Sugars

lecture

Importance of carbohydrates

- We use them as our major energy source (4 kcal/g)
  - Humans : starch, sucrose and fructose
  - 80% of our energy intake (average)
- We use them for their sweet taste
- We use them to provide structure and texture in food products
  - Bread & pudding (starch); Dextrin (soft drinks); Pectin (jellies)
- We use them to lower water activity of food products and also influence ice crystallization
  - Intermediate moist foods; Ice cream

Definition of a carbohydrate

- The word originates from "carbon" and "hydrate" or "hydrates of carbon"

$$C_x(H_2O)_y$$

- The empirical formula showed equal numbers of carbons and water
  - X=6 and Y=6 for glucose, galactose and fructose
- Simple carbs. are polyhydroxy aldehydes (aldoses) & ketones (ketoses)
- By definition carbs. are aldoses, ketoses and compounds derived from these via condensation, hydrolysis, reduction, oxidation and substitution

Sugars - definition

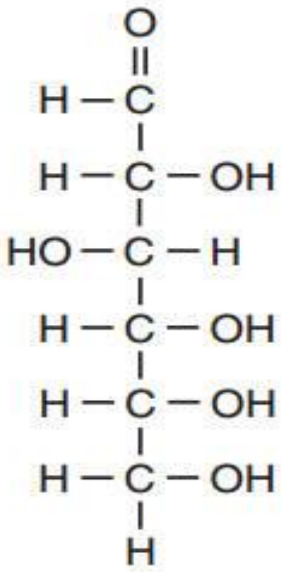
- Polyhydroxylic alcohol containing an aldehyde group (aldoses, i.e. glucose)

or

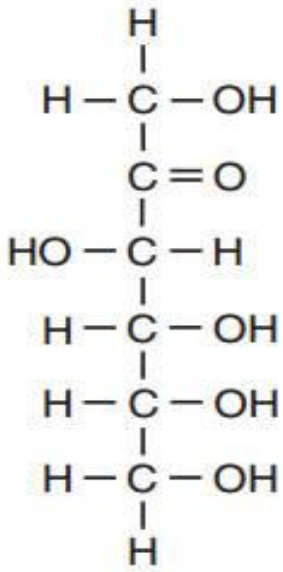
- Polyhydroxyl alcohol containing a ketone group (ketoses, i.e. fructose)

or

- Derivatives of aldoses and ketoses (polysaccharides)



Glucose

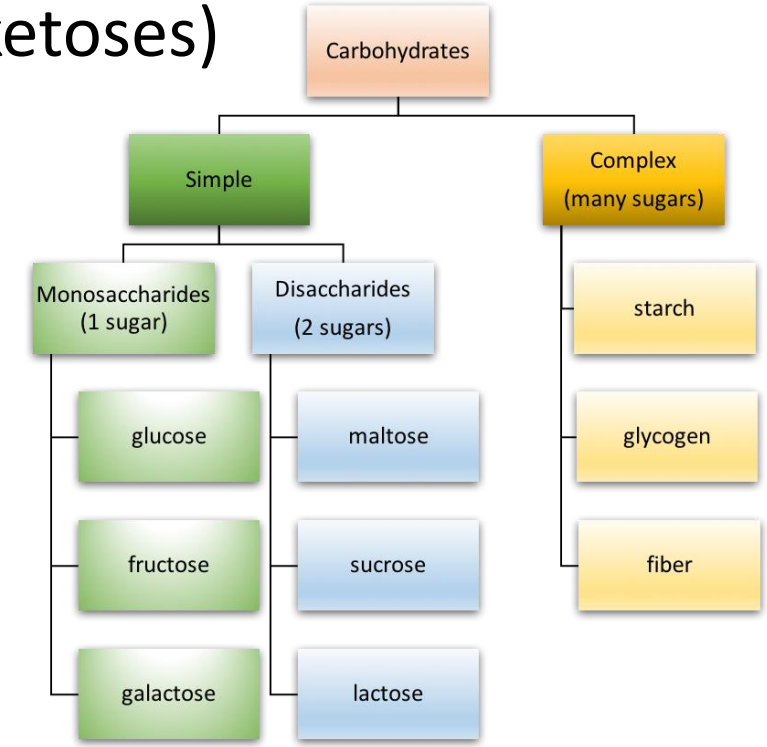


Fructose

Classifications

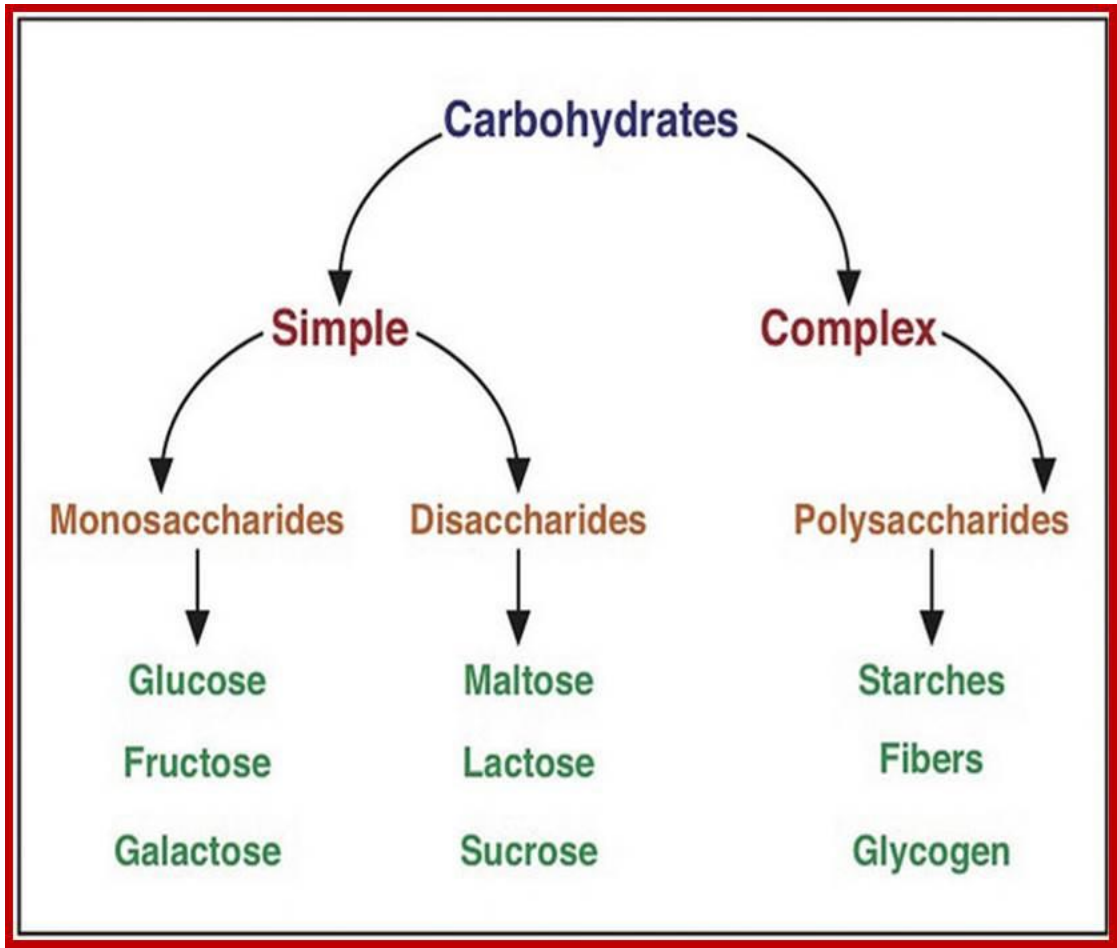
There are many classifications of sugars taking into account various criteria, for example:

- Amount of monosugars in the molecule (simpe sugars, complex sugars)
- Amount of carbon atoms in the molecule of monosugar
- Chemical nature (type of carbonyl group: aldoses vs ketoses)
- Isomeric forms (L vs D, alpha vs beta)

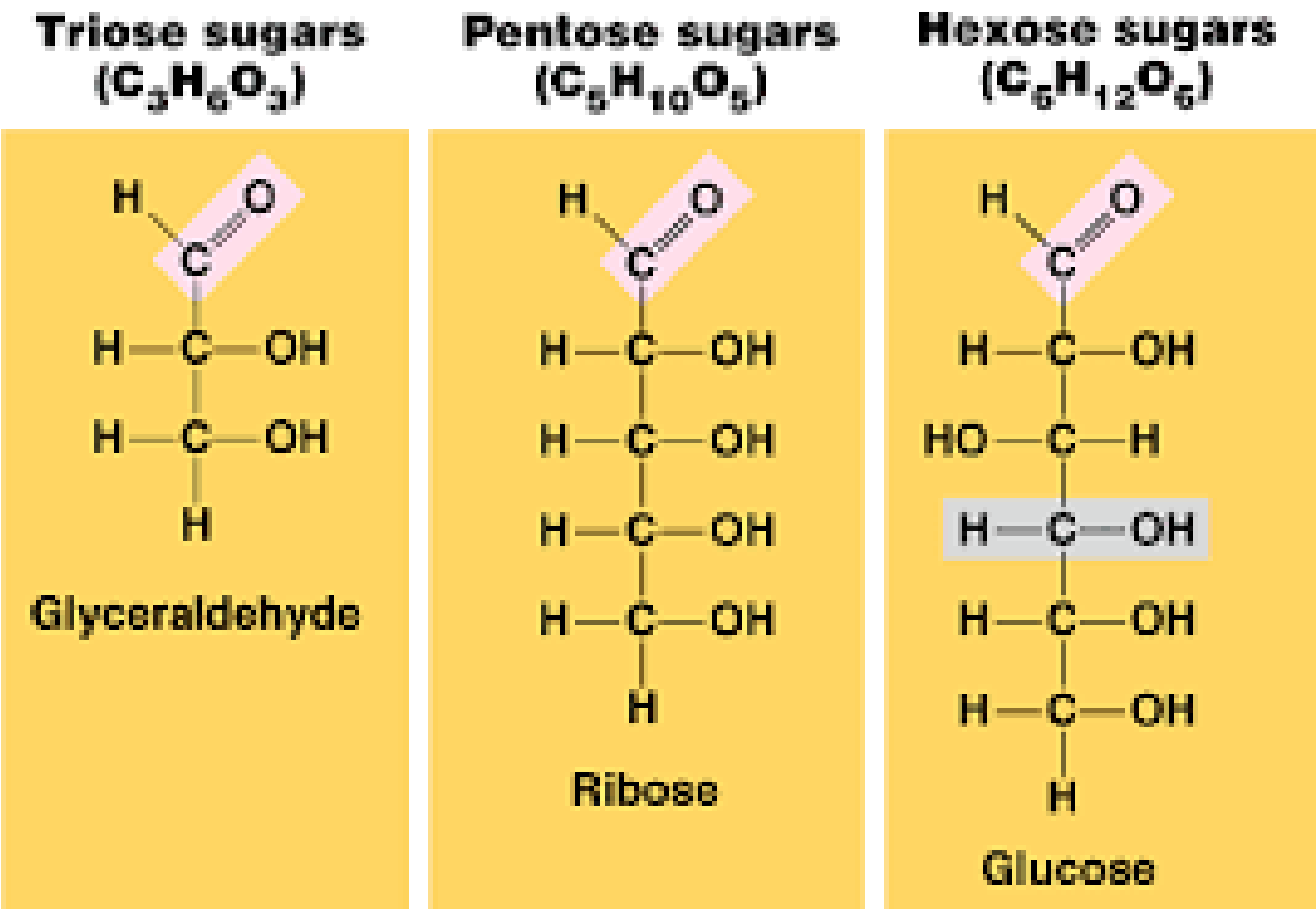


Classification of carbohydrates

- Monosaccharides
  - The simplest of the CHO forms
  - Building blocks of other higher carbohydrates
- Disaccharides
  - Two monosaccharide units
- Oligosaccharides
  - 2-10 monosaccharide units
- Polysaccharides
  - >10 monosaccharide units

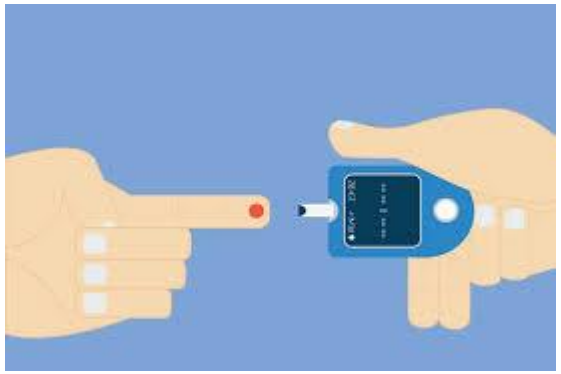


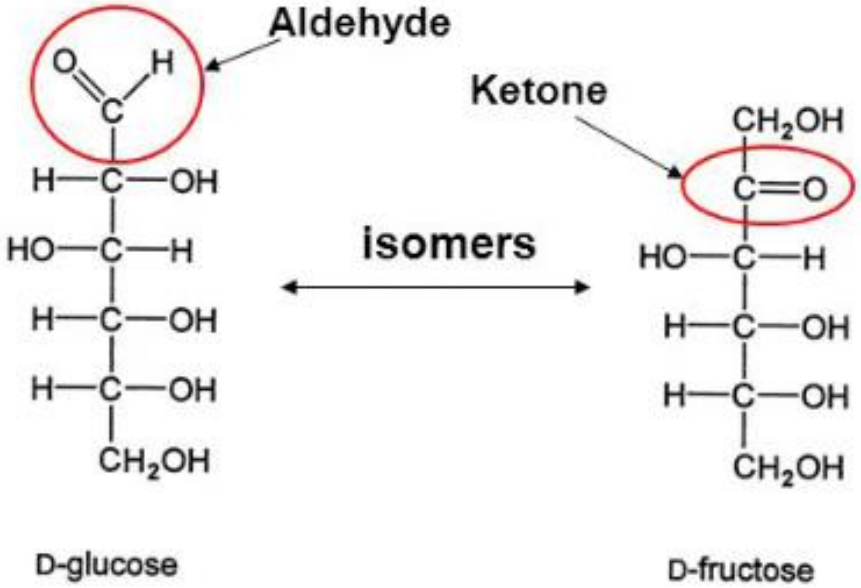
Amount of carbon atoms in molecule

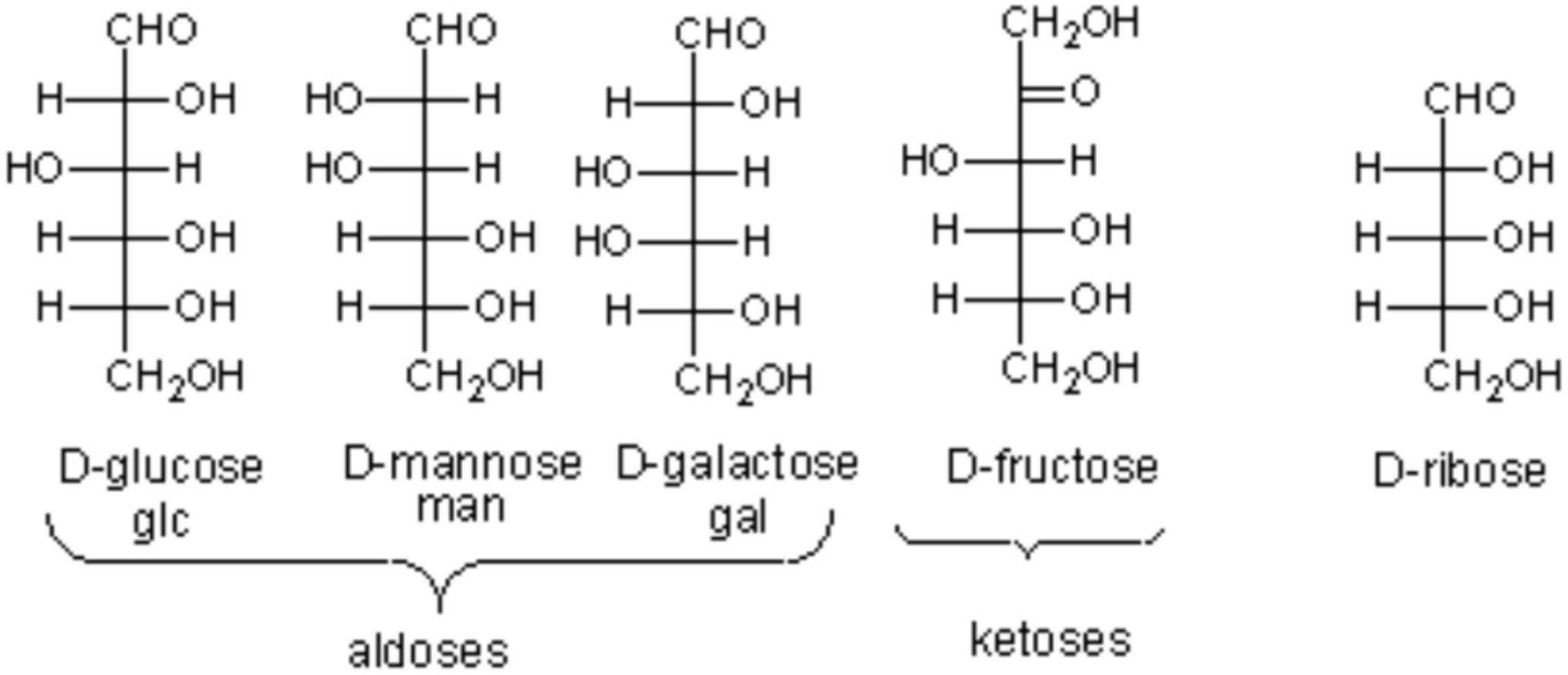


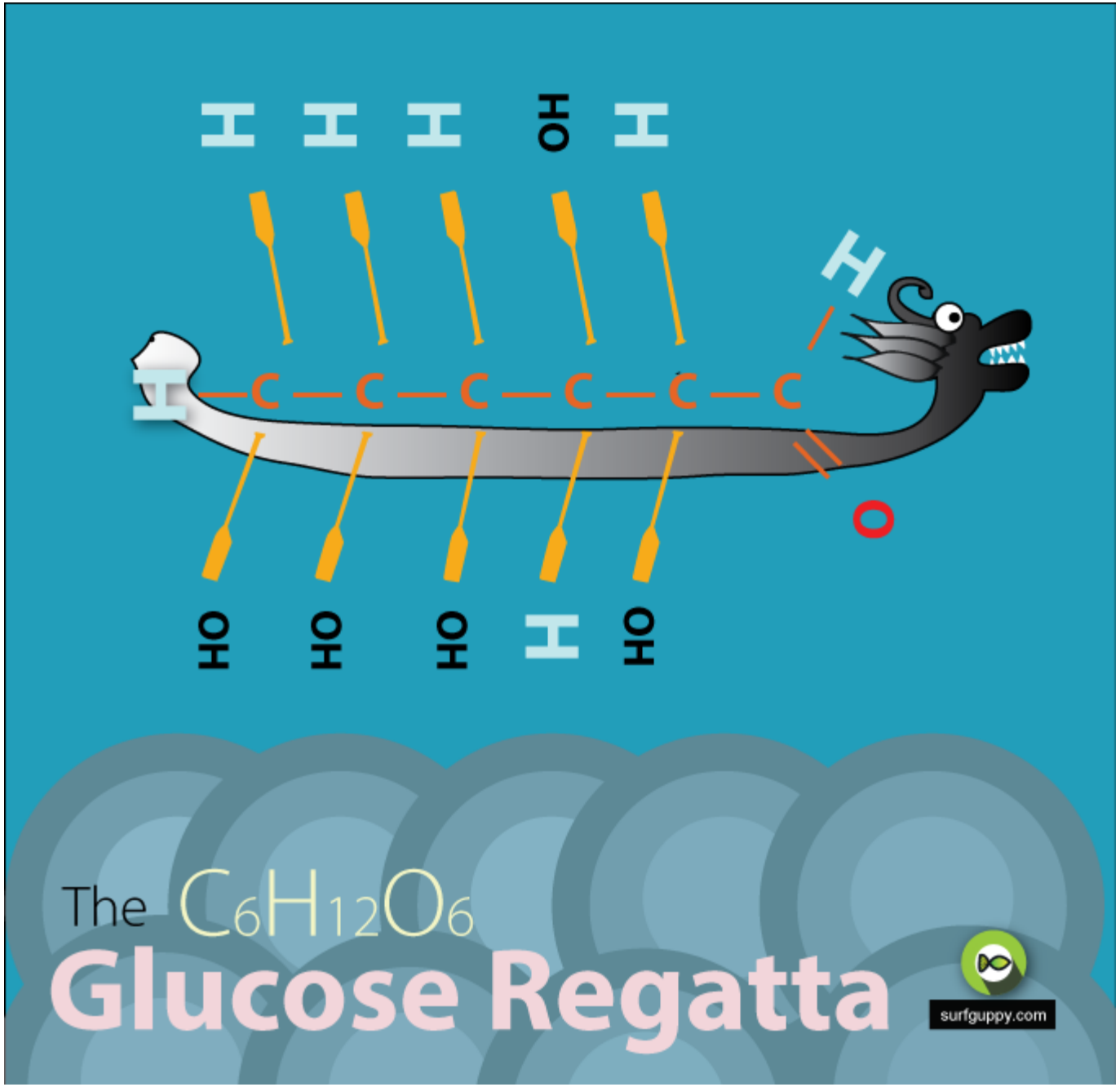
Monosaccharide classification

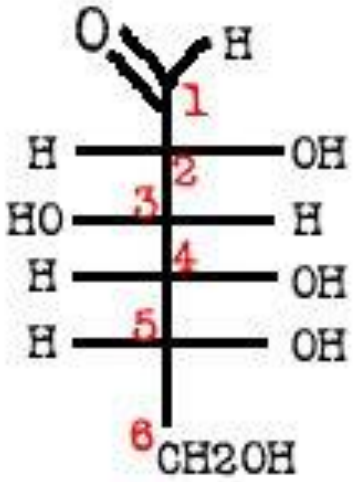
3. Type of carbonyl group
   - ALDOSE = Aldehyde group
     - Glucose, galactose and mannose most common in foods
   - KETOSE = Ketone group
     - Fructose most important





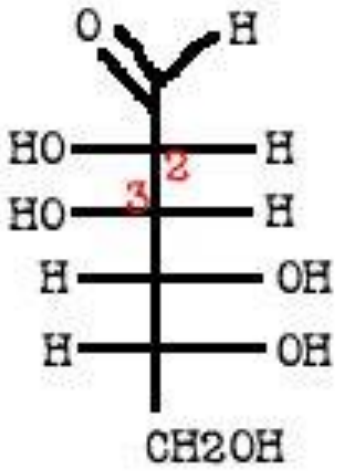

CHO
H OH
HO H
H OH
H OH
CH2OH
D-glucose
glc
CHO
HO H
HO H
H OH
H OH
CH2OH
D-mannose
man
CHO
H OH
HO H
HO H
H OH
CH2OH
D-galactose
gal
aldoses
CH2OH
O
HO H
H OH
H OH
CH2OH
D-fructose
ketoses
CHO
H OH
H OH
H OH
CH2OH
D-ribose


H H H OH H
H C C C C C C H
O
OH OH OH H OH
The $C_6H_{12}O_6$
Glucose Regatta
surfguppy.com



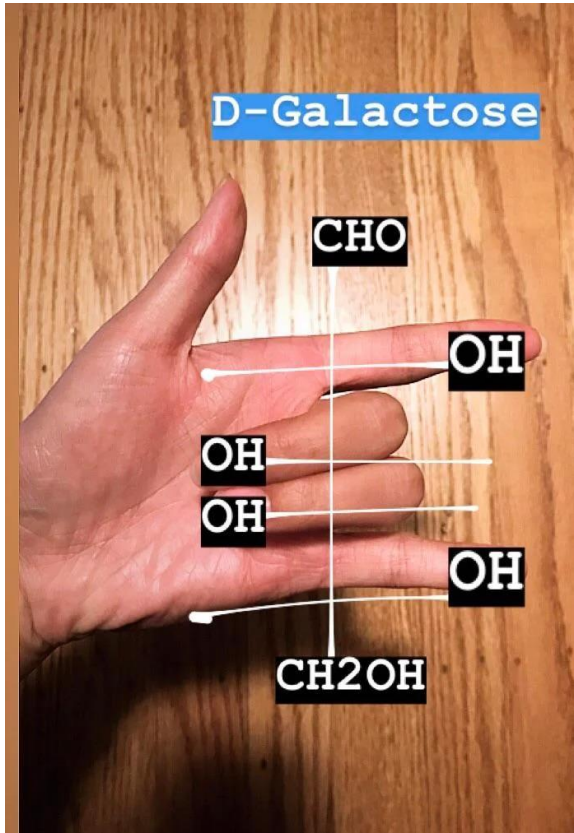
D-Glucose

"Eff memorizing carbohydrates!"



D-Mannose

"Manly man uses a gun."

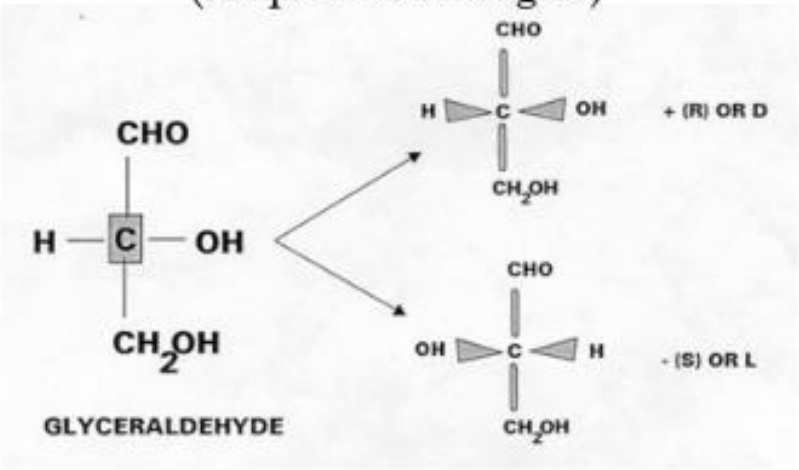


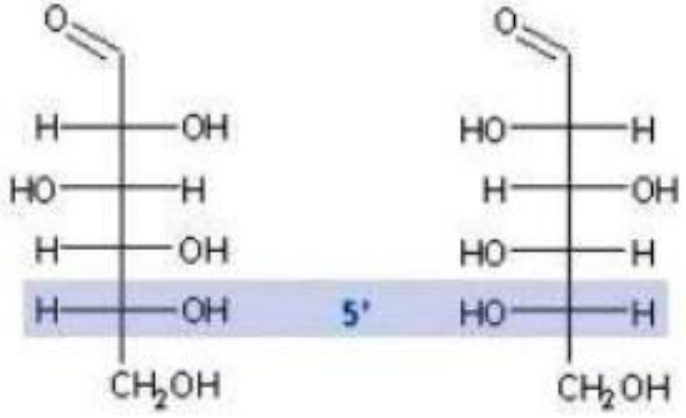
Monosaccharide classification

2. Configuration

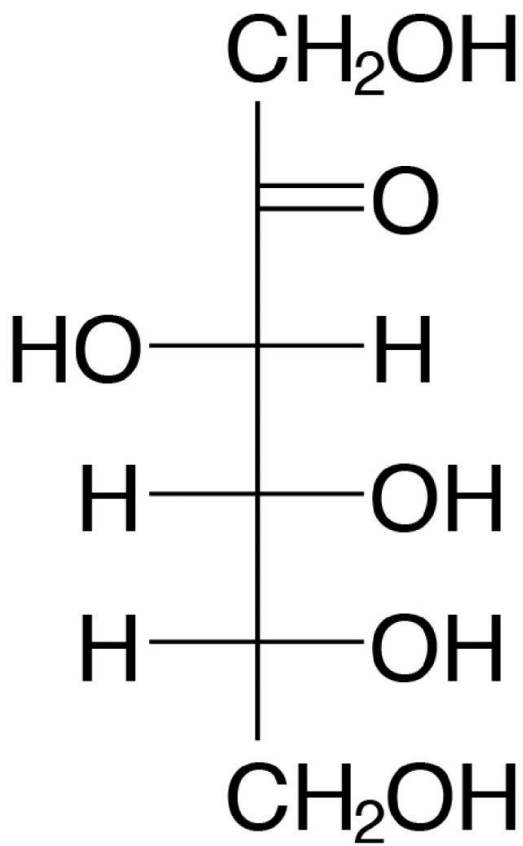
- Sugars have asymmetric (chiral) carbons and therefore can exist in two forms (enantiomers)
  - D-sugar vs. L-sugar, or +(R) vs. –(S)
  - Based on the location of the –OH group of the highest asymmetrical center (right = D; left = L)

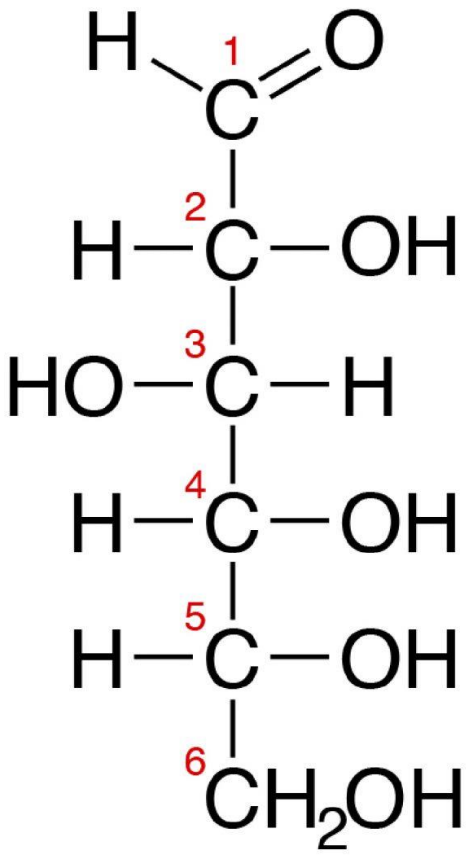
(simplest of all sugars)

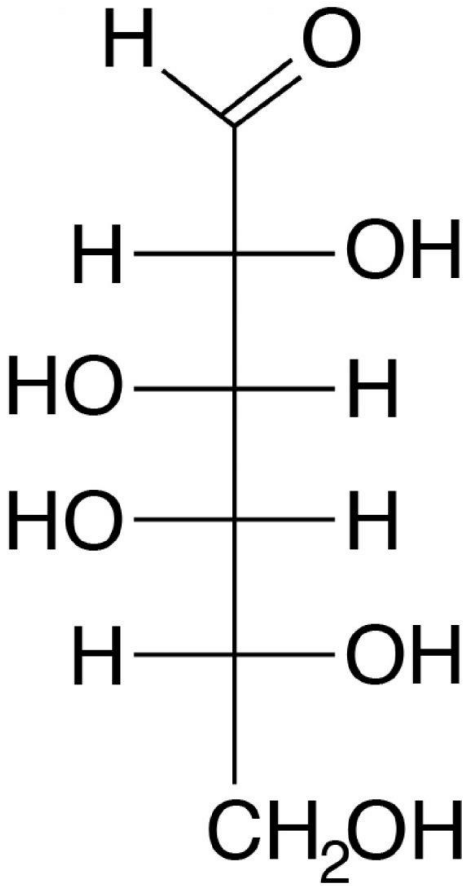




D-Glucose L-Glucose


CH2OH
O
HO
H
H
OH
H
OH
CH2OH

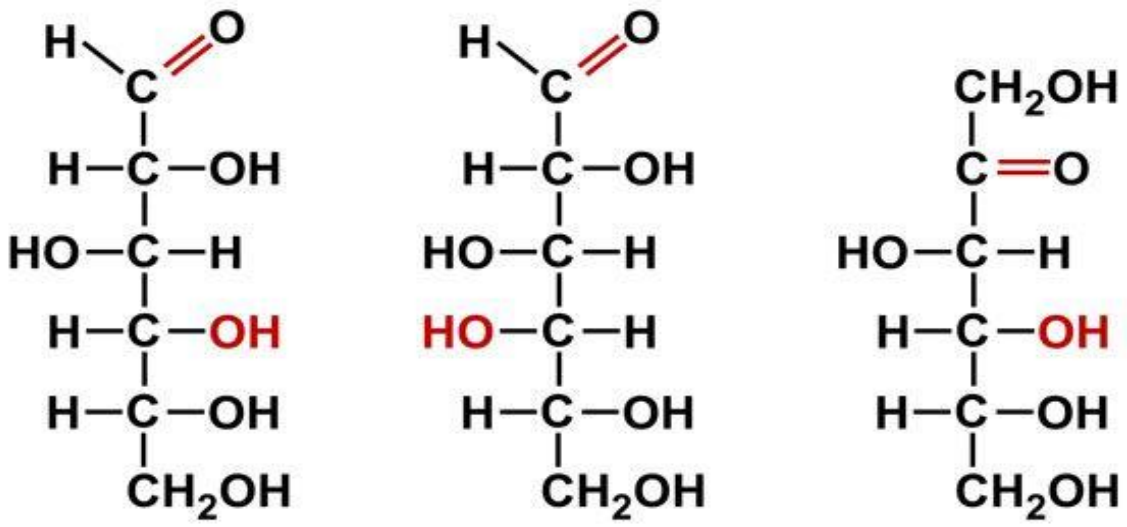

H
1
C
O
2
H
C
OH
3
HO
C
H
4
H
C
OH
5
H
C
OH
6
CH2OH

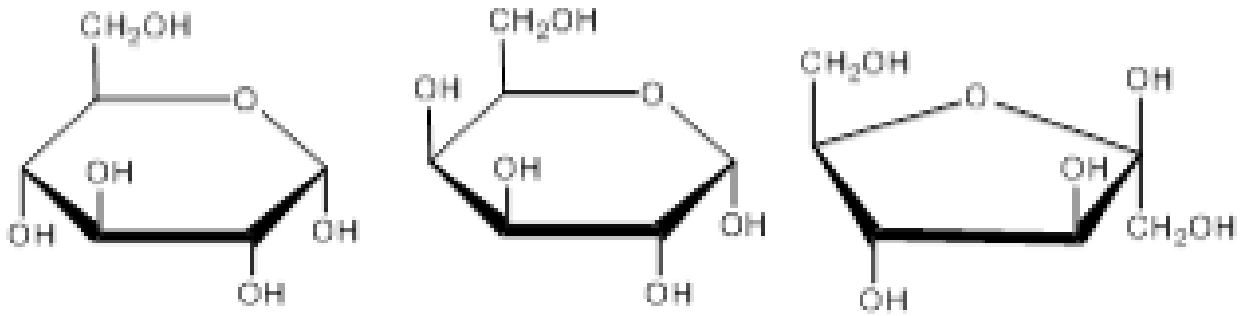

H
O
H
OH
HO
H
HO
H
H
OH
CH2OH

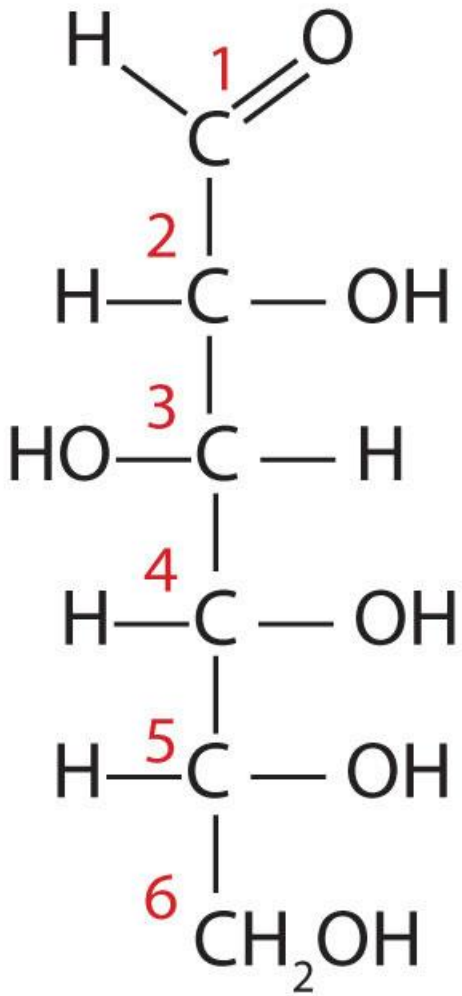
Sugar ring formation

- Most sugar units of carbohydrates in nature (and thus foods) have ring structures
- Formed by a reaction between the aldehyde or ketone group and an –OH group of the sugar
- This results in ring structures called:
  - Hemiacetal (aldoses)
  - Hemiketal (ketoses)
- These can further react to create di-, oligo- and polysaccharides (condensation reactions) and react with alcohols

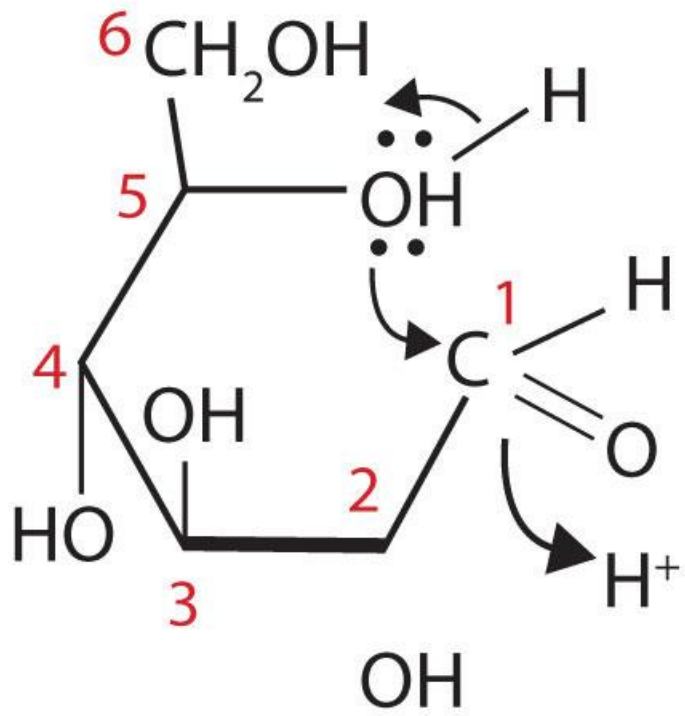
Carbohydrate Isomers



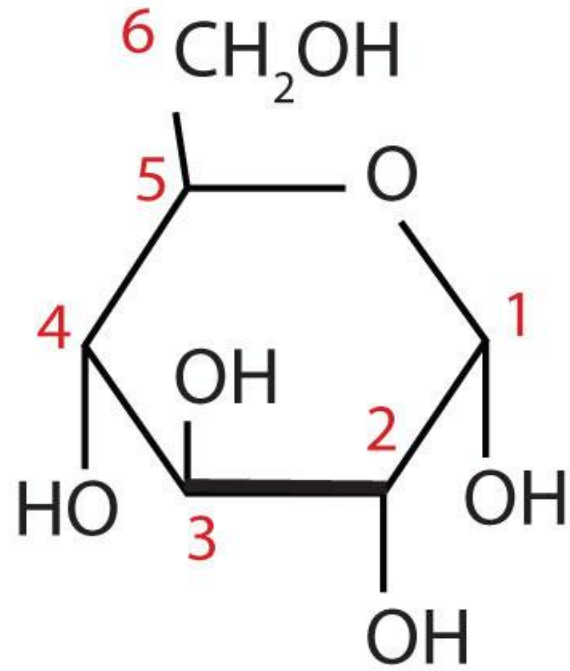




(a) Fischer projection

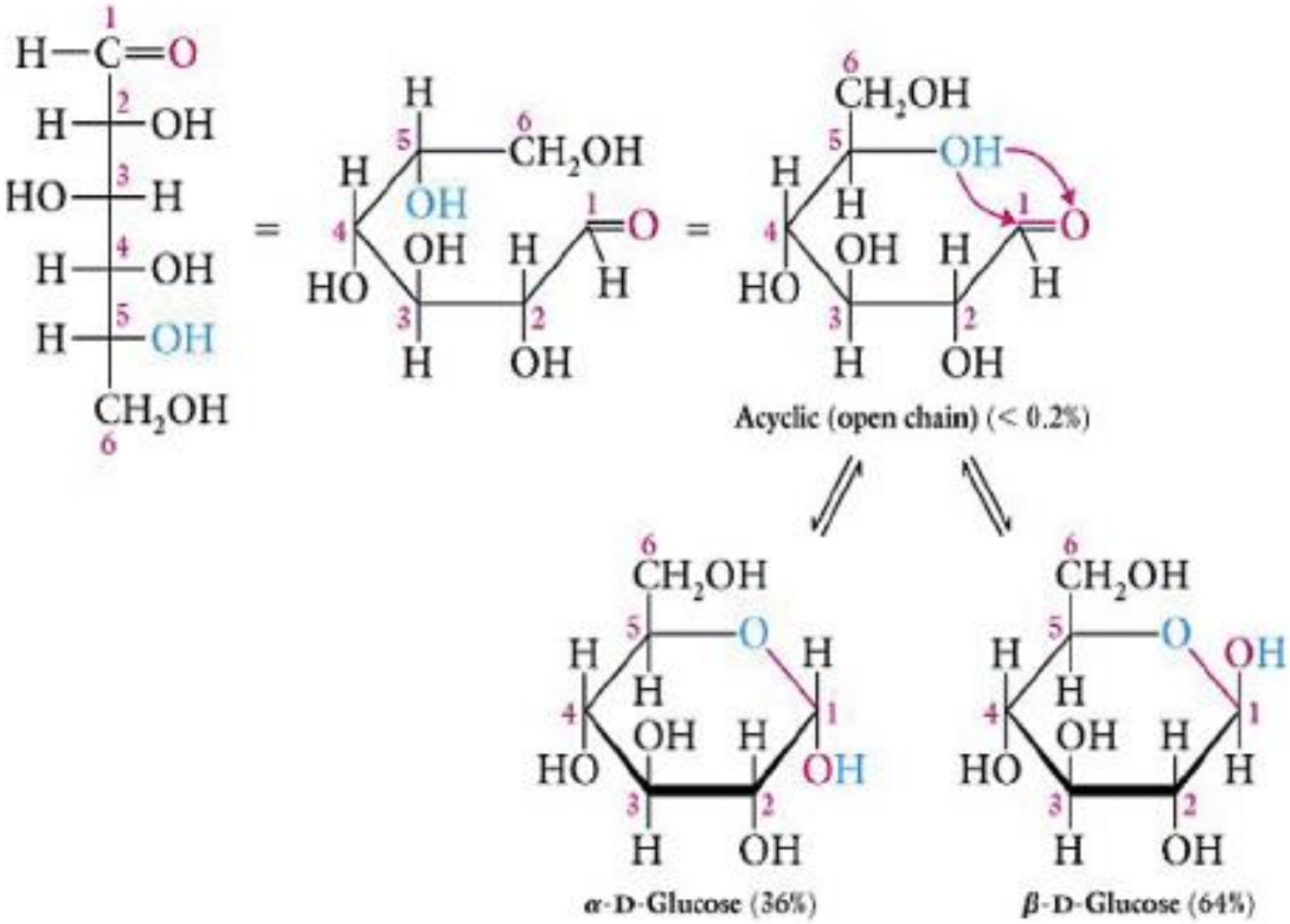


(b) Three-dimensional representantion



(c) Cyclic monosaccharide

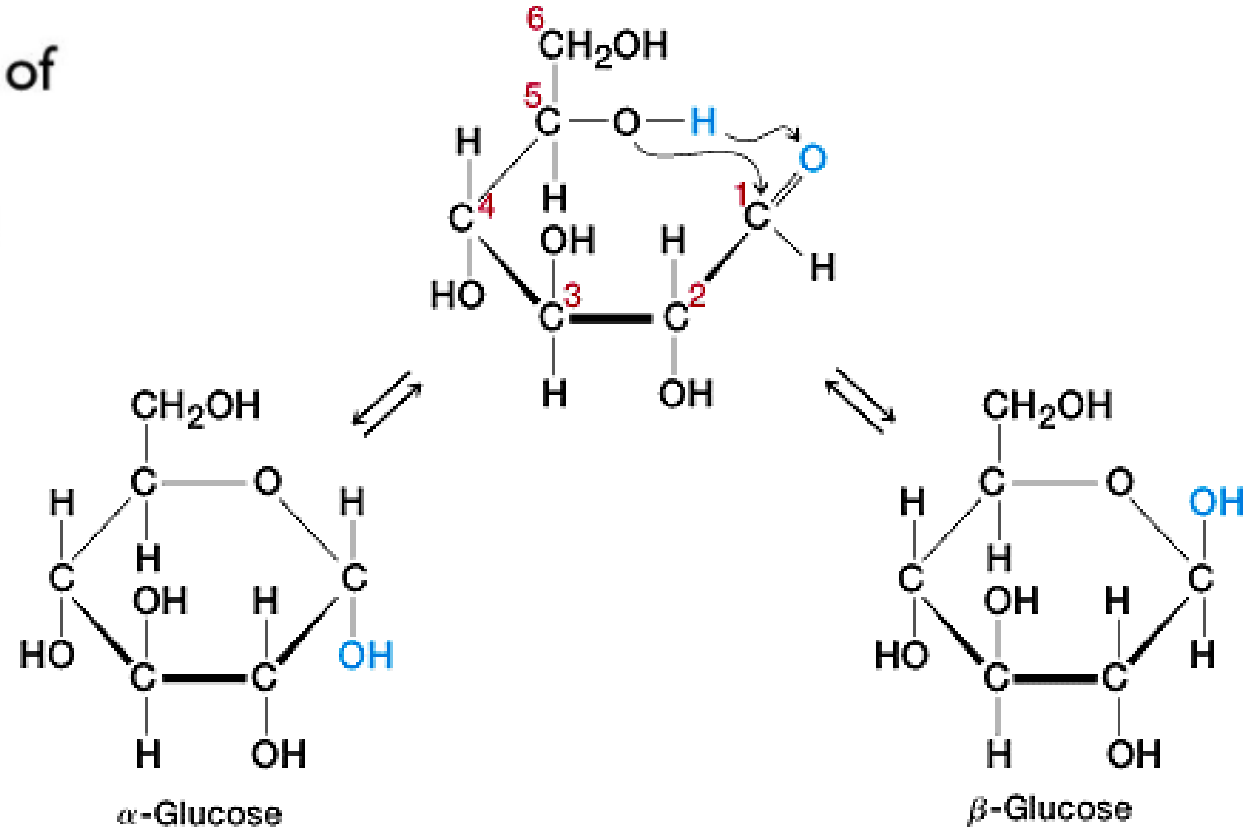
Glucose anomers



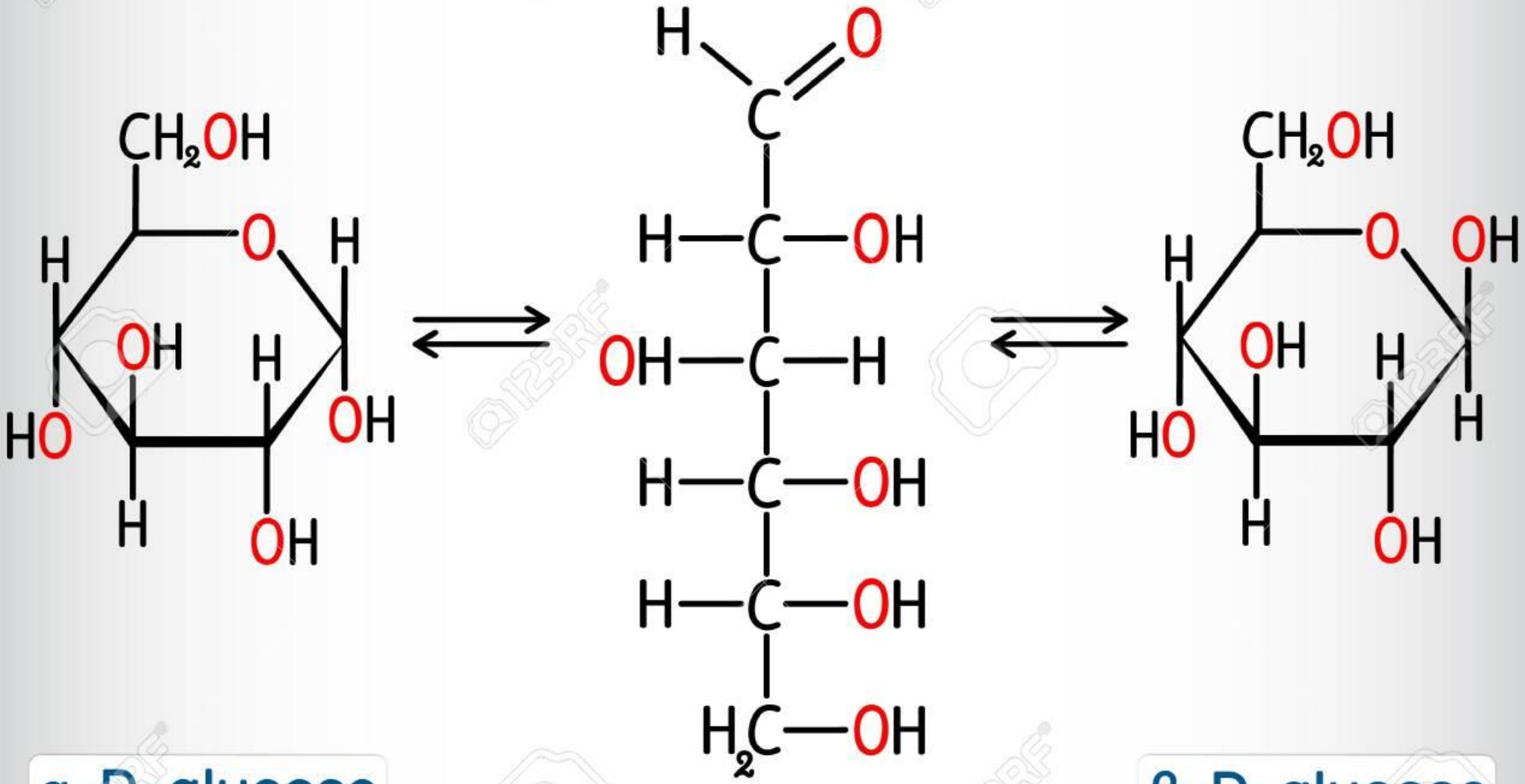
Chemical reactions

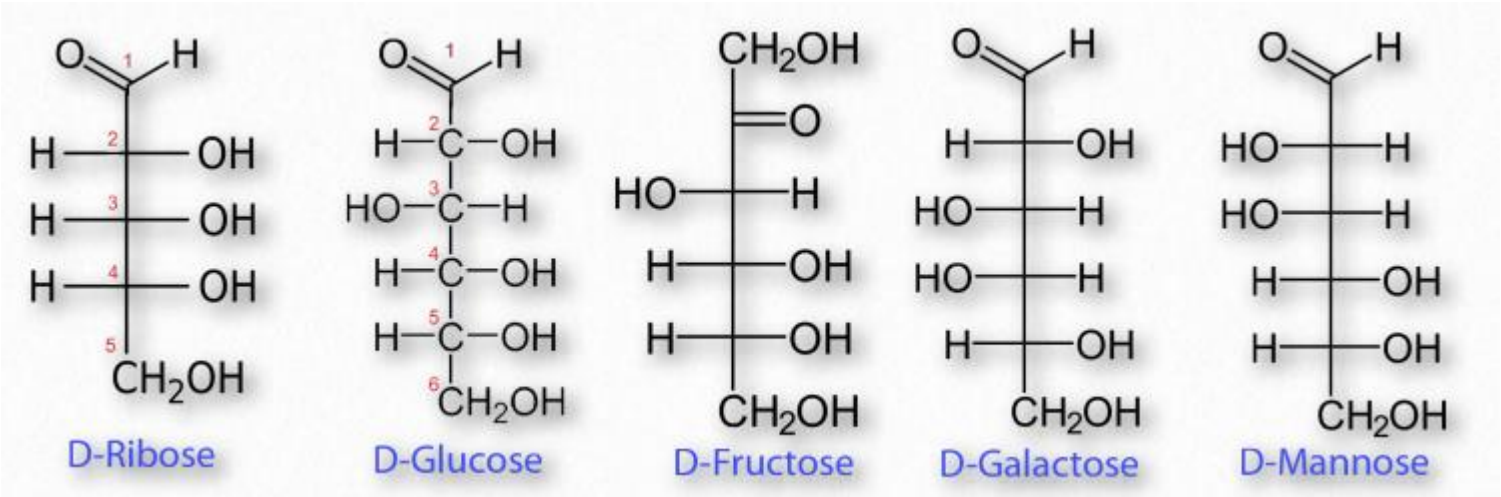
MUTAROTATION

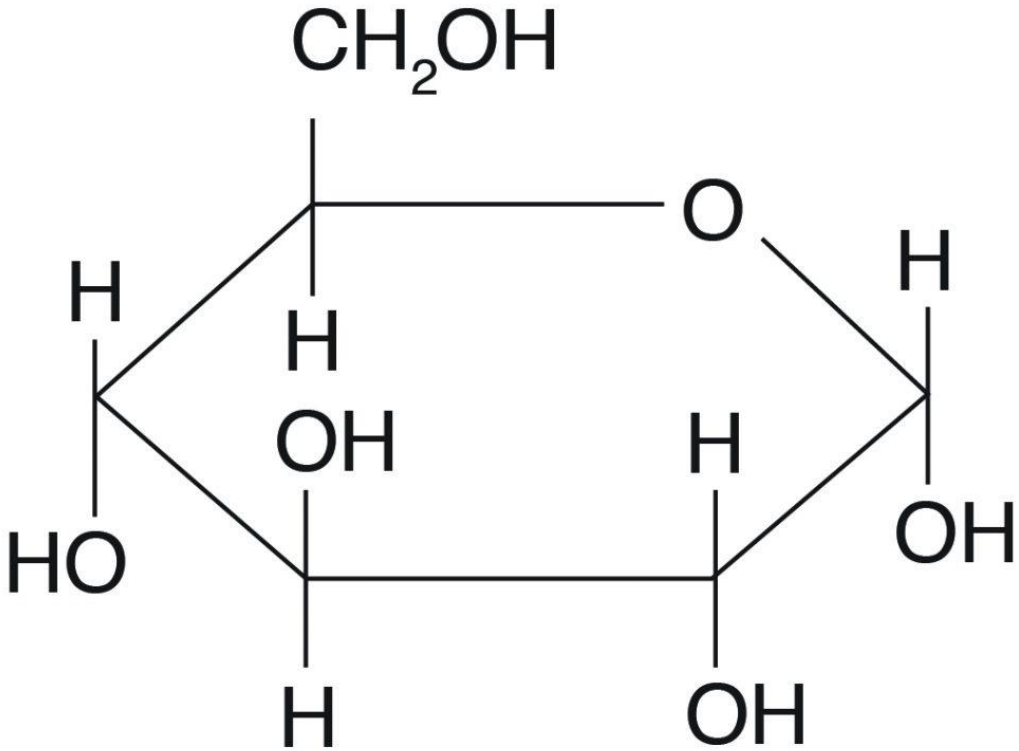
- Process by which various anomeric forms attain an equilibrium in solution
- First established studying spectral properties of sugars
  - Rotation of plane polarized light by an asymmetric center
  - Rotation varies from sugar to sugar and anomere



Glucose

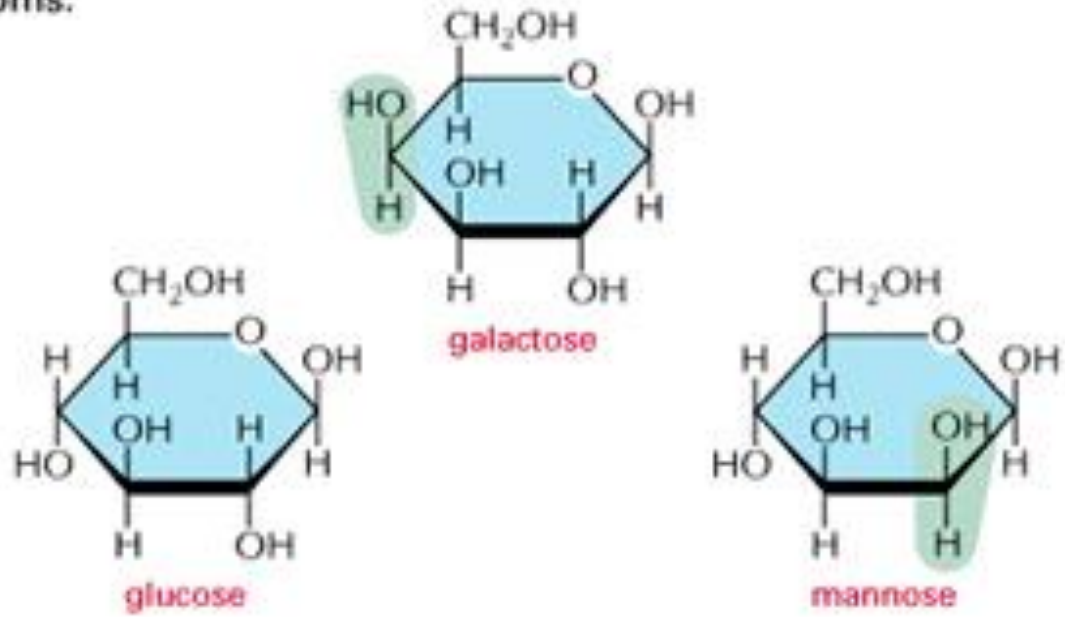



D-Ribose
D-Glucose
D-Fructose
D-Galactose
D-Mannose


CH2OH
O
H
H
H
OH
H
HO
OH
H
OH

ISOMERS

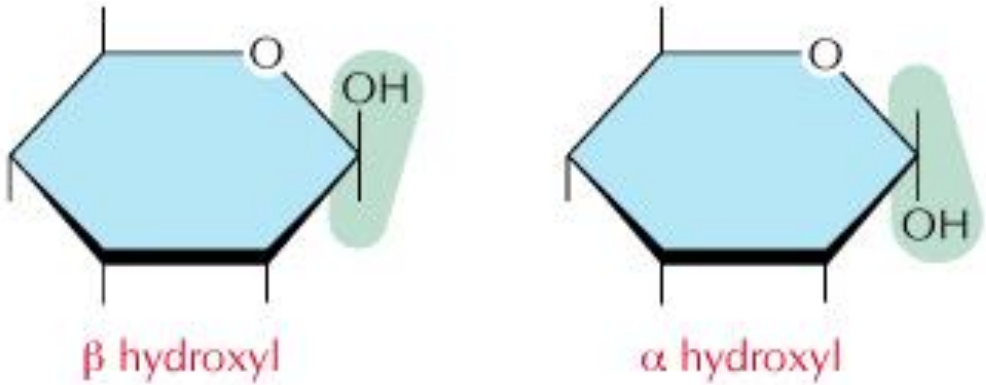
Many monosaccharides differ only in the spatial arrangement of atoms—that is, they are isomers. For example, glucose, galactose, and mannose have the same formula ($C_6H_{12}O_6$) but differ in the arrangement of groups around one or two carbon atoms.



These small differences make only minor changes in the chemical properties of the sugars. But they are recognized by enzymes and other proteins and therefore can have important biological effects.

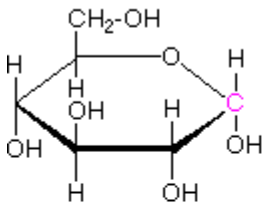
α AND β LINKS

The hydroxyl group on the carbon that carries the aldehyde or ketone can rapidly change from one position to the other. These two positions are called α and β.

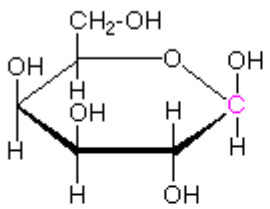


As soon as one sugar is linked to another, the α or β form is frozen.

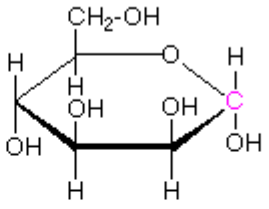
Examples of Some Pyranose Forms of Hexoses



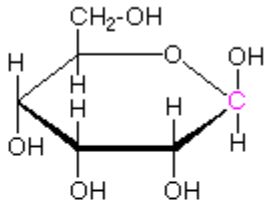
α-D-glucopyranose



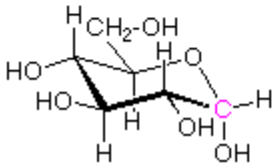
β-D-galactopyranose

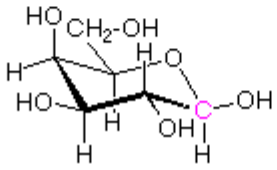


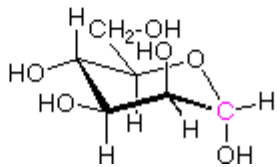
α-D-mannopyranose

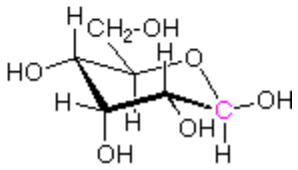


β-D-allopyranose



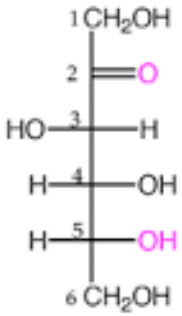




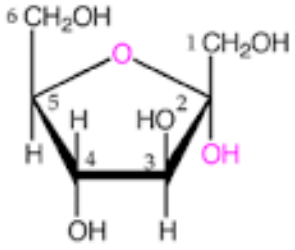


Furanoses:

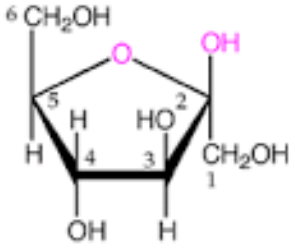
fructose



D-Fructose
(A ketohexose)

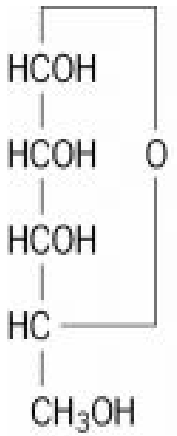


α-D-Fructofuranose
(α-D-Fructose)



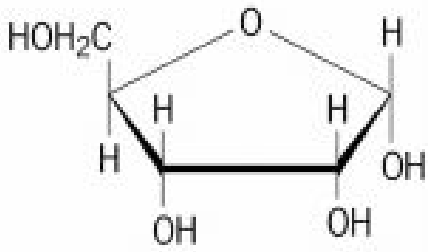
β-D-Fructofuranose
(β-D-Fructose)

ribose



D-Ribose

or

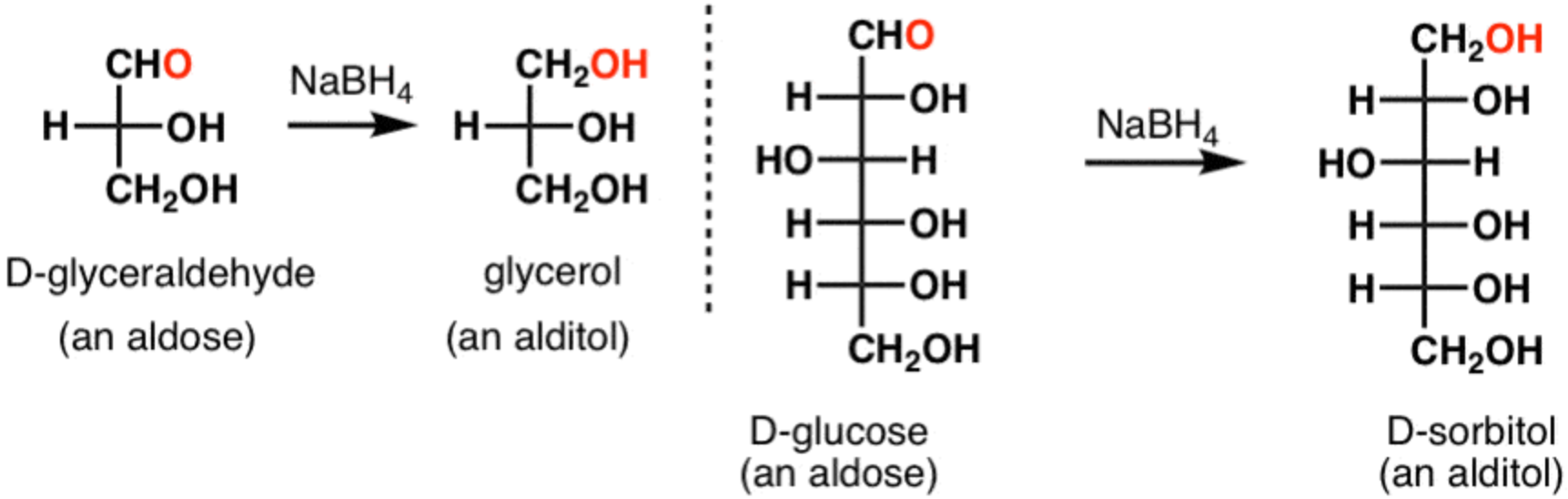


a-D-Ribofuranose

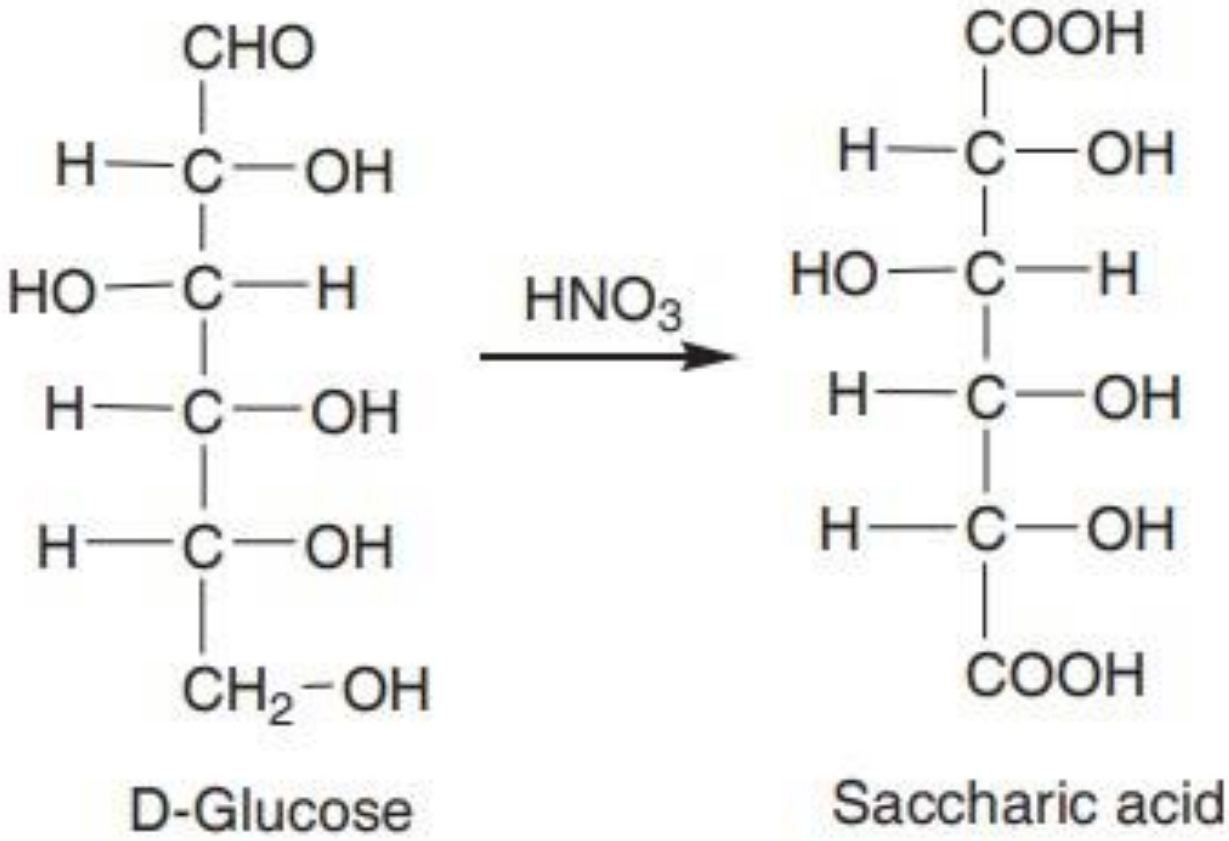
Chemical properties: reduction

Alditol

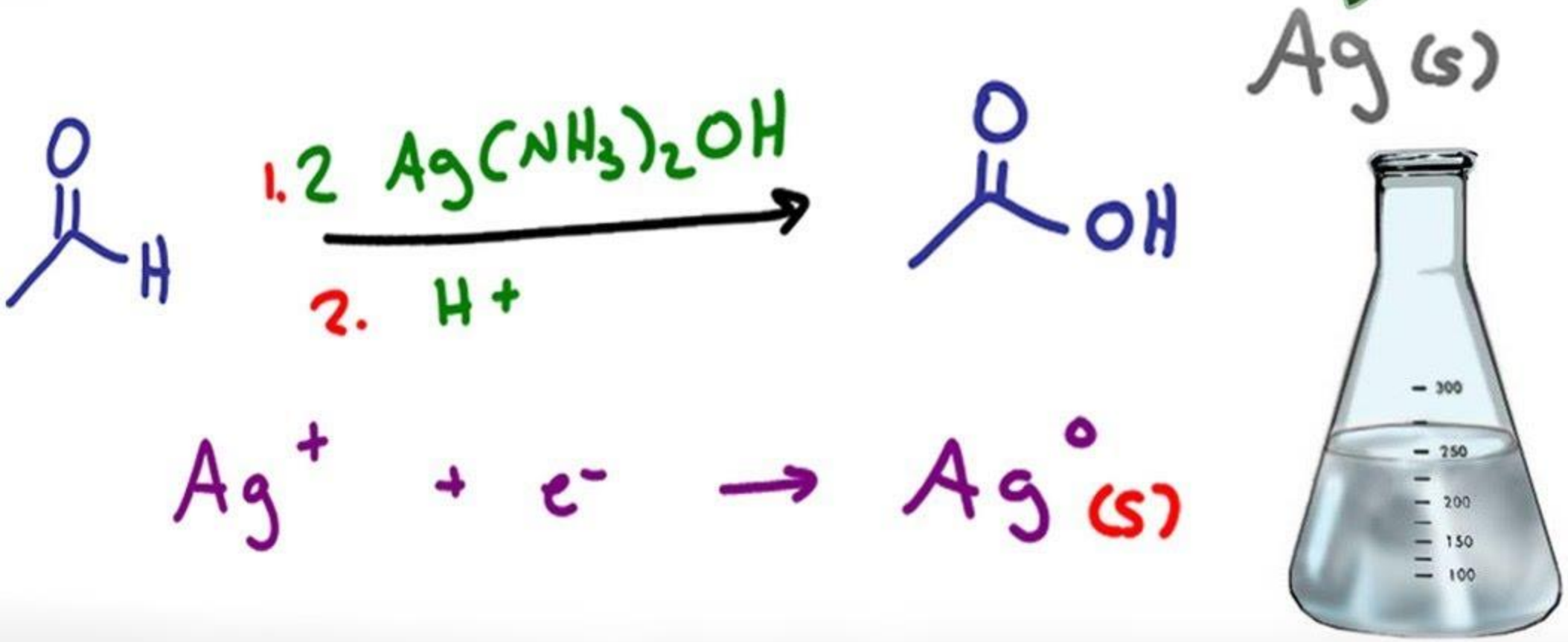
- an acyclic alcohol derived from the reduction of an aldose



Chemical properties: oxydation



Tollens Test for Aldehydes

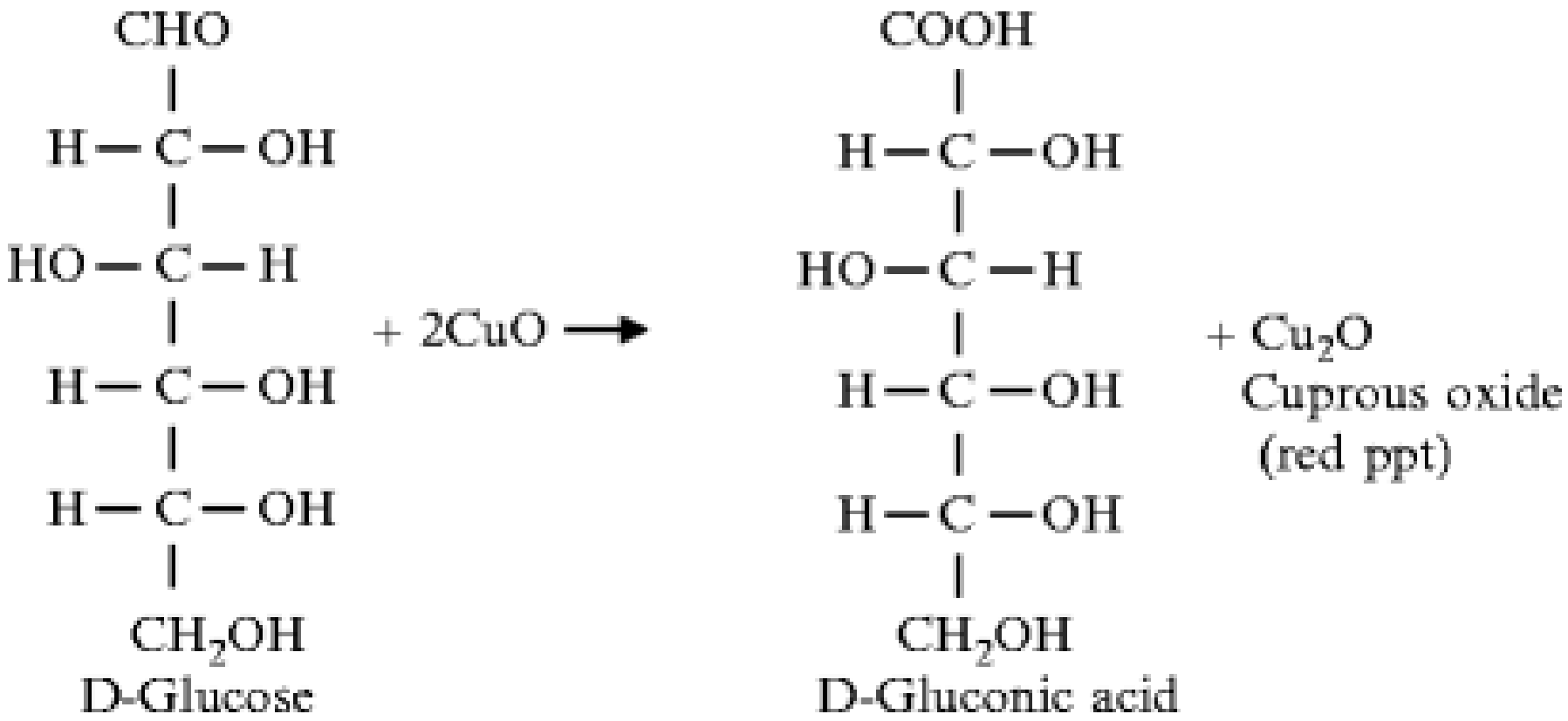


OXIDATION AND REDUCTION

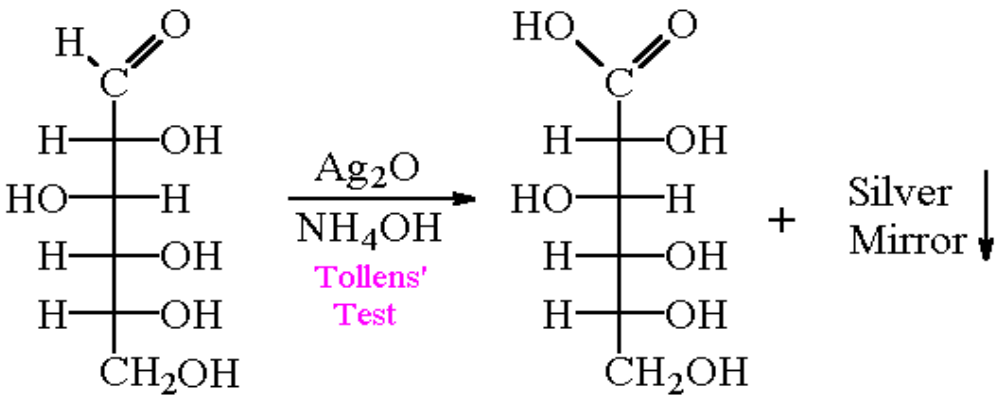
Leah4Sci

$$CuSO_4 + 2KOH \longrightarrow Cu(OH)_2 + K_2SO_4$$

$$Cu(OH)_2 \longrightarrow CuO + H_2O$$



Reducing Sugars



" $CuSO_4$, Na_2CO_3, sodium citrate (Benedict's Solution) → Cu_2O Brick Red Precipitate ↓

" $CuSO_4$, NaOH, sodium potassium tartrate (Fehling's Solution) → Cu_2O Brick Red Precipitate ↓

Benedict's Solution is not reduced by creatine and uric acid so it is preferred for detecting glucose in urine.

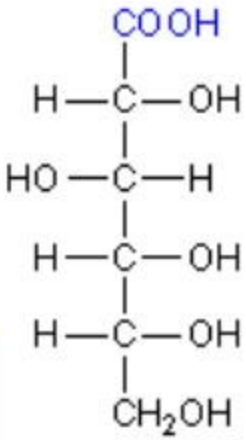
NOMENCLATURE:

- Sugar acids – aldehyde or hydroxyl is oxidized to carboxylic acid

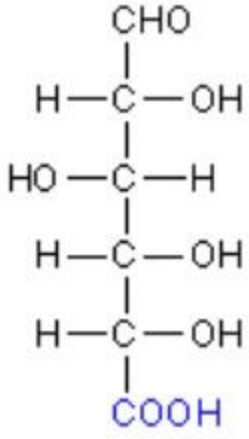
  ex. gluconic acid and glucuronic acid

- Amino sugar – amine group takes the place of one hydroxyl

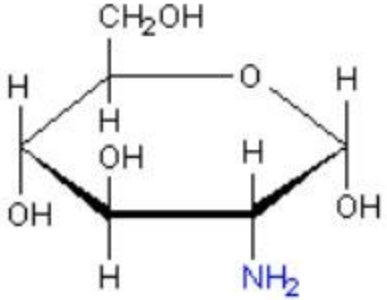
  ex. glucosamine



D-gluconic acid



D-glucuronic acid



α-D-glucosamine

Chemical reactions

REDUCTION

Reducing sugars

- Monosaccharides
  - Glucose
  - Fructose
  - All others
- Di and oligosaccharides s
  - Maltose
  - Lactose

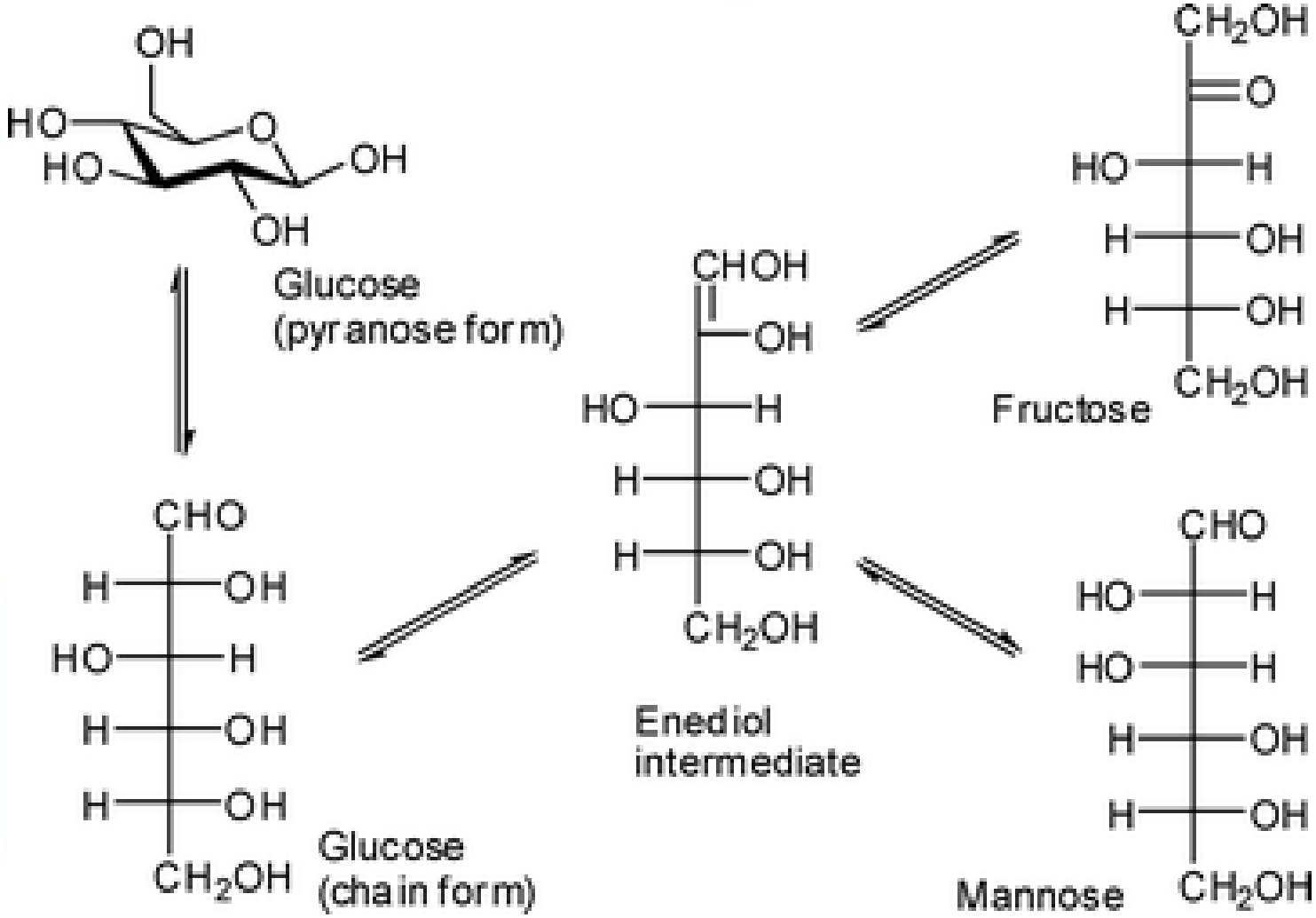
Non-reducing

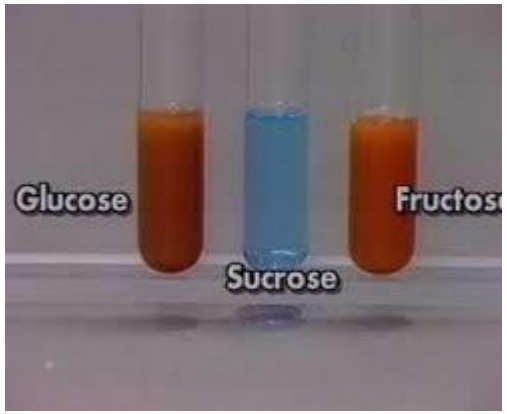
- Monosaccharides
  - None
- Di and oligosaccharides
  - Sucrose
  - Raffinose
  - Stacchyose

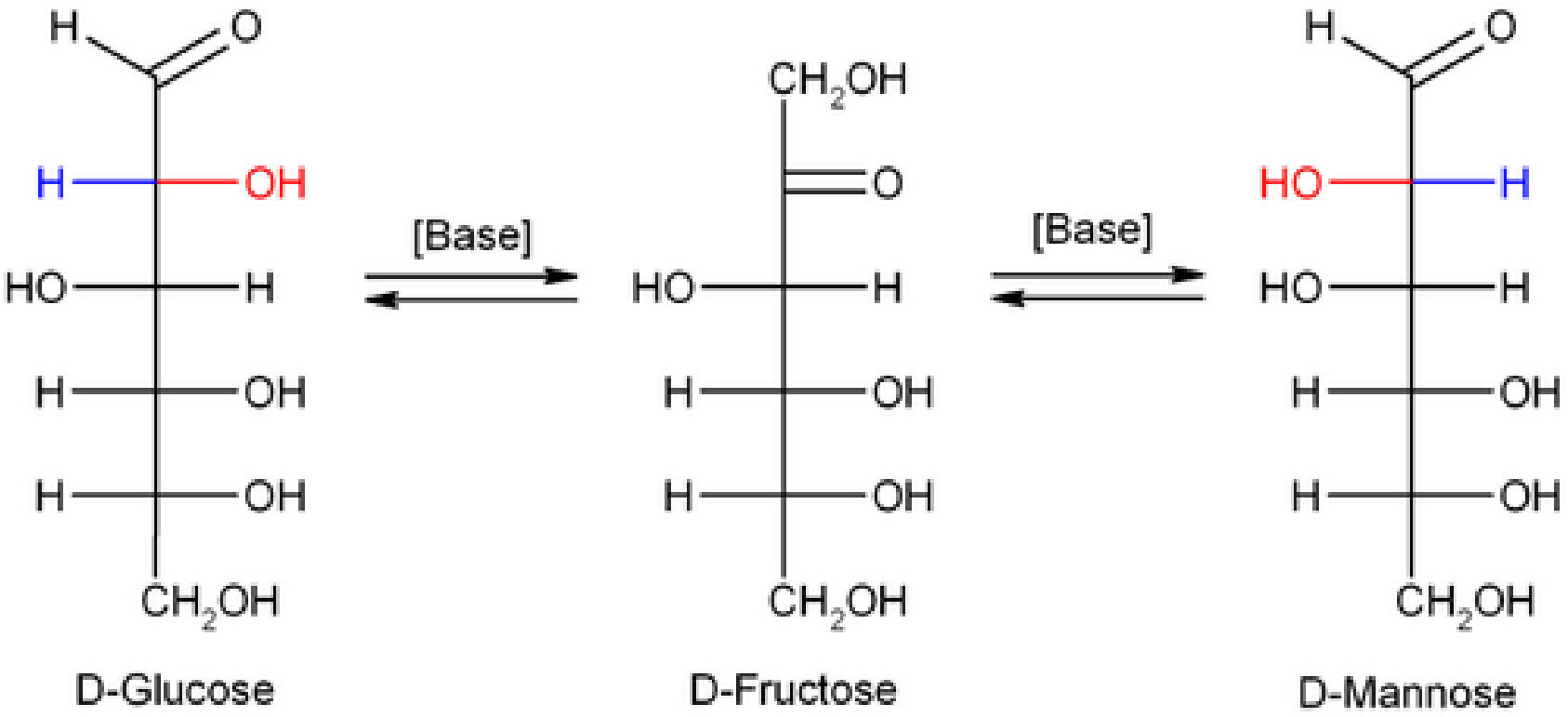
Chemical reactions

ENOLIZATION/ISOMERIZATION

- Aldose & ketose sugars are enolized in the presence of **alkali** solutions
- Thus **glucose**, **mannose** & **fructose** can be in equilibrium with each other through a 1,2-Endiol
- Therefore, you can get isomerization (transfer of 1 sugar type to another type) of varying yield
- Can happen during storage and heating




Glucose
Sucrose


[Base]
[Base]
D-Glucose
D-Fructose
D-Mannose

Chemical reactions

REDUCTION

Reducing sugars

- Monosaccharides
  - Glucose
  - Fructose
  - All others
- Di and oligosaccharides s
  - Maltose
  - Lactose

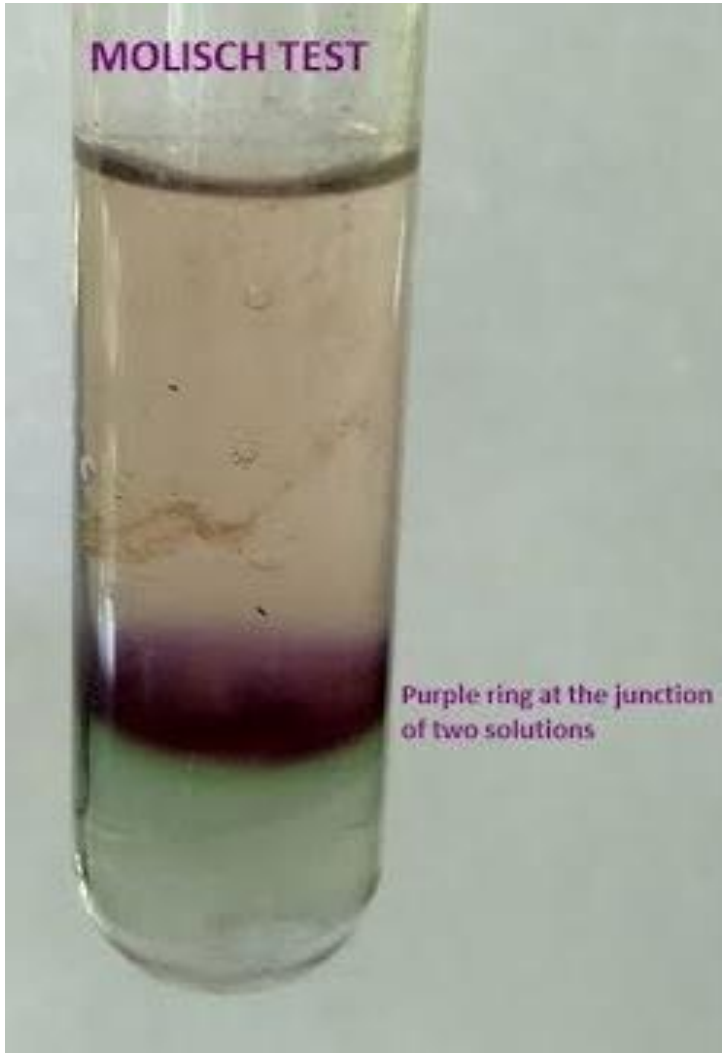
Non-reducing

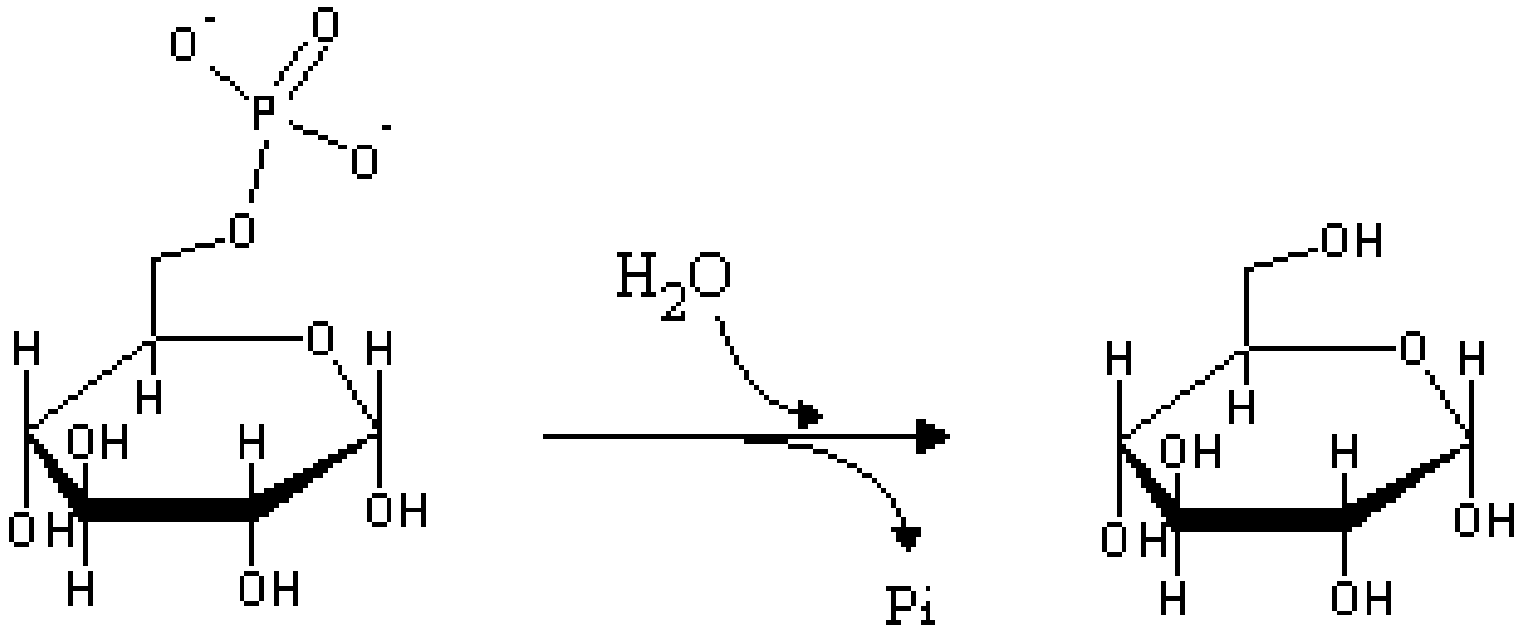
- Monosaccharides
  - None
- Di and oligosaccharides
  - Sucrose
  - Raffinose
  - Stacchyose

Chemical reactions

DEHYDRATION

- Favored at acid pH
- Occurs when you heat sugar solids or syrups with a dilute acid solution
- Leads to dehydration of sugars with the b-elimination of water
- Leads to **furan** end products
- HEXOSE → - 3 H_2O + HMF (Hydroxymethyl furfural)
  - Flowery odor, bitter/astringent flavor
- PENTOSE → - 3 H_2O + Furfural

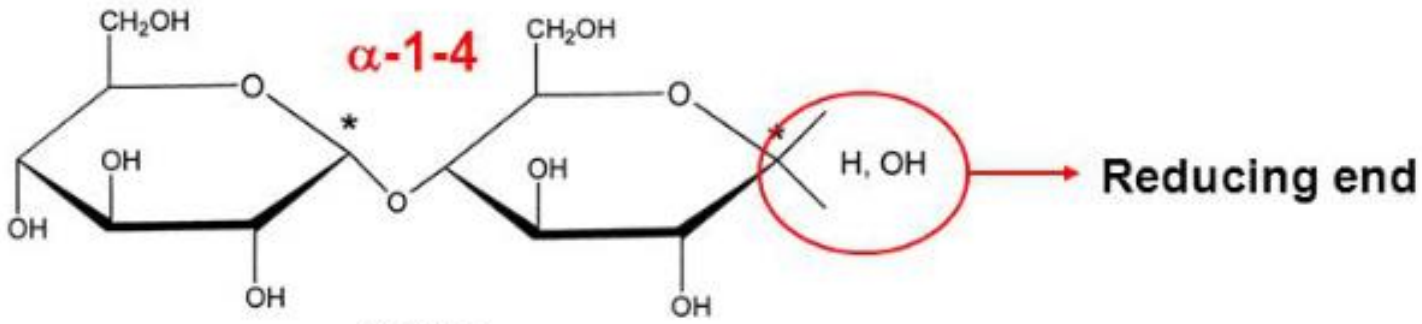




Glucose-6-P **Glucose**

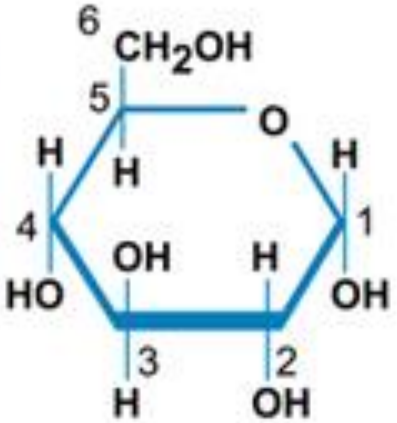
Maltose

- 2 units of glucose
- Forms from the breakdown of starch during malting of grains (barley) and commercially by using enzymes (β-amylase)
  - E.g. malt beverages; beer
- Used sparingly as mild sweetener in foods
- Very hygroscopic
- OH-group can be reactive and we term this as a **REDUCING SUGAR**
  - Is free to react with oxidants

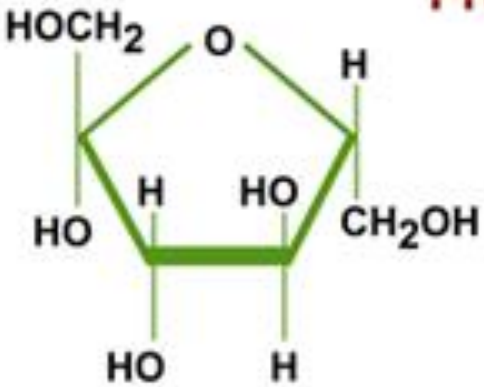


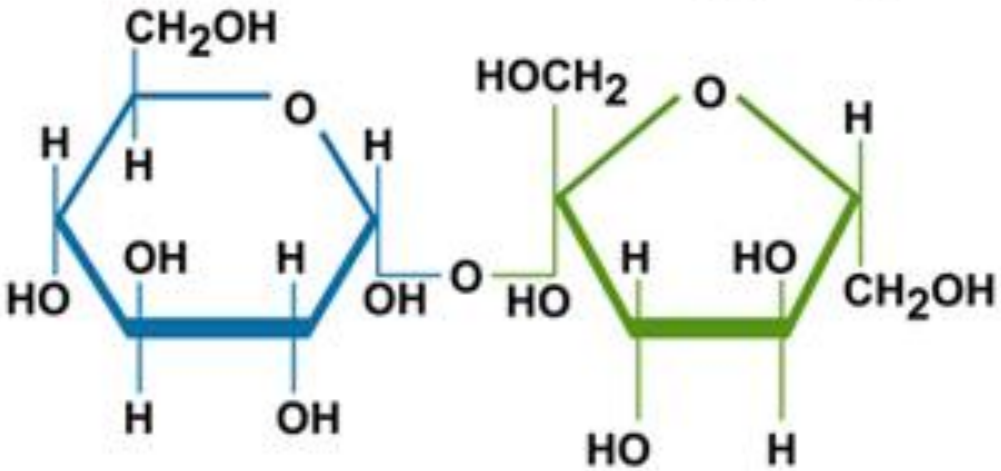
Maltose
4-O-(α-D-glucopyranosyl)-D-glucopyranose

Glucose

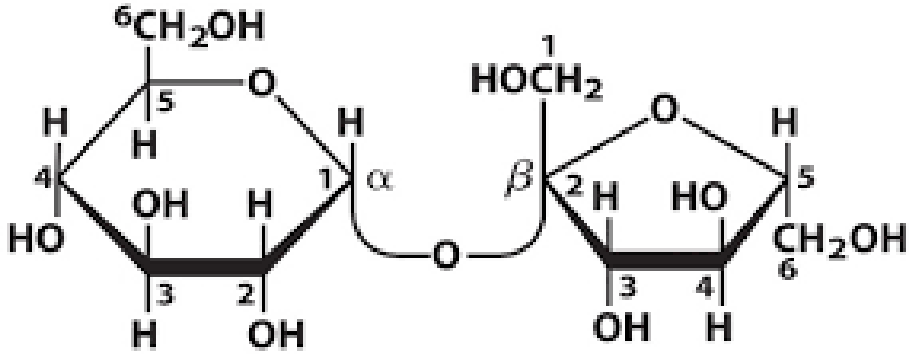


Fructose





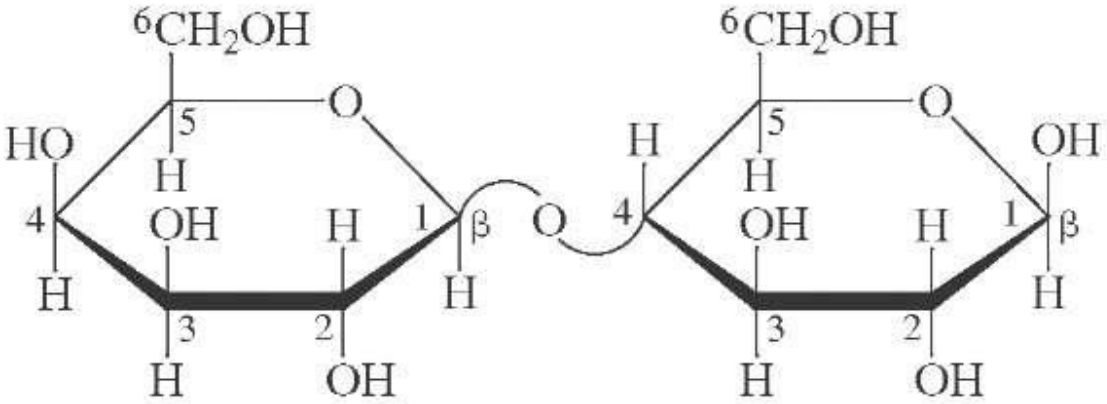
Sucrose



Sucrose

α-D-glucopyranosyl β-D-fructofuranoside

Glc(α1↔2β)Fru



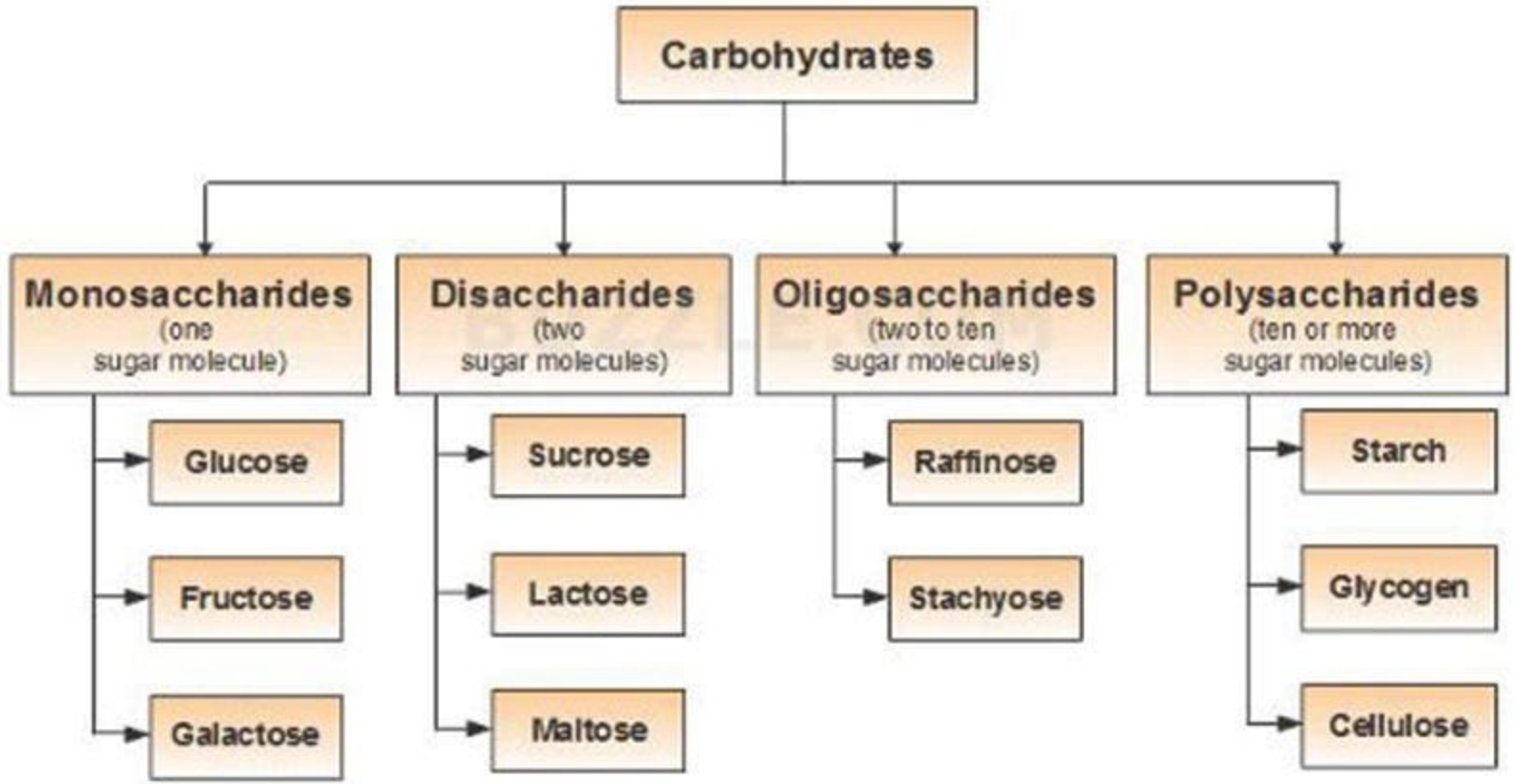
Lactose (β form)

β-D-galactopyranosyl-(1 → 4)-β-D-glucopyranose

Gal(β1 → 4)Glc

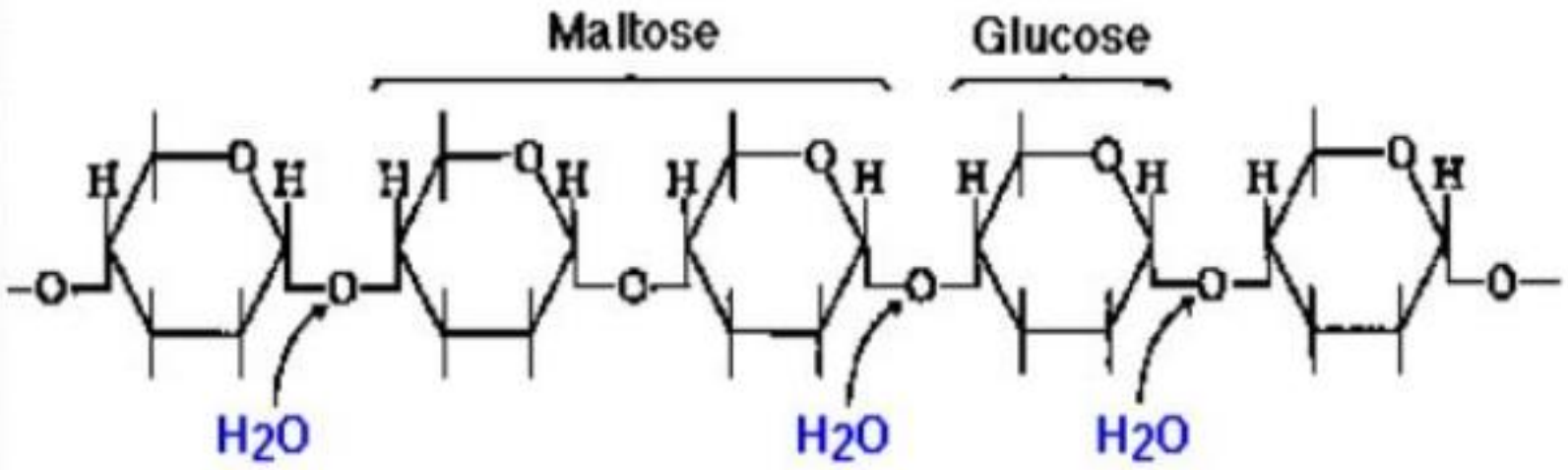
Relative sweetness

Sucrose	1.0
Lactose	0.16
Maltose	0.32
Glucose	0.74
Fructose	1.73
Invert sugar	1.30


Carbohydrates
Monosaccharides
(one
sugar molecule)
Disaccharides
(two
sugar molecules)
Oligosaccharides
(two to ten
sugar molecules)
Polysaccharides
(ten or more
sugar molecules)
Glucose
Fructose
Galactose
Sucrose
Lactose
Maltose
Raffinose
Stachyose
Starch
Glycogen
Cellulose

Definition

- Polysaccharides are high molecular weight polymers build up by repeated condensation of polyhydroxy aldehydes/ polyhydroxy ketones which are joined together by glycosidic linkages, and can be hydrolysed to a large no. of monosaccharides.



Types of polysaccharides

- **Homopolysaccharides :-also called as homoglycans.**

On hydrolysis yield only one type of monosaccharide unit.

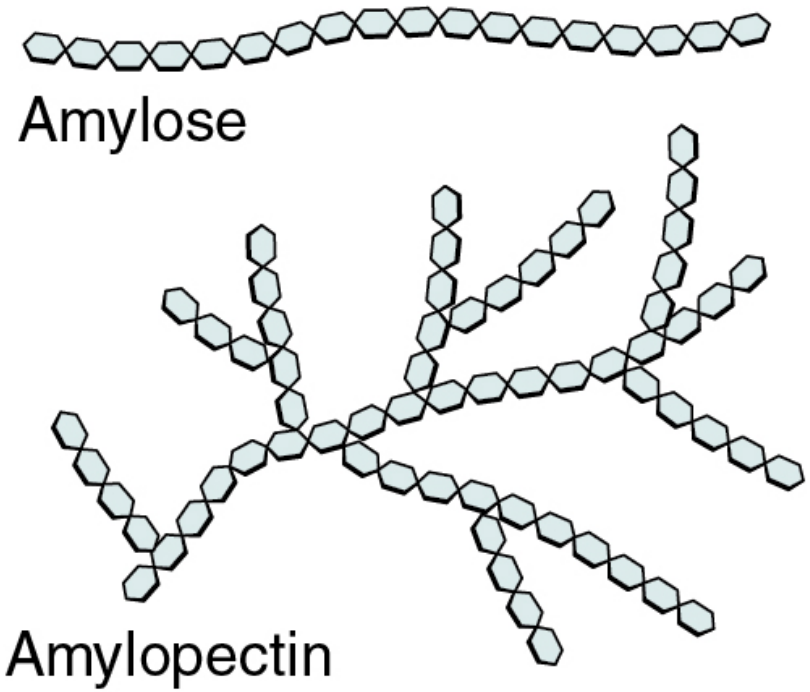
Example- cellulose, inulin, starch etc.

- **Heteropolysaccharides :- also called as heteroglycans.**

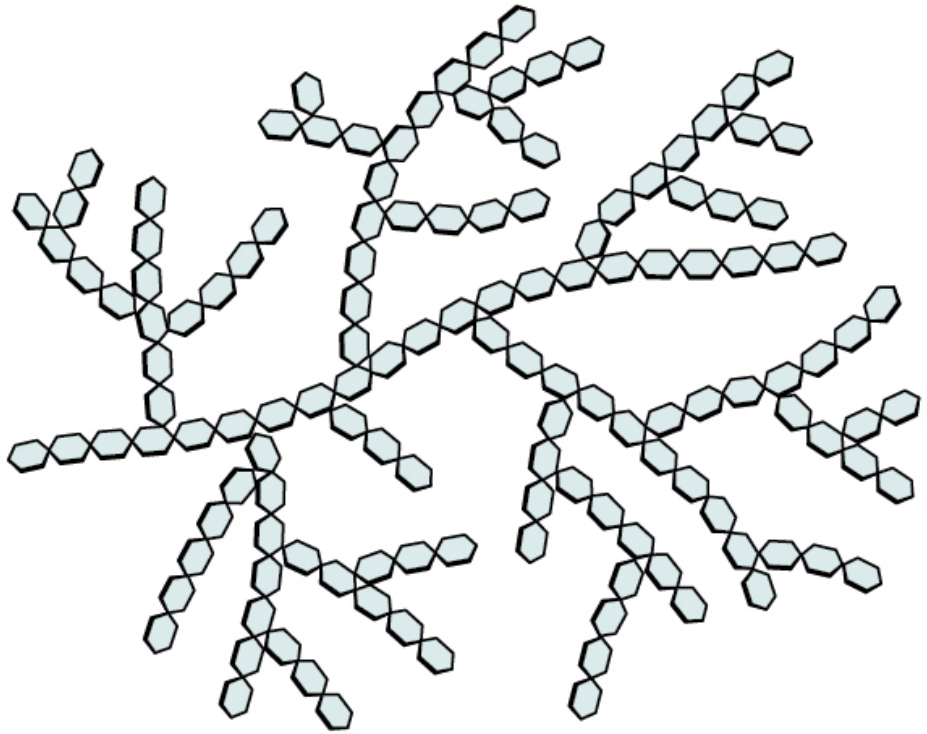
On hydrolysis yield more than one type of monosaccharide unit.

Example- α- heparin, hyaluronic acid etc.

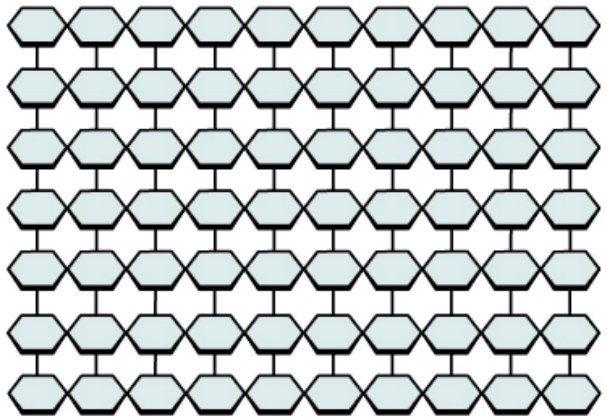
Homoglycans



Starch



Glycogen



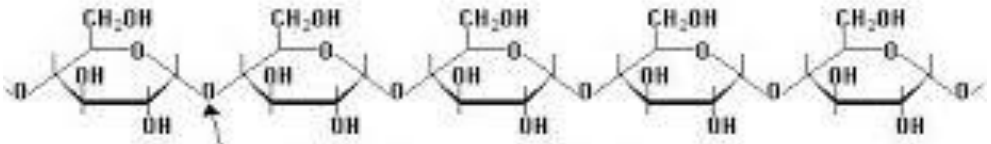
Cellulose (fiber)

Starch

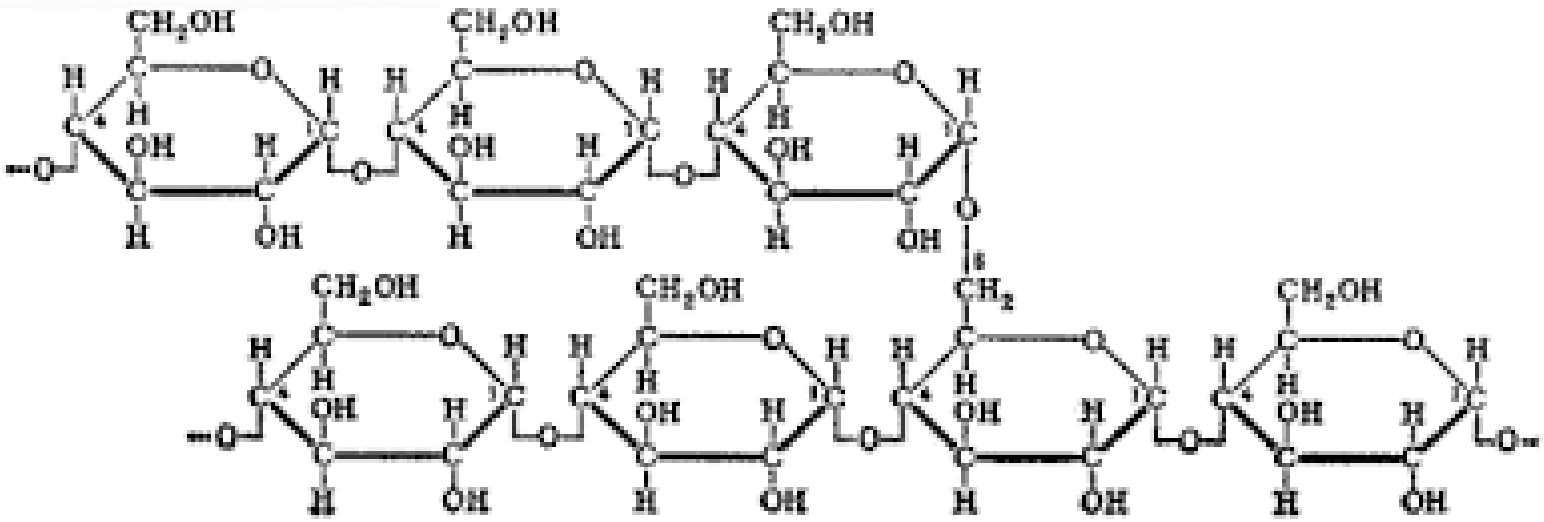
- **Starch** is a carbohydrate consisting of a large number of glucose units joined together by glycosidic bonds. This polysaccharide is produced by all green plants as an energy store.
- It is the most important carbohydrate in the human diet and is contained in such staple foods as potatoes, wheat, maize (corn), rice, and cassava.

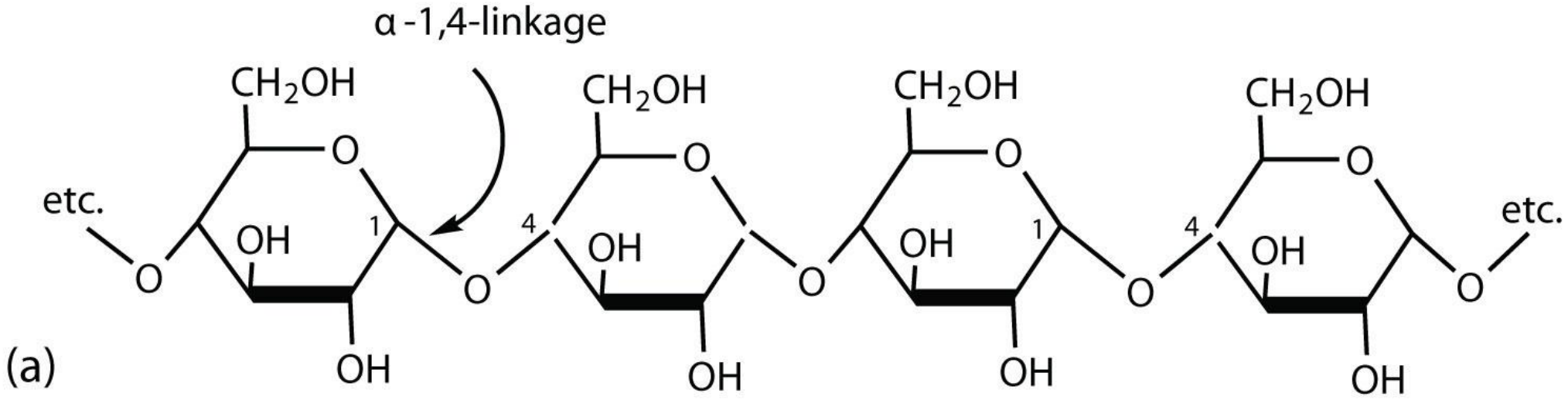
- It consists of two types of molecules:
- the linear and helical amylose:-**Amylose** is a linear polymer made up of D-glucose units.
- the branched amylopectin: Branching takes place with α(1→6) bonds occurring every 24 to 30 glucose units.
- Depending on the plant, starch generally contains 20 to 25% amylose and 75 to 80% amylopectin.

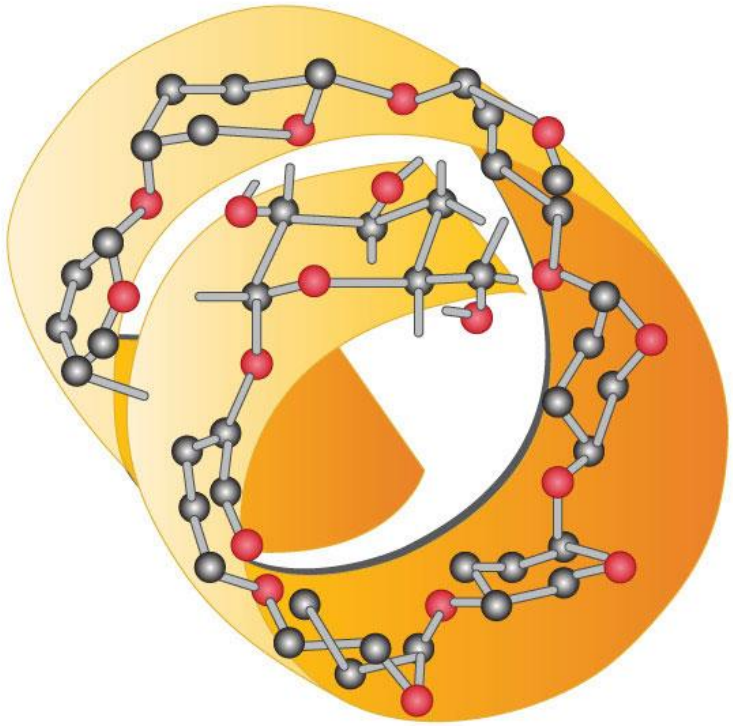
Amylose



α-1,4-glycosidic bonds

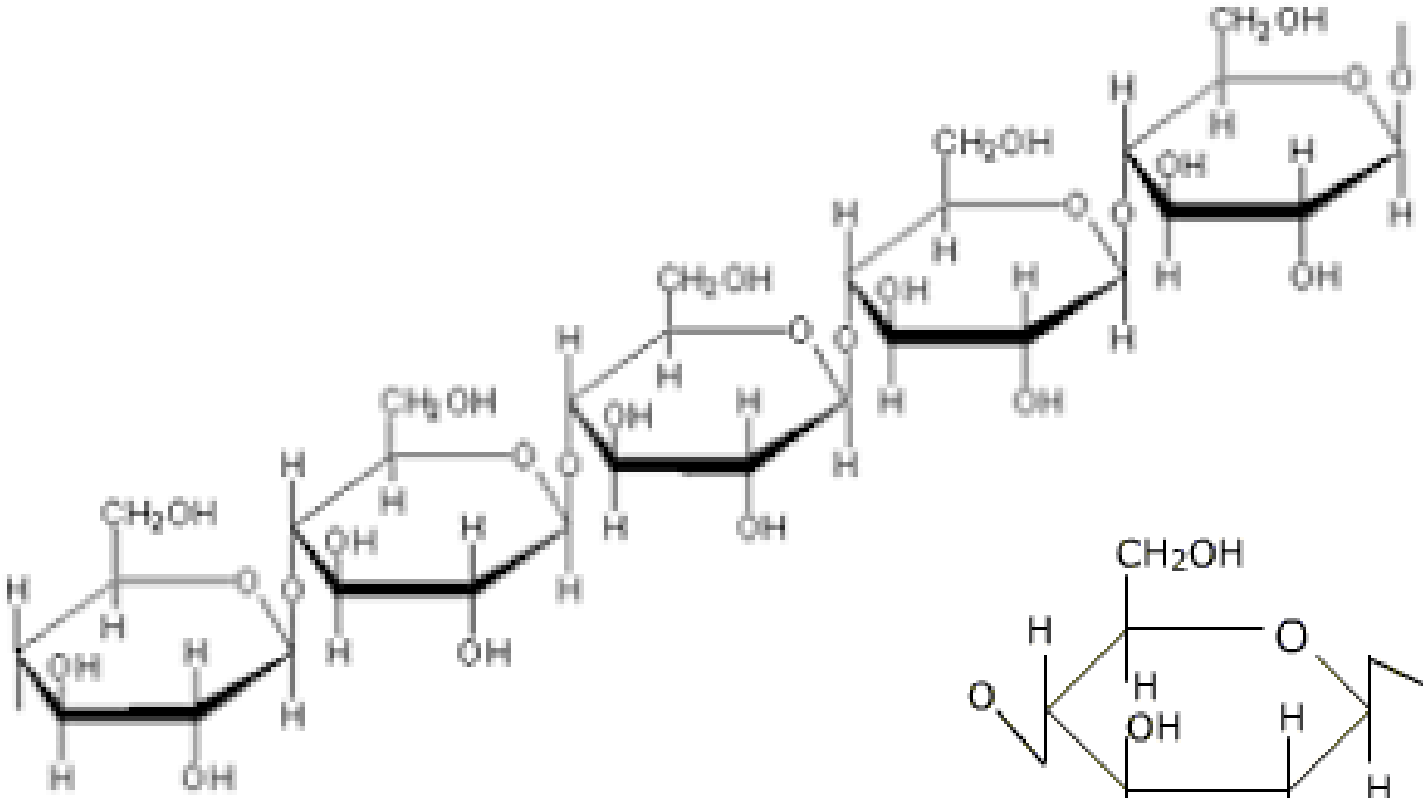


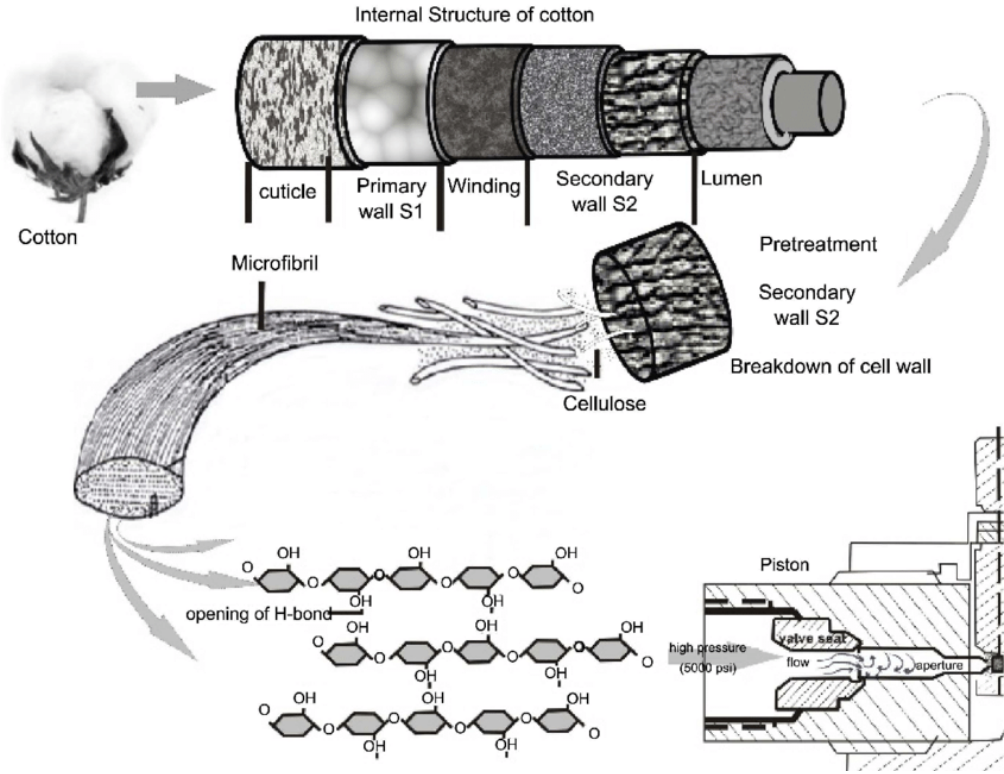


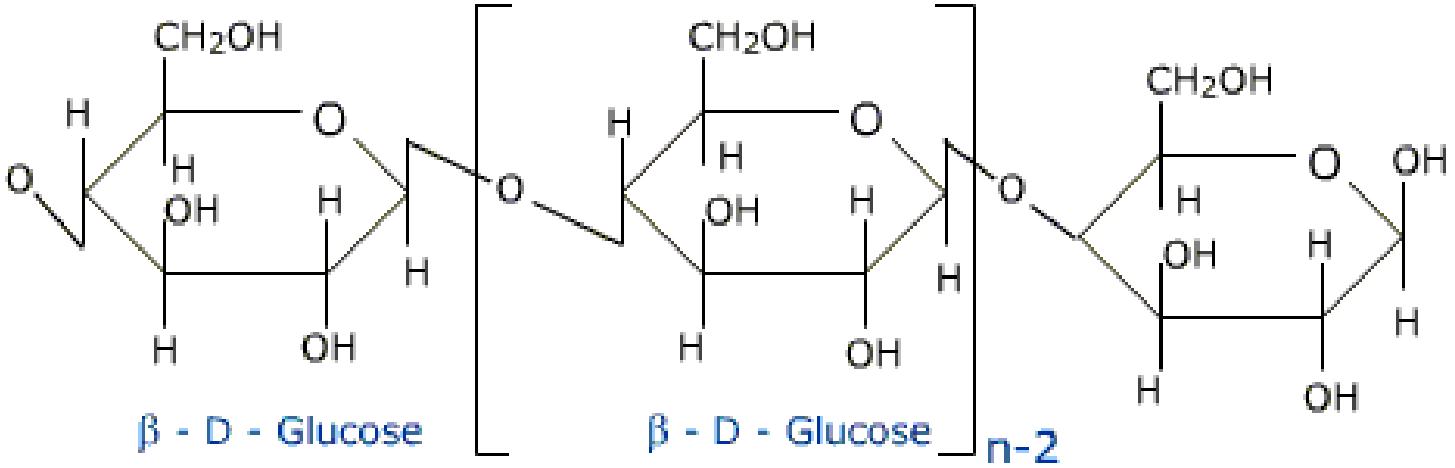


(b)

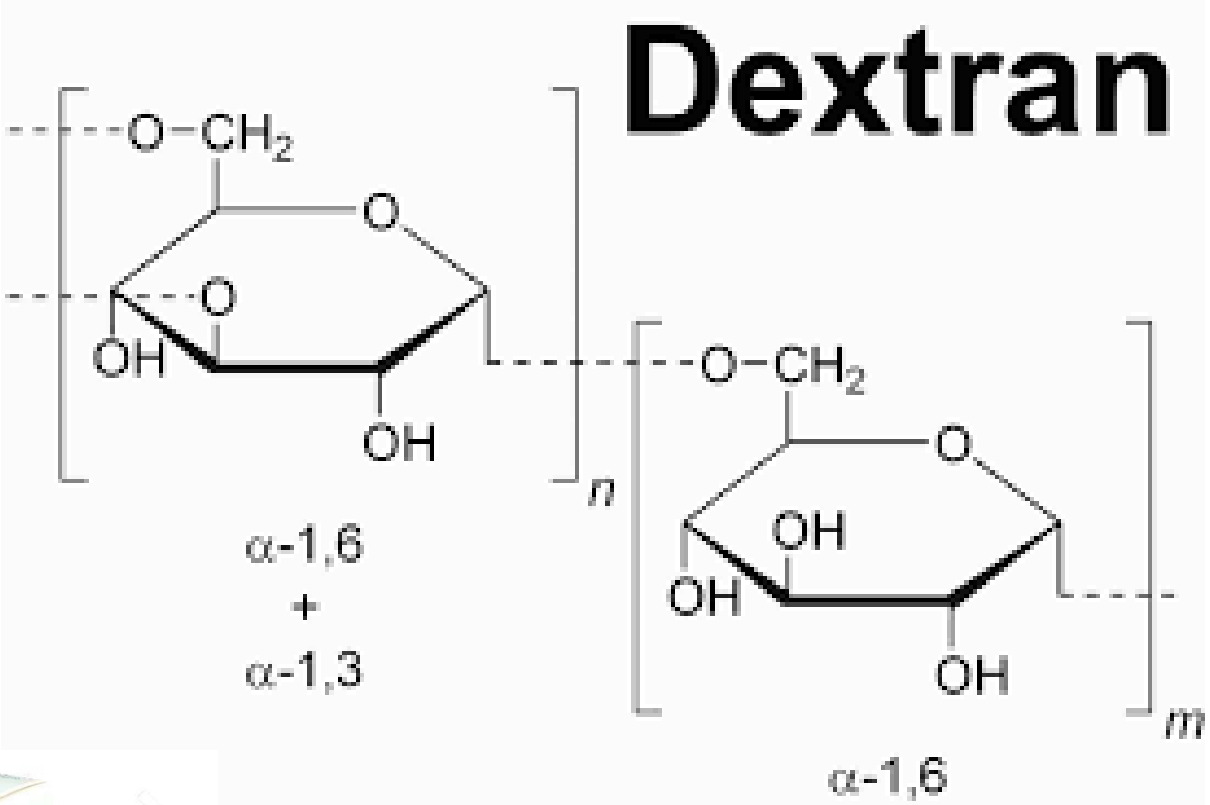
Cellulose (Fiber)







Dextran



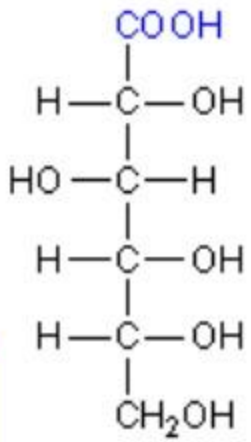
Used as:

- Injection fluids
- Eye drops
- Artificial tears

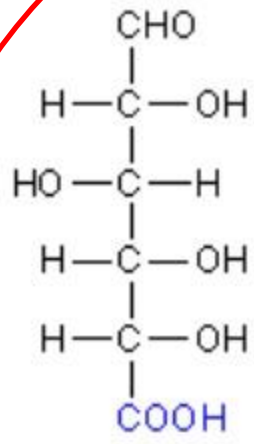
Sugars in other homoglycans and many heteroglycans

NOMENCLATURE:

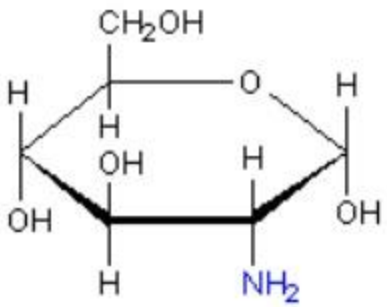
- Sugar acids – aldehyde or hydroxyl is oxidized to carboxylic acid
  ex. gluconic acid and glucuronic acid
- Amino sugar – amine group takes the place of one hydroxyl
  ex. glucosamine



D-gluconic acid



D-glucuronic acid



α-D-glucosamine

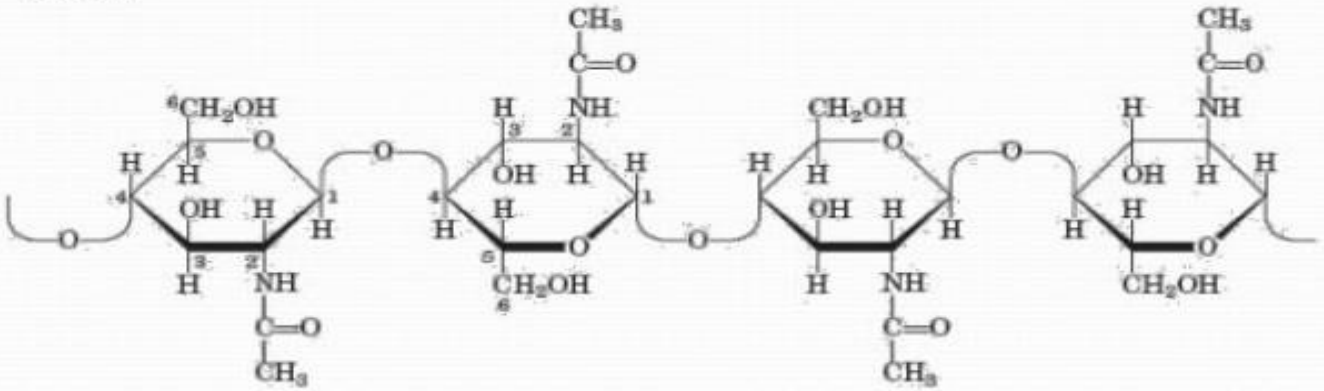
CHITIN

- **Linear homopolysaccharide composed of** *N-acetyl glucosamine residues in linkage*

- The only chemical difference from cellulose is the replacement of the hydroxyl group at C-2 with an acetylated amino group.
- Chitin forms extended fibers similar to those of cellulose, and like cellulose cannot be digested by vertebrates.

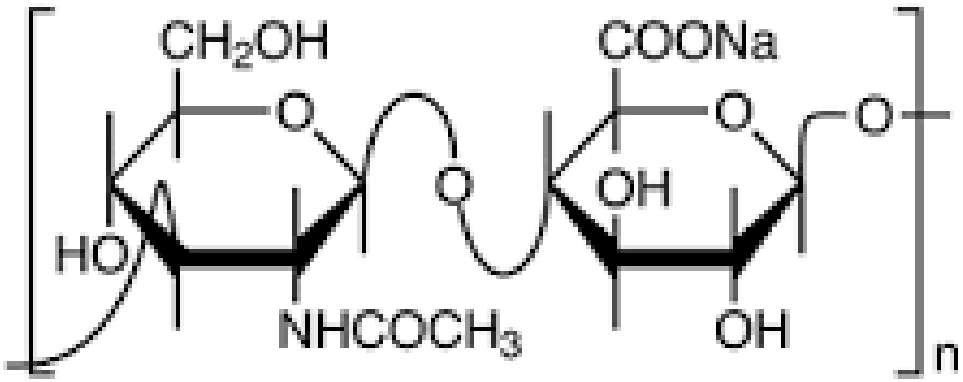
- Chitin is the principal component of the hard exoskeletons of nearly a million species of arthropods—insects, lobsters, and crabs, for example— and is probably the second most abundant polysaccharide, next to cellulose, in nature.

Chitin



Hetropolysaccharides

- **Hyaluronic acid**
- **Heparin**
- **Agarose**

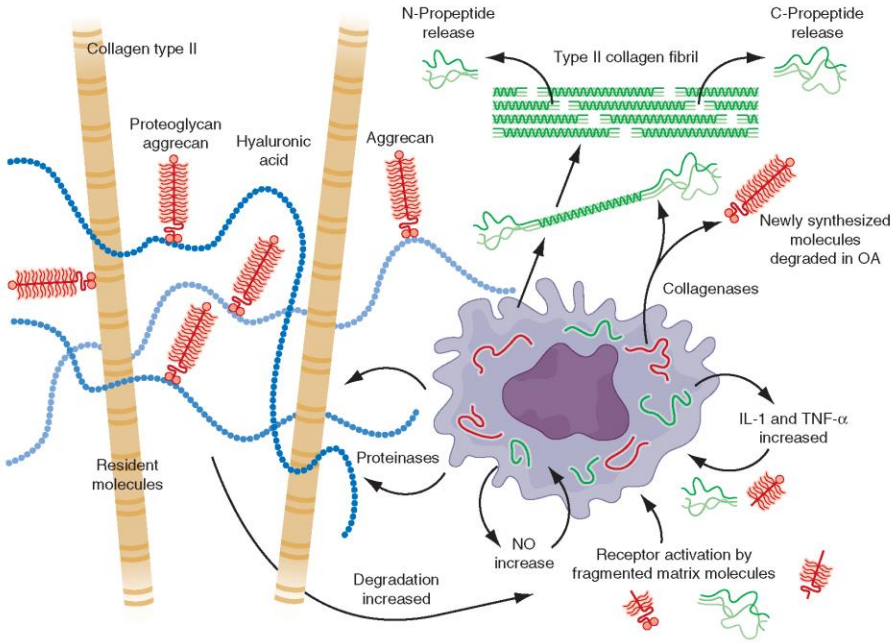


Hyaluronic acid

- Hyaluronic acid is an important GAG (Glycosamonoglycan) found in the ground substance of synovial fluid of joints and vitreous humor eye.

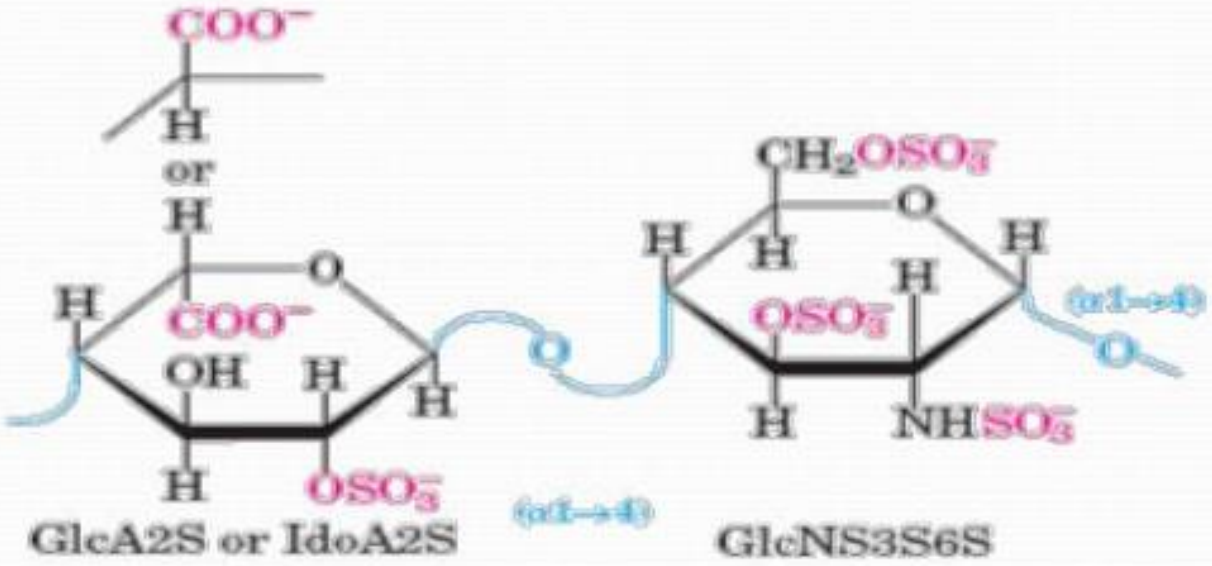
- serves as a lubricant and shock absorbant in joints.

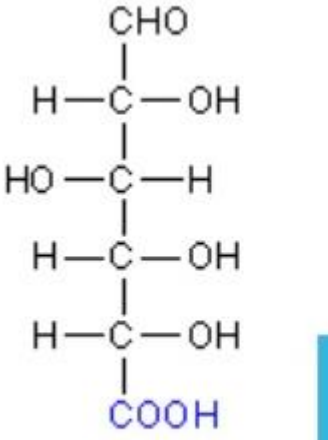
- composed of alternate unit of D-gluconic acidN-acetyl D-glucosamine.



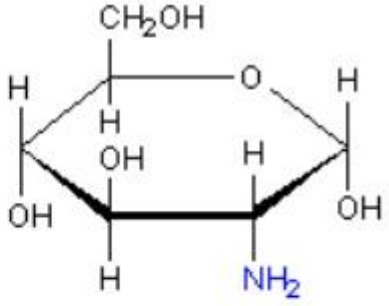
Heparin

- **Heparin is an anticoagulant(prevant blood clothing)** produced by basophils and mast cells **that occur in blood, lung, liver, kidney, spleen etc.**
- **Heparin** is composed of alternate unit of N-sulfo D-glucosamine 6-sulfate and glu 2-sulfate.



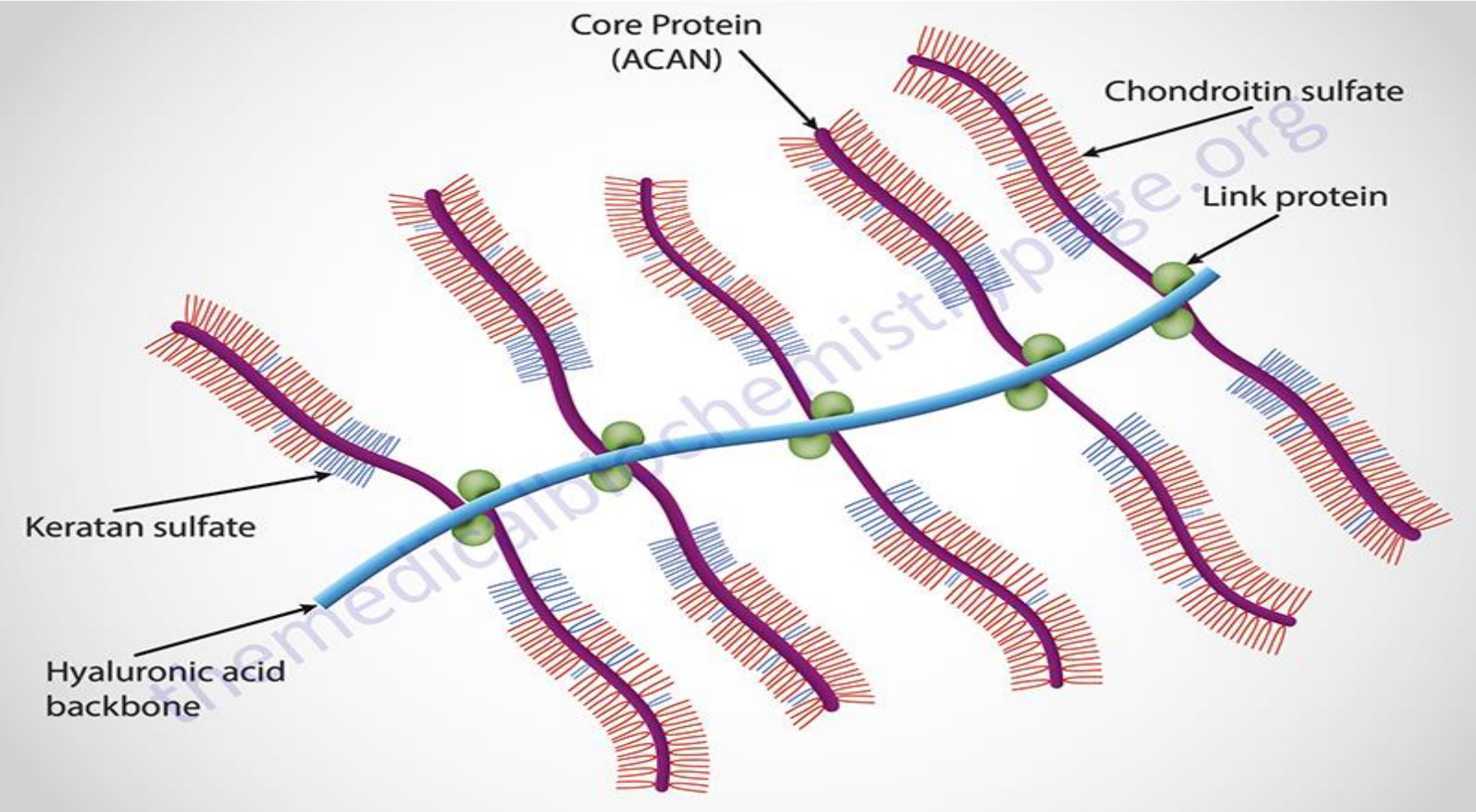


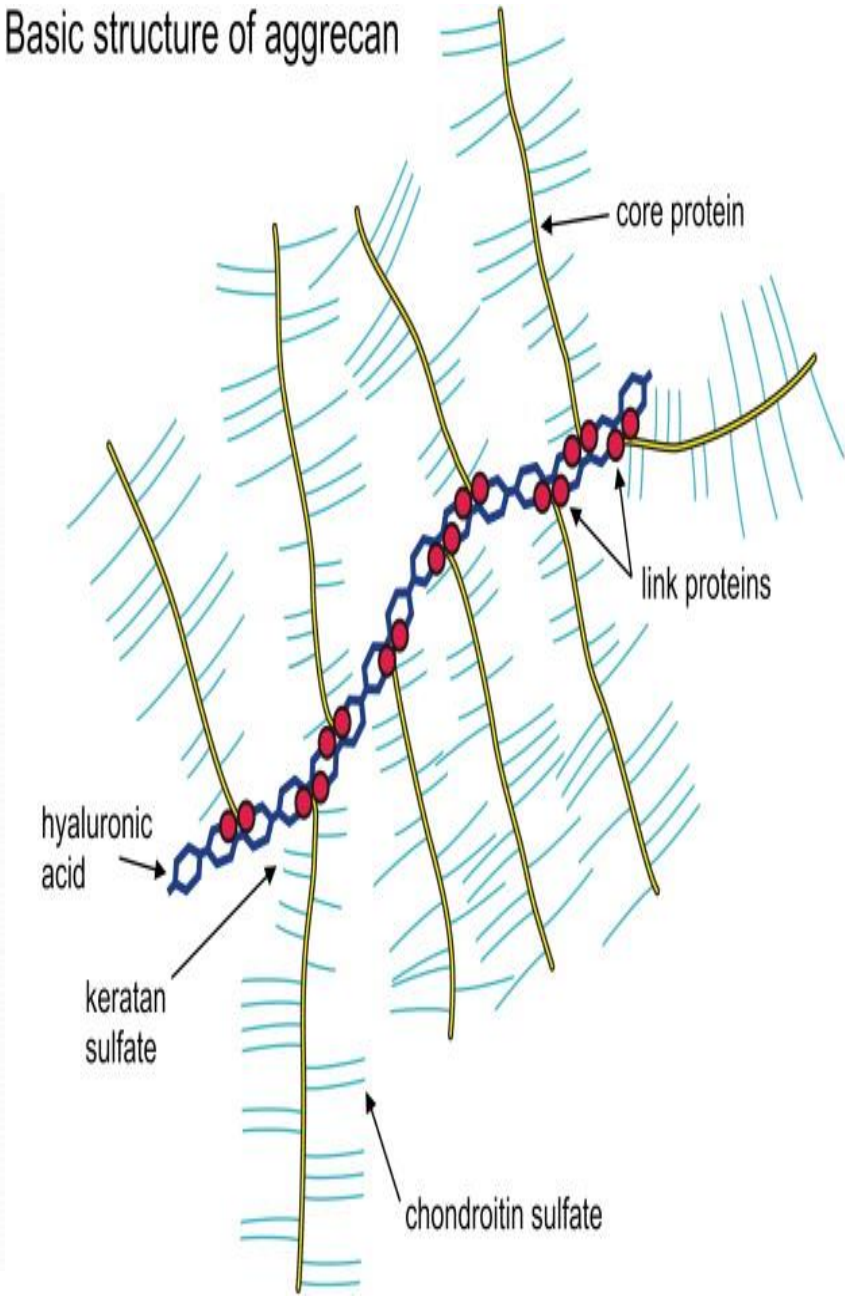
D-glucuronic acid



α-D-glucosamine

Extracellular matrix of connective tissue



To sum up:

- Glycosaminoglycans are extracellular heteropolysaccharides in which one of the two monosaccharide units is a uronic acid and the other an *N-acetylated amino sugar. Sulfate esters*on some of the hydroxyl groups give these polymers a high density of negative charge, forcing them to assume extended conformations. These polymers (hyaluronate, chondroitin sulfate, dermatan sulfate, keratan sulfate, and heparin) provide viscosity, adhesiveness, and tensile strength to the extracellular matrix.