Chapter 6

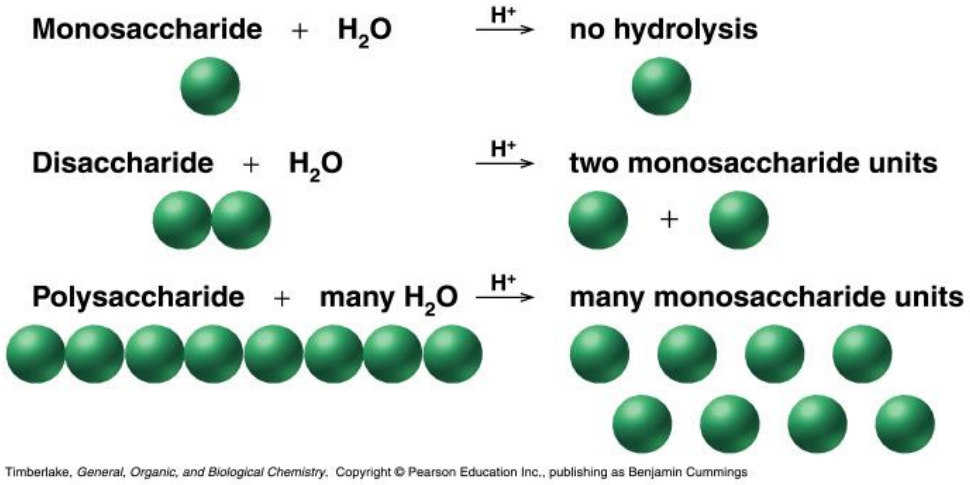
Carbohydrates

Definition

- Carbohydrates are polyhydroxylated aldehydes and ketones or their derivatives.
  - can also contain ether, amino, carboxylic, ester, amide and phosphate groups
- The term is literary to mean "**hydrates of carbon**"
  - Due to the fact that up on heating/dehydration carbohydrates give carbon
- They are the most abundant organic molecules on the planet
- Carbohydrates are formed in the plants by photosynthesis from carbon dioxide and water in the presence of sunlight

Classification of carbohydrates

- Carbohydrates can be classified based on the number of simpler (monomeric units) they contain as:-
  - **Monosaccharides**:-containing single monomeric unit
    - They cannot be further hydrolyzed to simpler units
  - **Oligosaccharides**:-containing 2-10 monomeric units
  - **Polysaccharides**:- are polymers containing more than 10 monomeric units



Monosaccharides

Introduction

- Are simple carbohydrates that can't be hydrolyzed further in to simpler units
  - General formula $(CH_2O)_m$ where $3 < m < 9$
- Are crystalline solids highly soluble in water
- Most of them have sweet taste
- They are rarely exist in free form
  - Rather exist in oligomeric or polymeric forms
- They are also called sugars

Monosaccharides

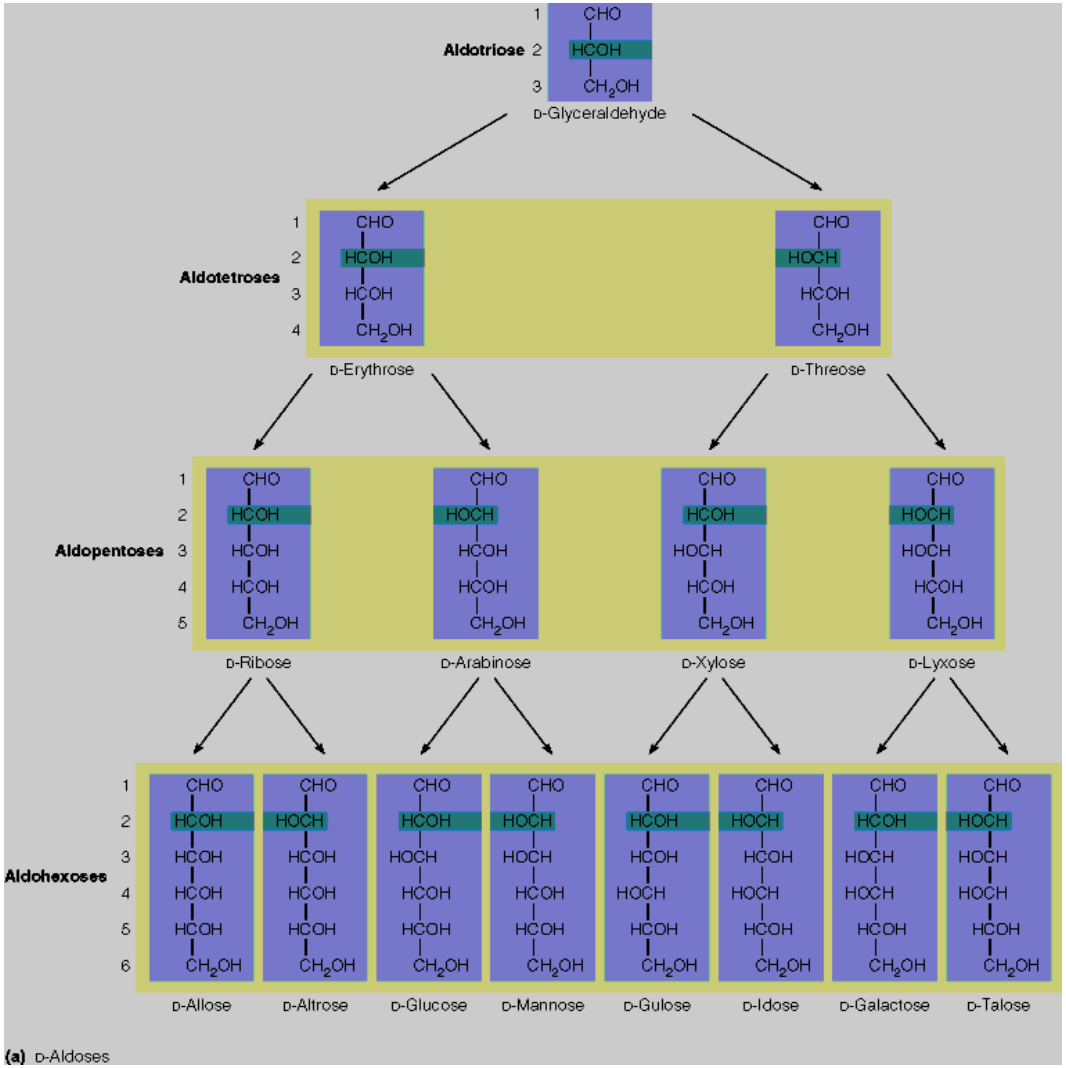
Classification

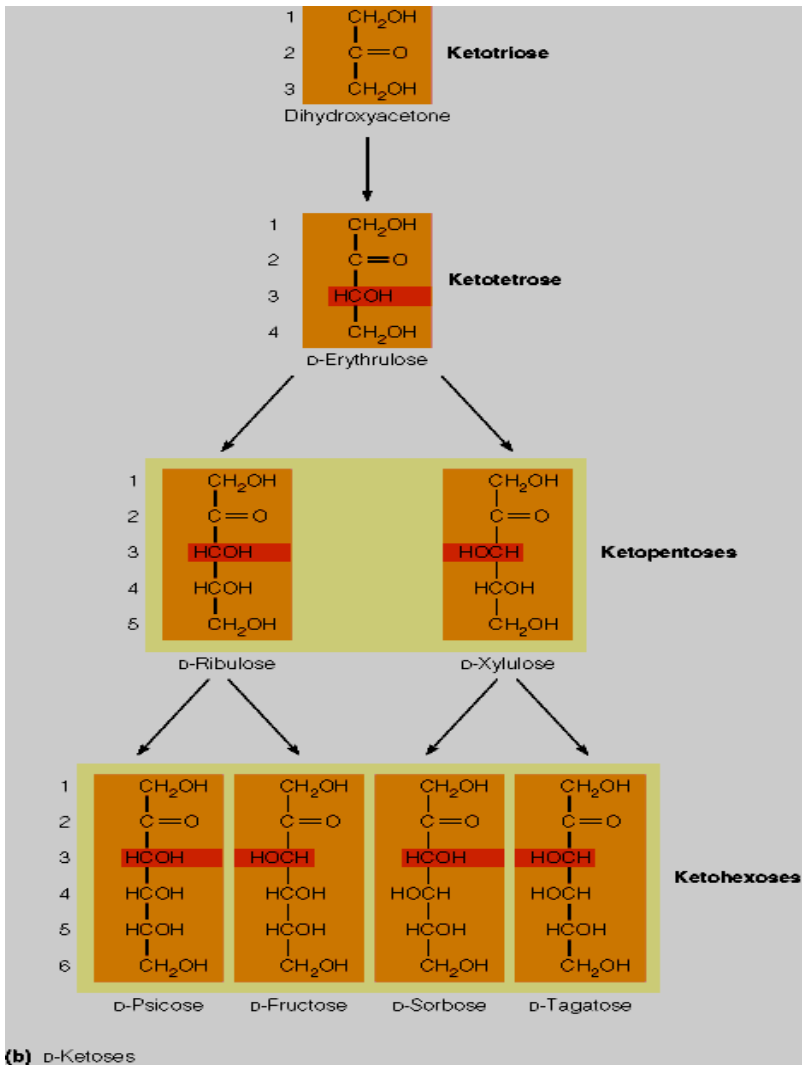
- Monosaccharides can be classified based on:-
  - Number of carbon atoms (3, 4, 5, 6….) as triose, tetrose, pentose,hexose…
  - Carbonyl functional they have on their C-1 or C-2 as aldose or ketose sugars
  - Or both as aldotriose, aldotetrose, aldopentose aldohexose or ketotriose, ketotetrose, ketopentose, ketohexose

# C-atoms	Aldoses	Ketose
3	Trios e.g Glyceraldehyde	Trulose e.g Dihydroxyacetone
4	Tetrose e.g Erythrose,threose	Tetrulose e.g Erythrulose
5	Pentose e.g Ribose, xylose, lyxose, arabonose	Pentulose e.g Ribulose, xylulose
6	Hexose e.g Allose, altrose , glucose, mannose, gulose, idose, galactose, tallose	Hexulose e.g Piscose,fructose, sorbose, tagarose
7	Heptose e.g Manneheptose	Heptulose e.g Sedoheptulose, manneheptulose
8	Octose	Octulose
9	Nanose e.g Neuraminic (sialic) acid	Nanulose

Monosaccharides

Classification

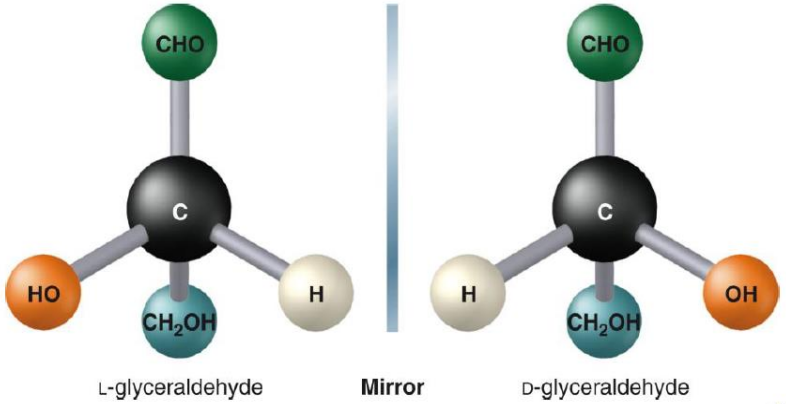




Monosaccharides

Stereochemistry

- Monosaccharides can exist in two isomeric forms (D or L)
- Assignment of D/L based on relative position of hydroxyl group as in glyceraldehyde
  - Naturally occurong monosaccharides are all exist in D-form



- With one exception (dihydroxyacetone) all monosaccharides contain one or more chiral centers
  - For "n" chiral centers 2^n stereoisomers are expected

Monosaccharides

Stereochemistry

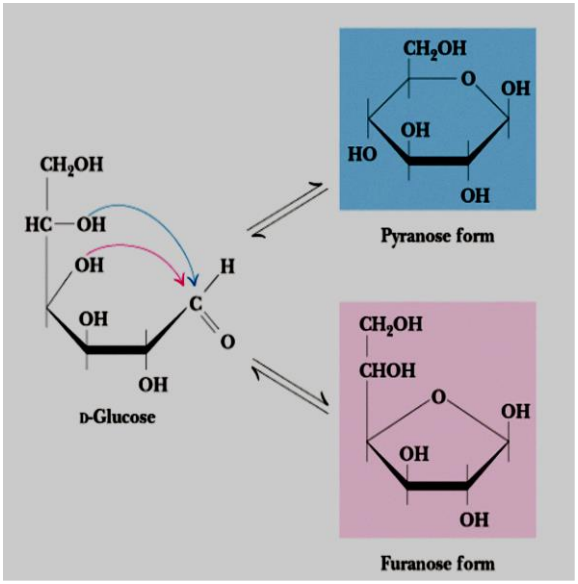
- Stereochemical relations
  - **Enantiomers**:- Pairs of isomers that have mirror image relationship.
    e.g D- and L-forms forms of each sugars
  - **Diastereomers**:-Pairs of isomers that have opposite configurations at one or more chiral centers but lacking a mirror images relationship
  - **Epimers**:- Special subset of diastereoisomers only differing in the configuration around one carbon
    e.g D-mannose & D-glucose (C-2 epimers)
    D-galactose & D-glucose (C-4 epimers)

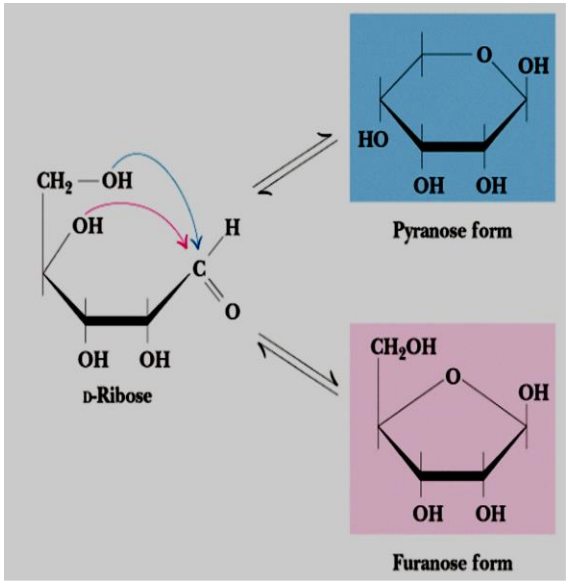
Monosaccharides

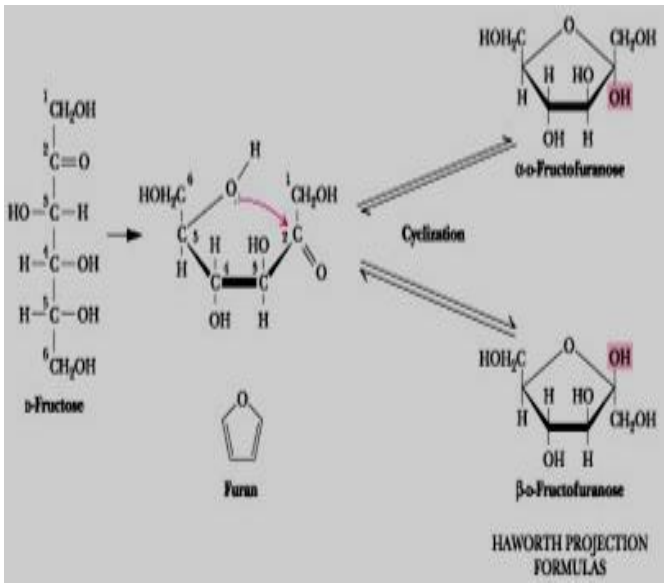
Cyclization

- In aqueous solution pentose and hexose sugars spontaneously cyclize in to **furanose** or **pyranose** rings
  - due intramolecular hemiacetal/hemiketal formation

- This leads to formation of a new chiral center
  - called **anomeric carbon**







Monosaccharides

Cyclization

- The OH group attached to anomeric carbon can have two orientations
  - Yielding the α and β anomers

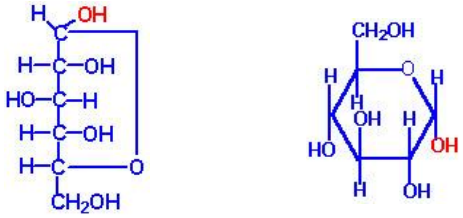
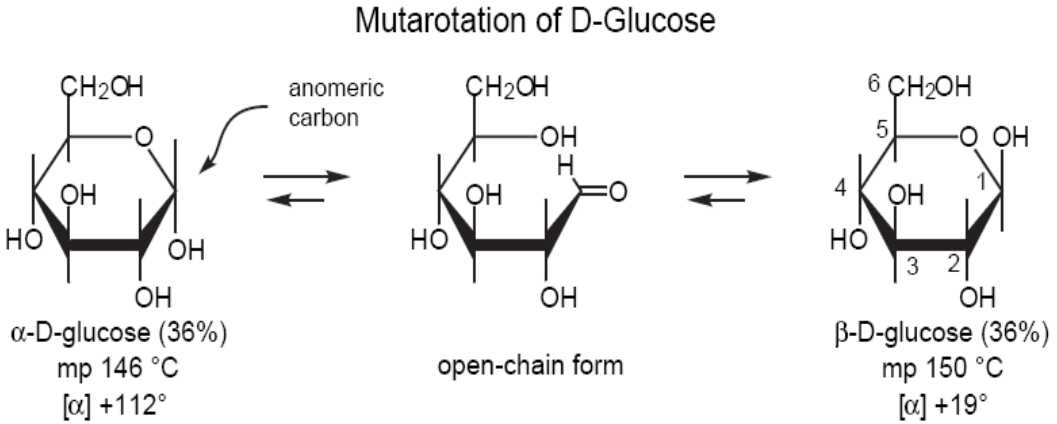


Fig. Orientation of OH of an α anomer in Fisher and Hawarth projections

- In aqueous solutions the α and β anomeric forms interchange through open structure.
  - Phenomena is called **mutarotation**



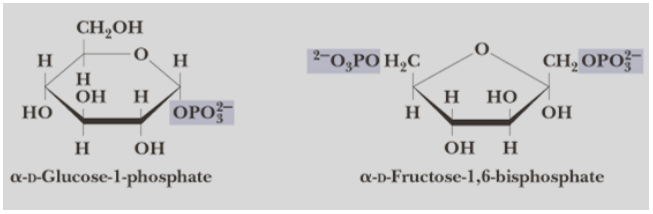
Monosaccharides

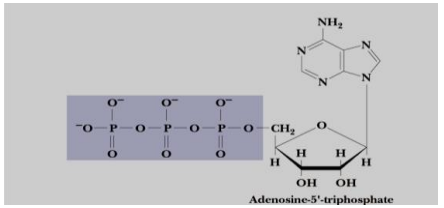
Derivatives of monosaccharides

❖ Are structures obtained when OH or carbonyl group of a monosaccharide is modified

i) Sugar Phosphates:-

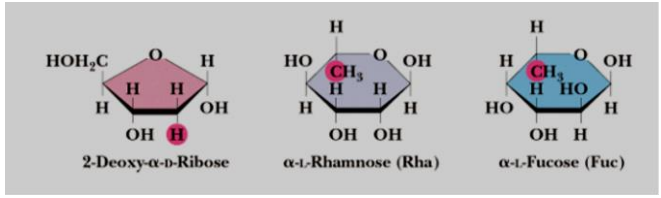
➢ Formed when OH group substituted by inorganic phosphate





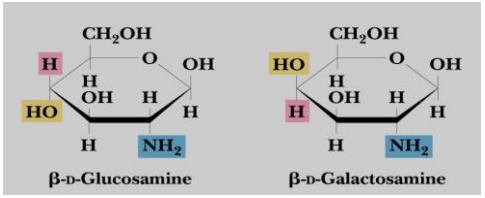
ii) Deoxy sugars :-

➢ Have some OH group reduced



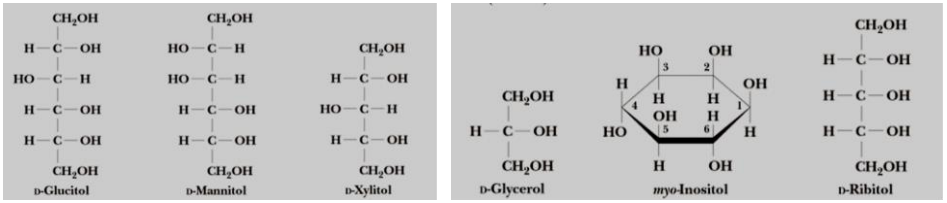
iii) Amino Sugars:-

➢ Formed when OH group substituted by amino group



iv) Sugar alcohols (Alditol)

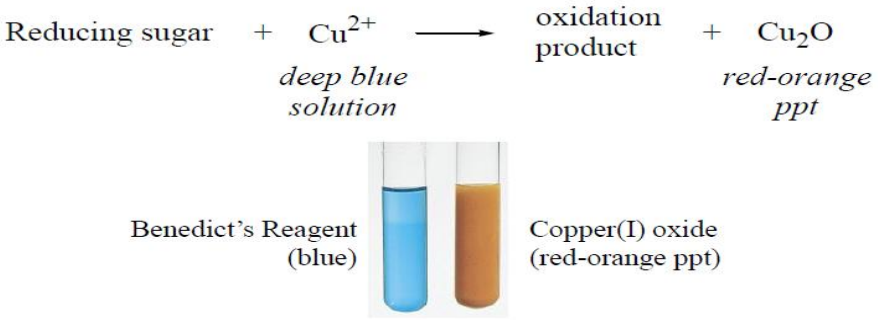
➢Formed when aldehyde/ketone groups are reduced in to alcohol



Monosaccharides

v) Oxidation of Sugars

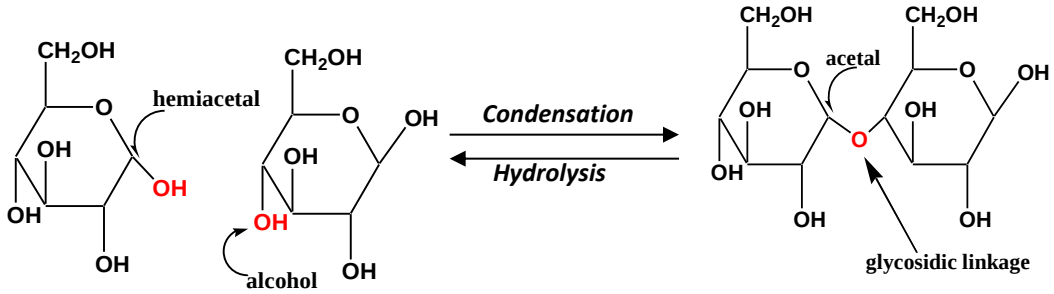
- Some sugars with free anomeric carbon atoms are reasonably good reducing agents to H2O2, Ferricyanide,Certain metals (e.g Cu2+, Ag+)
  - Such sugars are called reducing sugars
- Oxidation can give **Aldonic or aldaric acids**



Disaccharides

Introduction

- Dimers of monosaccharides formed by condensation reaction.



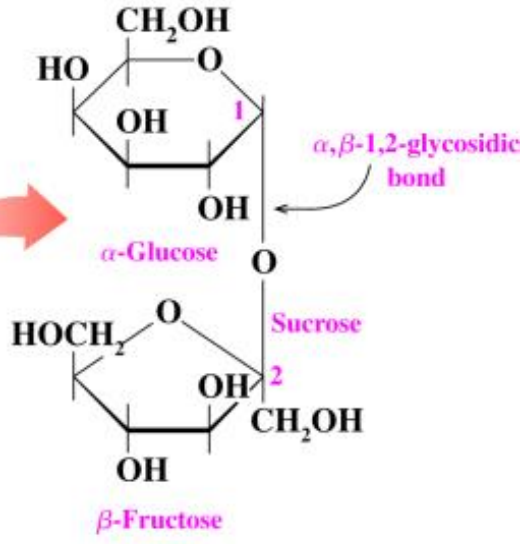
- The most important disaccrharides are fructose, maltose and lactose.

Disaccharide	Linkage type	Characteristics	Hydrolyzing Enzyme	Natural Source
Maltose	Glcα(1→4)Glc	reducing	maltase	Plants (starch) Animals (glycogen)
Lactose	Gal β(1→4)Glc	reducing	Lactase	Milk (major energy source)
Sucrose	Glcα(1→2)βFru	non-reducing	Sucrase (invertase)	Fruits seeds roots and honey

Disaccharides

Sucrose (cane sugar)

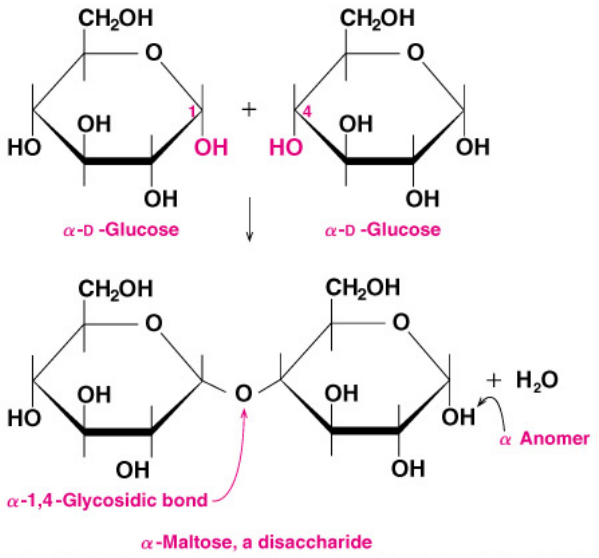
- Is obtained from sugar cane and sugar beets.
- Consists of α-D-glucose and β-D-fructose in 1:1 ratio.
- Has an α,β-1,2-glycosidic bond.



Disaccharides

Maltose (malt sugar)

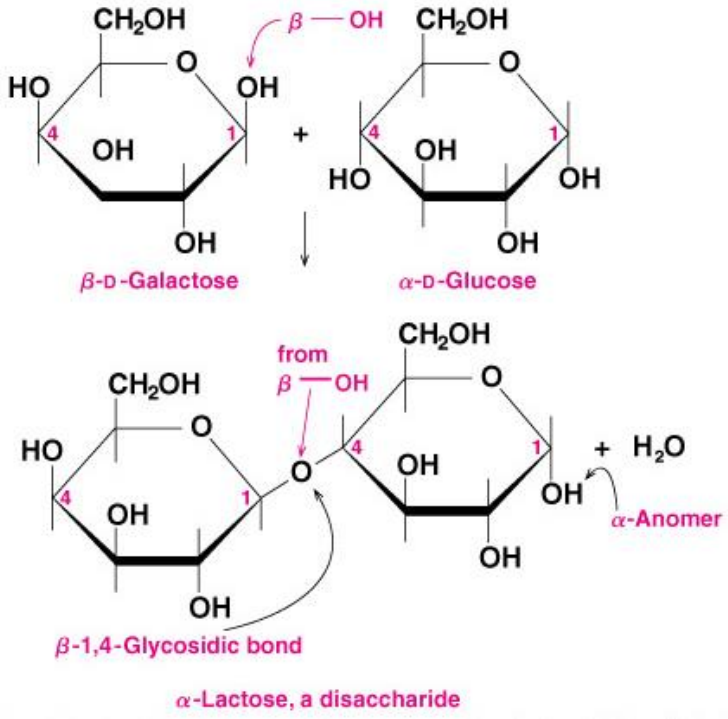
- It is produced in germinating seeds and during digestion of starch.
- It is made from two α-D-glucose units through an α-1,4-glycosidic linkage



Disaccharides

Lactose (Milk sugar)

- Is a disaccharide of β-D-galactose and α- or β-D-glucose.
- Contains a β -1,4-glycosidic bond.
- Is found in milk and milk products.



Polysaccharides

Introduction

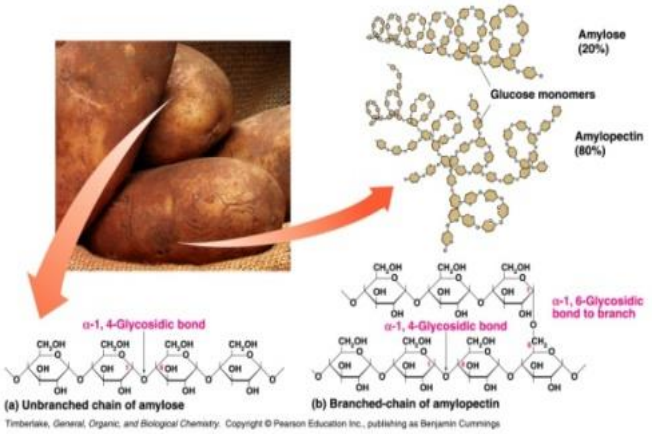
- Are polymers of monosacharides (containing >10 monomeric units)
- Are the most dominant forms of carbohydrates in nature
- The most common polysaccharides include
  - Starches (composed of polymers amylose and amylopectin)
  - Glycogen (animal starch in muscle)
  - Cellulose (plants and wood)
  - Dextrin
  - Chitin (in exoskeleton of insects)

Polysaccharide	Repeating units	Linkage type	Hydrolyzing Enzyme	Natural Source
Cellulose (unbranched)	Cellubiose (up to 15,000 glucose units)	All 1,4-β linkages	Cellulase	Plants
Starch **Amylose** (10-30%) (unbranched) **Amylopectin** (70-90%) (branched)	Glucose/Maltose(50-5,000 units) Glucose (up to 10^6 units)	1,4-α-glycosidic bonds 1,4-α-glycosidic bonds & 1,6-α-glycosidic bonds(every 15-25 residues)	Amylase	Plants
Glycogen (more branched)	Glucose (up to 500 units)	1,4-α-glycosidic bonds & 1,6-α-glycosidic bonds (every 8-12 units)		Liver
Dextrans (branched)	Glucose (wide range)	1,6-α-glycosidic bonds Branches can be (1,2), (1,3), or (1,4)		Plants, Bacteria, comp.of sephadex)
Chitin	*N*-acetylglucosamine (very large)	1,4-β-glycosidic bonds		

Polysaccharides

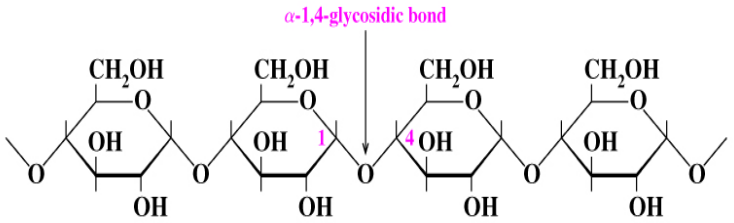
Starch

- A polymer of α-D-glucose
- Storage form of carbohydrate in plant roots and grain
- Is composed of amylose and amylopectin



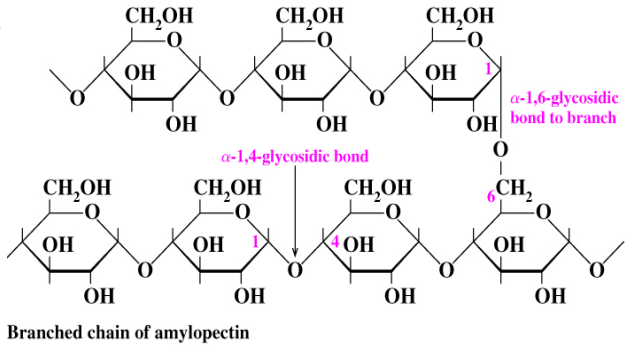
Amylose

- A polymer of α-D-glucose molecules (1000-2000) linked by α-1,4 glycosidic bonds.
- Form a continuous (unbranched) chain.
- May account for 10 -20% of starch



Amylopectin

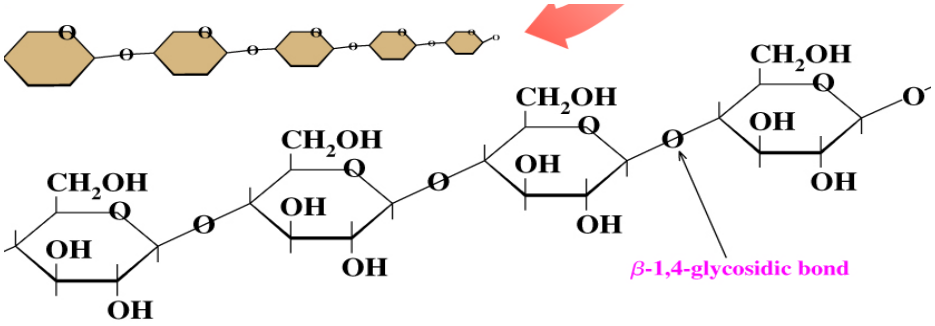
- Is a polymer of α-D-glucose (up to 10(E5) molecules) connected by
  - ✓ α-1,4-glycosidic bonds between glucose units and
  - ✓ α-1,6 bonds to branches (after every 25-30 units)
- It is therefore a branched-chain polysaccharide
- May account for 10 -20% of starch



Polysaccharides

Cellulose

- Is a polysaccharide of glucose units in unbranched chains.
- Has β-1,4-glycosidic bonds.
- Cannot be digested by humans because humans cannot break down β-1,4-glycosidic bonds.

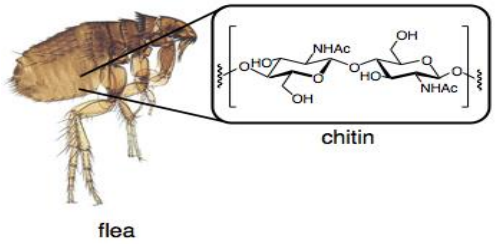


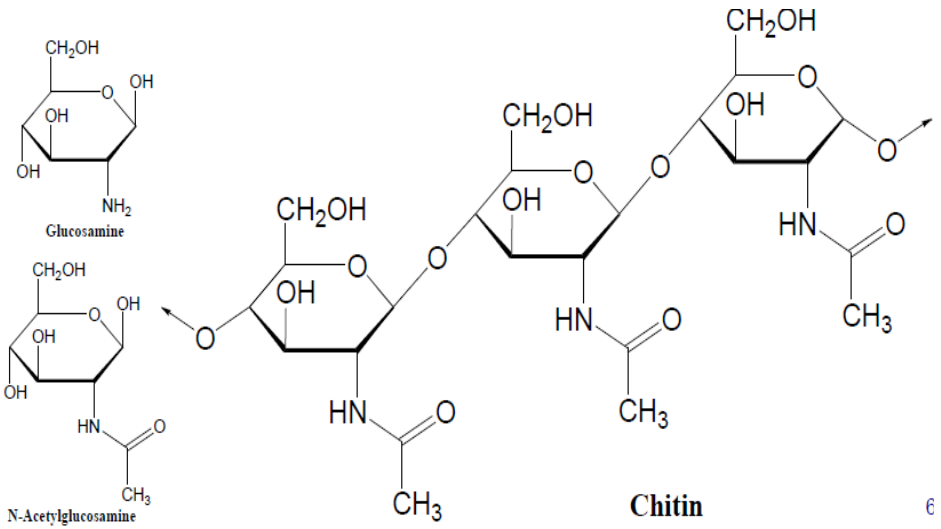
Polysaccharides

Chitin

- A tough, protective, semitransparent polysaccharide composed primarily of N- aGlucosamine(N-containing monomer)

- Is the principal component of arthropod exoskeletons and the cell walls of certain fungi.

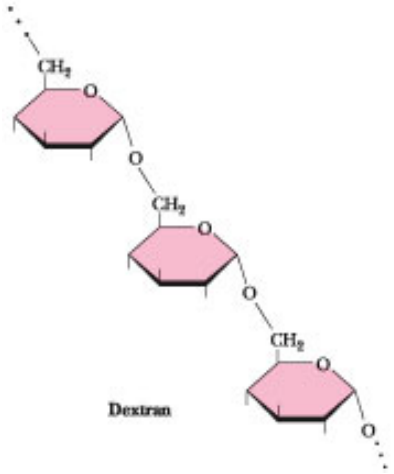


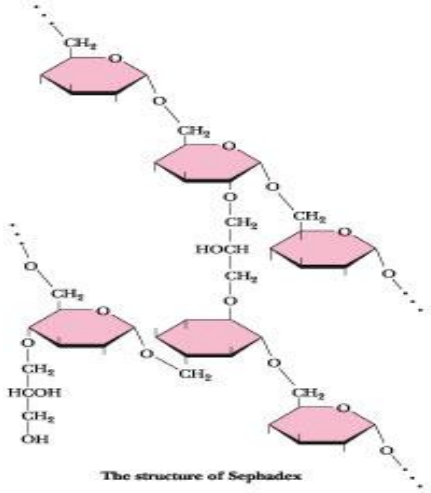


Polysaccharides

Dextrans

- Are are α-1,6 -linked polysaccharides of D-glucose with 1,2; 1,3, or 1,4 branching in various species.



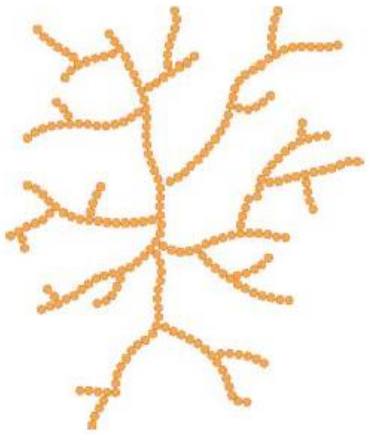


- The degree of branching and the average chain length between branches depend on the species and strain of the organism.
- Sephadex gels (used in electrophoresis) are formed from dextran chains cross-linked with epichlorohydrin.

Polysaccharides

Glycogen

- Is the polysaccharide that stores α-D-glucose in liver and muscles.
- Consists of both α-1,4 and *α*-1,6 α-1,4-glycosidic bonds between glucose units
  - i.e similar to amylopectin but is more highly branched (after 8-12 glucose units)



Polysaccharides

Classification

- Can be classified based on monomeric units they are composed of in to:-

i) Homopolysaccharides (Homoglycans):- Contain only one type of monosaccharide residue

e.g Cellulose (from glucose), starch (from glucose), Chitin (from *N*-acetylglucosamine)

ii) Heteroploysaccharides (hetroglycans) :- Contain mixture of monosaccharide residues

e.g Hemicellulose

Functional role of Carbohydrates

Biological

- Structural component of cell & nucleic acids (cellulose, chitin, ribose and 2-deoxyribose)
- Energy storage (glycogen, starch)
- Cellular recognition (Cell surface polysaccharides & **c**arbohydrate derivatives (glycoproteins , glycolipids)
- Sweeteners (flavor) in foods (fructose is found in many fruits)
- Fermentation

Pharmaceutical agents:- Emulsifier, bulking agent (filler), binder, suspending agent etc.

Dietary role :- energy source, fiber

Industrial: - Pulp and paper industry

Chromatographic separation:- Stationary phase, support

Drugs:-Sugars, oligosaccharide and polysaccharide groups are incorporated in to many drug structures