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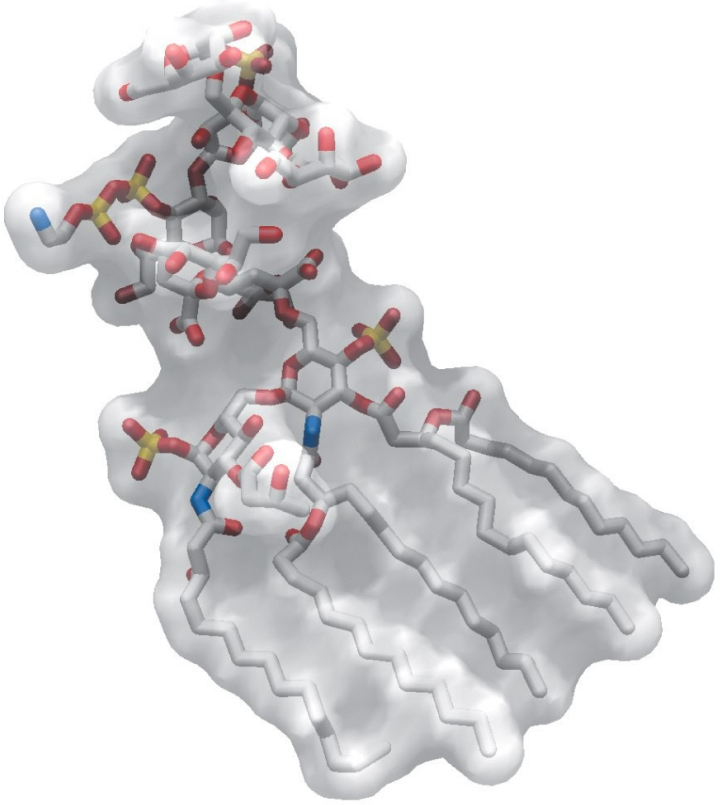
Chapter 11: Sugars and Polysaccharides

Voet & Voet: Chapter 11



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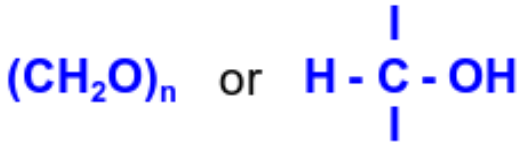
Carbohydrates

Carbohydrates (saccharides) are essential components of all living organisms

- **carbohydrate** means "carbon hydrate" and reflects the chemical composition of simple monosaccharides



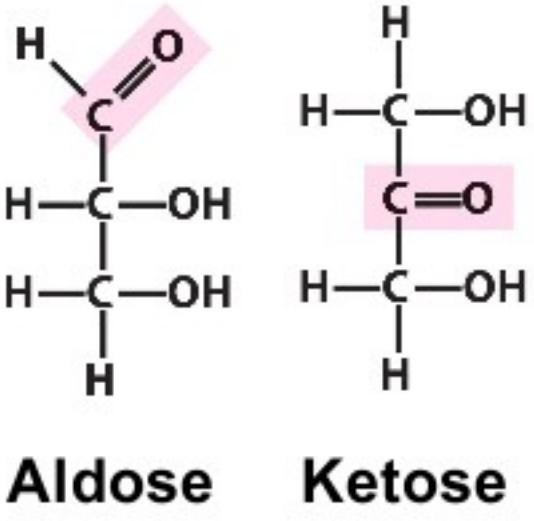
- polyhydroxyl aldehyde or polyhydroxyl ketose are particularly important in biological systems

Structural and functional studies of carbohydrates are <u>less advanced</u> than for nucleic acids and proteins as:

1) complex carbohydrates are heterogeneous in size and composition

2) saccharide sequences are not subject to standard genetic analysis

3) difficult to establish functional assays as typically have structural roles



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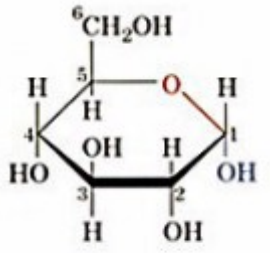
Saccharide Classification

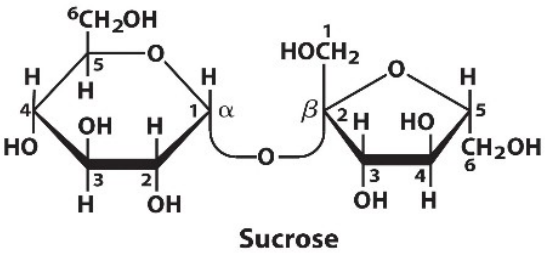
Monosaccharides are the basic unit of carbohydrates

- synthesized from simpler substances in gluconeogenesis or photosynthesis
- major energy source & components of nucleic acids and many lipids



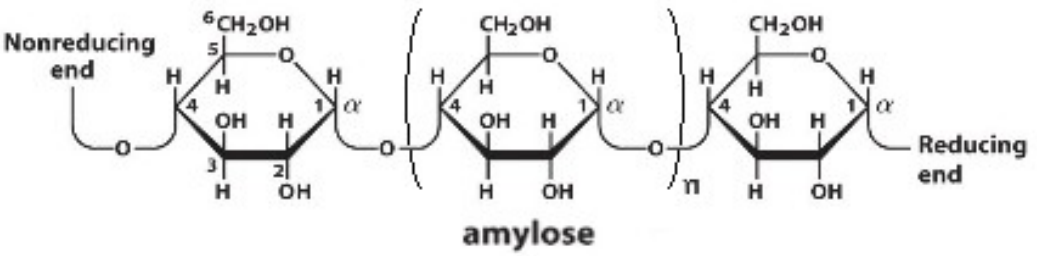
Oligosaccharides consist of a few (up to 20) covalently linked monosaccharides

- associated with proteins (glycoproteins) and lipids (glycolipids)
- serve structural and regulatory roles



Polysaccharides consist of many covalently linked monosaccharides

- structural function in all organism (*ie* cellulose in plants)
- nutritional reserve (*ie* starch in plants, glycogen in animals)



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Monosaccharide Classification

Classified according to chemical nature of carbonyl group and number of C atoms

- **Aldose or Ketose**
- **Triose, tetrose, pentose, hexose**

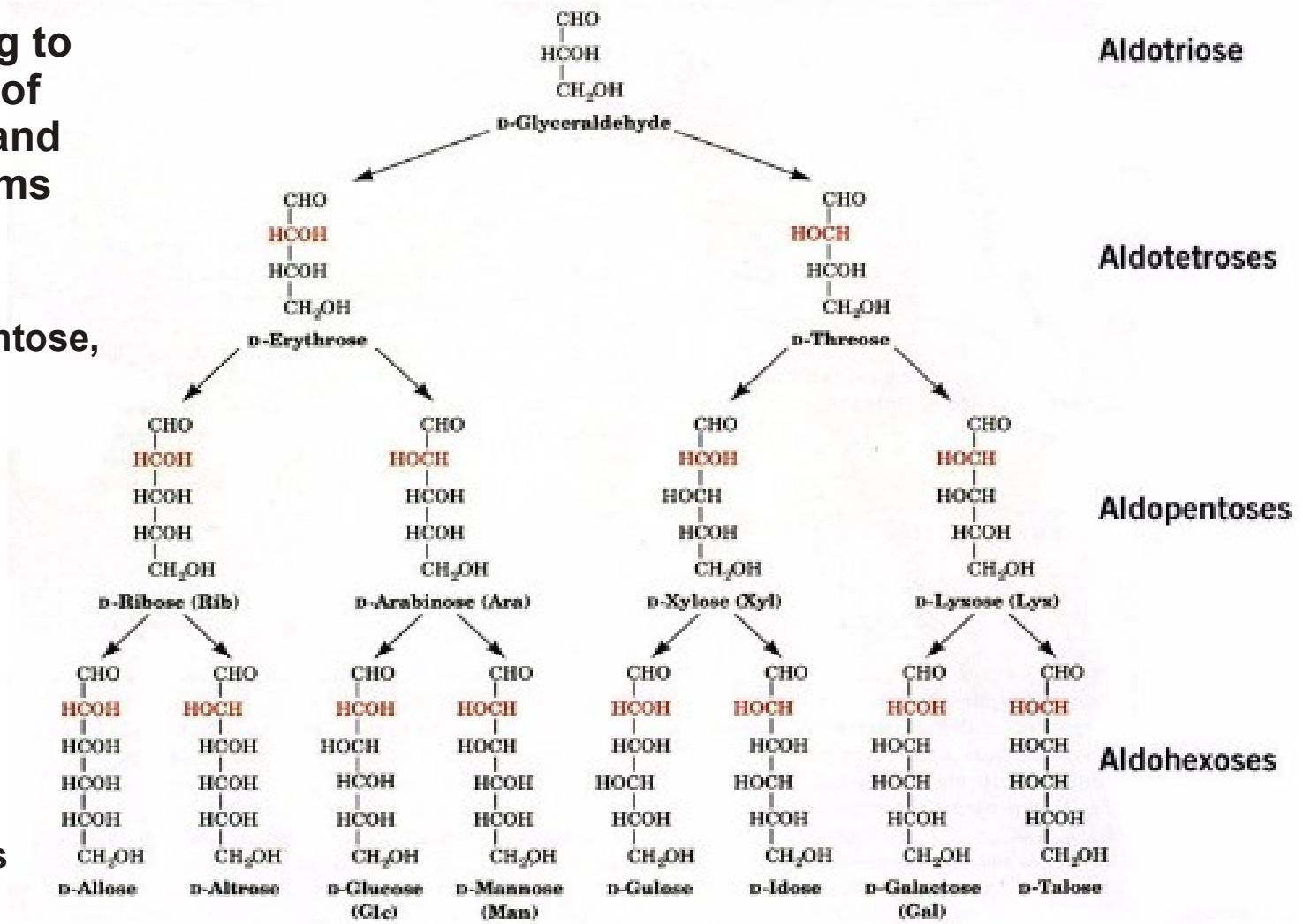

Figure: D-aldose family of monosaccharides

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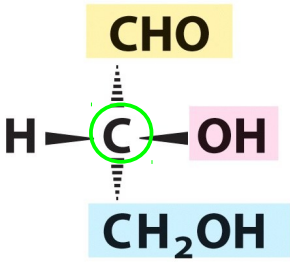
Saccharide Stereochemistry

Based upon configuration of chiral C in glyceraldehyde

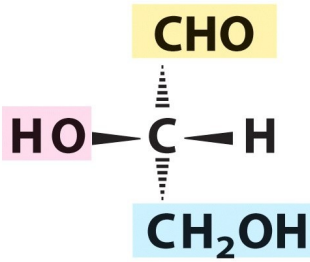
- chiral C furthest from carbonyl for sugars with n > 3
- Number of stereoisomers is 2^n (n is number of chiral centers)

Stereochemical terminology (review)

- **Enantiomers**: differ at all chiral centers (mirror image molecules)
- **Diastereomers**: differ at one or more chiral centers
- **Epimers**: differ at one chiral center

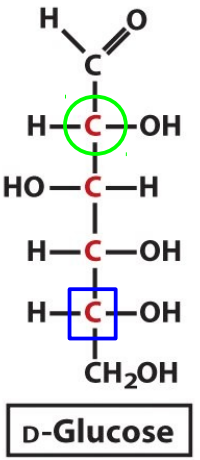


D-Glyceraldehyde

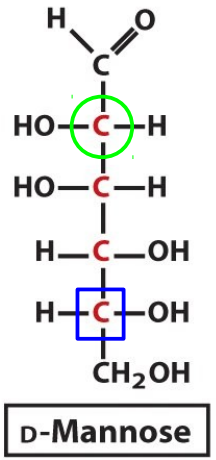


L-Glyceraldehyde

Example of epimers



D-Glucose



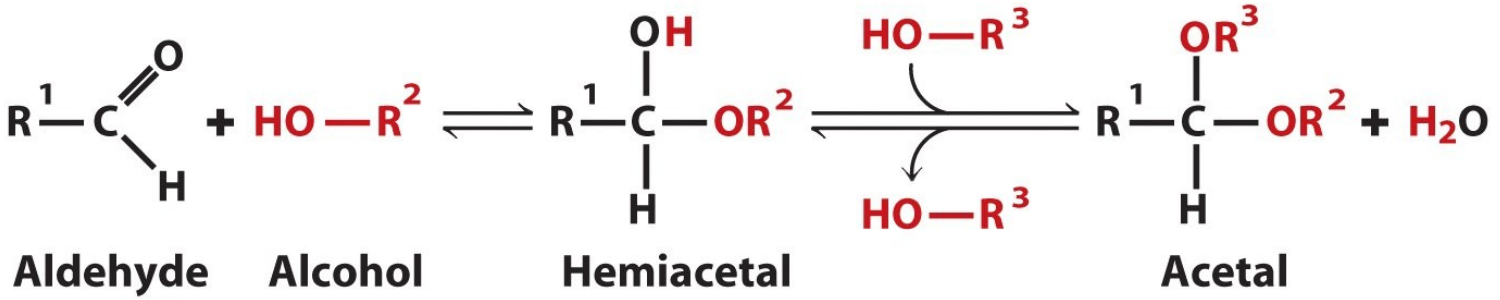
D-Mannose

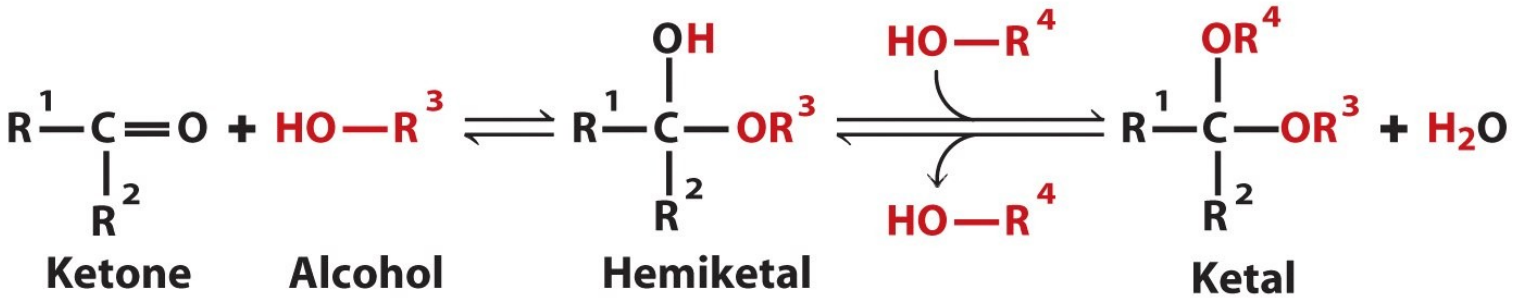
Circles: Epimeric Carbons

Squares: D-configuration

Reactivity (review)

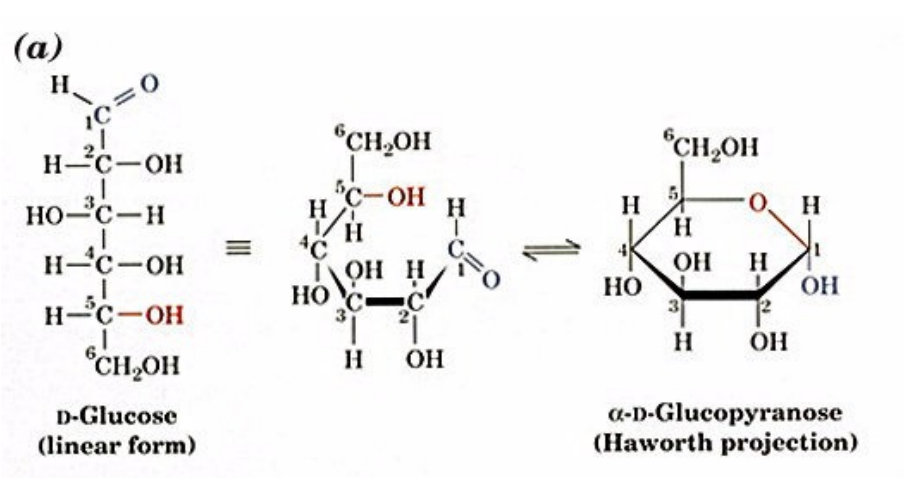
- Alcohols react with aldehydes (1:1 ratio) to form hemiacetals and (2:1 ratio) acetals
- Alcohols react with ketones (1:1 ratio) to form hemiketals and (2:1 ratio) ketals

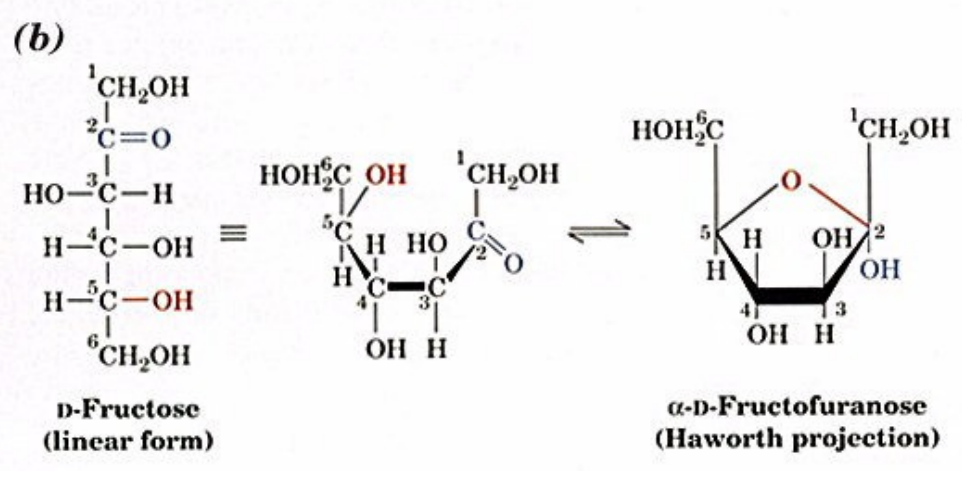


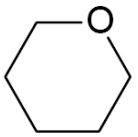


Saccharide Configurations

- **Aldoses can react with self forming cyclic hemiacetals(left) and ketoses can react with self forming cyclic hemiketals (right)**
  - **saccharides forming 5 and 6 member rings are referred to as a furanose and pyranose, respectively**







Pyranose

Furanose

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Cyclic Saccharide Anomers

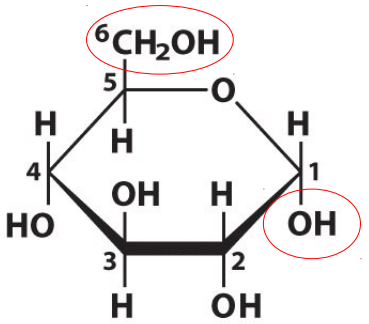
Cyclization of saccharides can generate two diastereomers or anomers

- hemiacetal or hemiketal carbon is referred to as the anomeric carbon

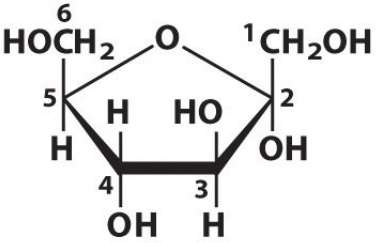
α anomer : anomeric carbon OH is on the opposite side of the ring from the CH_2OH of the chiral center defining D- or L-

β anomer : anomeric carbon OH is on the same side of the ring as the CH_2OH of the chiral center defining D- or L-

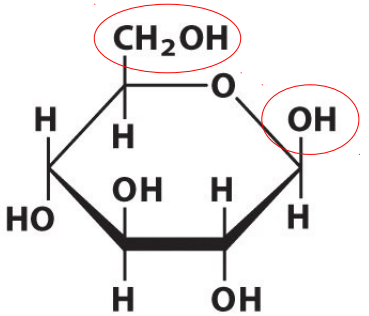
Need to learn the structures of glucose (an aldose) and fructose (a ketose) and their anomers



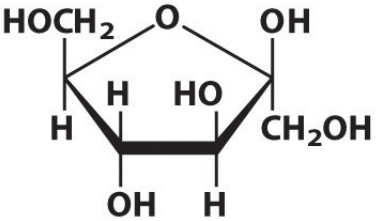
α-D-Glucopyranose



α-D-Fructofuranose



β-D-Glucopyranose



β-D-Fructofuranose

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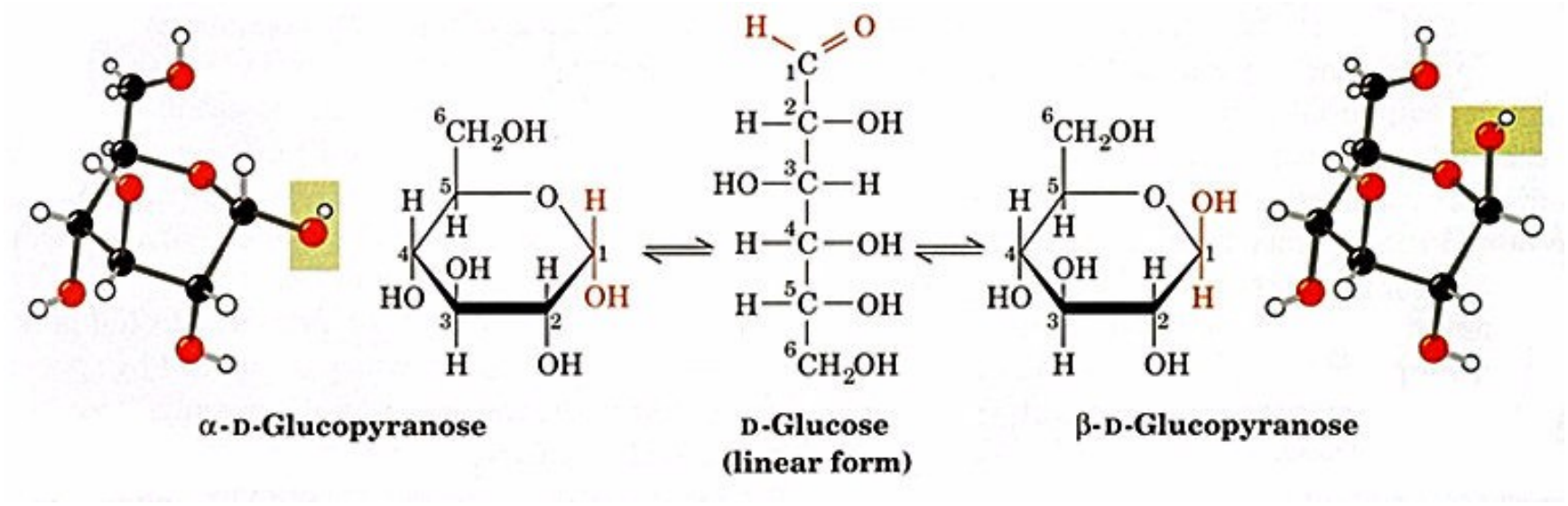
Mutarotation

An **equilibrium exists** between the **α and β anomeric forms** of saccharides

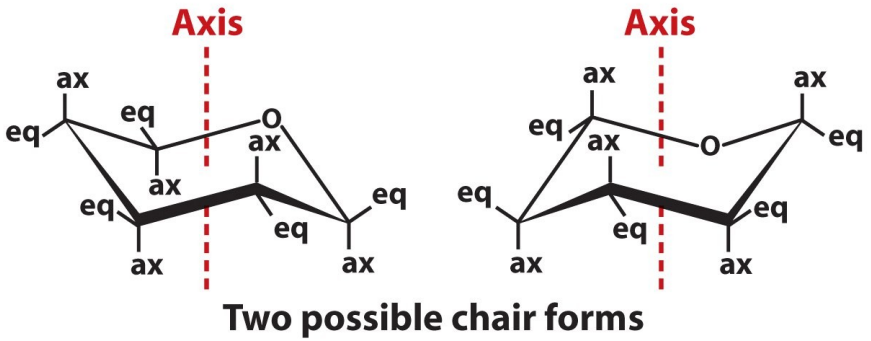
- interconversion between anomeric forms is referred to as **mutarotation**

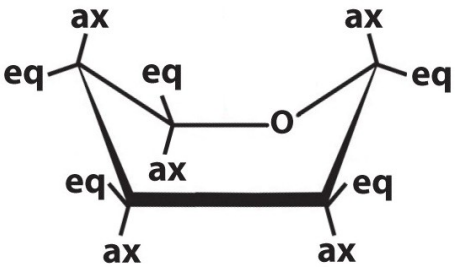


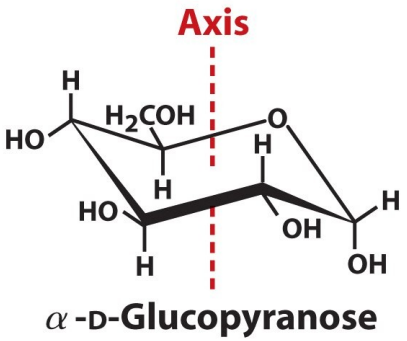
~33 % ~1 % ~66 %

Conformational Variability

- Pyranose adopt "chair" or "boat" conformations due to the tetrahedral configuration of carbon atoms







Boat form is only observed when bulky substituents are present (rare in biological saccharides)

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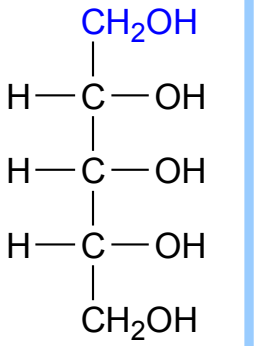
Saccharide Derivatives

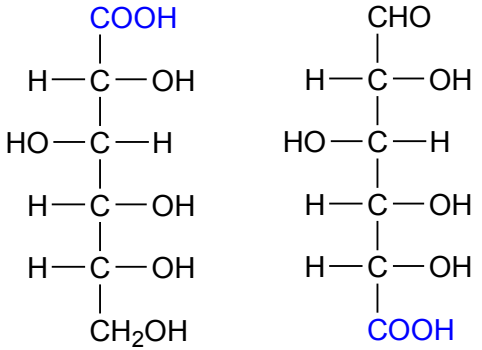
Sugar Alcohols – alcohol replaces aldehyde or ketone (suffix *-itol*)

Sugar Acids – C1 oxidized (suffix *-onic*); C6 oxidized (suffix *-uronic*)

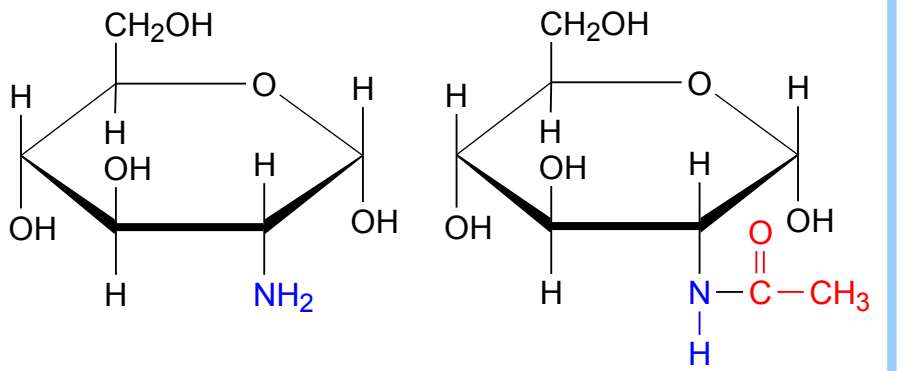
Sugar Amines – amine or acetylated amine replaces a hydroxyl



D-ribitol



D-gluconic acid D-glucuronic acid



α-D-glucosamine α-D-*N*-acetylglucosamine

You must be able to recognize the different saccharide derivatives and the appropriate suffix. You are not responsible for learning the exact names of the derivatives

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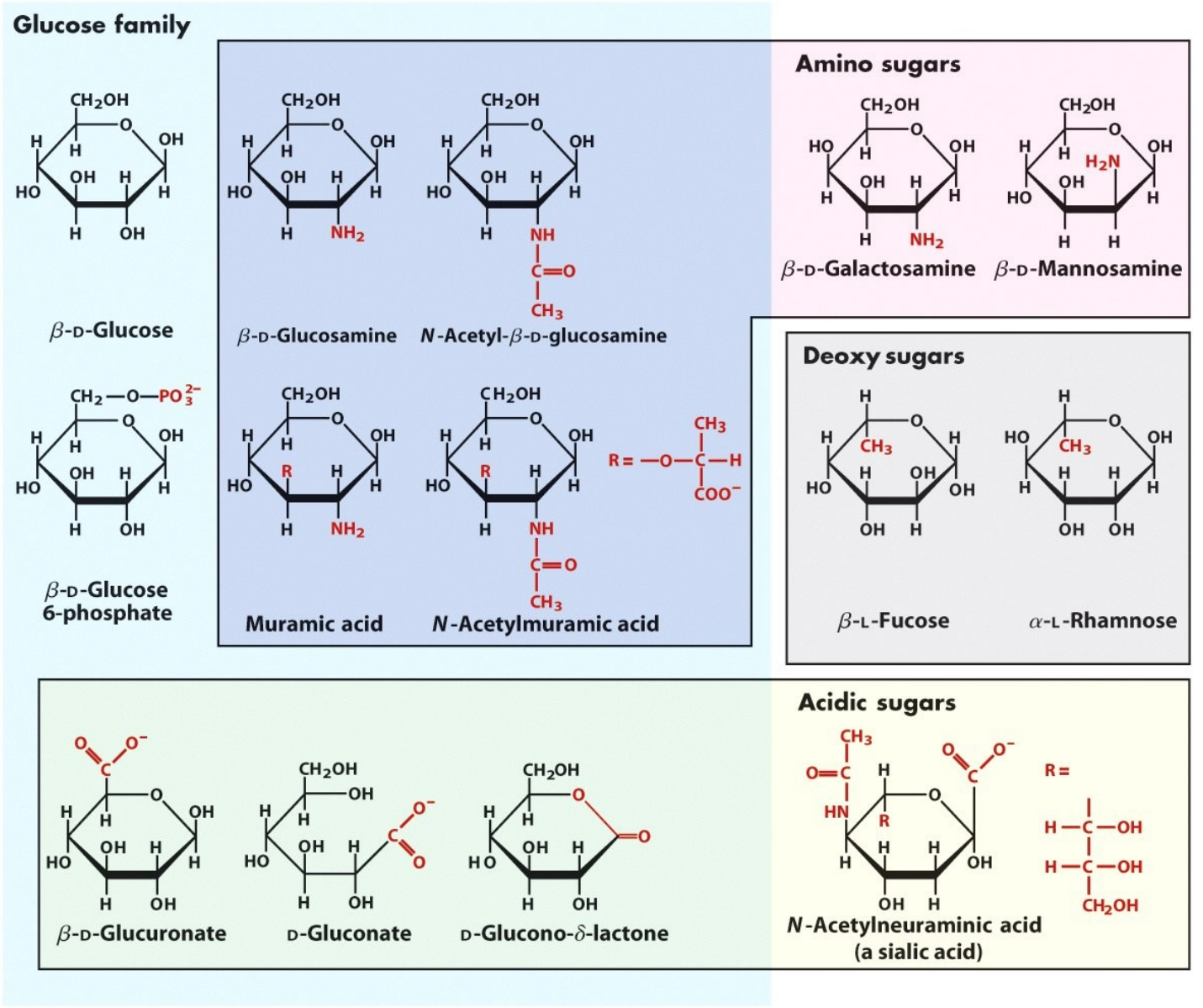
Important Hexose Derivatives

For information only



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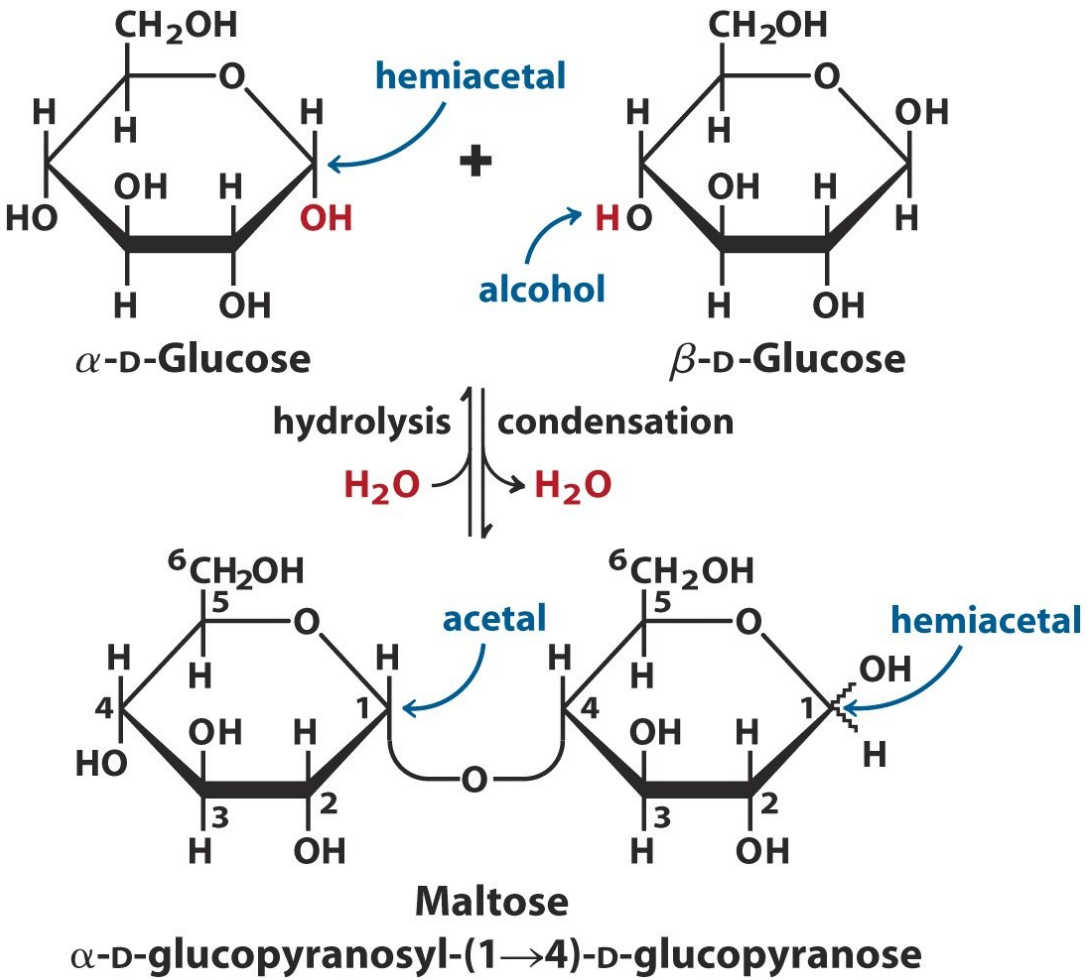
Glycosidic Bonds

Condensation reaction between anomeric carbon and any other hydroxyl containing compound produces a glycosidic bond

- In disaccharides, the glycosidic bond is typically between C1 and C4
- glycosidic bonds between C1 & C6, C1 & C1 of aldoses are also common



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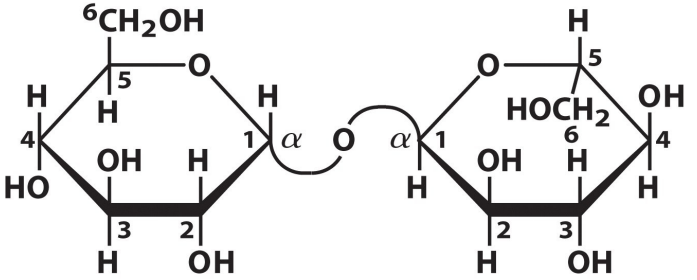
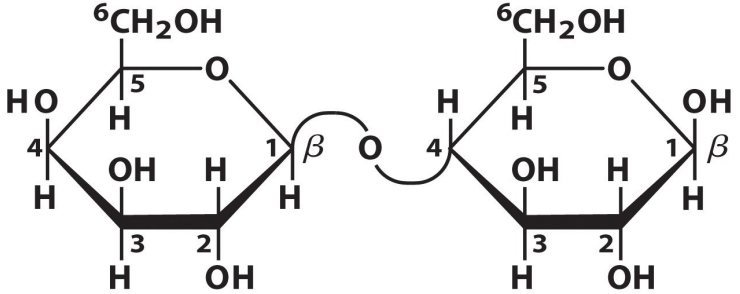
Disaccharides

Examples of glycosidic bonds between sugars

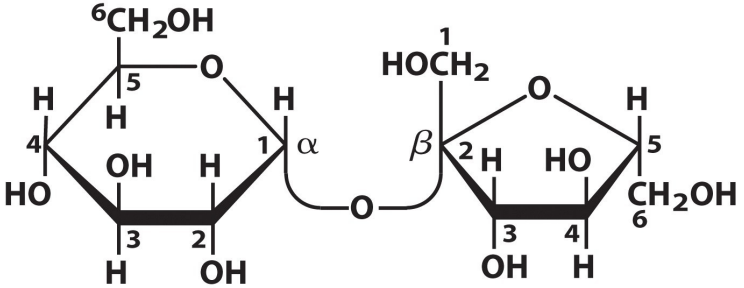
- **lactose – milk sugar (β1-4)**
- **trehalose – insect hemolymph (α1-α1)**
- **sucrose – common sugar (α1-β2)**



Trehalose
α-D-glucopyranosyl α-D-glucopyranoside
Glc(α1↔1α)Glc



Lactose (β form)
β-D-galactopyranosyl-(1→4)-β-D-glucopyranose
Gal(β1→4)Glc



Sucrose
α-D-glucopyranosyl β-D-fructofuranoside
Glc(α1↔2β)Fru

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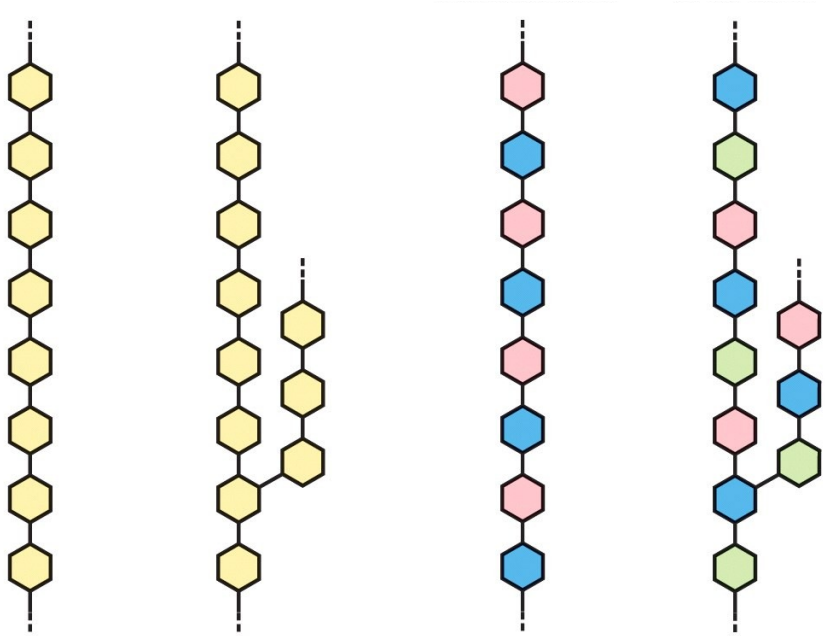
Polysaccharides

Polysaccharides are variable in length, can be composed of one or more types of monosaccharide and can be linear or branched

- **Homopolysaccharides are composed of one monosaccharide type**
- **Heteropolysaccharides are composed of two or more monosaccharide types**



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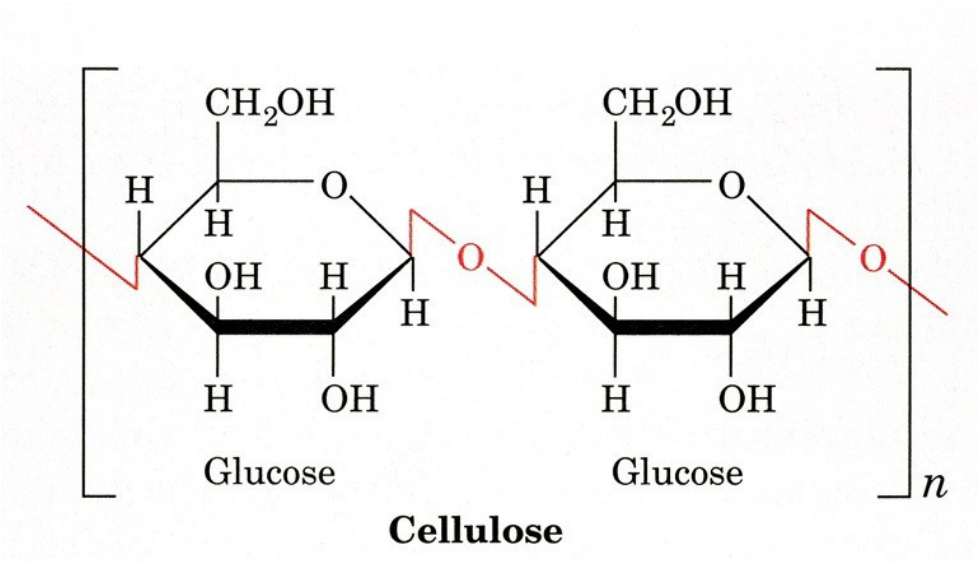
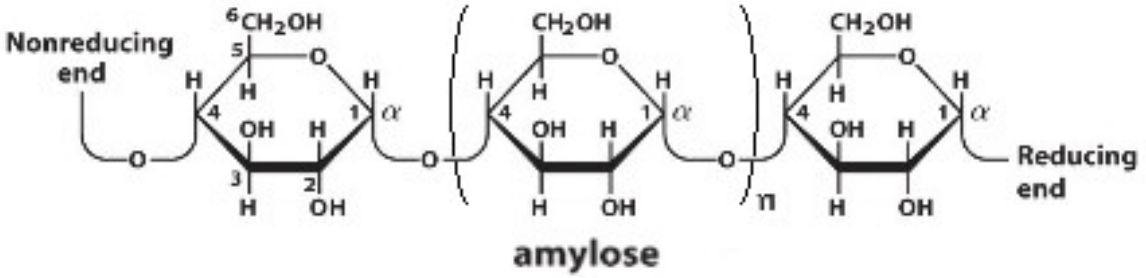
Homopolysaccharides

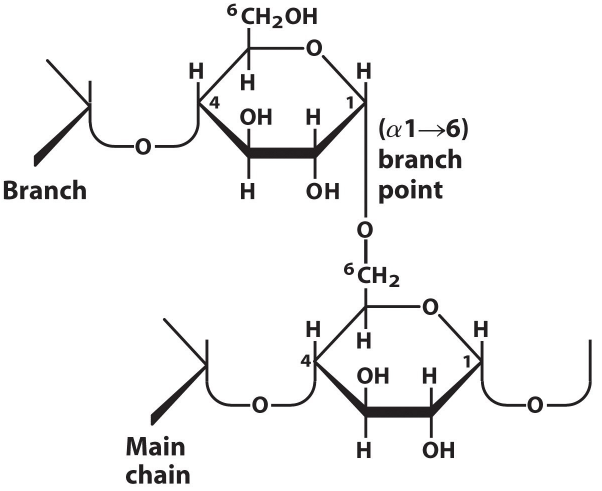


Cellulose: unbranched β1-4 linked glucose; serves structural role in plants; indigestible by mammals

Amylose: unbranched α1-4 linked D-glucose

Glycogen: amylose with α1-6 branch every 8-12 residues





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Heteropolysaccharides

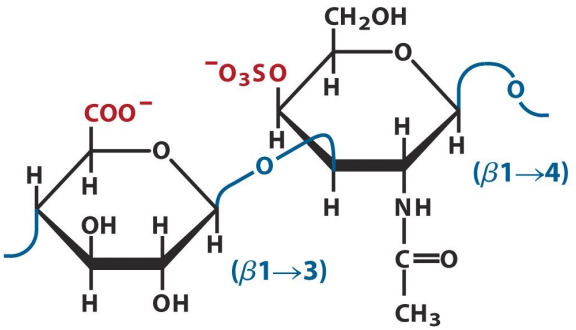
Glycosaminoglycans: family of linear polymers composed of repeating disaccharide units

- one saccharide is N-acetylglucosamine (or N-acetylgalactosamine) and the other is an acid sugar (D-glucuronic or L-iduronic)
- hydroxyl groups can be esterified with sulfate

- Covalently attach to proteins forming **proteoglycans**

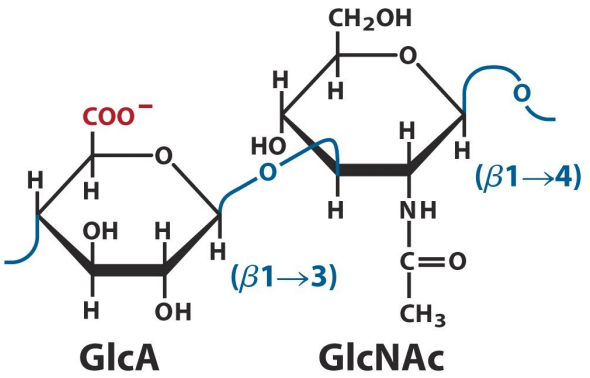
Chondroitin 4-sulfate

20–60



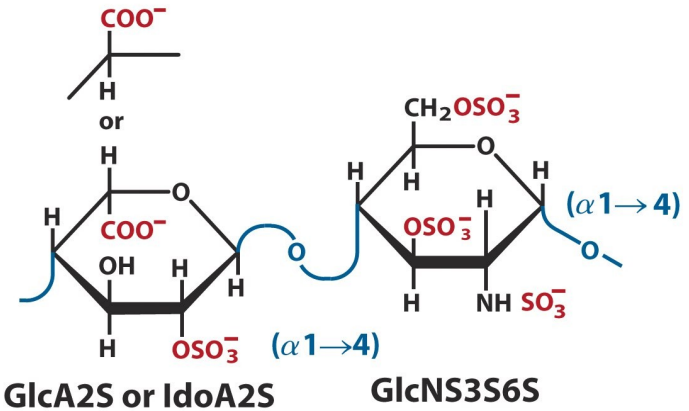
Hyaluronate

~50,000



Heparin

15–90



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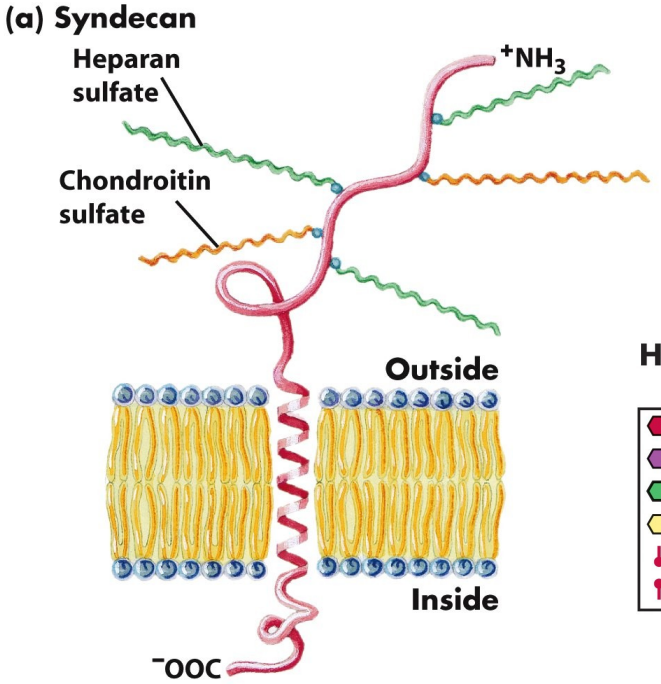
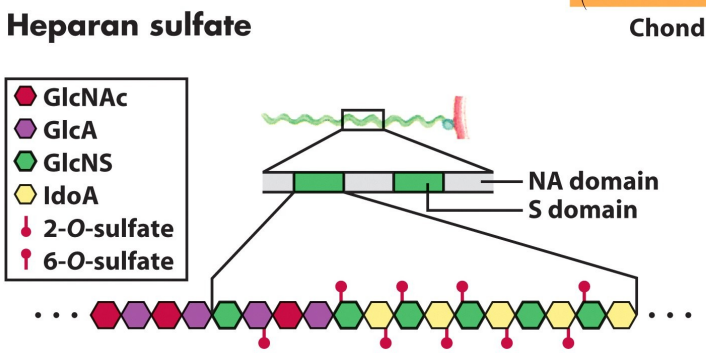
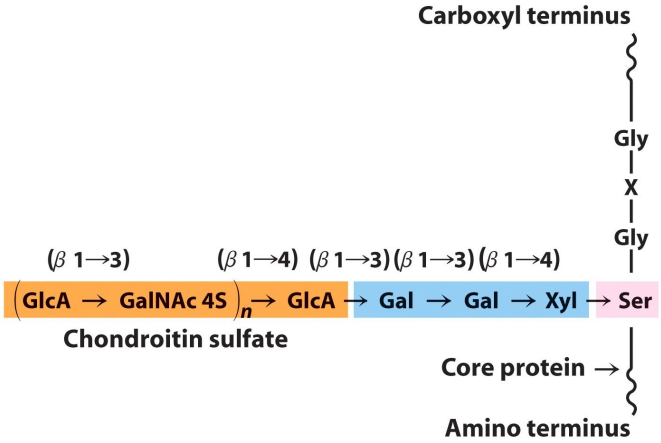
Proteoglycans

Proteoglycans: macromolecules of cell surface or extracellular matrix

- composed of a membrane or secreted protein and one or more glycosaminoglycan chains covalently attached to Ser-Gly-X-Gly sequence







Proteoglycans are one type of glycoconjugate – an oligo- or polysaccharide attached to protein or lipid

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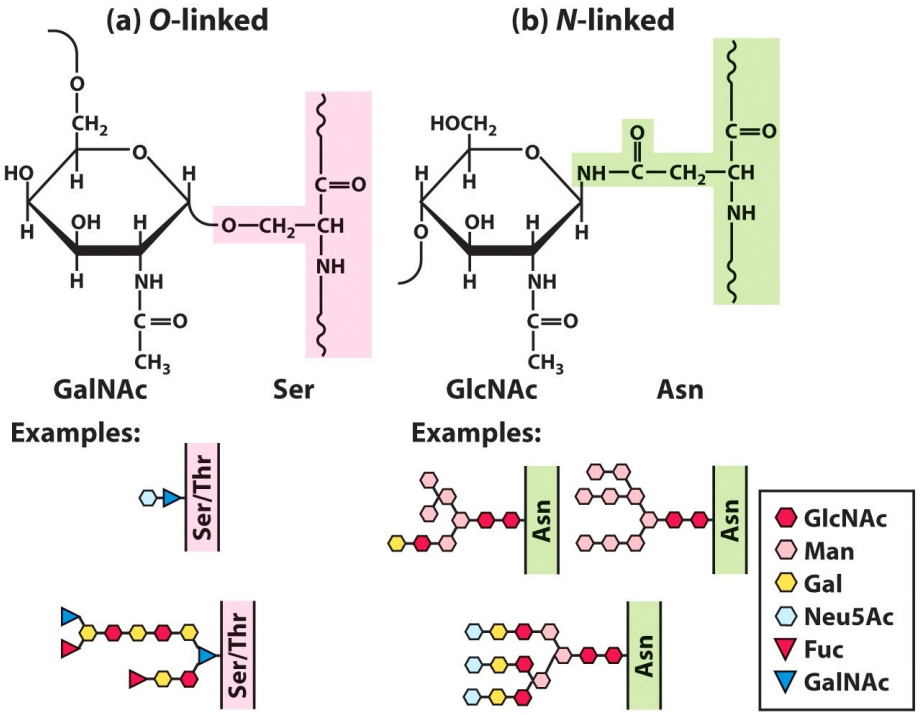
Glycoproteins

Glycoproteins: glycoconjugates composed of a protein and one or more oligosaccharides

- oligosaccharides are smaller and structurally diverse
- covalently attached to Ser/Thr (O-linked) or Asn (N-linked)



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Glycolipids

Glycolipids: glycoconjugates composed of a membrane lipid and an oligosaccharides (eg. gangliosides)

- oligosaccharides are attached to polar head group
- specific recognition site for carbohydrate binding proteins