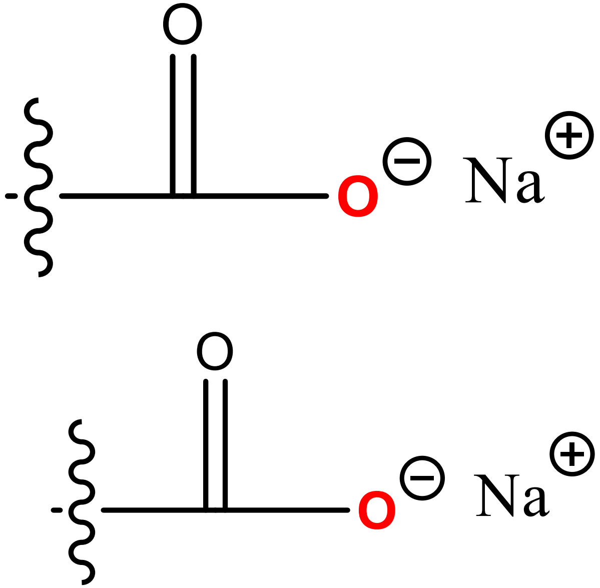


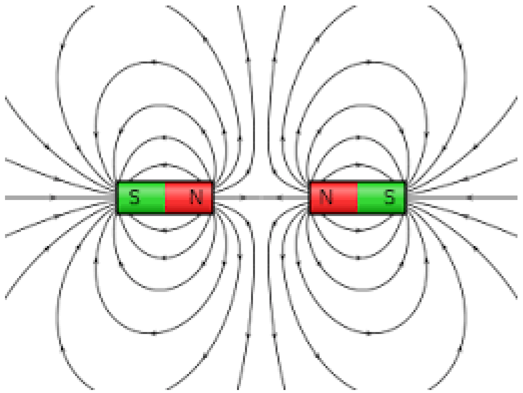


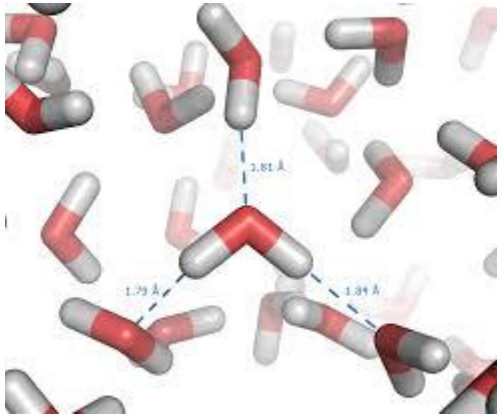


Hetero-polysaccharide chemistry will play a major role in cell wall architecture

The molecular level of wood will be impacted by charged groups and more hydrophobic groups







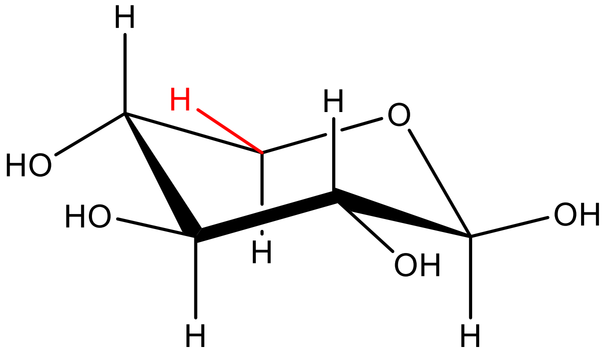
Hetero-polysaccharides are composed of 4 principle carbohydrates

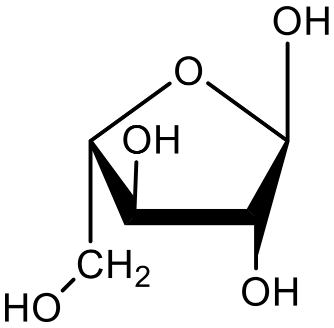
Xylose (like cellulose but missing the 6th carbon)

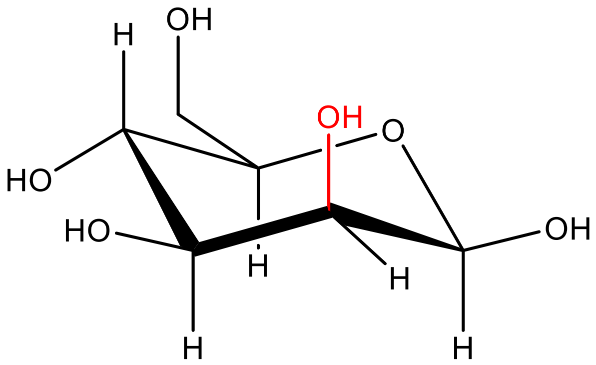
Arabinose (usually the only furanose ring, and in L configuration)

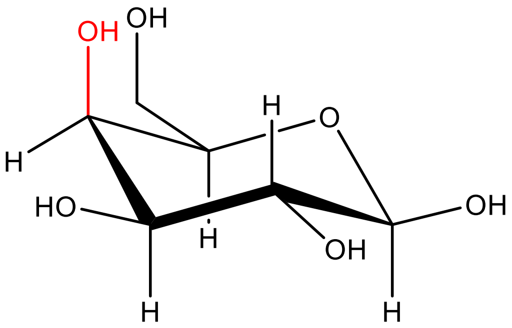
Mannose (Has a hydroxyl axial at the 2 position)

Galactose (Linked at the 4 position in an axial conformation)

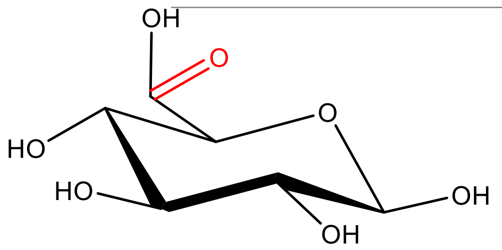


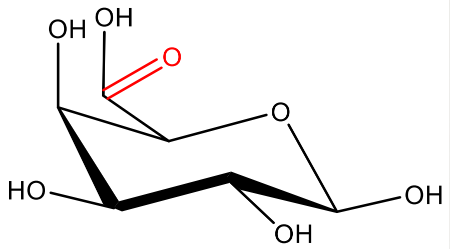






Gymnosperms/conifers/softwoods have different types of hetero-polysaccharides than angiosperms/broadleaf/hardwoods



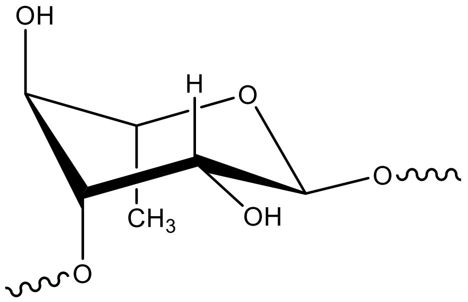


Previous results in the field of polyoses chemi...
Schuerch (1963), Timell (1964a, 1965, 1967) and Aspinall (1964a, 1973).

Table 5–1. Non-glucosic units of the polyoses in various woods

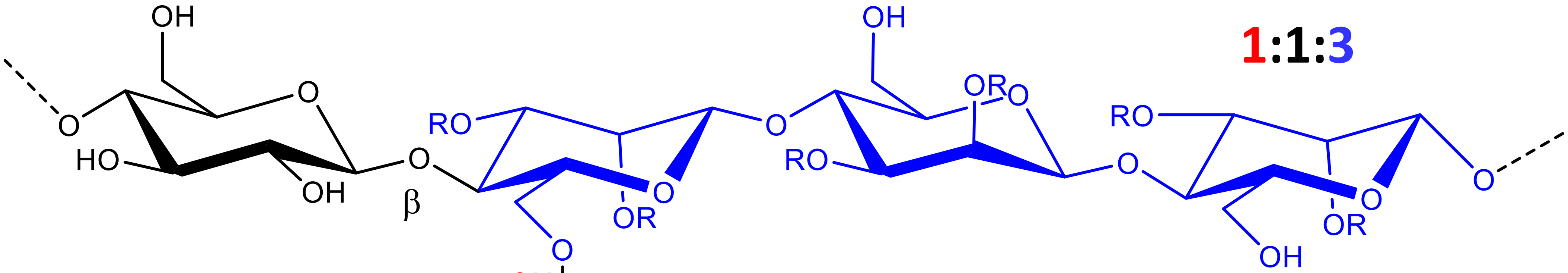
Species	Man %	Xyl %	Gal %	Ara %	Uron.A. %	Rha %	Acetyl %	References
Abies balsamea	10.0	5.2	1.0	1.1	4.8		1.4	Côté et al. 1966
Larix decidua	11.5	5.1	6.1	2.0	2.2*	0.0		Fengel et al. 1978
Larix laricina	12.3	6.0	2.4	1.3	2.8		1.6	Côté et al. 1966
Picea abies	13.6	5.6	2.8	1.2	1.8*	0.3		Fengel et al. 1978
Picea glauca	12.0	7.0	1.9	1.1	4.4		1.2	Côté et al. 1966
Picea mariana	9.4	6.0	2.0	1.5	5.1		1.3	Côté et al. 1966
Pinus strobus	8.1	7.0	3.8	1.7	5.2		1.2	Côté et al. 1966
Pinus sylvestris	12.4	7.6	1.9	1.5	5.0		1.6	Côté et al. 1966
Tsuga canadensis	10.6	3.3	1.8	1.0	4.7		1.4	Côté et al. 1966
Thuja occidentalis	7.4	3.8	1.5	1.7	5.8		0.9	Côté et al. 1966
Acer rubrum	3.3	18.1	1.0	1.0	4.9		3.6	Timell 1969
Betula alleghaniensis	1.8	18.5	0.9	0.3	6.3		3.7	Timell 1969
Betula papyrifera	2.0	23.9	1.3	0.5	5.7		3.9	Timell 1969
Betula verrucosa	3.2	24.9	0.7	0.4	3.6*	0.6		Fengel et al. 1978
Fagus grandifolia	1.8	21.7	0.8	0.9	5.9		4.3	Timell 1969
Fagus sylvatica	0.9	19.0	1.4	0.7	4.8*	0.5		Fengel et al. 1978
Fraxinus excelsior	3.8	18.3	0.9	0.6	6.0*	0.5		Fengel et al. 1978
Populus tremuloides	3.5	21.2	1.1	0.9	3.7		3.9	Timell 1969
Robinia pseudoacacia	2.2	16.7	0.8	0.4	4.7		2.7	Timell 1969
Ulmus americana	3.4	15.1	0.9	0.4	4.7		3.0	Timell 1969

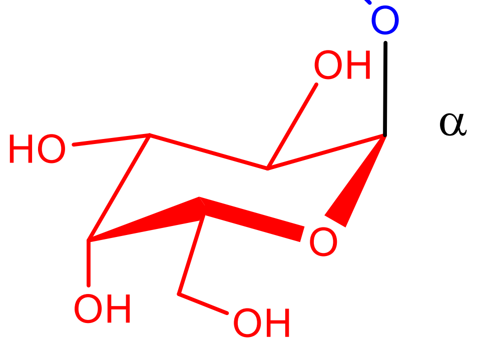
* 4-O-Methylglucuronic acid



Heteropolysaccharides: Softwoods

Galactoglucomannan



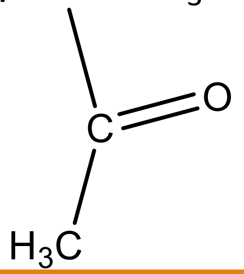


Two types

0.1:1:4

1:1:3

R is equal to CH_3CO or H

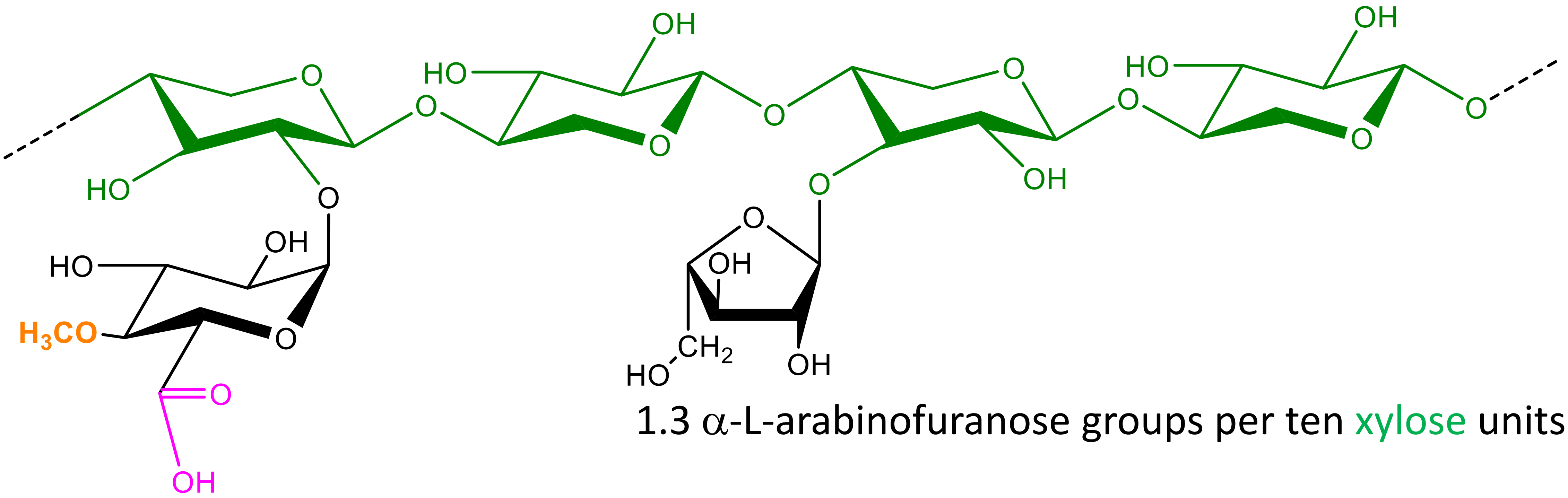


~1 acetyl group per 3-4 hexose units

20% by weight

Heteropolysaccharides: Softwoods

Arabinoglucuronoxylan



1.3 α-L-arabinofuranose groups per ten xylose units

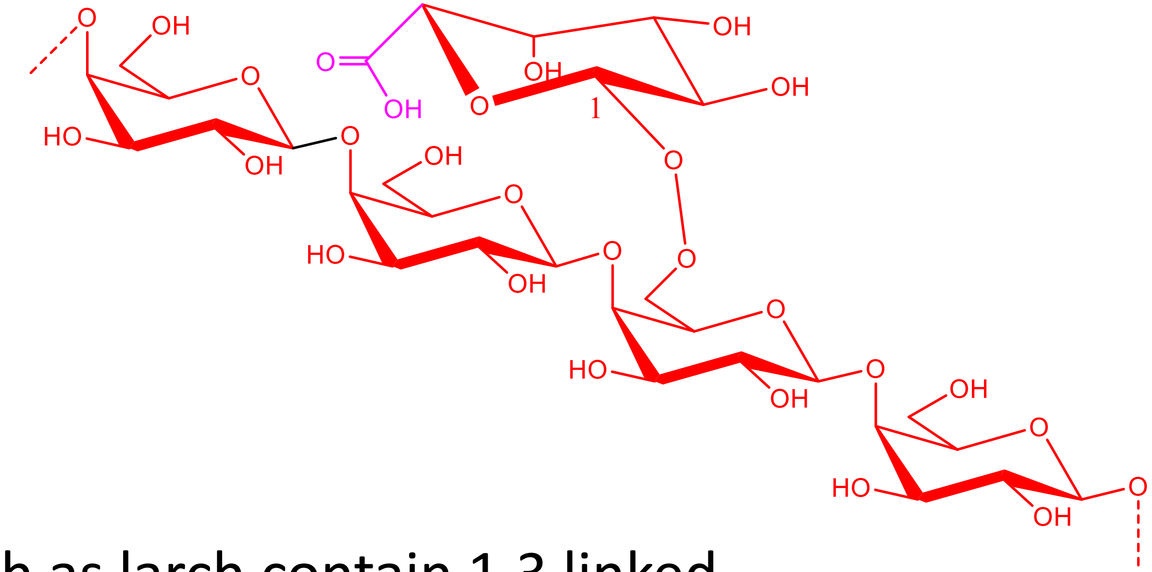
two 4-O-methyl-α-D-glucuronic acid groups per ten xylose units

5-10% by weight

Heteropolysaccharides: Softwoods

Galactan

Galacturonic acid

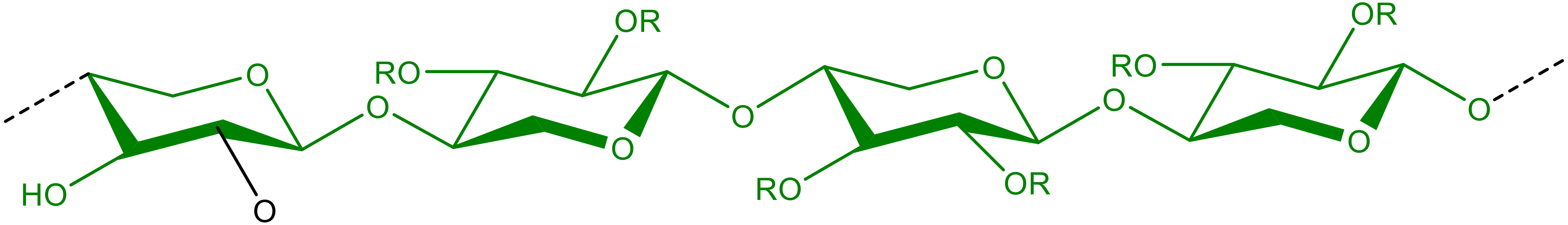


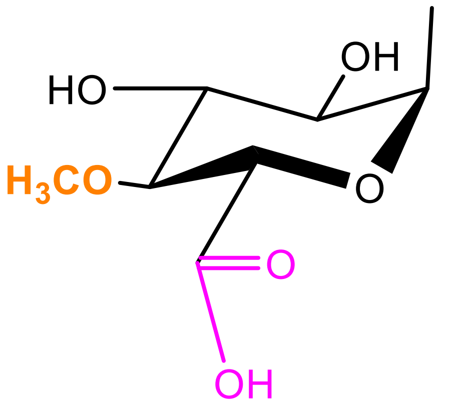
Up to 10% in compression wood

Note, softwoods such as larch contain 1,3 linked galactan with substitution of arabinan or 1,6 galactan at the 6 carbon position

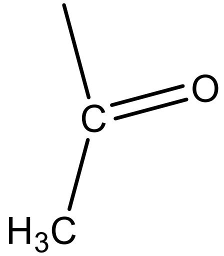
Heteropolysaccharides: Hardwoods

Glucuronoxylan





R is equal to acetyl or H

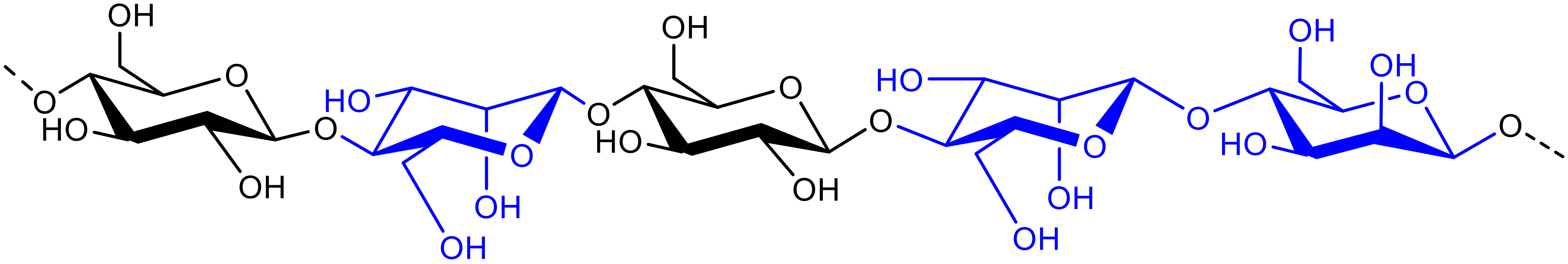


Hardwood xylan is heavily acetylated with 7 acetyl groups per 10 xylose units and 1 glucuronic acid group per 10 xylose units

15-30% by weight

Heteropolysaccharides: Hardwoods

Glucomannan



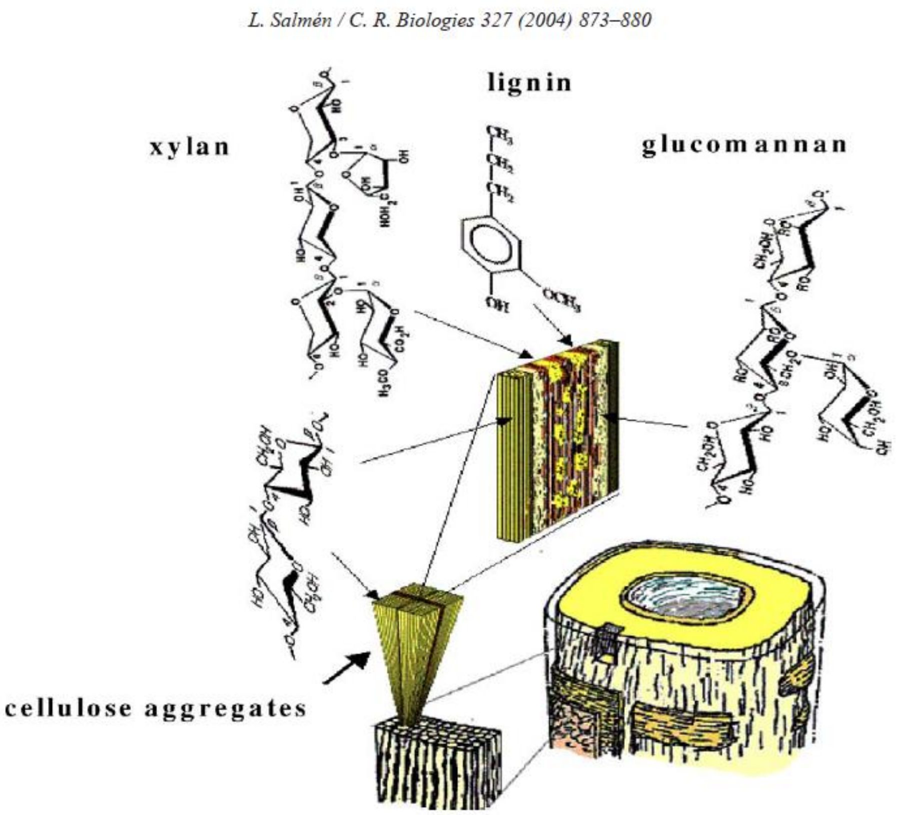
Typically about 1.5 to 2: 1 and it is a random co-polymer

3-5% by weight

Some literature points to a stratified structure of the hemicelluloses

Cellulose and glucomannan are closely associated

Lignin and xylan are closely associated



This schematic is from an article "Micromechanical Understanding of the cell-wall structure" by Lennart Salmén in C.R. Biologies 327 (2004) 873-880

Many of the hetero-polysaccharides can be extracted and solubilized in alkali

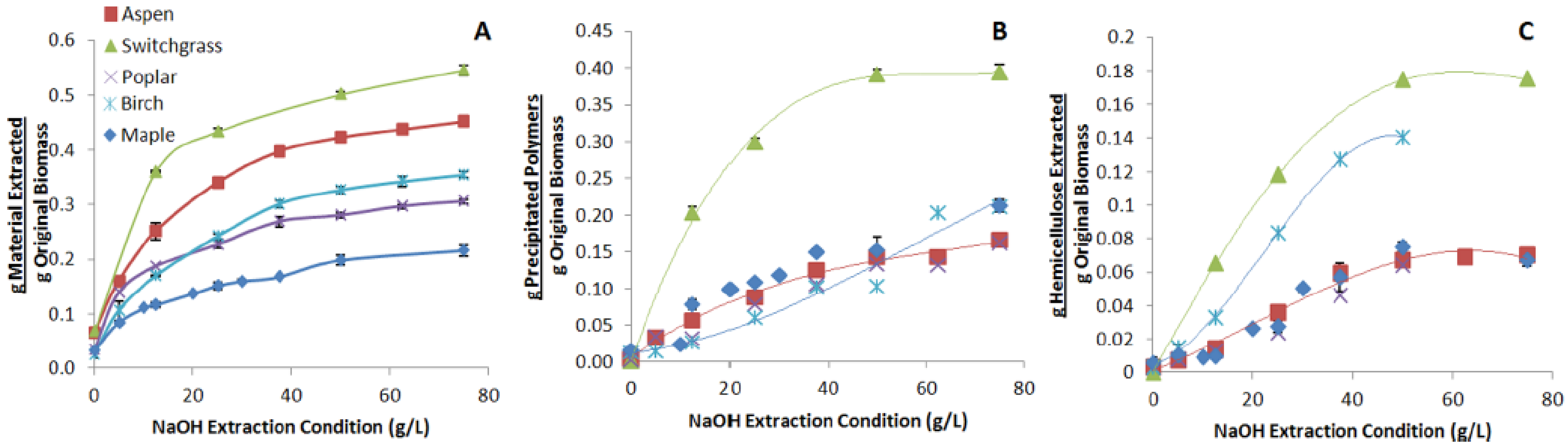


Figure 1. Comparison of the five biomass sources for (A) total mass extractability by alkali, (B) recoverability of the extracted polymers with 2:1 (v:v) ethanol precipitation, and (C) hemicellulose extractability by alkali.

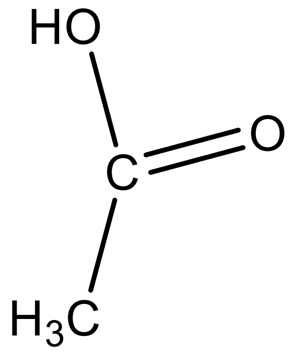
Ind. Eng. Chem. Res. 2012, 51, 11045-11053

Sulfite pulping and acidolysis conditions can break down hemicelluloses significantly

Hemicelluloses are very sensitive to acids

Xylan can become deacetylated and generate acetic acid

Acid groups can attack glycosidic linkages forming oligosaccharides



Retention of hetero-polysaccharides can impact paper yield and paper properties

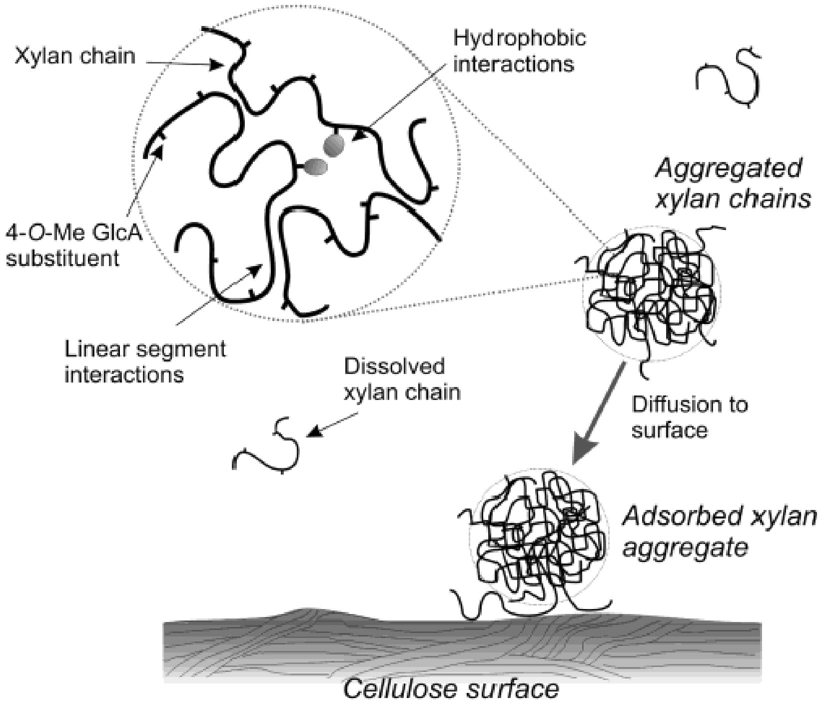


Figure 6. Schematic illustration showing the mechanisms for xylan aggregation in solution and interaction with cellulose surfaces.

Langmuir 2003 19(12)5072-5077

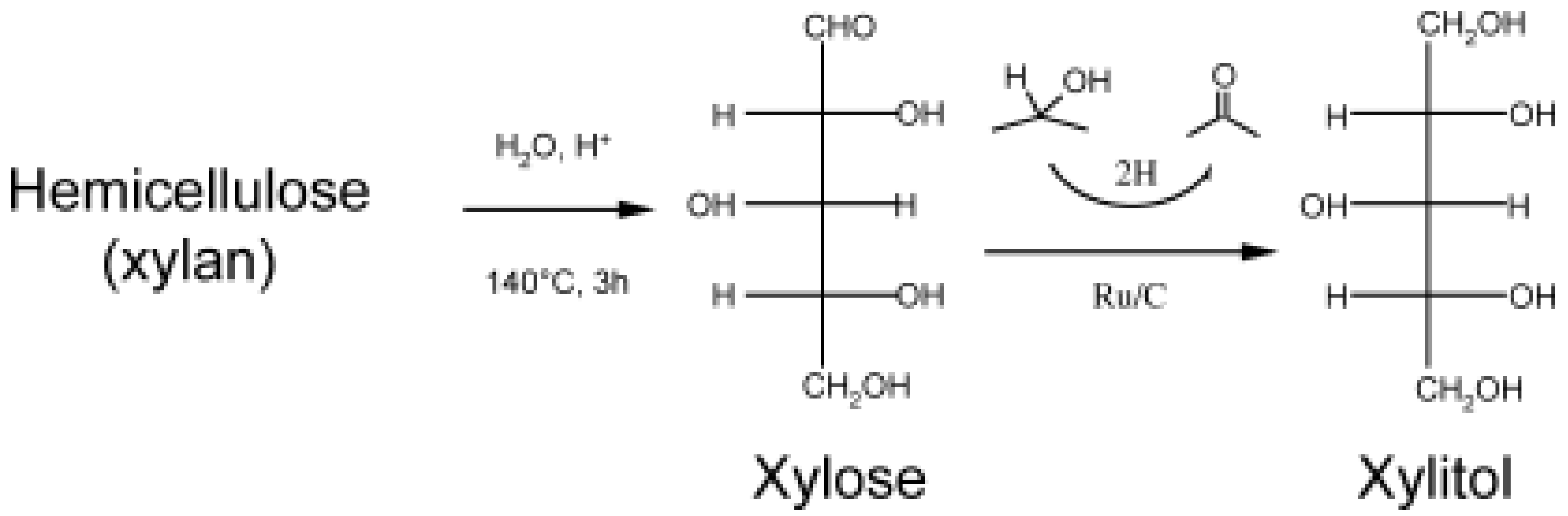
Xylans have been used for packaging materials because of tremendous O_2 barrier properties

1534 *Biomacromolecules, Vol. 5, No. 4, 2004* Gröndahl et al.

Table 1. Oxygen Permeability Data on Plasticized Glucuronoxylan Film and Comparable Values for Plasticized Starch Polymers, Ethylene Vinyl Alcohol, and Low Density Polyethylene

material	oxygen permeability [(cm^3 μm)/(m^2 d kPa)]	source and conditions
glucuronoxylan with 35 wt. % sorbitol	0.21	present study, 50% RH
amylose with 40 wt. % glycerol	7	[42] 50% RH
amylopectin with 40 wt. % glycerol	14	[42] 50% RH
poly(vinyl alcohol) (PVA)	0.21	present study, 50% RH,
ethylene vinyl alcohol (EVOH)	0.1−12	[43] 70% VOH, 0−95% RH
low-density polyethylene (LDPE)	1870	[43] 50% RH

Xylan can be readily hydrolyzed to xylose and converted into xylitol, an important sweetener



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http://onlinelibrary.wiley.com/doi/10.1002/cssc.201200290/full#sch1

Summary

Hetero-polysaccharides make up a significant part of the biomass of wood

They add complexity to the cell wall with various functional groups

Isolation of hetero-polysaccharides in pulping processes are usually not done because of the sensitivity

There is great potential for the utilization of these polysaccharides