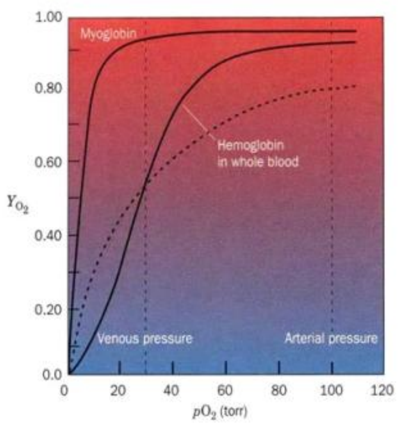
Notes 10/15

Monday, October 15, 2007
10:00 AM

Carbohydrates

October 15, 2007

Oxygen dissociation curves of Mb and Hb in whole blood



- **Hemoglobin: $Y_{O2} = P_{50}$ a little below 30 torr**
- **Myoglobin: $Y_{O2} = P_{50}$ at 2.8 torr**
- Hb dissociates more readily from O_2 than Mb

Biochemistry

- What are the chemical and 3D structures of biological molecules and assemblies?
- How do they form these structures?
- How do their properties vary with them.
- We have considered proteins.
- Now let's consider carbohydrates.

Proteins vs Carbohydrates

- Proteins
- Polymer of amino acid residues
- 20 species of amino acids
- Chirality
- Amide linkages
- Linear
- Sequences are genetically dictated
- Self assembly
- 4 kcal/g

- Carbohydrates
- Polymer of sugar residues
- About 8 common species of sugars
- Chirality
- Glycosidic linkages
- Linear and branched
- Sequences are not genetically dictated
- Most abundant class of biological molecules
- 4 kcal/g

Carbohydrates

- Saccharide (Greek: sakcharon, sugar)
- Most abundant class of biomolecules
- $(C \cdot H_2O)_n$ where $n \geq 3$
- Simplest unit = monosaccharide
- Many produced by gluconeogenesis (animals) glucose new creation
- Many produced by photosynthesis (plants)
- Breakdown of monosaccharides provides most of the E to power biological processes

Carbohydrates

- Monosaccharides
  - Classification
  - Configuration and Conformation
  - Sugar Derivatives
- Polysaccharides
  - Disaccharides
  - Structural Polysaccharides
  - Storage Polysaccharides
- Glycoproteins (next lecture)

General Characteristics

- Most carbohydrates are found naturally in bound form rather than as simple sugars
  - Polysaccharides (starch, cellulose, inulin, gums)
  - Glycoproteins and proteoglycans (hormones, blood group substances, antibodies)
  - Glycolipids (cerebrosides, gangliosides)
  - Glycosides (
  - Mucopolysaccharides (hyaluronic acid)
  - Nucleic acids
- Carb. compounds are often heterogenous in size and composition

Functions

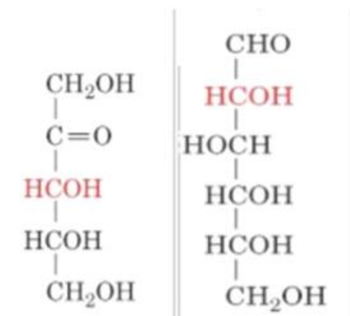
- sources of energy
- intermediates in the biosynthesis of other basic biochemical entities (fats and proteins)
- associated with other entities such as glycosides, vitamins and antibiotics
- form structural tissues in plants and in microorganisms (cellulose, lignin, murein)
- participate in biological transport, cell-cell recognition, activation of growth factors, modulation of the immune system

Monosaccharides

- Biomolecules
- Simple sugars
- Aldehyde or ketone derivatives
- Polyhydroxy alcohols
- Contain at least 3 carbon atoms
- Cannot be hydrolyzed into simple saccharides

Classification of Monosaccharides

- 1. Chemical nature of carbonyl group
  - Aldehyde: aldose
  - Ketone: ketose
- 2. Number of carbon atoms
  - 3: triose, 4: tetrose, 5: pentose, 6: hexose, etc.
  - Examples: glucose = aldohexose
  - Ribulose: ketopentose

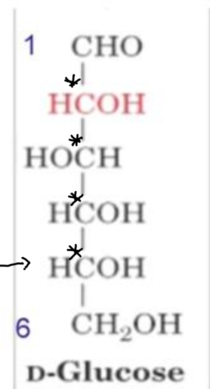


D-Ribulose D-Glucose

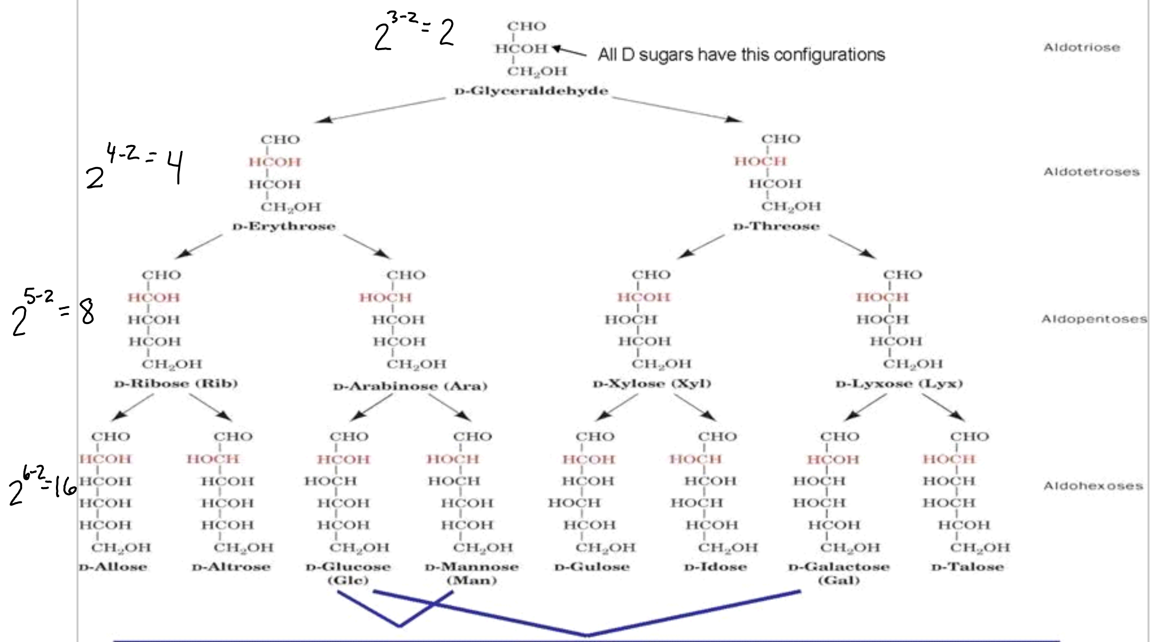
Stereochemistry of aldoses

- Chiral centers except C1 and C6
- $2^4 = 16$ aldohexose stereoisomers
- In general, n-carbon aldoses have 2^{n-2} stereoisomers
- D sugars have the same absolute configuration at the chiral center farthest away from the carbonyl groups as does D-glyceraldehyde
- D sugars are more biologically abundant
- D-glucose is only aldose that commonly occurs naturally as a monosaccharide

D/L carb



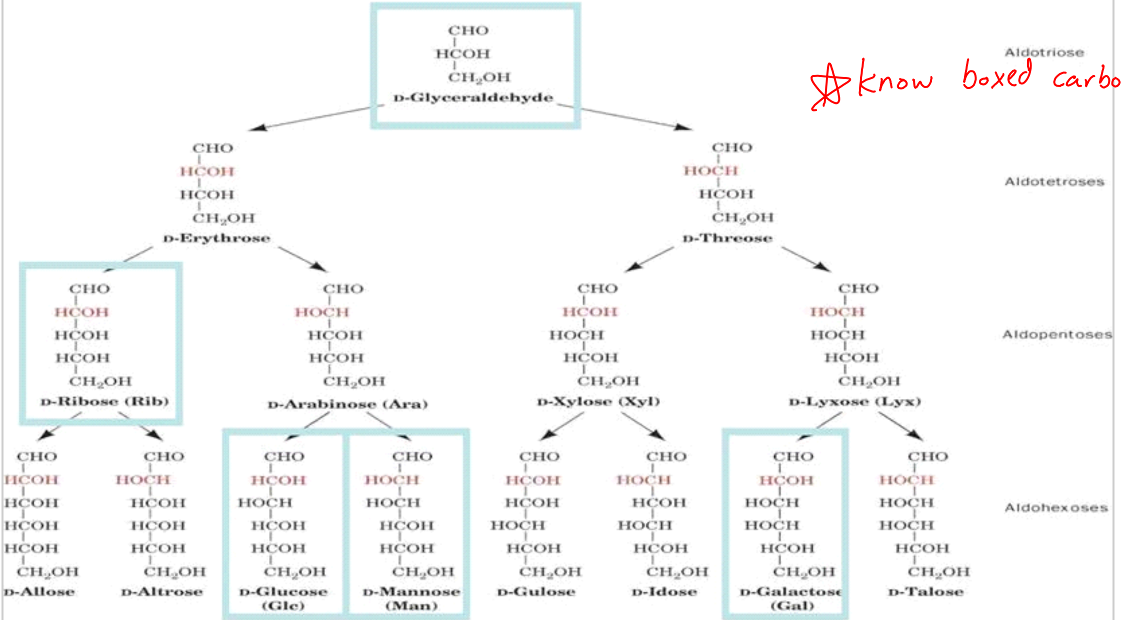
The stereochemical relationships, shown in Fischer projection, among the D-aldoses with three to six carbon atoms.



Epimers: sugars that differ only by the configuration about one C atom

The stereochemical relationships, shown in Fischer projection, among the D-aldoses with three to six carbon atoms.

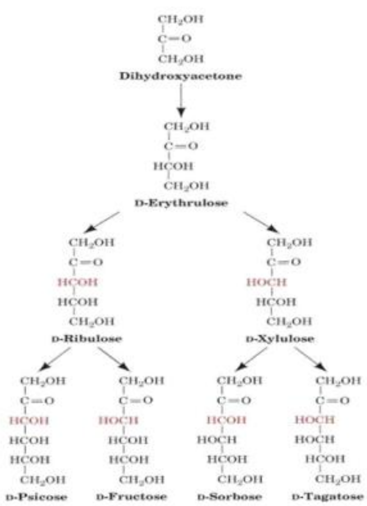
★ know boxed carbohydrates



Reducing sugars: aldehyde group reduces mild oxidizing agents

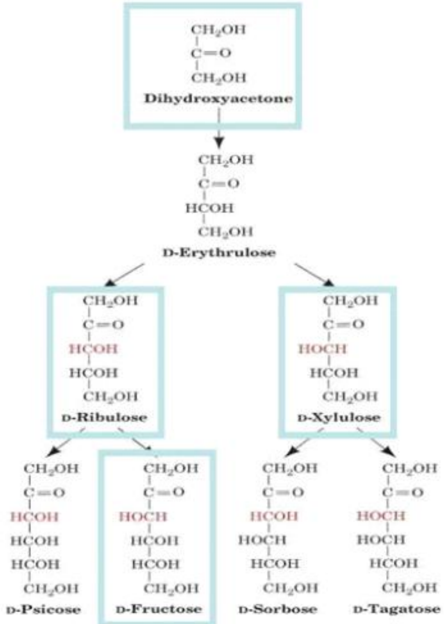
Tollen's reagent is used to detect reducing sugars (Ag+ in reagent gets reduced)

The stereochemical relationships among the D-ketoses with three to six carbon atoms.



- Ketoses have 2^{n-3} stereoisomers

The stereochemical relationships among the D-ketoses with three to six carbon atoms.

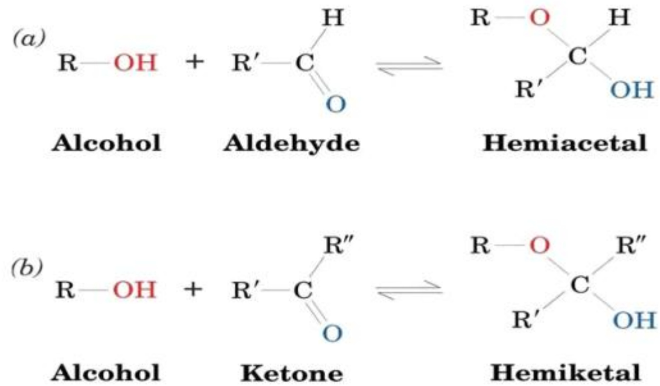


- Ketoses have 2^{n-3} stereoisomers

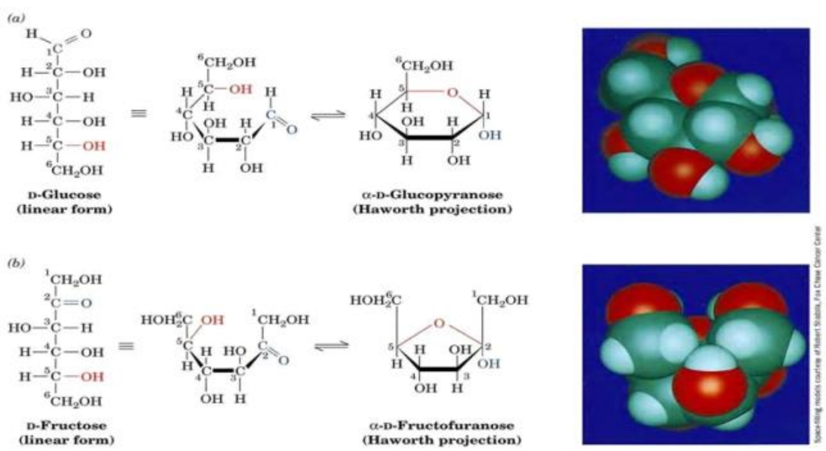
Configurations and conformations of monosaccharides

- Reactions with alcohols
- Haworth projection formulas
- Cyclic sugars have two anomeric forms
- Sugars are conformationally variable

The reactions of alcohols with (*a*) aldehydes to form hemiacetals and (*b*) ketones to form hemiketals.

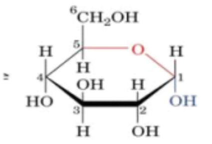


Cyclization reactions for hexoses

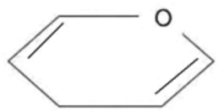


Space filling model

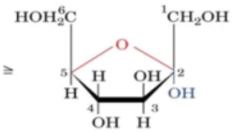
Cyclization reactions for hexoses.



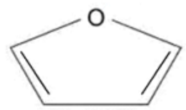
α-D-Glucopyranose
(Haworth projection)



Pyran



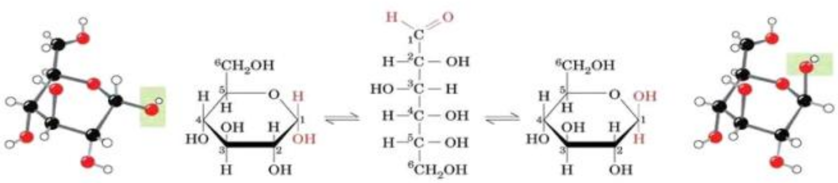
α-D-Fructofuranose
(Haworth projection)



Furan

Cyclic sugars have two anomeric forms

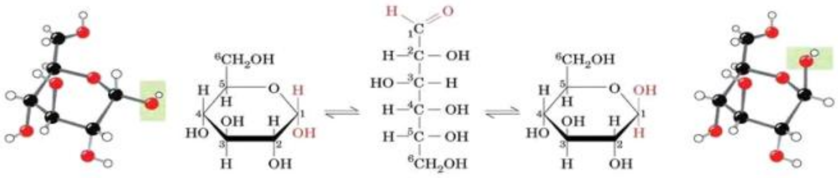
- Anomers: diastereomers that result from cyclization of monosaccharide
- Anomeric carbon (shown in red): the hemiacetal or hemiketal carbon
- Alpha or beta designation



α-D-Glucopyranose D-Glucose (linear form) β-D-Glucopyranose

Properties of anomers

- Anomers are diastereomers
- Any pair of diastereomers will have different physical and chemical properties
- Alpha and beta differ in optical rotation
- Dissolve either pure alpha or pure beta in water and interconversion will occur
- Mutarotation: phenomenon that occurs due to the formation of an equilibrium mixture between two anomers



α-D-Glucopyranose + 112.2°

D-Glucose (linear form)

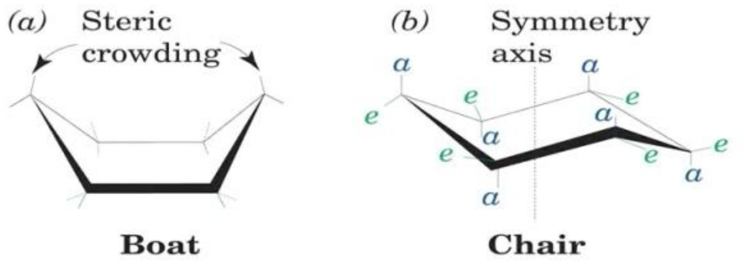
β-D-Glucopyranose +18.7°

At equilibrium + 52.7°

Sugars are conformationally variable

- Five- and six-membered hexose rings are more stable
  - Stability depends on interactions between substituents on the ring
- Haworth formulas are just models and not what the rings really look like naturally
- Atoms in the rings are sp^3 hybridized so tetrahedrally shaped

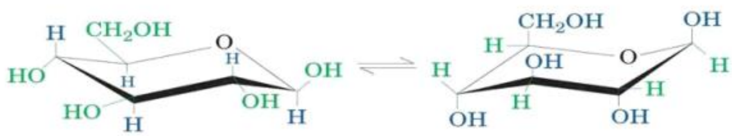
Conformations of a cyclohexane ring



Substituents (green) are eclipsed

e = equatorial
a = axial
a and e are interconvertable

The two alternative chair conformations of β-D-glucopyranose.



Predominant conformation

Bulky substituents are equatorial

Beta-D-glucose is the only D-aldohexose that can have all 5 non-H groups in the e position

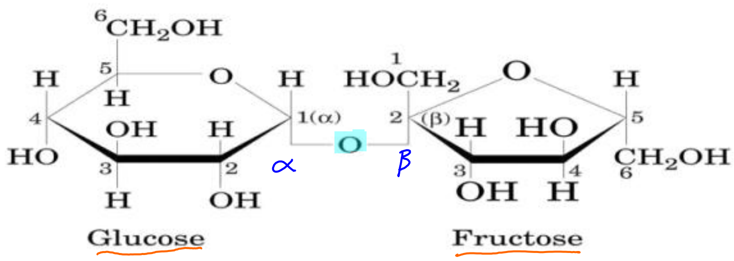
Glycosidic Bond

- Glycosidic bond forms when an anomeric hydroxyl group of a sugar reversibly condenses with an alcohol of another sugar
- Links monsaccharides
  - disaccharides
  - polysaccharides
- Carb analog of the peptide bond
- Glycosidases hydrolyze this bond
- Bond is acid catalyzed
- Stable in basic and neutral conditions in absence of glycosidase

Disaccharides

- Two monosaccharides linked by a glycosidic bond
- Several common disaccharides
  - Sucrose, lactose, maltose, isomaltose, cellobiose
- Naming
  - Component monosaccharides
  - Ring types
  - Anomeric forms
  - linkage

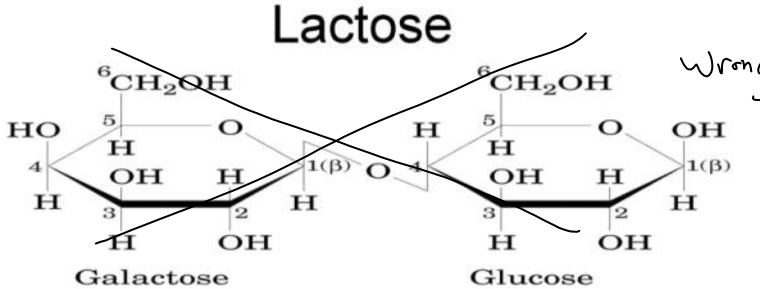
Sucrose



- O-alpha-D-glucopyranosyl-(1-->2)-beta-D-fructofuranoside
- Most abundant
- Found in plant kingdom
- Table sugar
- Not a reducing sugar
- Hydrolysis leads to a change in optical rotation from dextro to levo and it is referred to as invert sugar
- Invertase (alpha-D-glucosidase)

Do not need to know polysaccharide nomenclature but need to know the full names of the ones on these notes.

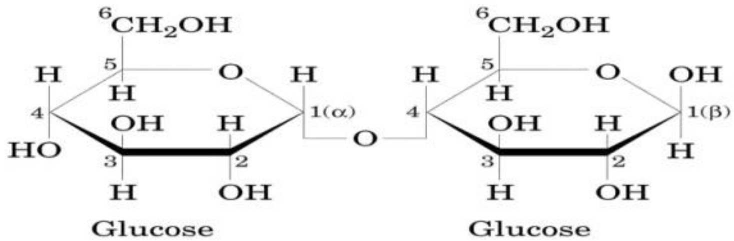
Lactose



Wrong see 10/17 notes

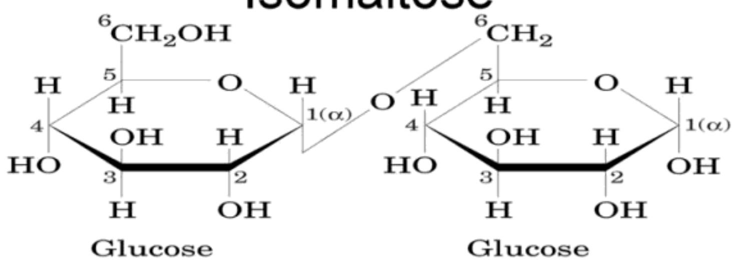
- O-beta-D-galactopyranosyl-(1-->4)-D-glucopyranose
- Milk sugar (0 to 7% of milk)
- Reducing sugar because free anomeric C on glucose is present
- Lactase (beta-D-galactosidase)

Maltose



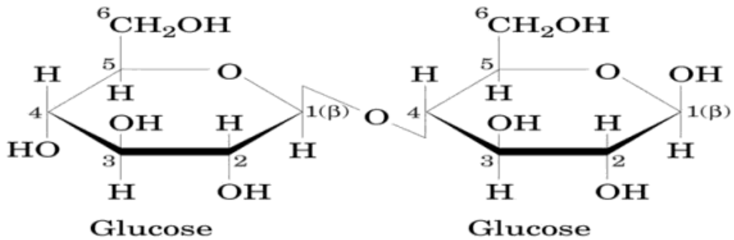
- Enzymatic hydrolysis product of starch
- O-alpha-D-glucopyranosyl-(1-->4)-D-glucopyranose
- Reducing sugar

Isomaltose



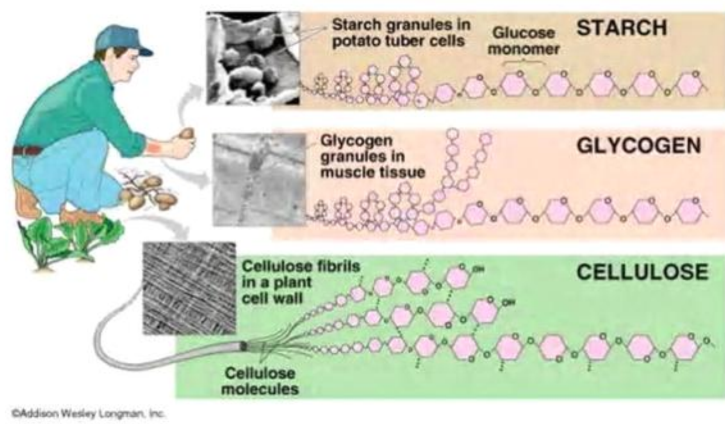
- O-alpha-D-glucopyranosyl-(1-->6)-D-glucopyranose

Cellobiose



- O-beta-D-glucopyranosyl-(1-->4)-D-glucopyranose

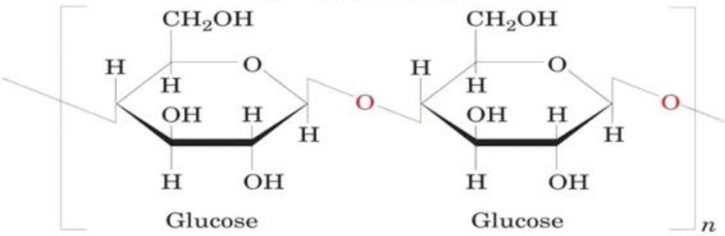
Examples of Polysaccharides



Structural Polysaccharides

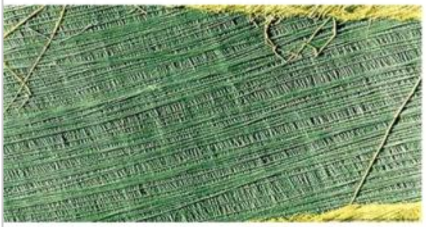
- Cellulose
  - Primary structural component of plant cell walls
  - Accounts for over half of C in biosphere
  - Predominately in plants
  - Also found in tunicates (invertebrates)
- Chitin
  - Primary structural component of ✓ lobster, crab
    - Exoskeletons: Crustaceans, insects, spiders
    - Cell walls: Fungi, algae
  - Almost as abundant as cellulose

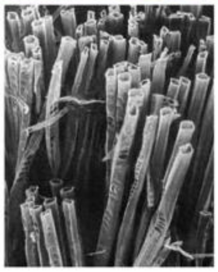
The primary structure of cellulose



- Linear polymer of up to 15,000 D-glucose residues
- Beta(1-->4) glycosidic bonds
- No defined size
- Invertebrates cannot hydrolzye Beta(1-->4) glycosidic bond, but microbes and termite can using cellulase

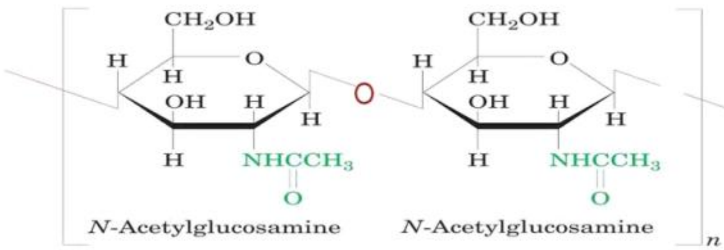
Electron micrograph of cellulose fibers





- The fibers are held together by a matrix of polysaccharides
- In wood the matrix is called lignin (plasticlike phenolic polymer)
- Cellulose fibers are held in position by intra- and interchain H-bonds

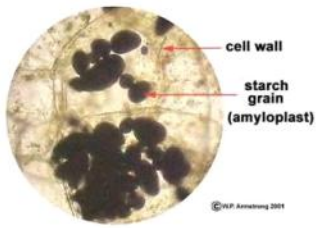
Structure of chitin

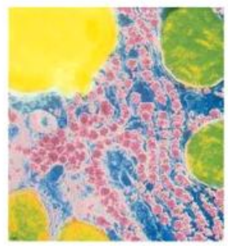


- Homopolymer of beta(1-->4)-linked N-acetyl-D-glucosamine
- Acetamido group
- Similar in structure compared to cellulose

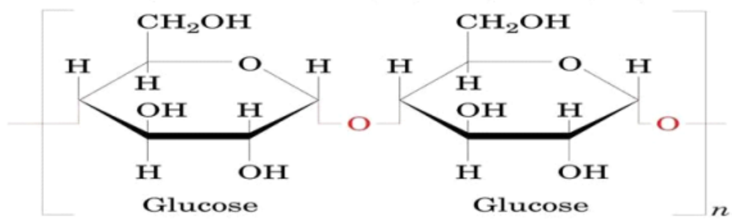
Storage Polysaccharides

- Starch
  - Plant synthesized
  - Mixture of glucans
  - Food reserve
  - Deposited in plant cell cytoplasm as insoluble granules
  - Main carb source in human diet
  - Alpha-amylose, amylopepctin
- Glycogen
  - Animal synthesized
  - Mixture of glucans
  - More branched than starch
  - Present in all cells but most prevalent in skeletal muscle and liver



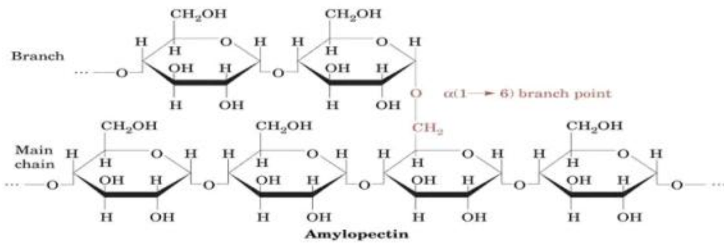


The D-glucose residues of α-amylose are linked by α(1 ® 4) bonds (*red*).



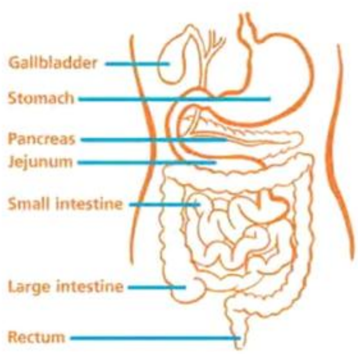
- n = several thousand
- Linear polymer
- Isomer of cellulose but different structure
- Left-handed helix conformation as a result of the alpha linkage

Amylopectin primary structure near one of its α(1 ® 6) branch points (*red*).



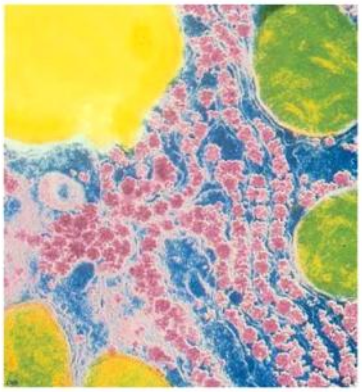
- Branched every 24 to 30 molecules on average
- May contain up to 10^6 glucose residues
- One of the largest biomolecules

Starch digestion occurs in stages



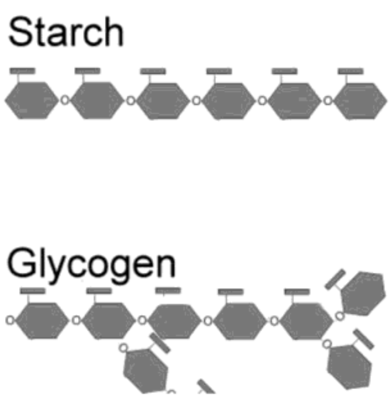
- Alpha-amylase in saliva hydrolyzes alpha(1-->4) glucosidic bonds
  - Oligosaccharides of 8 glucose units or less
- Pancreatic alpha-amylase in sm. intestine continues to hydrolyze
  - Maltose
  - Maltotriose
  - dextrins (contain the alpha(1-->6) branches)
- Brush border membrane enzymes of the intestinal mucosa hydrolyze to monosaccharides
  - Alpha-glucosidase
  - Alpha-dextrinase
  - Sucrase
  - Lactase (in infants)
- Monosaccharides are absorbed by intestine and transported to bloodstream

Photomicrograph showing the glycogen granules (*pink*) in the cytoplasm of a liver cell



- 1º structure resembles amylopectin
- Branched every 8 to 12 glucose residues
- Degraded in cell by glycogen phosphorylase to make glucose-1-phosphate

Why bother with polysaccharides?



- Polysaccharides have a lower osmotic pressure compared to monomers
- Osmotic pressure is proportional to the number of solute molecules in a given volume