Notes 10/16

Tuesday, October 16, 2007
10:00 AM

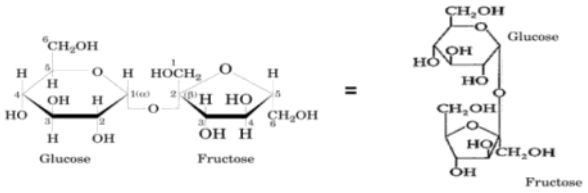
Carbohydrates: Part II

Oct. 16, 2007

Carbohydrate Nomenclature

- You are responsible for the nomenclature that you see in lecture, problem sets, and quizzes.
- We will not focus on how to name carbohydrates systematically in this course.
- Know the systematic names (the "long" names) for the sugars that are written out for you in lecture, problems sets, and quizzes

Sucrose

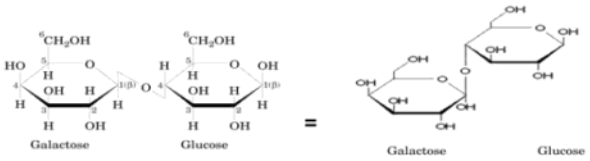


- O-alpha-D-glucopyranosyl-(1-->2)-beta-D-fructofuranoside
- Voet and Voet structure is correct, but not very intuitive so study this structure on this slide if it's better for you
- The same thing applies to the rest of the disaccharides

Carbohydrate Nomenclature (if you are dying to know but you don't need to know this)

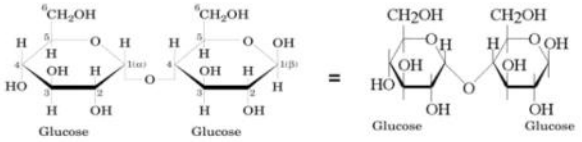
- Always name sugar polymers showing the non-reducing sugar residue(s) as substituents of the reducing sugar residue.
- Identify monosaccharide units
- Specify D or L form
- Specify the ring form (pyranose or furanose)
- Name the anomeric carbon first, and the other carbon involved in the linkage second.
- Identify the properties of the anomeric carbon of the sugar unit and add one of the following suffixes:
  - "-ose" if the anomeric carbon is free to convert from alpha to beta
  - "-oside" to the parent's name if all anomeric carbons form glycosidic linkages. The same goes for monosaccharides that are linked to a substituent via a glycosidic bond.
- "osyl" if the sugar residue is being named as a substituent of another residue to which its anomeric carbon is linked in a glycosidic bond. An example of this is sucrose, where both anomeric carbons are linked. The sugar can be named with either monosaccharide as the substituent (ending in -osyl) and the other named as the parent compoun ending in -oside.
- Specify how they are linked together (alpha or beta linkage and the identity of the carbons involved)
- There are several ways to order a carbohydrate's name.
- This list here isn't entirely complete.
- Reference: IUPAC Commission (1972) JBC 277: 613-635

Lactose



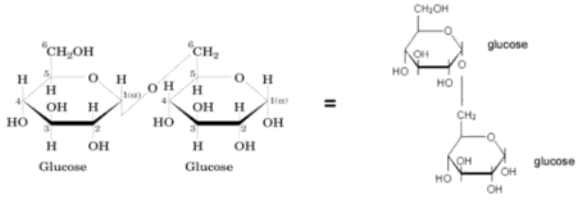
- **O-beta-D-galactopyranosyl-(1-->4)-D-glucopyranose**
- "O" is for the atom that links the two monosaccharides
- "beta" because galactose is in the beta configuration (and won't change to alpha)
- "Pyran" because the ring resembles a pyran
- "-osyl" because its anomeric C is linked in a glycosidic bond
- "D" because it is in the D configuration
- "-ose" because the anomeric C is in the hemiacetal form
- The anomeric configuration (alpha or beta) isn't mentioned when naming the glucopyranose because it is free to convert between the alpha and beta configuration

Maltose



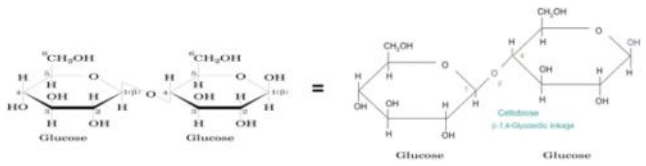
- Enzymatic hydrolysis product of starch
- O-alpha-D-glucopyranosyl-(1-->4)-D-glucopyranose
- Reducing sugar

Isomaltose



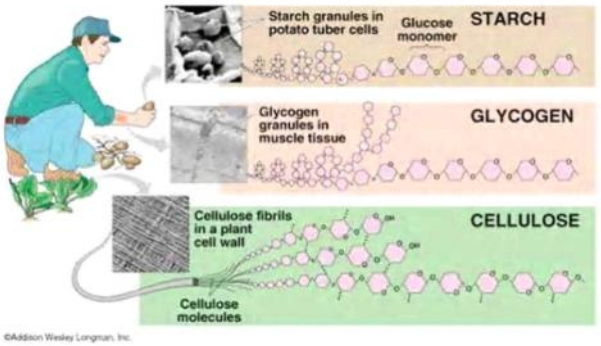
- O-alpha-D-glucopyranosyl-(1-->6)-D-glucopyranose

Cellobiose



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

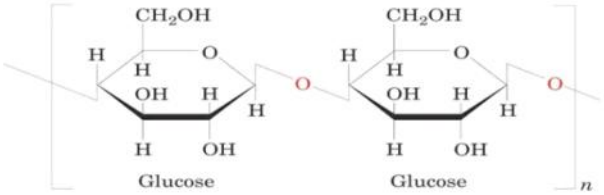
Examples of Polysaccharides



Structural Polysaccharides

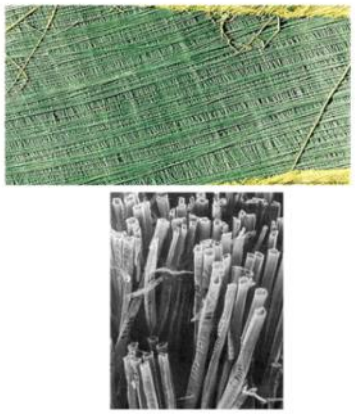
- Cellulose
  - Primary structural component of plant cell walls
  - Accounts for over half of C in biosphere
  - Predominately in plants
  - Also found in tunicates (invertebrates)
- Chitin
  - Primary structural component of (lobster, crab)
    - Exoskeletons: Crustaceans, insects, spiders
    - Cell 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 bonds, but microbes and termites can using cellulase

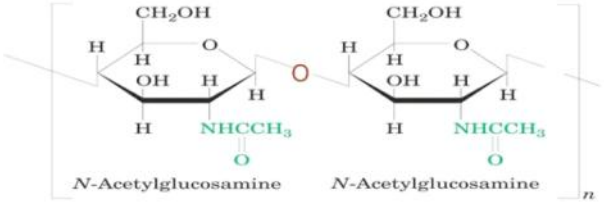
Electron micrograph of cellulose fibers



- 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
- Cotton balls are 100% cellulose

crunchy stuff in insects
most insects 401 chitin

Structure of chitin

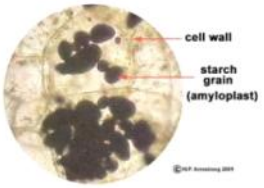


- Homopolymer of beta(1-->4)-linked N-acetyl-D-glucosamine
- Acetamido group
- Similar in structure compared to cellulose

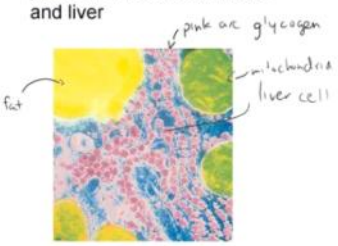
Storage Polysaccharides

a molecule that is a polysaccharide of D-glucose molecules that are linked by glycosidic bonds

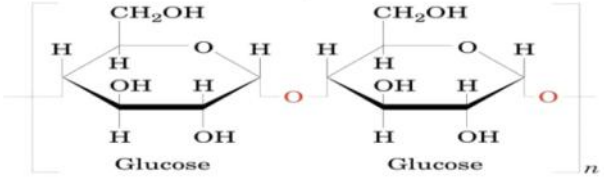
- Starch
  - Plant synthesized
  - Mixture of glucans
  - Food reserve
  - Deposited in plant cell cytoplasm as insoluble granules
  - Main carb source in human diet
  - Alpha-amylose, amylopectin



- Glycogen
  - Animal synthesized
  - Mixture of glucans
  - More branched than starch
  - Present in all cells but most prevalent in skeletal muscle and liver

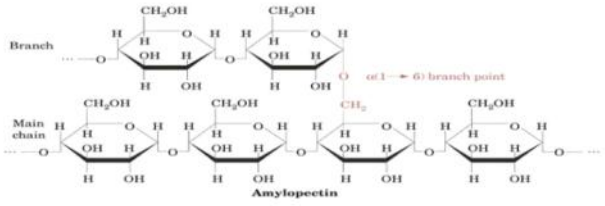


The D-glucose residues of α-amylose are linked by α(1 → 4) bonds (*red*).



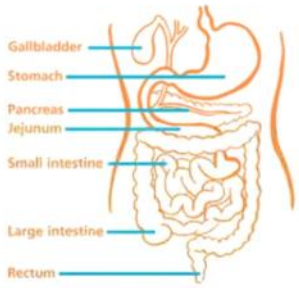
- n = several thousand
- Linear polymer
- Isomer of cellulose but different structure
- Left-handed helix conformation as a result of the alpha linkage

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



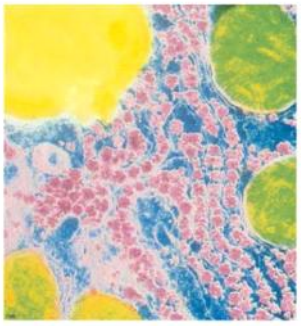
- Branched every 24 to 30 molecules on average
- May contain up to 10^6 glucose residues
- One of the largest biomolecules

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

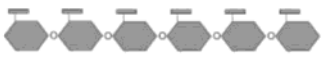
Photomicrograph showing the glycogen granules (*pink*) in the cytoplasm of a liver cell



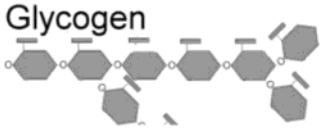
- 1° structure resembles amylopectin
- Branched every 8 to 12 glucose residues
- Degraded in cell by glycogen phosphorylase to make glucose-1-phosphate

Why bother with polysaccharides?

Starch



Glycogen



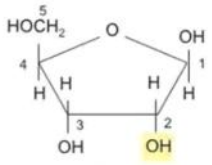
- Polysaccharides have a lower osmotic pressure compared to monomers
- Osmotic pressure is proportional to the number of solute molecules in a given volume

Sugar Derivatives

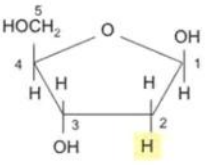
- Deoxy sugars
  - A monosaccharide in which an OH group is replaced by H
  - Beta-D-2-deoxyribose
- Amino sugar
  - One or more OH groups are replaced by an often acetylated amino group
  - D-glucosamine, D-galactosamine
- Sugar alcohols
  - Reduced aldoses and ketoses
  - Ribitol, glycerol, sorbitol

Deoxy Sugar Derivatives

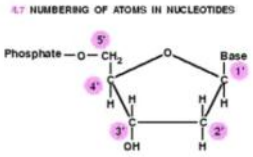
Chemical structures of sugars found in nucleotides



Ribose



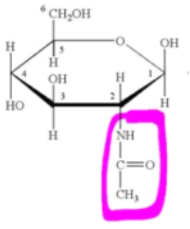
Deoxyribose



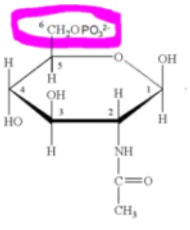
Nucelotide: PHOSPHATE-SUGAR-BASE

The 3'-OH of one nucleotide is linked to the 5'-phosphate of the next nucleotide.

Amino Sugars

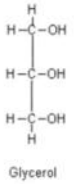


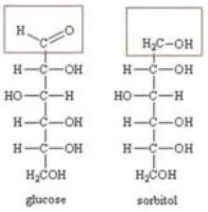
N-Acetyl-D-glucosamine

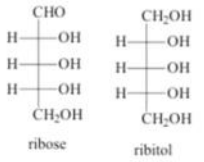


N-Acetyl-D-glucosamine 6-phophate

Sugar alcohols







Glycerol: important lipid component

Ribitol: component of flavin coenzymes

Sorbitol: "sugarless" sweetener

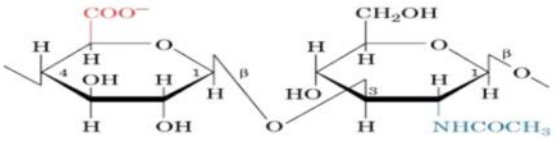
L-ascorbic acid (Vitamin C) is a sugar derivative

- Synthesized in plants and most animals (except primates and guinea pigs)
- Scurvy
  - Results from Vit. C deficiency
  - Impairment of collagen formation
  - Prolyl hydroxylase requires Vitamin C to hydroxylate prolines in collagen

Glycosaminoglycans (a.k.a. mucopolysaccharides)

- are linear polysaccharides found in extracellular matrices
- makes up a gel-like matrix called ground substance
- Ground substance is found in connective tissues and lubrication fluids
  - cartilage, tendon, skin, blood vessel walls, vitreous humor of eye, synovial fluid that lubricates joints
- Slimy, mucuslike texture
- Viscous, elastic

Hyaluronic acid (structure shown below) is an example of a glycosaminoglycan



Glucoronic acid N-acetylglucosamine

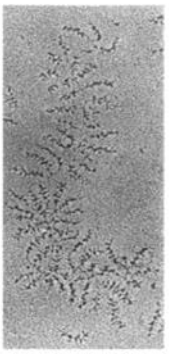
- Linear sequence of dimers consisting of two glucose derivatives
- Specifically it consists of glucoronic acid linked beta(1--->3) to N-acetylglucosamine
- Can be 25,000 to 50,000 dimers

Glycoproteins

- Glycoproteins are proteins that contain oligosaccharide chains covalently attached to their polypeptide backbones.
- Proteoglycans represent a special class of glycoproteins that have at least one glycosaminoglycan chain

Proteoglycans (a core protein + glycosaminoglycan chain) are seen in cartilage

- Cartilage is a meshwork of collagen fibrils filled in by proteoglycans
- The glycosaminoglycans are most often keratin sulfate and/or chondroitin sulfate



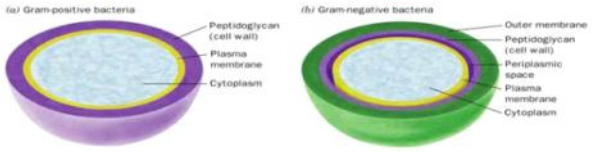
Electron micrograph of a proteoglycan

Peptidoglycan (a.k.a. murein) is a polysaccharide that serves a structural role in bacterial cell walls

latin for wall (mural = wall)

- Covalently linked polysaccharide and polypeptide chains form the peptidoglycan framework
- Medically significant because the cell wall is responsible for bacterial virulence
- Cell walls alone can induce disease symptoms in humans
- The thickness of the cell wall that encloses the plasma membrane distinguishes bacteria as either gram-positive or gram-negative

Schematic diagram comparing the cell envelopes of (*a*) gram-positive bacteria and (*b*) gram-negative bacteria.



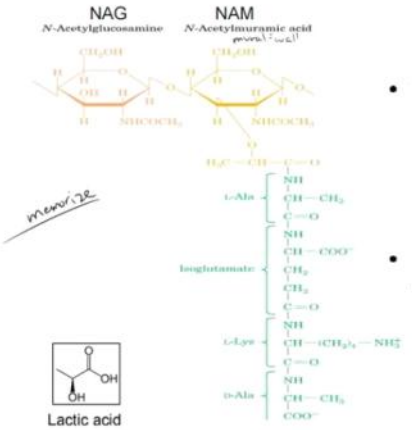
- Gram-positive wall is about 250 angstroms thick

takes up a gram stain

- Gram-negative wall is about 30 angstroms thick

Last slide for 10-16

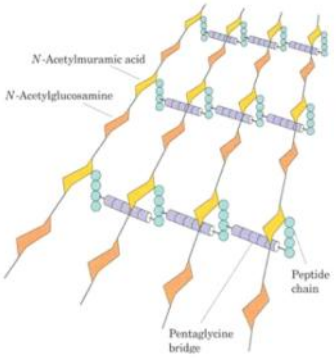
Chemical structure of the repeating unit of peptidoglycan



memorize

- The polysaccharide portion is an alternating NAG and NAM linked beta(1-->4)
- NAM has a tetrapeptide linked by an amide bond to its lactic acid moiety

Structure of the gram positive *Staphylococcus aureus* bacterial cell wall peptidoglycan



- Peptidoglycan chains form parallel layers that are cross-linked by a pentaglycine bridge
- The pentaglycine bridge extends from the terminal carboxyl group of one tetrapeptide to the epsilon-amino group of the K in the neighboring tetrapeptide

Wednesday we start discussing lipids