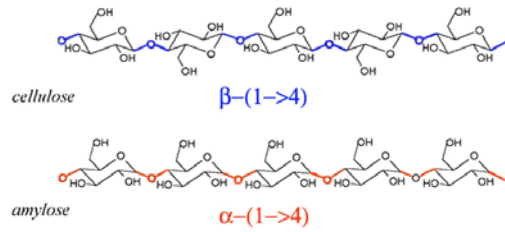


# Polysaccharides

## Lesson 3

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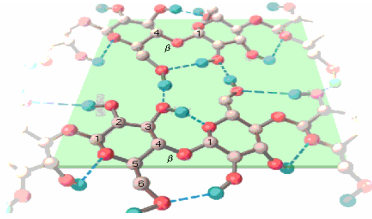
# Cellulose and Amylose



The difference between cellulose and amylose can be seen more easily if we look at more than two residues

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# Cellulose



- Forms a fibrous planar structure with individual parallel chains held together by hydrogen bonds
- Water insoluble - luckily if you wear cotton!
- Most animals cannot digest the  $\beta$ -(1- $\rightarrow$ 4) linkages in cellulose

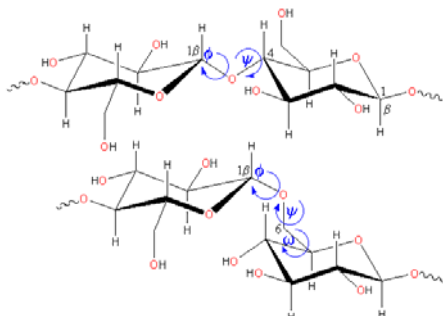
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# Rotation about linkage

- Regular ordered polysaccharides, in general, are capable of assuming only a limited number of conformations due to severe steric restrictions on the freedom of rotation of sugar units about the interunit glycosidic bonds

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# Rotation about linkage



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# Cellulose, Amylose and Amylopectin

All are polyglucans, polymers of glucose or glucopyranose.

Both cellulose and amylose are 1,4 linked.

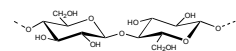
Cellulose is  $\beta$ -D-(1- $\rightarrow$ 4) and amylose is  $\alpha$ -D-(1- $\rightarrow$ 4)

Amylopectin also has  $\alpha$ -D-(1- $\rightarrow$ 6) linkages

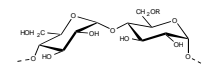
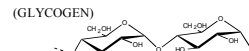
Starch is made up of two different chains, amylose and amylopectin primary storage polysaccharides of plants

© Caroline Sc

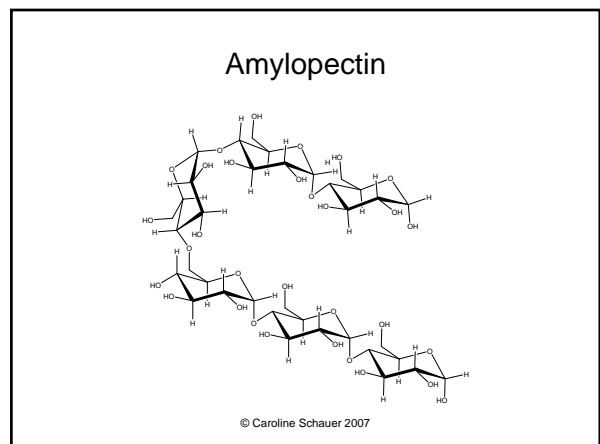
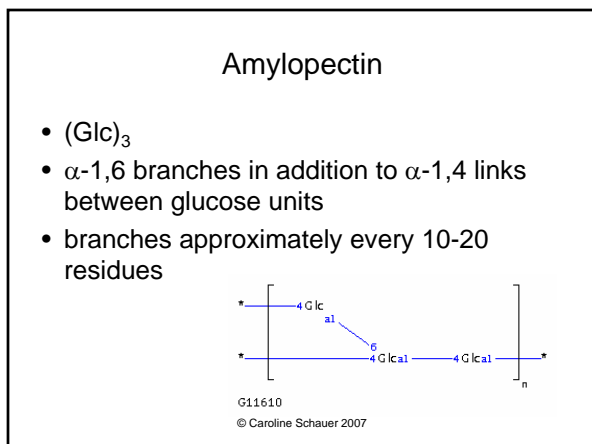
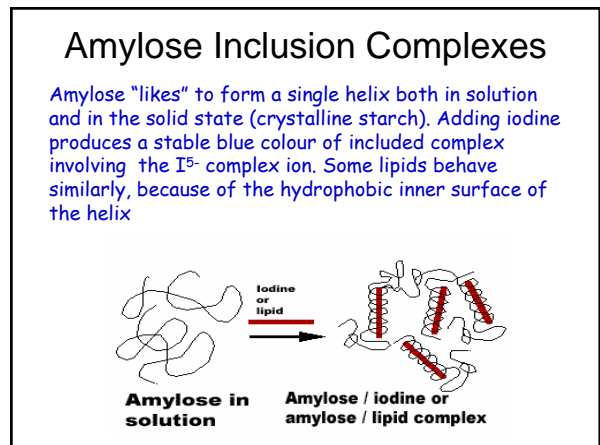
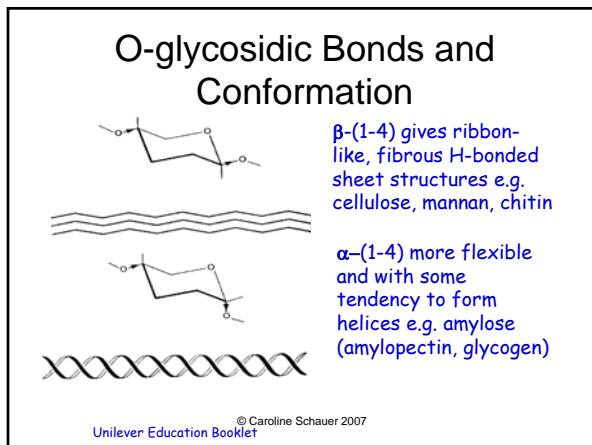
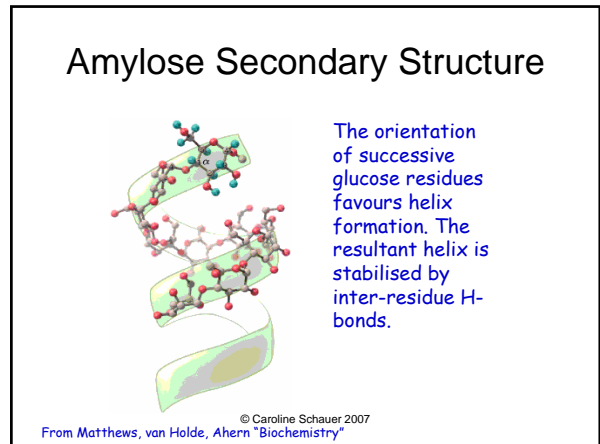
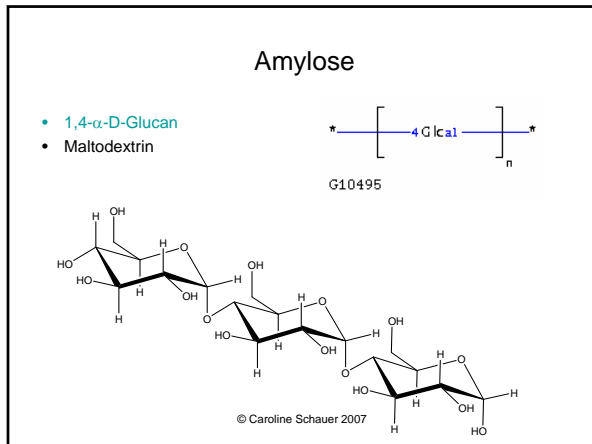
CELLULOSE BACKBONE



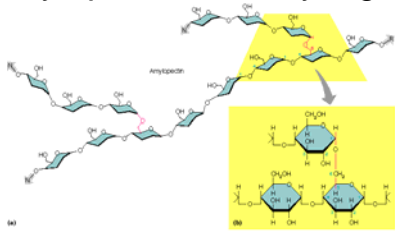
STARCH:  
AMYLOSE R=H  
AMYLOPECTIN R=



STARCH BACKBONE



## Amylopectin and Glycogen



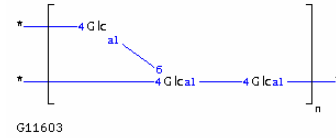
From Matthews, van Holde, Ahern "Biochemistry"

Glycogen and amylopectin have very similar (tree-like) structures but the branching frequency (~ every 6 glucans) is more frequent in glycogen than amylopectin (~12-20). [Some plant mutant amylopectins are essentially the same!] RMMs are ~50,000,000.

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## Glycogen

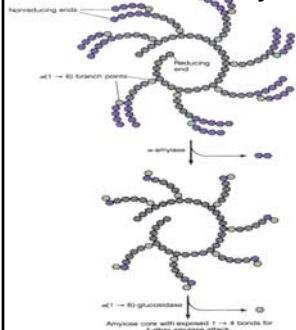
- (Glc)<sub>3</sub>



G11603

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## Digestion of Amylopectin and Glycogen



Amylopectin and glycogen are stores of glucose, but to release this requires two enzymes, one to cleave  $\alpha$ -1-4 (amylose) bonds and another to break the 1-6 branch-points.

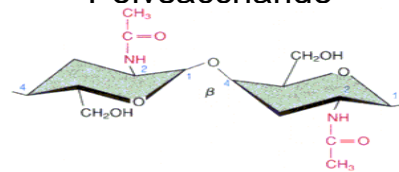
The 1-4 glycosidases include  $\alpha$ -amylase (in saliva) and the glycogen and starch phosphorylases.

1-6 cleavage employs an appropriate debranching enzyme.

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From Matthews, van Holde, Ahern "Biochemistry"

## Chitin - an Acetylated Polysaccharide



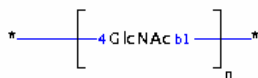
Chitin

From Matthews, van Holde, Ahern "Biochemistry"  
Chitin occurs widely in the exo-skeleton of invertebrates (especially crustacea). Like cellulose, also  $\beta$ -(1-4), it is fibrous and water insoluble. The partially deacetylated water soluble product chitosan (e.g. from krill chitin) has a number of important bio-pharmaceutical applications

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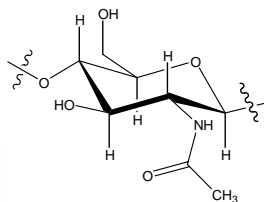
## Chitin

- beta-1,4-Poly-N-acetyl-D-glucosamine
- Second most abundant polysaccharide after cellulose

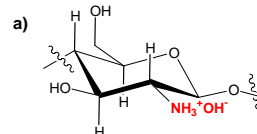


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## Chitosan



- Deacetylate chitin, using 50% NaOH and you get chitosan
- Soluble in dilute acid
- Amine functionality to attach functional groups

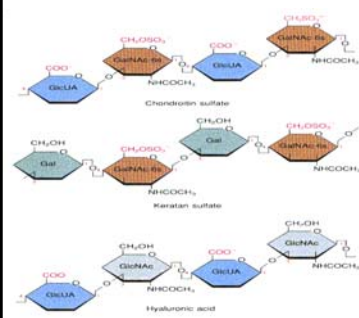
© Caroline Schauer 2007

## Chitosan uses

- Separation membranes
- Drug and enzyme immobilization
- Polyelectrolyte
- Metal adsorbent for the removal of Hg(II), Cu(II), Cr(III) and Cr(VI), Ag(I), Fe(III), Mo(VI), Cd(II), Pb(II), Zn(II), Pt(IV) and Sn(II)

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## Glycosaminoglycans (GAGs)

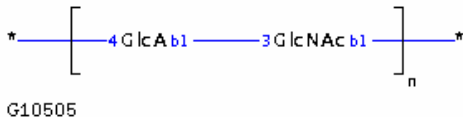


- Poly(disaccharides) one of which is N-acetylated at the 2-position
- They carry a -ve charge (as sulphate or acetyl) and form an important part of the connective tissue matrix
- Hyaluronic acid, for example, is a major constituent of cartilage

From Matthews, van Holde, Ahern Biochemistry © Caroline Schauer 2007

## Hyaluronic acid

- Hyaluronate
- (GlcNAc)<sub>1</sub> (GlcA)<sub>1</sub> D-galactosamine and D-glucuronic acid
- Glycoprotein; Glycosaminoglycan



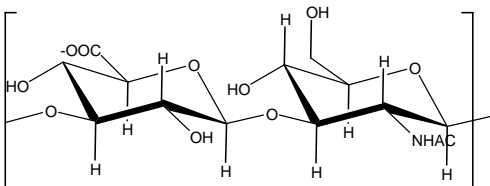
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## Hyaluronic Acid

- present in every tissue of the body
- Retention of water is one of the most important biological functions
- providing nutrients and removing waste from cells that do not have a direct blood supply, such as cartilage cells
- synovial joint fluid, the vitreous humor of the eye, the cartilage, blood vessels, extracellular matrix, skin and the umbilical cord
- popular choice for [facial augmentation](#)

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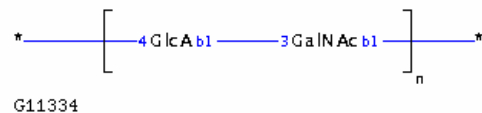
## Hyaluronic Acid (HA) β(1,3)



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## Chondroitin

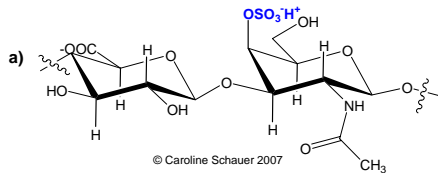
- (GlcA)<sub>1</sub> (GalNAc)<sub>1</sub> D-galactosamine and D-glucuronic acid
- Glycoprotein; Glycosaminoglycan



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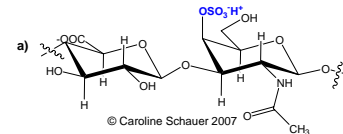
## Chondroitin sulfate $\beta(1,3)$

- Chondroitin sulfate is a major constituent of [cartilage](#), providing structure, holding water and nutrients, and allowing other molecules to move through cartilage usually paired up with HA
- degenerative joint disease, such as [osteoarthritis](#), there is a loss of chondroitin sulfate as the cartilage erodes



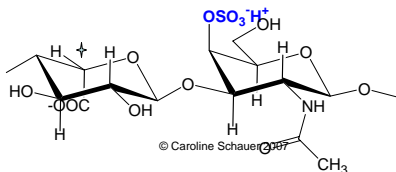
## Chondroitin sulfate A

- in humans in cartilage, bone, cornea, skin and the arterial wall
- galactosamines in the basic unit of chondroitin sulfate A is acetylated
- sulfate group esterified to the 4-position in N-acetyl-galactosamine (chondroitin 4-sulfate)
- molecular weight of chondroitin sulfate ranges from 5,000 to 50,000 daltons and contains about 15 to 150 basic units of D-galactosamine and D-glucuronic acid



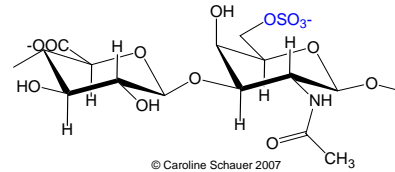
## Chondroitin sulfate B

- a.k.a. dermatan sulfate
- abundant in skin and is also found in heart valves, tendons and arterial walls
- linear repeating units containing D-galactosamine and either L-iduronic acid or D-glucuronic acid.
- molecular weight ranges from 15,000 to 40,000 daltons.



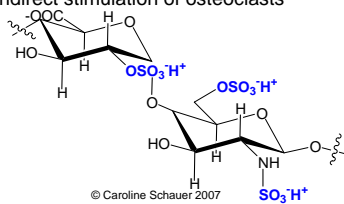
## Chondroitin sulfate C

- found in fish and shark cartilage
- sulfate group is esterified to the 6-position in N-acetyl-galactosamine
- chondroitin 6-sulfate



## Heparin $\alpha(1,4)$

- Anticoagulant/ Treat frostbite
- Heparin is strongly acidic because of its content of covalently linked sulfate and carboxylic acid groups
- most abundant in the liver and lungs
- direct or indirect stimulation of osteoclasts



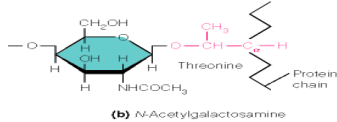
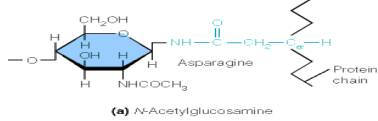
## Heparin

- Natural heparin is a complex mixture of carbohydrates
- in various medical devices such as test tubes and extracorporeal circulation devices such as renal dialysis machines- advantage over [EDTA](#) as an anticoagulant, as it does not affect levels of ions (such as [calcium](#)).
- Heparin was originally isolated from liver cells, hence its name (*hepato-* means "of the liver").
- Heparin is acetylated at the amine rather than sulfonated like Heparin

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## Glycoprotein linkages

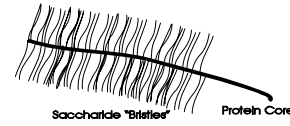
Glycoproteins are, as the name suggests, glycosylated proteins usually formed from N-acetylated saccharides, and either Asn (asparagine) or Thr (threonine)



From Matthews, van Holde, Ahern "Biochemistry"

## Glycoproteins and Proteoglycans

Many common "proteins" are actually glycoproteins, including ovalbumin, ribonuclease and human IgG! The blood group antigens (ABO) are distinguished by the different patterns of saccharide substitution



If the predominant species is the polysaccharide, the alternative name of **proteoglycan** is used. Many of these consist of a peptide core with saccharide chains attached to give a "beads-on-a-string" structure

## Glycosylation

- >70% of all proteins are glycosylated (recent comment)
- Glycobiology is still in its infancy
- Structural techniques still being developed
- Sequence methods for saccharides include
  - Chemical analysis after acid treatment (largely historical)
  - Enzymatic determination of structure
    - breakdown into oligosaccharides
  - FAB mass spectrometry

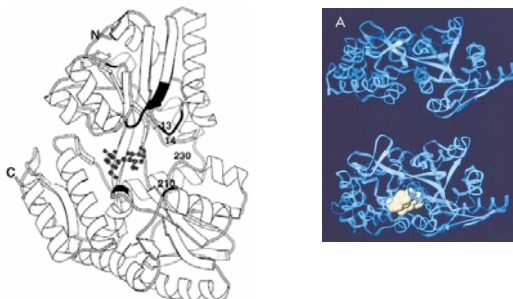
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## Hydrophobicity

- affected by the degree of polysaccharide hydration
- intra-molecular hydrogen bonding
- more hydrophobic if they have a greater number of internal hydrogen bonds
- their hydrophobicity increases there is less direct interaction with water
- Carbohydrates contain alcohol groups that preferentially interact with two water molecules each if they are not interacting with other hydroxyl groups on the molecule
- preferentially interact with water if the hydroxyl groups are equatorial on the pyranose rings

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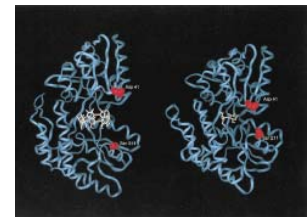
Maltose binding protein is a hinge protein that changes conformation upon binding to maltose



The figure is from the recent review of the maltose resistance system in E. coli by W. Boos & H. Shuman, Microbiology and Molecular Biology Reviews, 62, 204-229 (1998)

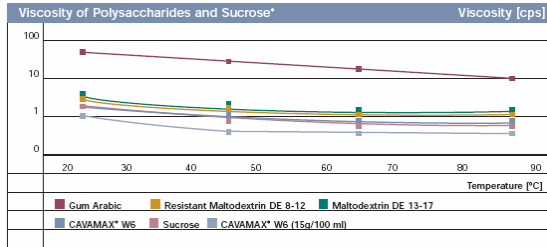
## Competitive binding

- Structure of Maltose Binding protein with maltose on the right and  $\beta$ -cyclodextrin on the left



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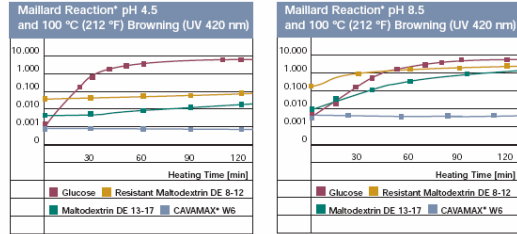
## Viscosity



\*30 grams/100 ml

Alpha cyclodextrin is marketed under the "widely recognized" CAVAMAX® W6 brand name.

## Browning



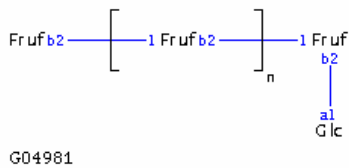
\*10 % Solution with 1% glycine

\*10 % Solution with 1% glycine

Many dietary fibers contain reducing sugars. Their reaction with proteins (Maillard reaction) can lead to browning and undesirable color changes of certain foods and beverages. © Caroline Schauer 2007

## Inulin

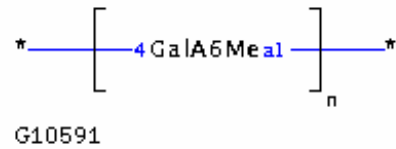
- (Glc)1 (Fruf)3



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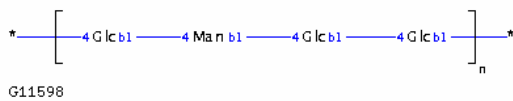
## Pectin

- (GalA6Me)<sub>1</sub>
- containing galacturonic acid residues flexible extended conformations and also have regular "hairy" regions with pendant arabinogalactans



## Glucmann

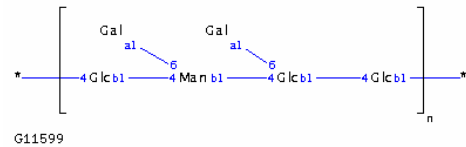
- (Glc)3 (Man)1
- The ratio of Man:Glc is 2:1 ~ 3:1.



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## Galactoglucomannan

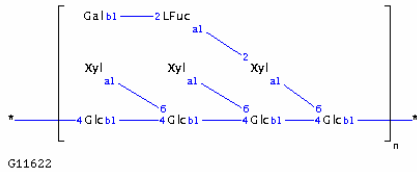
- The ratio of Man:Glc:Gal is 1:3:2. (Glc)3 (Gal)2 (Man)1



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## Xyloglucan

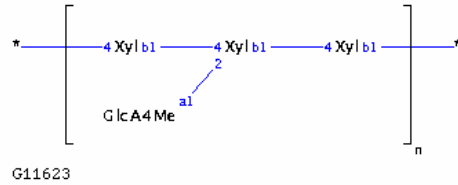
- (Glc)4 (Gal)1 (LFuc)1 (Xyl)3



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## 4-O-Methylglucuronoxylan

- (Xyl)3 (\*)2 (GlcA4Me)1



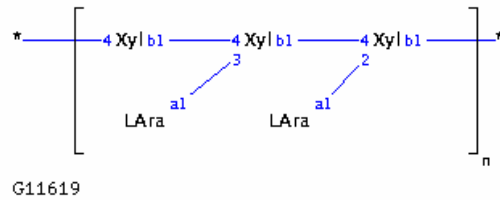
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## Arabinoxylan

- (Xyl)<sub>3</sub> (LAra)<sub>2</sub>
- The flexibility of arabinoxylans is decreased with increasing arabinosylation, but the key parameter is likely to be the distribution of these side-chains along the backbone since this will have the most direct effect on conformation.
- Because of extended conformations arabinoxylans exhibit a very high viscosity in aqueous solution
- Cereal arabinoxylans are composed of β-linked xylan chains and are relatively stiff molecules with extended conformations

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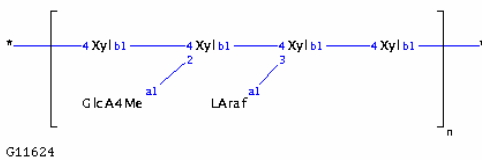
## Arabinoxylan



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## 4-O-Methylglucuronoarabinoxylan

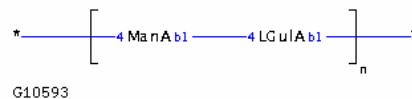
- (Xyl)4 (\*)2 (GlcA4Me)1 (LAráf)1



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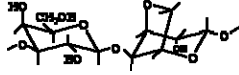
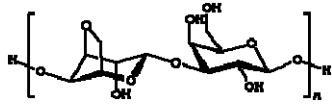
## Alginate

- (LGulA)1 (ManA)1
- Alginic acid
- Polysaccharide consisting of ManA and LGulA.
- There are several modes of glycoside bond.



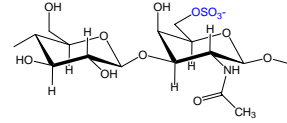
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## Agarose



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## Keratan Sulfate



- Found in cornea bone cartilage
- Usually aggregated with CS
- $\beta(1,4)$

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