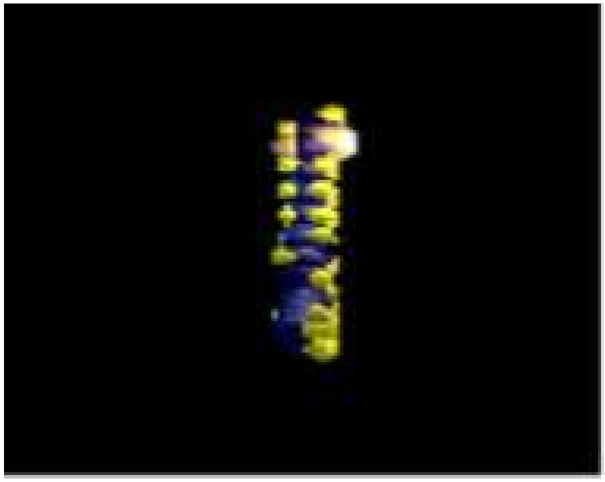
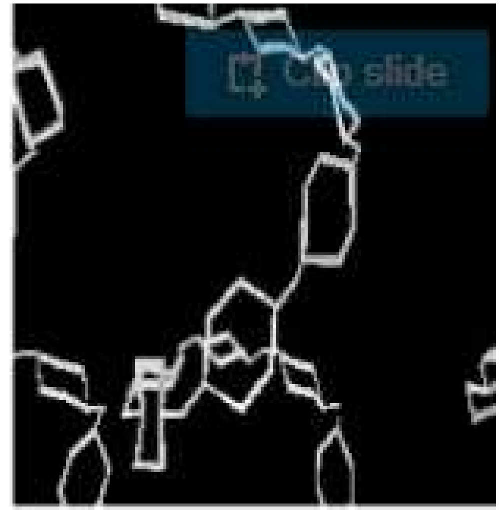
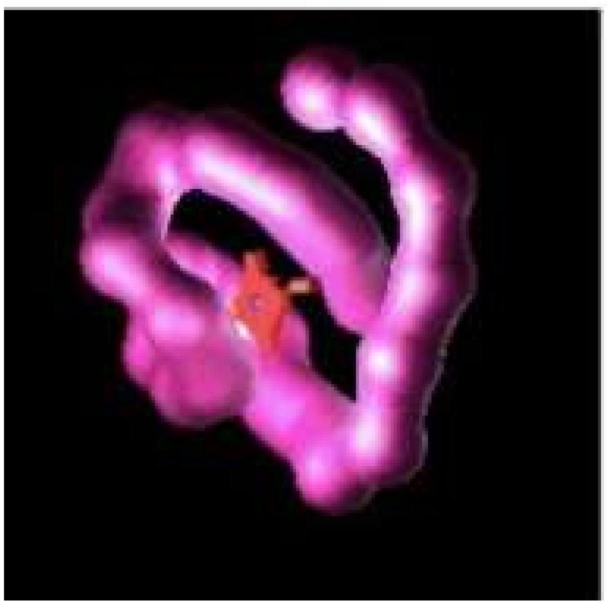
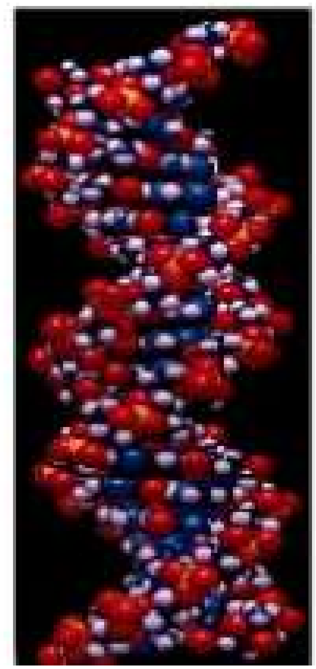




Biomolecules

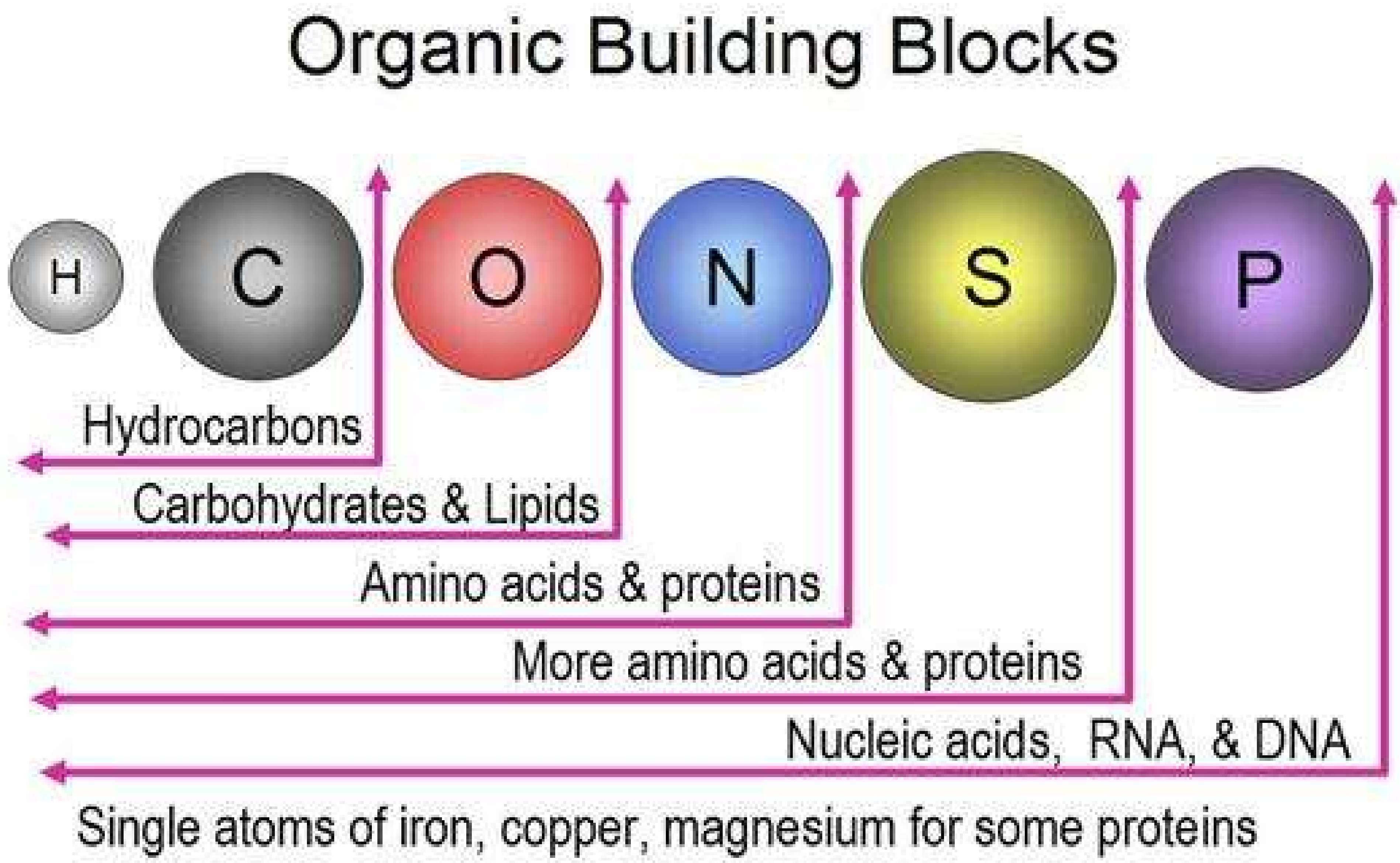




What molecules keep us alive, and how do they do so?

- All living organisms require several compounds to continue to live.
- We call these compounds **biomolecules.** All of these biomolecules are **organic**, which means that they contain carbon.
  - Carbon has four valence electrons, which means this element forms strong covalent bonds with many other elements.

Biomolecules of life consists of six basic elements



Biomolecules

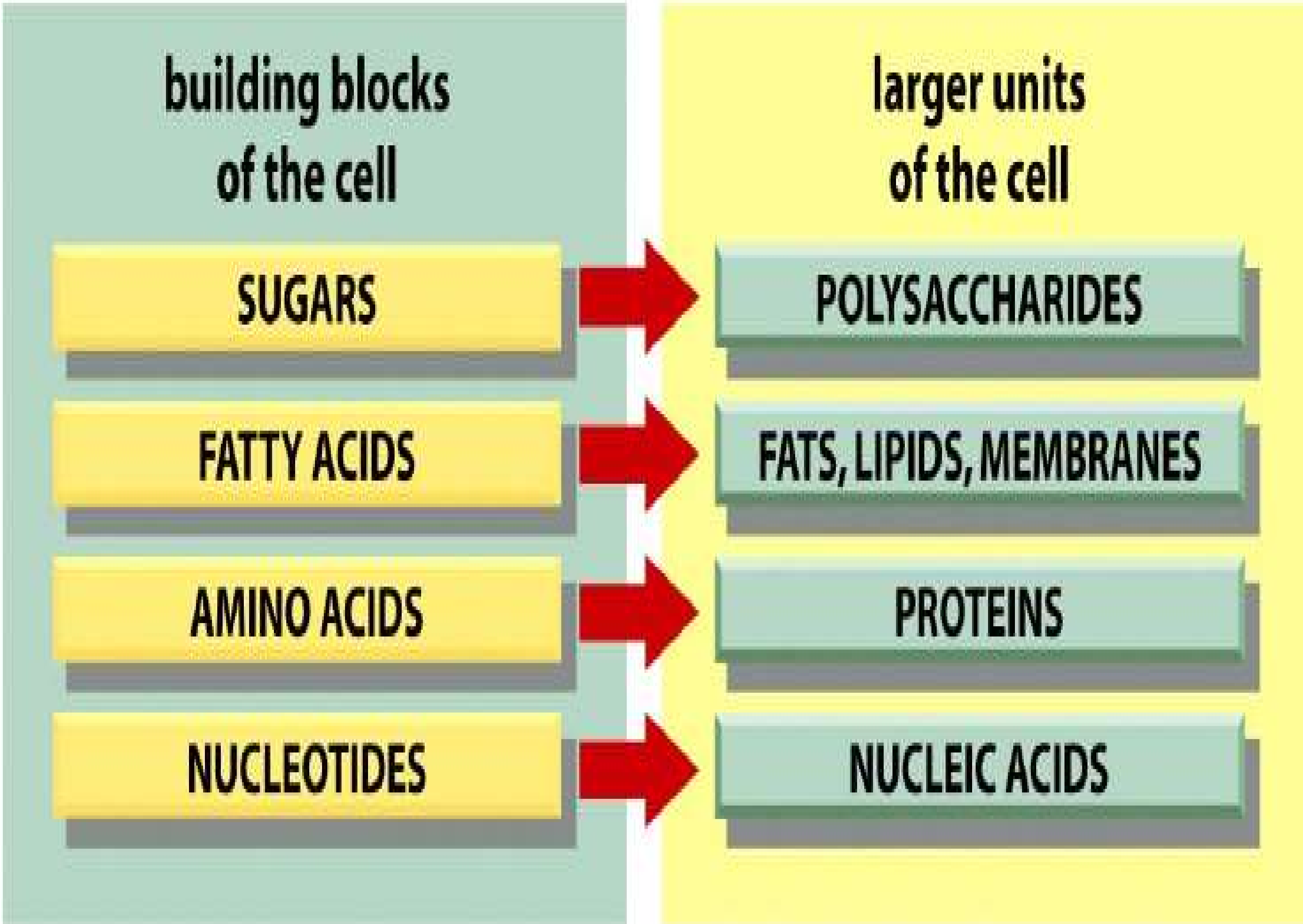
Macromolecules (Biomolecules)

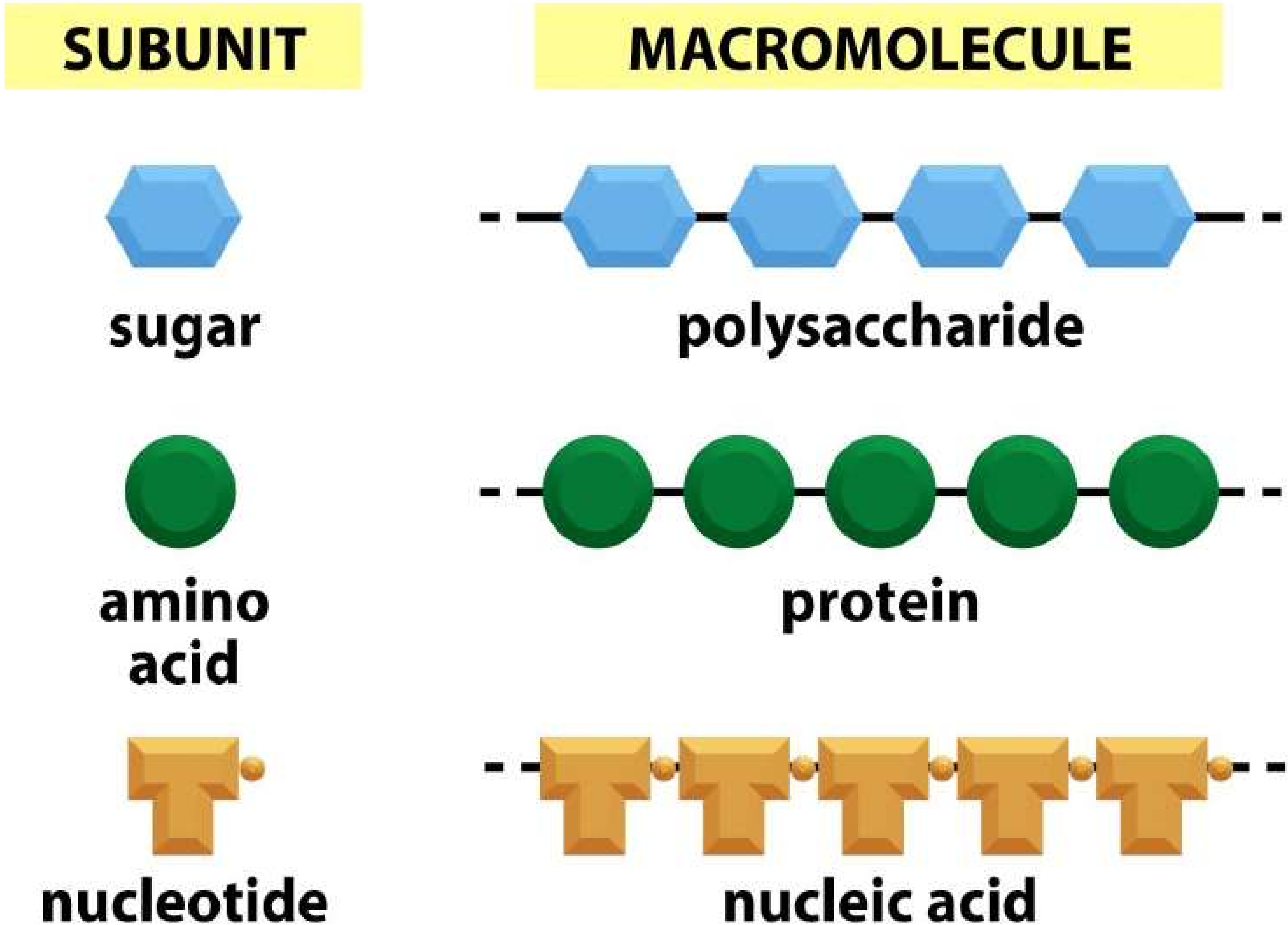
made through POLYMERIZATION

MONOMER – building block

POLYMER – large compound made of monomers

1. Carbohydrates
2. Lipids
3. Proteins
4. Nucleic Acids


building blocks of the cell
larger units of the cell
SUGARS
POLYSACCHARIDES
FATTY ACIDS
FATS, LIPIDS, MEMBRANES
AMINO ACIDS
PROTEINS
NUCLEOTIDES
NUCLEIC ACIDS


SUBUNIT
MACROMOLECULE
sugar
polysaccharide
amino acid
protein
nucleotide
nucleic acid

Function:

- Carbohydrates
  - Energy, support and recognition
- Proteins
  - Enzymes, structure, recognition, transport pigments, signals, mov't
- Lipids
  - Cell membrane structure energy storage, signals cellular metabolism (VitK..)
- Nucleic Acids
  - Hereditary and protein information, energy, signals

The Nature of Carbohydrates

Carbohydrates are compounds of great importance in both the biological and commercial world

They are used as a source of energy in all organisms and as structural materials in membranes, cell walls and the exoskeletons of many arthropods

All carbohydrates contain the elements carbon (C), hydrogen (H) and oxygen (O) with the hydrogen and oxygen being present in a 2 : 1 ratio

THE GENERAL FORMULA OF A CARBOHYDRATE IS:

$$Cx(H_2O)y$$

EXAMPLES

The formula for glucose is $C_6H_{12}O_6$

The formula for sucrose is $C_{12}H_{22}O_{11}$

Definition

Carbohydrates are polyhydroxyaldehydes or polyhydroxyketones or compounds that give polyhydroxyaldehydes or polyhydroxyketones on hydrolysis

OR

Carbohydrates are aldehyde or ketone derivatives of polyhydric alcohols

BIOLOGICAL IMPORTANCE OF CARBOHYDRATES

1. Energy source
2. Storage source
3. Precursors
4. Structural component
5. Drugs component

- Most abundant dietary source of energy. Brain cells and RBCs are almost wholly dependent on carbohydrates as the energy source.
- Also serve as storage form of energy –Glycogen.
- Carbohydrates are precursors for many organic compounds (fats, amino acids).
- Participate in the structure of cell membrane & cellular functions (cell growth, adhesion and fertilization).
- Certain carbohydrate derivatives are used as drugs, like cardiac glycosides / antibiotics.
- DM (diabetes mellitus)

Classification of Carbohydrates

Carbohydrates

Monosaccharides
1 sugar unit

e.g.Glucose,
fructose etc

Disaccharides
2 sugar units

e.g.Sucrose

Oligosaccharides
3-10 units

e.g. Maltotriose

Polysaccharides
>10

Homoglycans

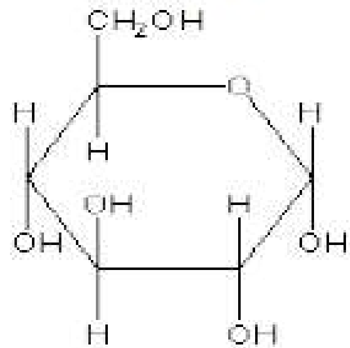
e.g. starch,
glycogen

Heteroglycans

e.g. GAGs or
glycosaminoglycans

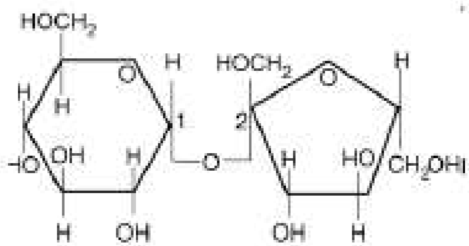
3 types of sugars:

- **Monosaccharides-**
  simple sugars (1 sugar carbohydrate)
  - Glucose & Fructose



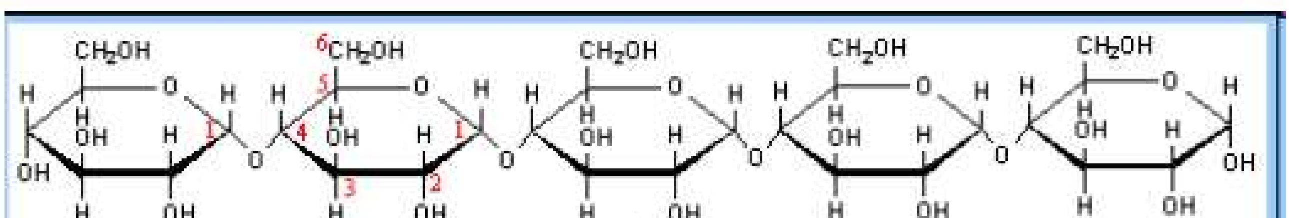
Glucose

- **Disaccharides**
  - sucrose & Lactose (2 sugars linked together)



Sucrose

- **Polysaccharides**
  - many simple sugars linked together



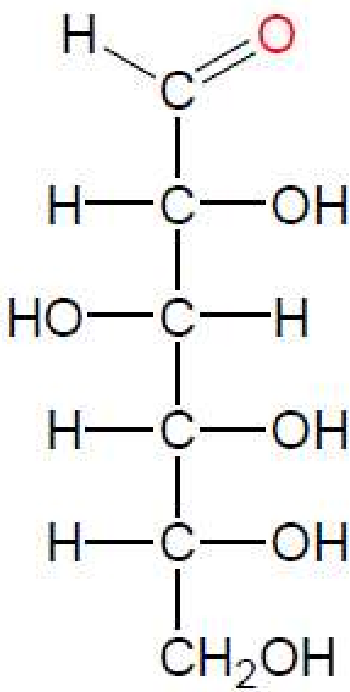
amylose

Monosaccharides

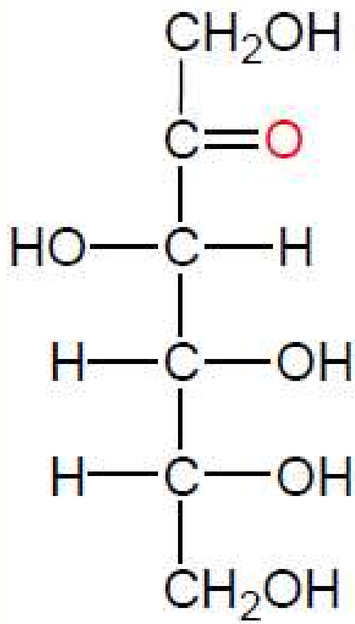
- What are monosaccharides?
- About aldoses and Ketoses
- Isomerism in monosaccharides: Enantiomers, epimers, Anomers
- Cyclization of monosaccharides
- Physical properties of monosaccharides

Monosaccharides:

They are the simplest carbohydrates that cannot be broken into smaller units on hydrolysis.



D-glucose



D-fructose

- Aldoses (e.g., glucose) have an aldehyde group at one end
- Ketoses (e.g., fructose) have a keto group, usually at C2.

Aldoses	Monosaccharides having an aldehyde group
Ketoses	Monosaccharides having a keto group

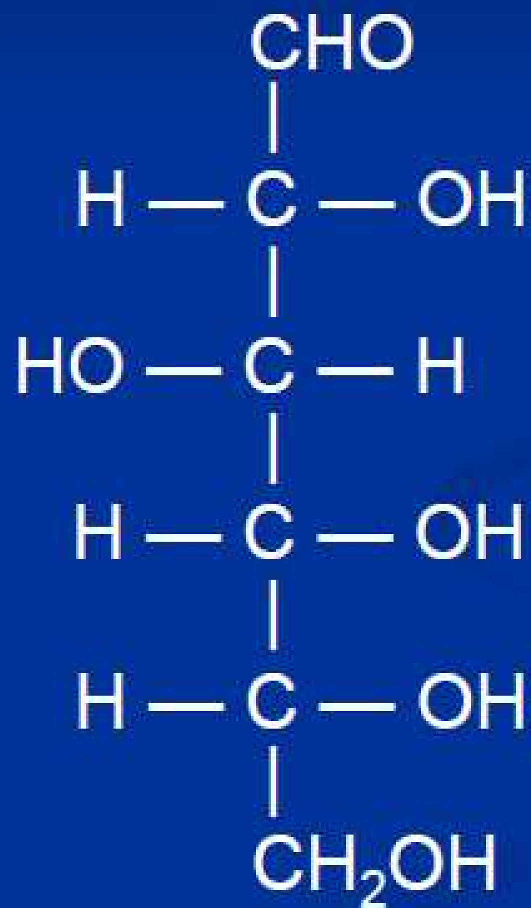
Monosaccharide further classified on the basis of functional group and number of carbon atoms present in their structure

On the basis of no. of carbon atom

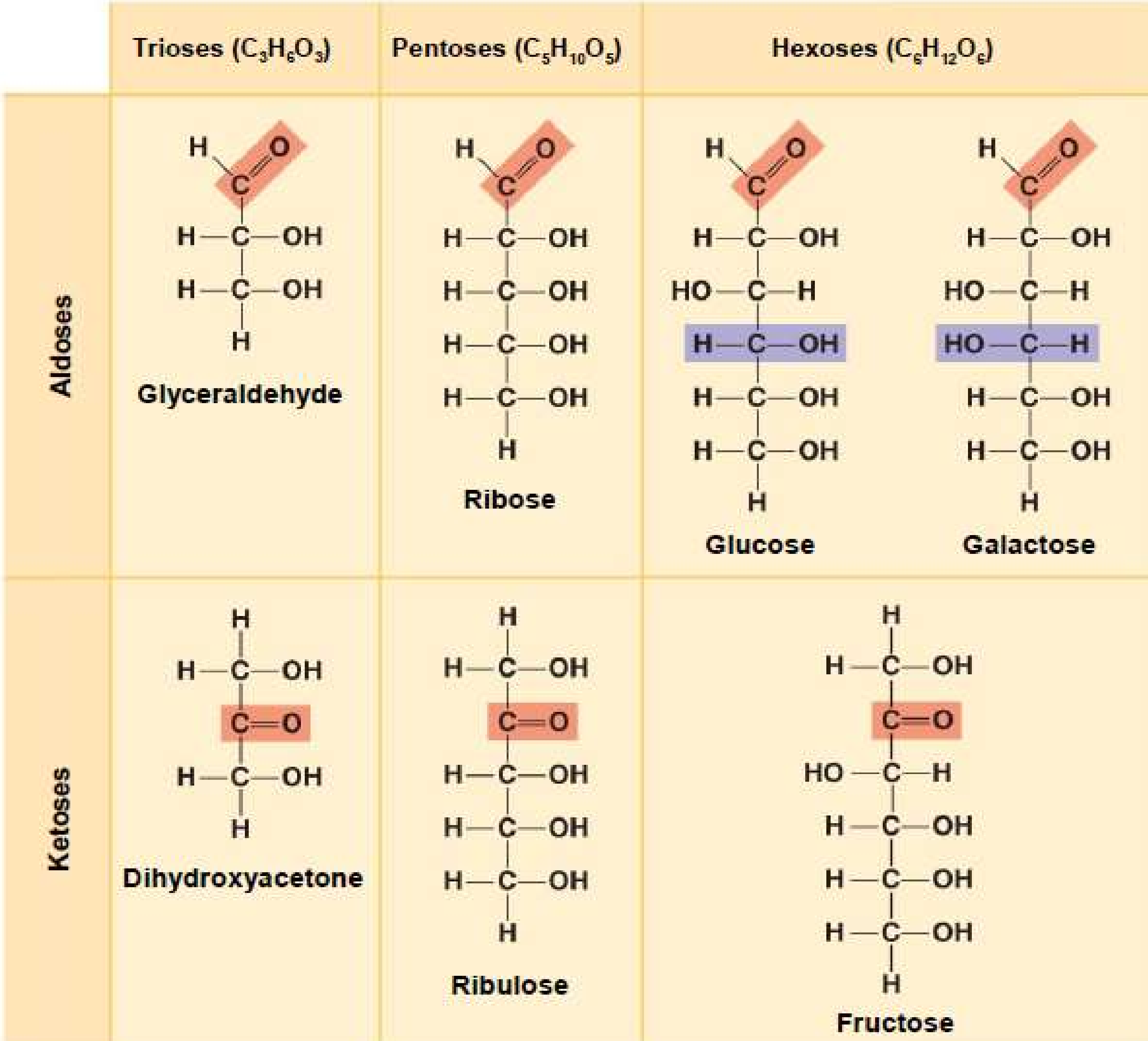
On the basis of functional group

No. of carbon atom	Generic name	ALDOSE	KETOSE
3	Trioses	Aldotriose e.g. glyceraldehyde	Ketotriose e.g. Dihydroxyacetone
4	Tetroses	Aldotetrose e.g. Erythrose	Ketotetrose e.g. Erythrulose
5	Pentoses	Aldopentoses e.g Arabinose, Xylose, Ribose	Ketopentoses e.g. Xylulose, Ribulose
6	Hexoses	Aldohexose e.g. Glucose, Galactose, Mannose	Ketohexose e.g. Fructose
7	Heptoses	Aldoheptose: Glucoheptose	Ketoheptose e.g Sedoheptulose

D-Glucose is the most important carbohydrate in human beings



D-Glucose


Trioses ($C_3H_6O_3$)
Pentoses ($C_5H_{10}O_5$)
Hexoses ($C_6H_{12}O_6$)
Aldoses
Ketoses
Glyceraldehyde
Ribose
Glucose
Galactose
Dihydroxyacetone
Ribulose
Fructose

Isomerism in monosaccharides

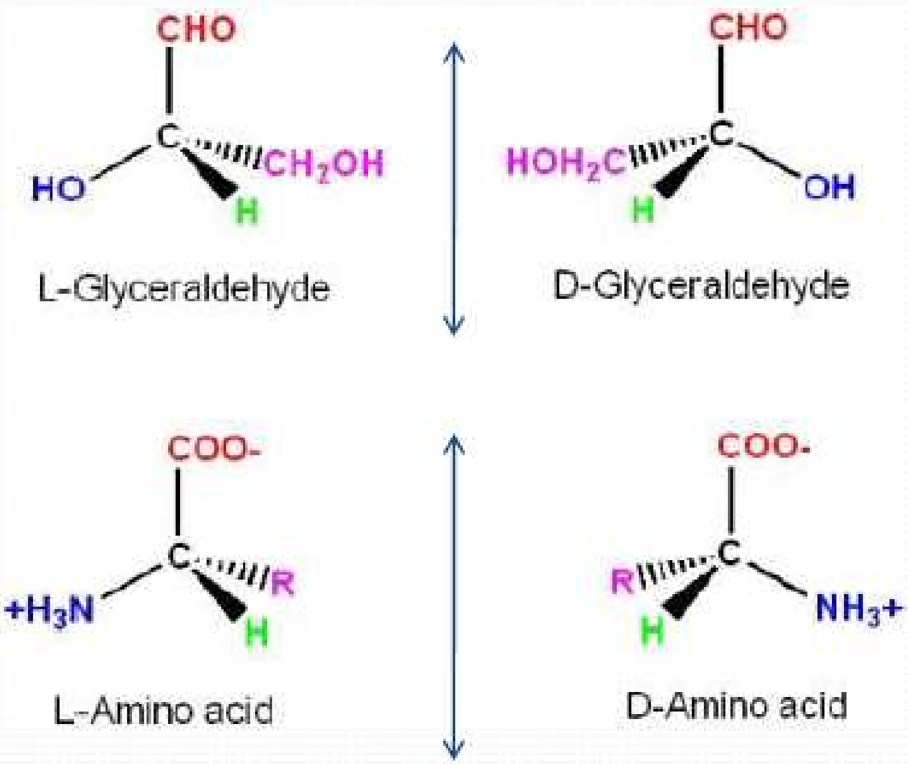
Many biological important molecules such as sugars exist as **stereoisomers**. Our body can make a difference.

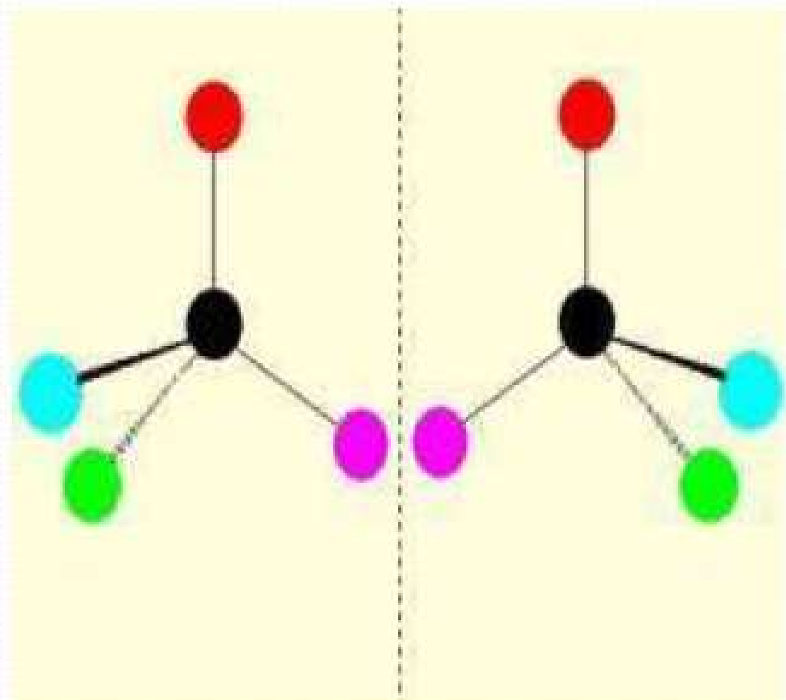
Stereoisomers

- **The same order and type of bonds.**
- **Different spatial arrangements.**
- **Different properties**

Optical activity/ Optical Isomerism

Optical activity is a characteristic feature of compounds with asymmetric carbon atom. Carbon atom can have four different groups then the carbon atom will possess asymmetry. A carbon atom is said to be asymmetric when its mirror images are non-super imposable on each other.



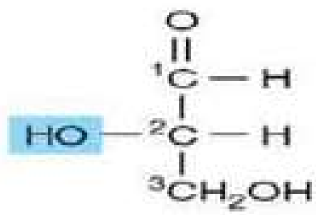


D- and L- isomers

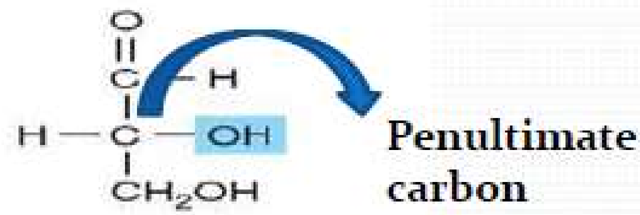
D and L Isomers are mirror images of each other.

The *spatial orientation of H & OH groups on the C- atom (C_5 for glucose), adjacent to the terminal primary alcohol carbon determines whether the sugar is D or L Isomer.*

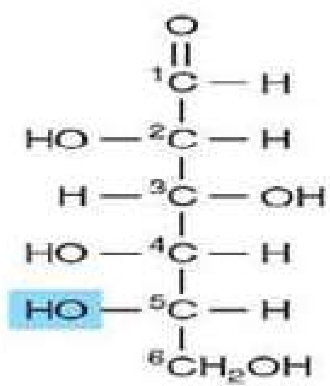
If the OH group is on the right side, the sugar is of D- Isomer. If the OH group is on the Left side, the sugar is of L- Isomer. Mammalian tissues have D- sugars.



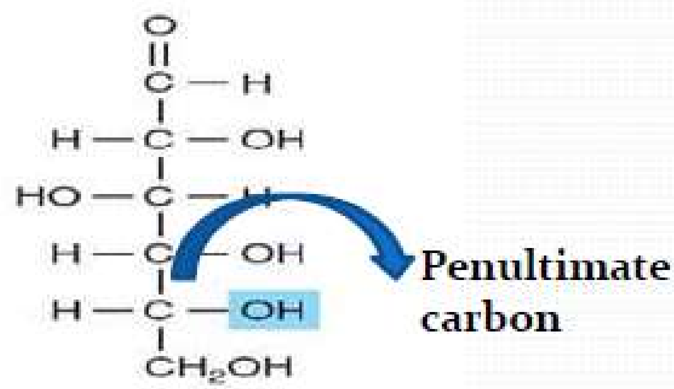
L-Glycerose
(L-glyceraldehyde)



D-Glycerose
(D-glyceraldehyde)

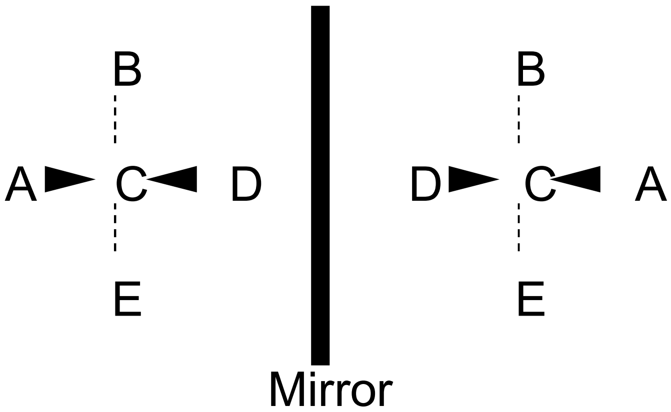


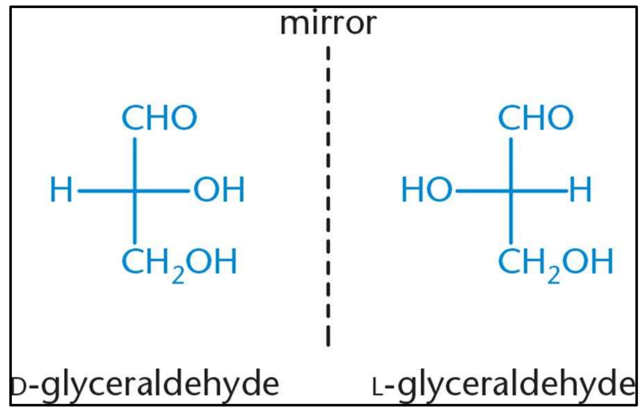
L-Glucose

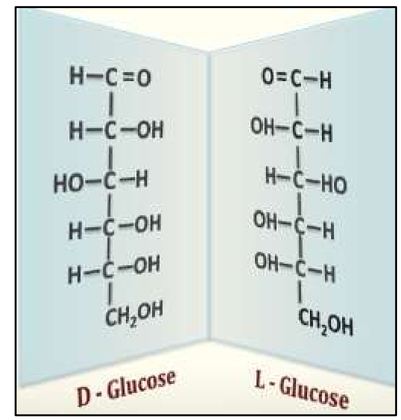


D-Glucose

Enantiomers- The mirror images non superimposable on each other







Diastereomers

- **Not mirror images (enantiomers) and non superimposable**

- **Dextrorotatory (D)** which is labelled (+) rotate a plane of polarized light in a clockwise direction.

- **Levorotatory** (L) which is labelled (-) rotate the light in a counterclockwise direction.

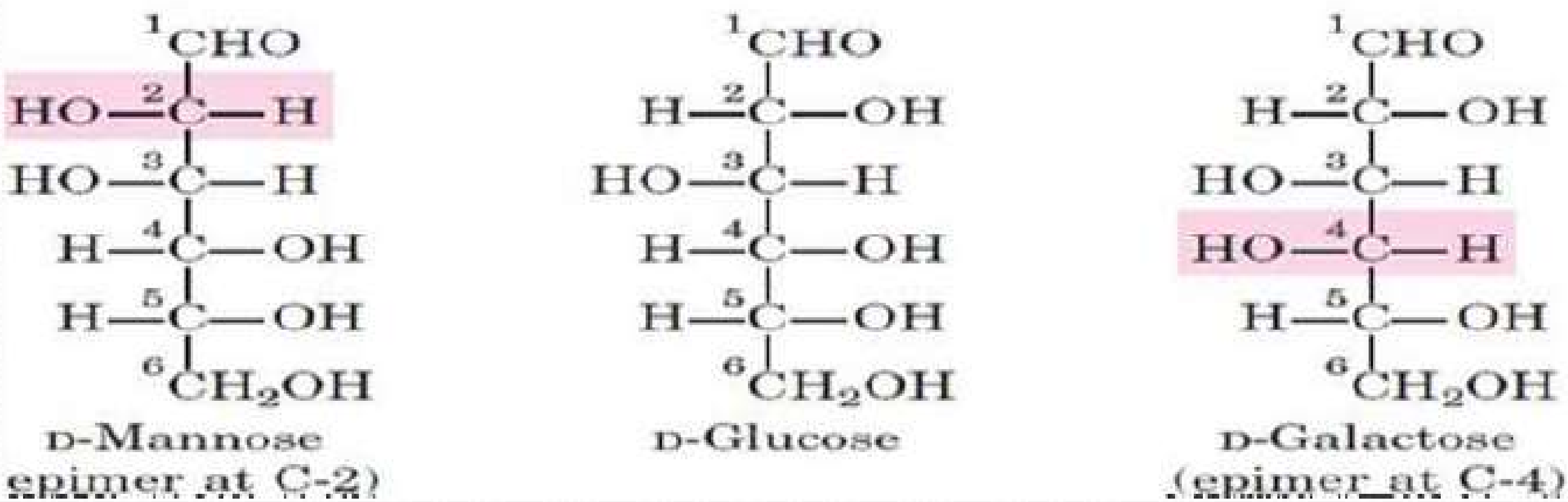
Epimers

If two monosaccharides differ from each other in their configuration around a single specific carbon atom, they are referred as epimers to each other.

Glucose & galactose are C4-epimers.

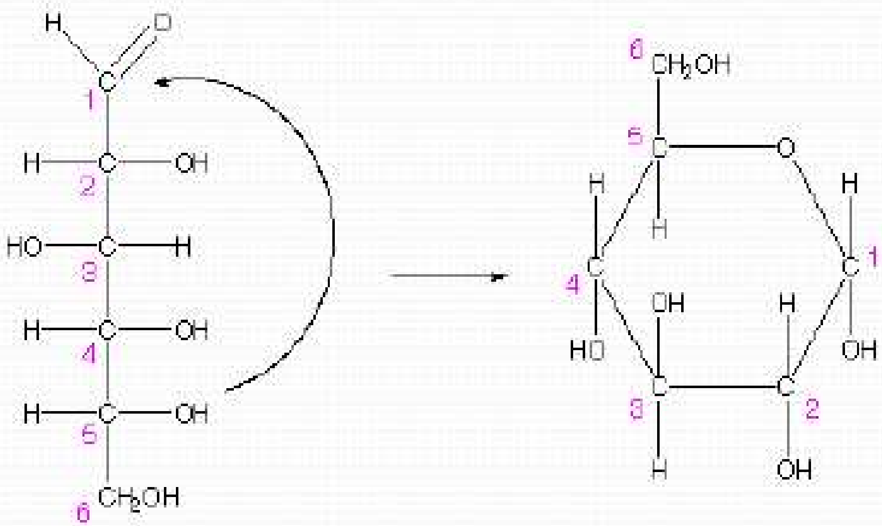
Glucose & mannose are C2-epimers

Inter-conversion of epimers is known as epimerization, epimerase catalyzes this reaction.

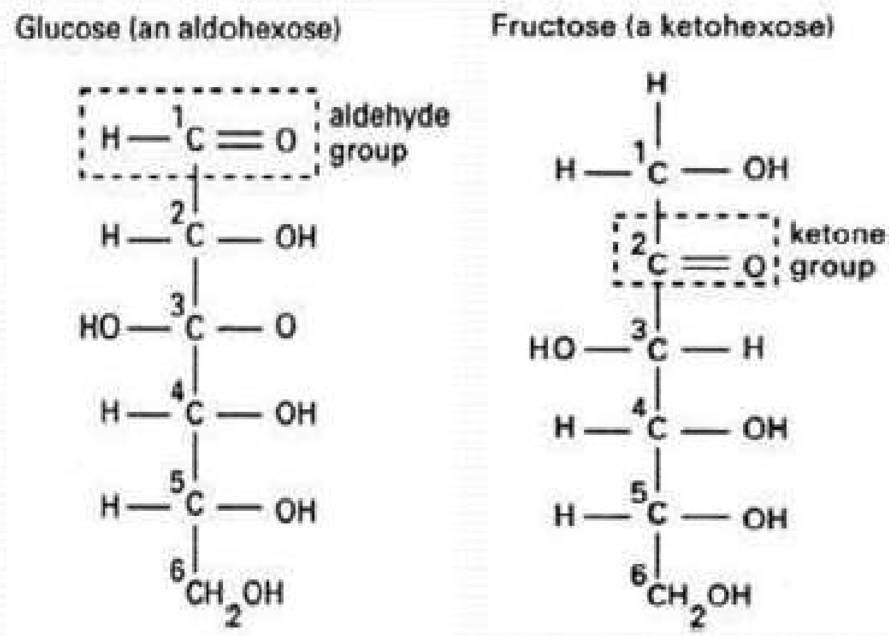


Cyclization

- Less then 1% of CHO exist in an open chain form.
- Predominantly found in **ring form**.
- involving reaction of C-5 OH group with the C-1 aldehyde group or C-2 of keto group.
- Six membered ring structures are called **Pyranoses .**
- Five membered ring structures are called **Furanoses .**



Straight chain form



Anomerism – Mutarotation

Anomers have same composition but differ in the orientation of groups around anomeric carbon atom.

Anomeric carbon is a hemiacetal or carbonyl carbon atom, e.g. 1st carbon atom in glucose is anomeric carbon atom.
Carbonyl carbon atom becomes asymmetric because of ring structures of monosaccharides in solution thus anomers are encountered in cyclic structures of monosaccaharides.

The alpha & beta cyclic forms of D-glucose are known as Anomers.
They differ from each other in the configuration only around C1 known as anomeric carbon.

In case of alpha anomer, the OH group held by anomeric carbon is on the opposite side of the group CH_2OH of sugar ring

Anomers are expressed as α and β forms.

In α form "OH" group is below the plane (OH group is oriented away from the oxygen atom)

In β form "OH" group is above the plane (OH group is oriented towards the oxygen atom)

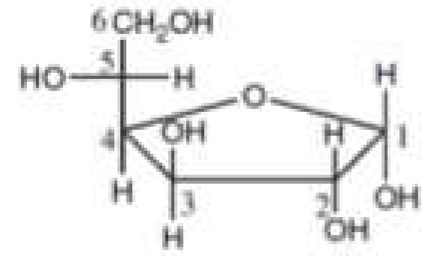
Mutarotation:

When D-glucose is crystallized at room temperature and a fresh solution is prepared, its specific rotation of polarized light is 112°; but after 12- 18 hrs it changes to +52.5 °

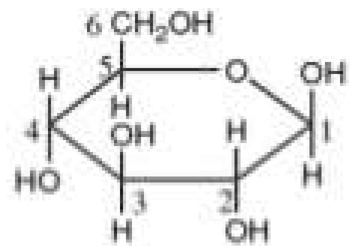
Mutarotation is defined as the change in the specific optical rotation representing the interconversion of α and β forms of D-glucose to an equilibrium mixture.

Haworth Projection (Cyclic Form)

W. N. Haworth (Nobel Prize, 1937)



42, α-D-glucofuranose



41, β-D-glucopyranose

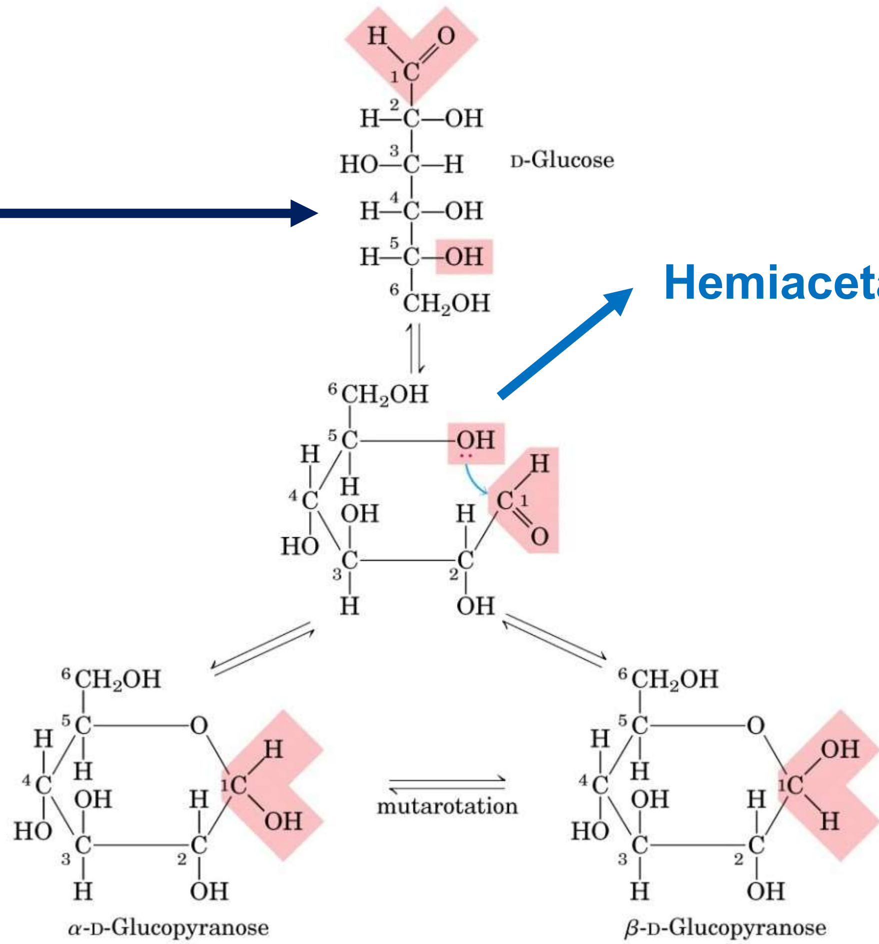
- Cyclization via intramolecular hemiacetal (hemiketal) formation
- C-1 becomes chiral upon cyclization - anomeric carbon
- Anomeric C contains -OH group which may be **α** or **β** (mutarotation **α** ⇔ **β**)

Glucose

- **C-1 and C-5-intramolecular hemiacetal formation give rise to a pyranose ring**

Open chain / Fischer projection

Hemiacetal formation



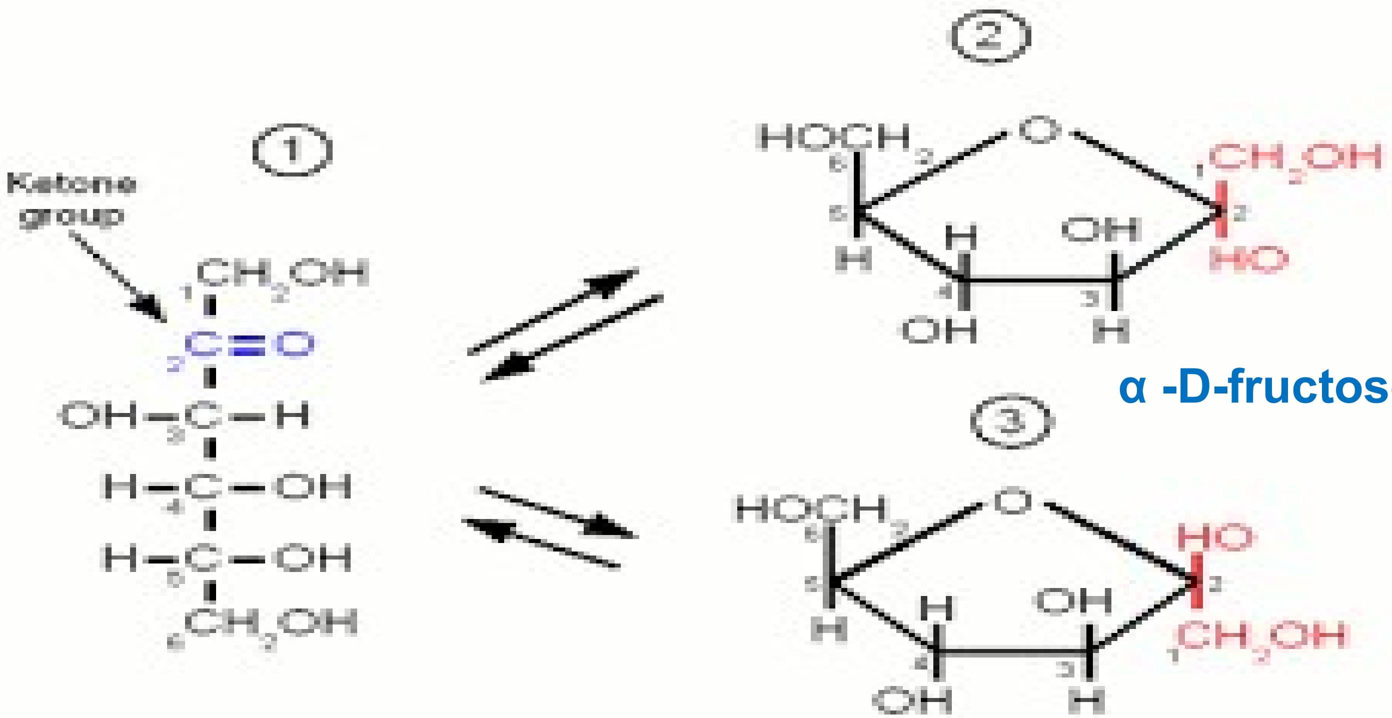
Ring form/ Haworth projection

C-1 is called anomeric carbon

Pyranose ring

Fructose

- **C-2 and C-5-intramolecular hemiketal formation in fructose forms furanose ring**

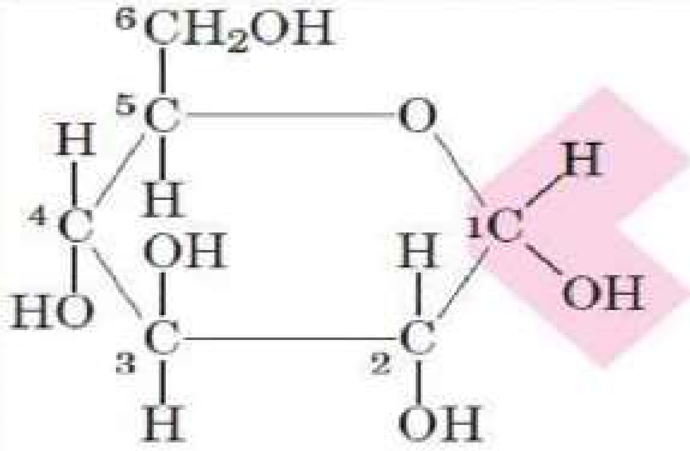


α -D-fructose

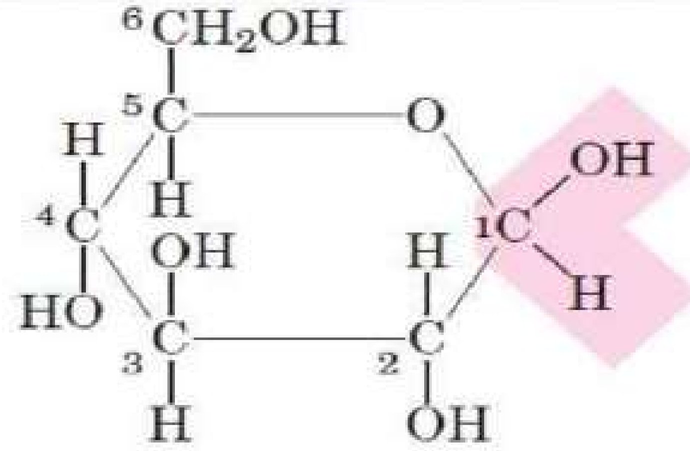
C-2 is called anomeric carbon

β -D-fructose

Furanose ring

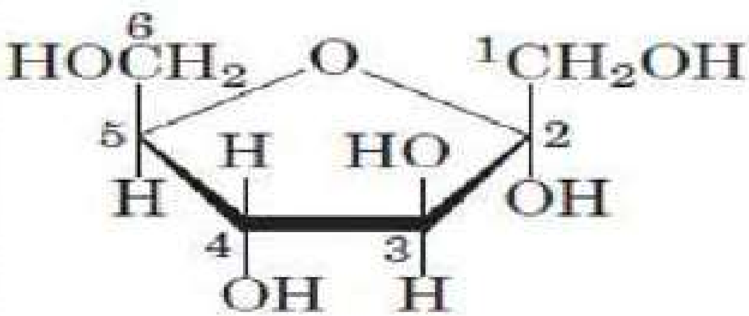


α-D-Glucopyranose

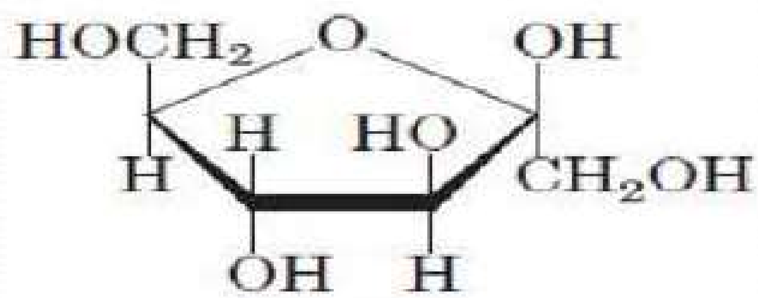


β-D-Glucopyranose

Glucose and Fructose has two anomers α and β



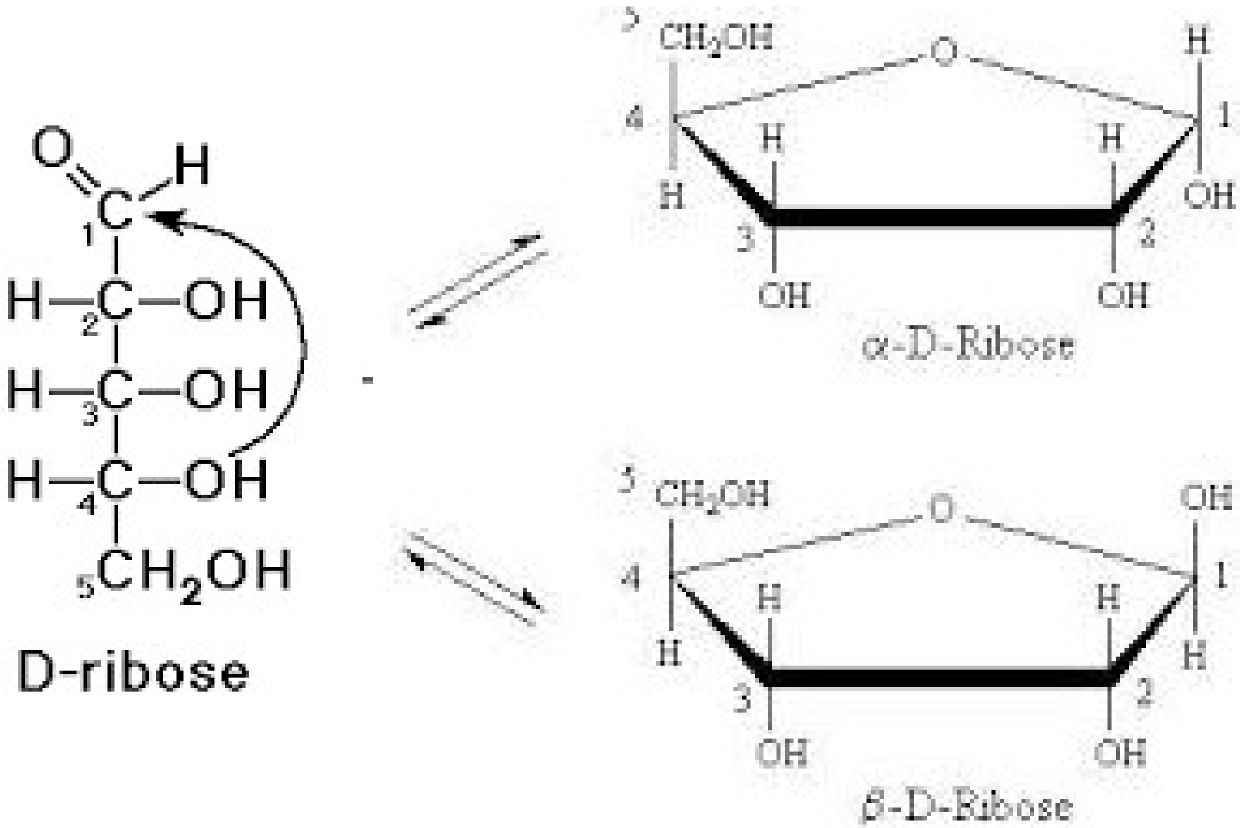
α-D-Fructofuranose



β-D-Fructofuranose

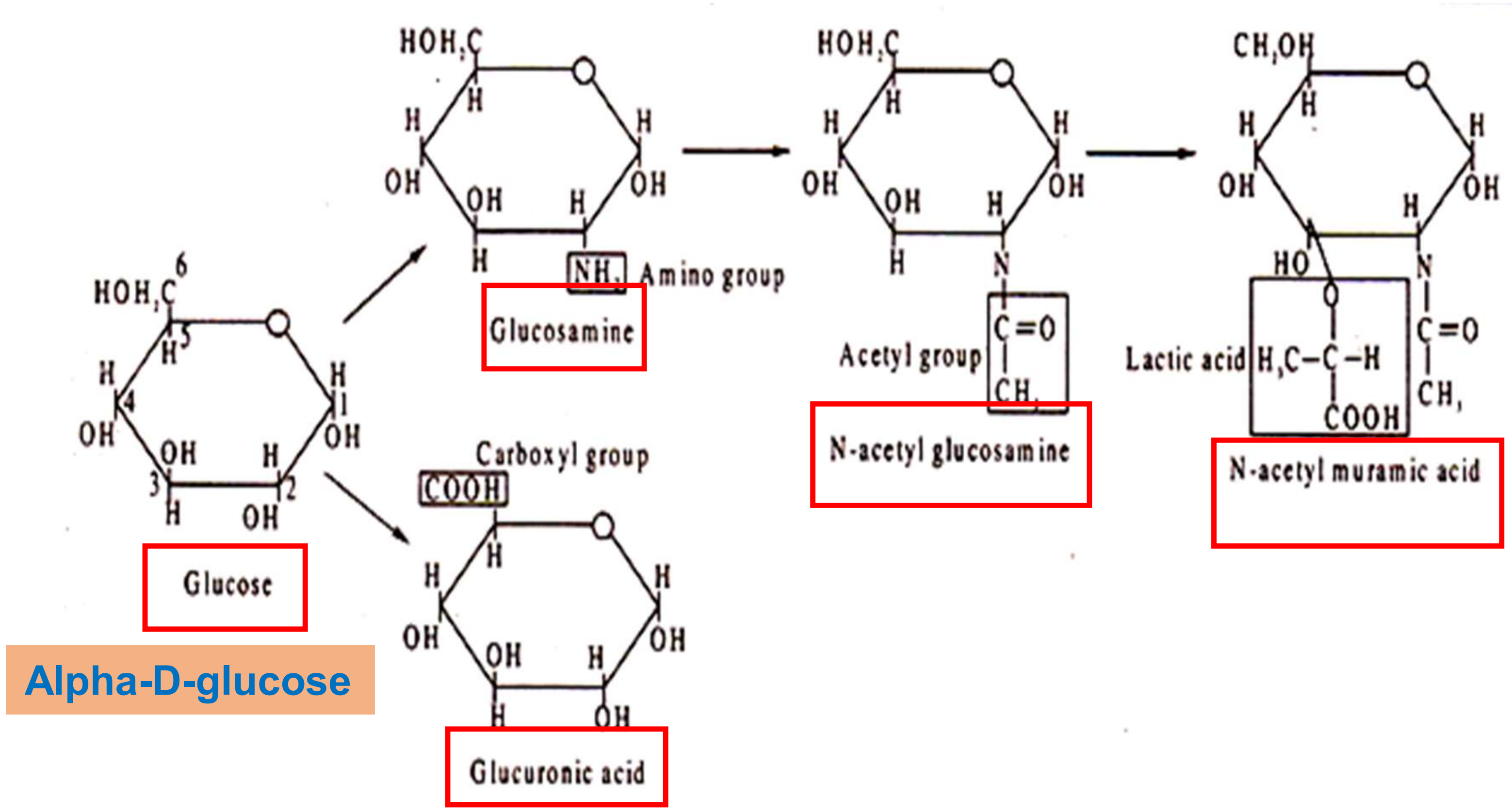
Ribose

- **C-1 and C-4-hemiacetal formation**



furanose ring

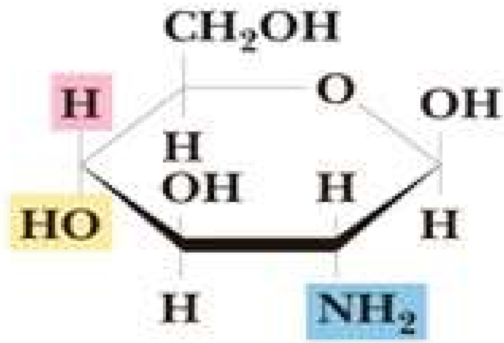
Important glucose derivatives in biological system



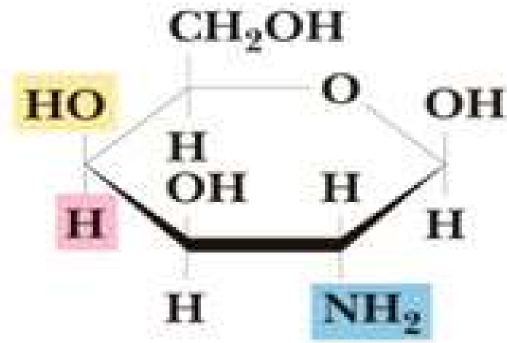
All derivatives are in alpha confguration

Other monosaccharide derivatives

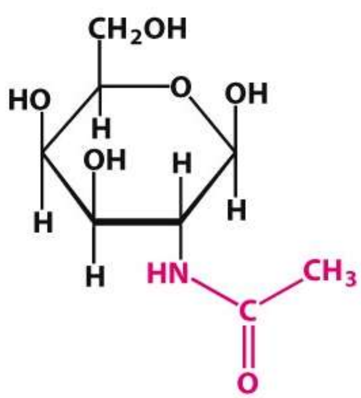
- **Amino sugars found in animal cells**



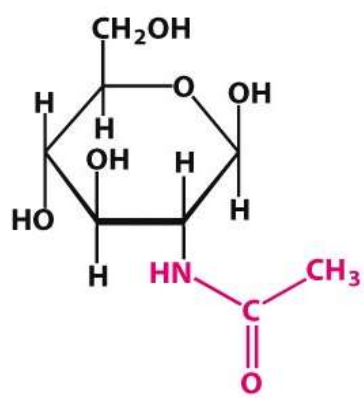
β-D-Glucosamine



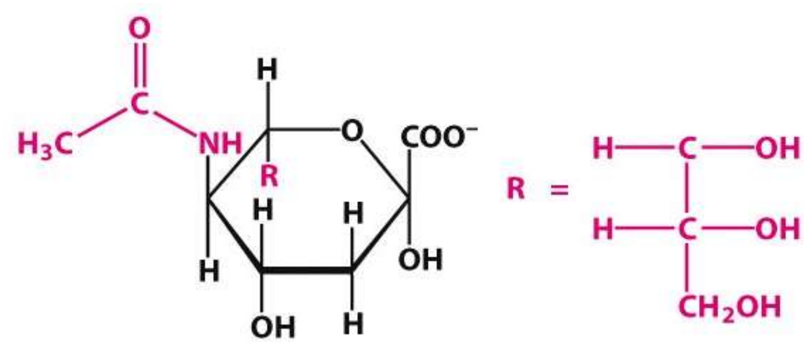
β-D-Galactosamine



β-D-Acetylgalactosamine
(GalNAc)



β-D-Acetylglucosamine
(GlcNAc)



Sialic acid (Sia)
(*N*-Acetylneuraminate)

PROPERTIES OF MONOSACCHARIDES

1. **Physical properties:**

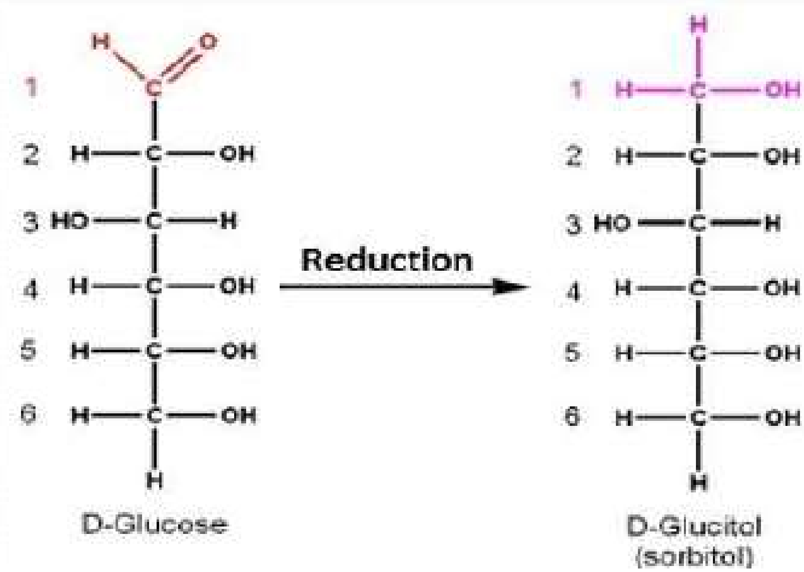
   Monosaccharides are colourless, crystalline compounds, readily soluble in water and sweet in taste. Their solutions are optically active and exhibit mutarotation.

2. **Chemical properties:**

   a) **Reduction:** When treated with reducing agents such as sodium amalgam, hydrogen can reduce sugars. Aldose yields corresponding alcohol. Ketoses form two alcohols because of appearance of new asymmetric carbon in this process.

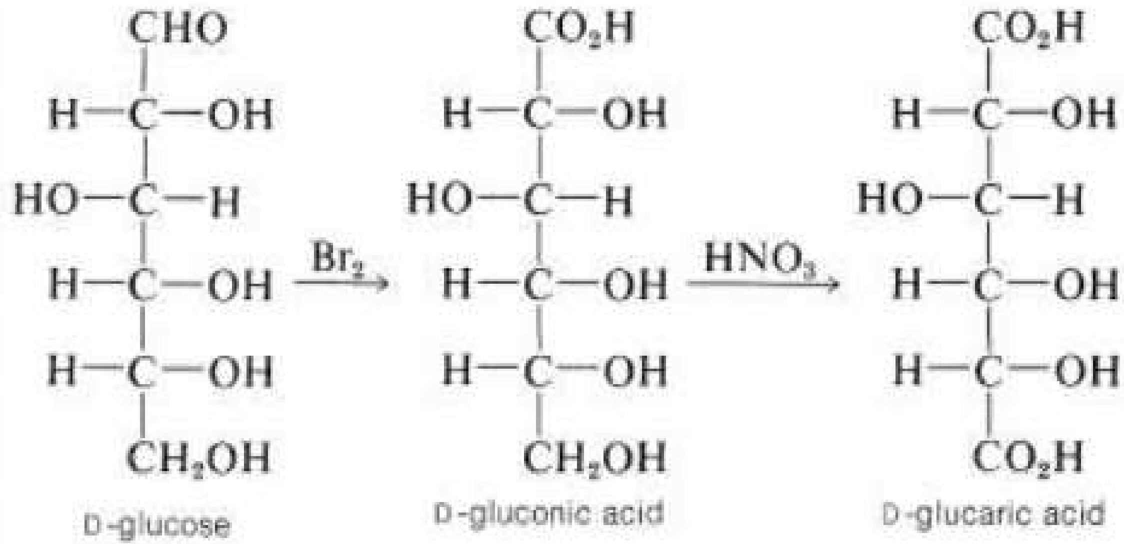
   D-Glucose→ D-Sorbitol

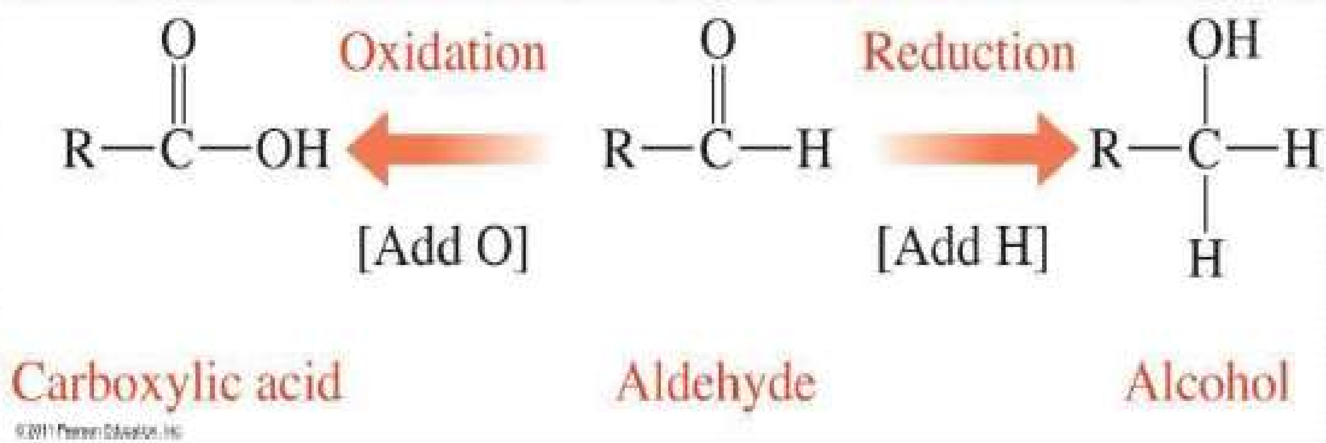
   D-Fructose →D-Sorbitol+D-Mannitol



b) Oxidation: upon oxidation aldose sugars like glucose yields carboxylic acid, *the aldehyde group is oxidized to carboxyl group to produce respective acids.*

Glucose → Gluconic acid
Mannose → Mannonic acid
Galactose → Galactonic acid

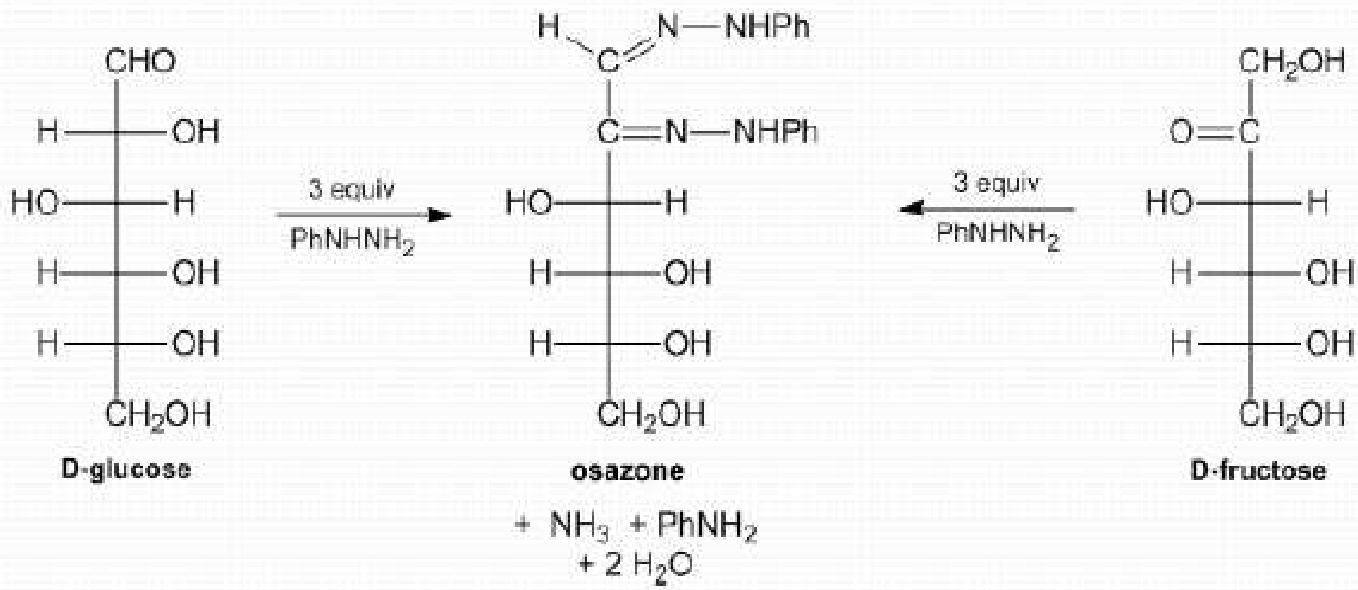




c) Formation of esters: Hydroxyl groups of sugars can be esterified to form acetates, propionates, benzoates, etc. Sugar phosphates are of great biological importance. Metabolism of sugars inside the body starts with phosphorylation.

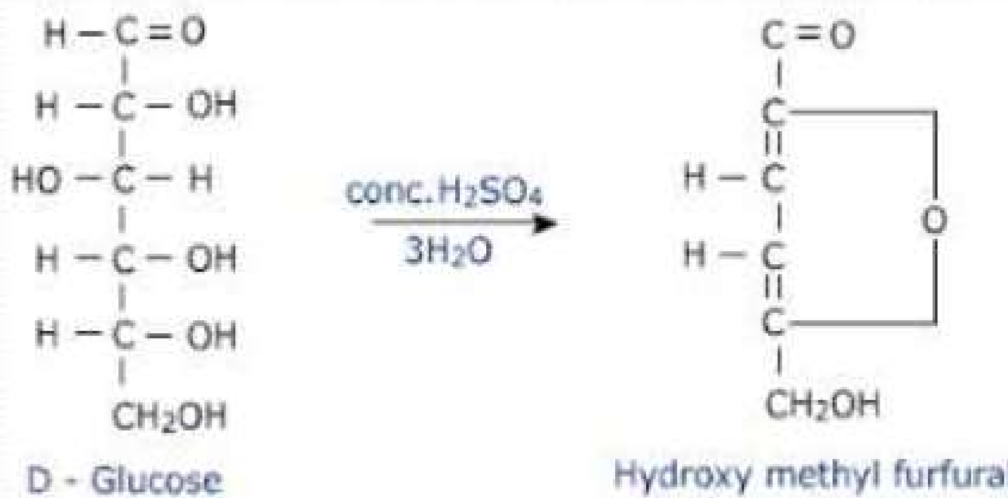
e.g Glucose 6-Po_4

d) Formation of osazone: this test is given by reducing sugar like, glucose, fructose, lactose and maltose. In this test phenyl hydrazine is reduced to phenyl hydrazone by sugar solution. Phenyl hydrazone when heated with more amount of phenyl hydrazine forms yellow crystals of osazone.



e) Furfural formation/Dehydration: Monosaccharides when treated with concentrated H_2SO_4 undergoes dehydration with the removal of 3 molecules of water. Hexoses give hydroxymethyl furfural and pentoses give furfural. Furfurals condense with phenolic compounds to give various colors.

E.g. Molisch's test: General test for carbohydrates (H_2SO_4 and α-naphthol). Rapid Furfural and Seliwanoff's test: Tests for presence of keto group



Some important Monosaccharides

Pentoses of Physiological importance

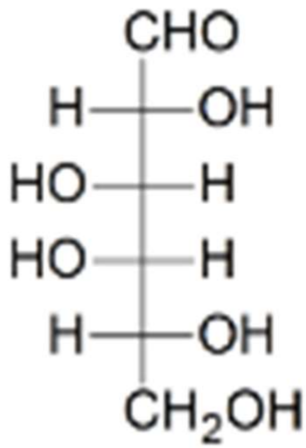
Sugar	Where Found	Biochemical Importance	Clinical Significance
D-Ribose	Nucleic acids.	Structural elements of nucleic acids and coenzymes, eg, ATP, NAD, NADP, flavoproteins. Ribose phosphates are intermediates in pentose phosphate pathway.	
D-Ribulose	Formed in metabolic processes.	Ribulose phosphate is an intermediate in pentose phosphate pathway.	
D-Arabinose	Gum arabic. Plum and cherry gums.	Constituent of glycoproteins.	
D-Xylose	Wood gums, proteoglycans, glycosaminoglycans.	Constituent of glycoproteins.	
D-Lyxose	Heart muscle.	A constituent of a lyxoflavin isolated from human heart muscle.	

Hexoses of Physiological Importance

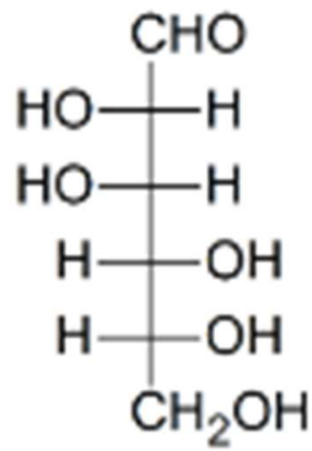
Sugar	Source	Importance	Clinical Significance
D-Glucose	Fruit juices. Hydrolysis of starch, cane sugar, maltose, and lactose.	The "sugar" of the body. The sugar carried by the blood, and the principal one used by the tissues.	Present in the urine (glycosuria) in diabetes mellitus owing to raised blood glucose (hyper-glycemia).
D-Fructose	Fruit juices. Honey. Hydrolysis of cane sugar and of inulin (from the Jerusalem artichoke).	Can be changed to glucose in the liver and so used in the body.	Hereditary fructose intolerance leads to fructose accumulation and hypoglycemia.
D-Galactose	Hydrolysis of lactose.	Can be changed to glucose in the liver and metabolized. Synthesized in the mammary gland to make the lactose of milk. A constituent of glycolipids and glycoproteins.	Failure to metabolize leads to galactosemia and cataract.
D-Mannose	Hydrolysis of plant mannans and gums.	A constituent of many glycoproteins.	

Sample questions

(01) Study the following Fischer projections to answer the questions below.



galactose



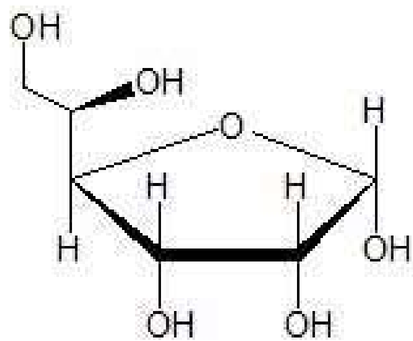
mannose

I. Is galactose a D-sugar or an L-sugar?
II. Is mannose a D-sugar or an L-sugar?
III. Choose either one, and sketch it as it would appear if it was an L-sugar.
IV. Are these two carbohydrates enantiomers? If not, in how many places do they differ?
V. What is the term to describe the relationship between galactose and mannose?

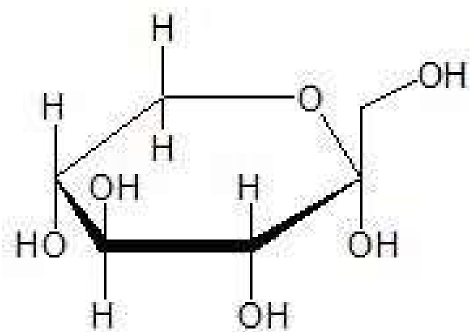
(02) Which carbon is considered the anomeric carbon? How do you distinguish between the alpha and beta types of anomers?

(03) Study these Haworth projections to answer the following for each of them.

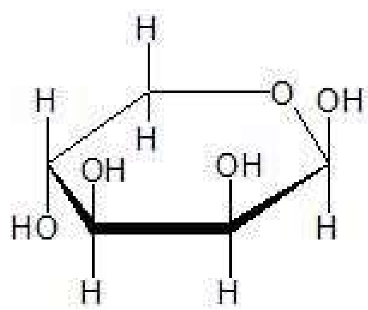
A)



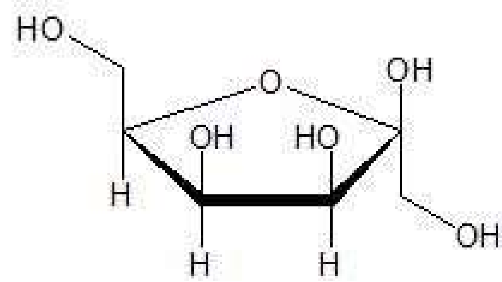
B)



C)



D)



i. Is it a furanose or a pyranose?
ii. Is it an alpha or beta anomer?
iii. Circle the anomeric carbon.

DISACCHARIDES

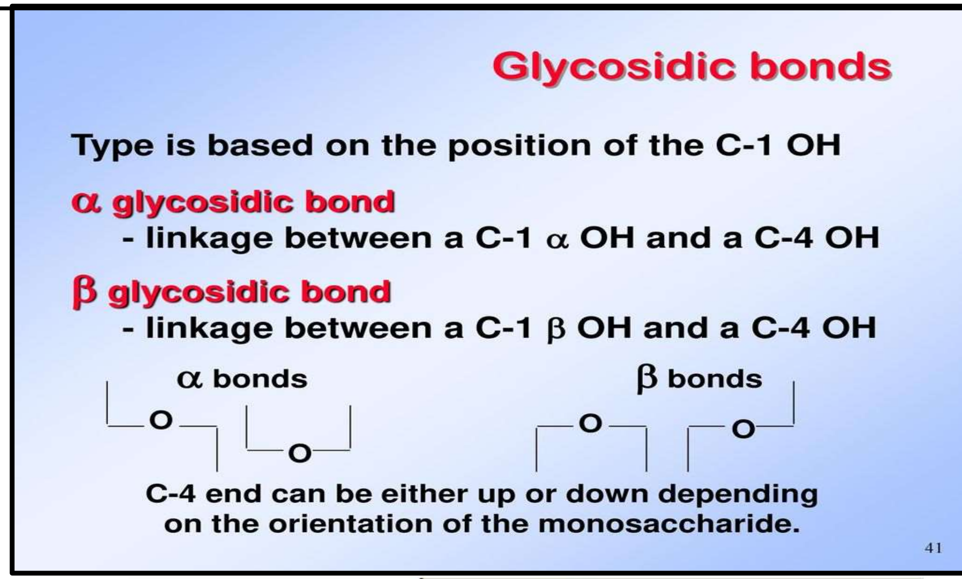
- **Disaccharides are composed of two sugar unit linked through glycosidic bond, that is formed by dehydration process with removal of one water molecule.**
- **Hydrolysis of disaccharide in the presence of water molecule releases its two units.**
- **Disaccharides consumed by us through foods,** is digested and hydrolyzed by enzymes called disaccharidases, and then individual units of disaccharide is absorbed by the cells of our body for various cellular functions. For example: sucrase hydrolyses sucrose; maltase hydrolyses maltose; lactase hydrolyses lactose
- The disaccharides of physiological importance are as follows-
  1)Maltose
  2)isomaltose
  3)Sucrose
  4)Lactose
  5)Lactulose
  6) Trehalose

Glycosidic bonds

Linkage formed between a two sugar unit involving –OH groups or a sugar unit with –OH group and N-atom containing compound such as amino acid asparangine, and glutamine; purine and pyrimidine bases

O-glycosidic bond: formed between sugar units or monosaccharides to form disaccharides, oligosaccharides or polysaccharides. Also found between sugar unit and –OH containing amino acid

They are either alpha-glycosidic bond or Beta glycosidic bond in disaccharides



N-glycosidic bond: formed between a sugar unit with –OH group and N-atom containing compound **such as amino acid asparangine, and glutamine; purine and pyrimidine bases**.

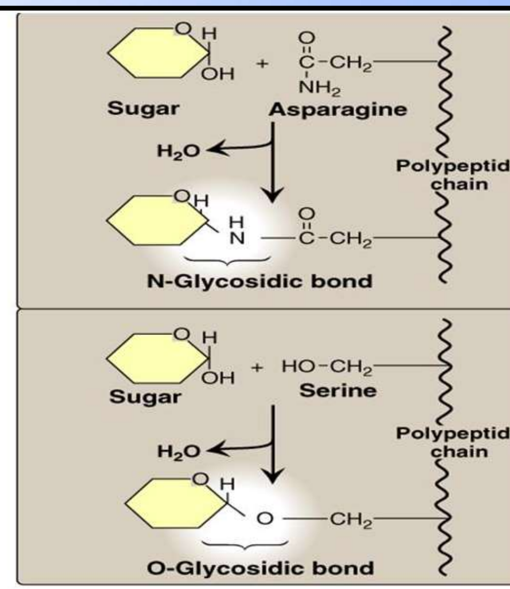
Found in heteropolysaccharide such as proteoglycans, glycoproteins, and nucleic acids (DNA and RNA that has purine and pyrimidine bases

N-Glycosidic

(C-N-C link)

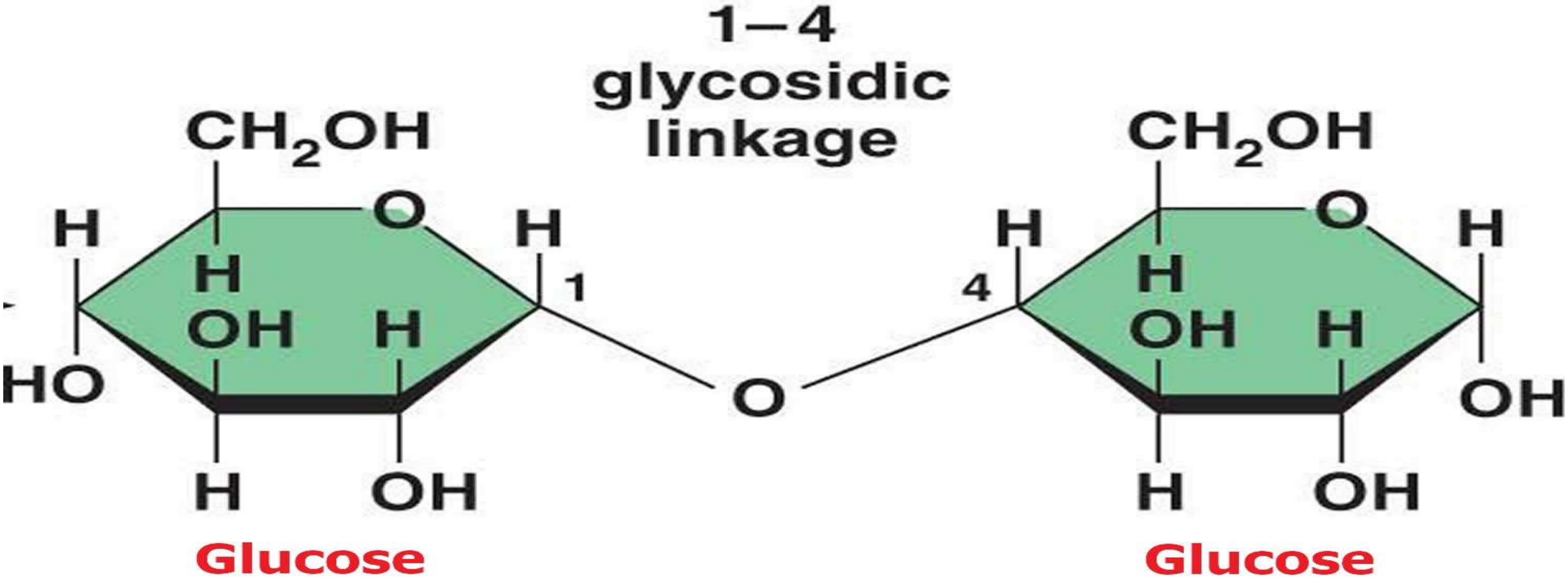
O-Glycosidic

(C-O-C link)



MALTOSE (Malt sugar)

- Maltose is formed by joining of 2 glucose units by α-(1,4) glycosidic bond.



Maltose

α -D-glucopyranosyl- (1-4) -D -glucopyranose

- Produced by partial hydrolysis of starch either by Salivary or Pancreatic amylase.

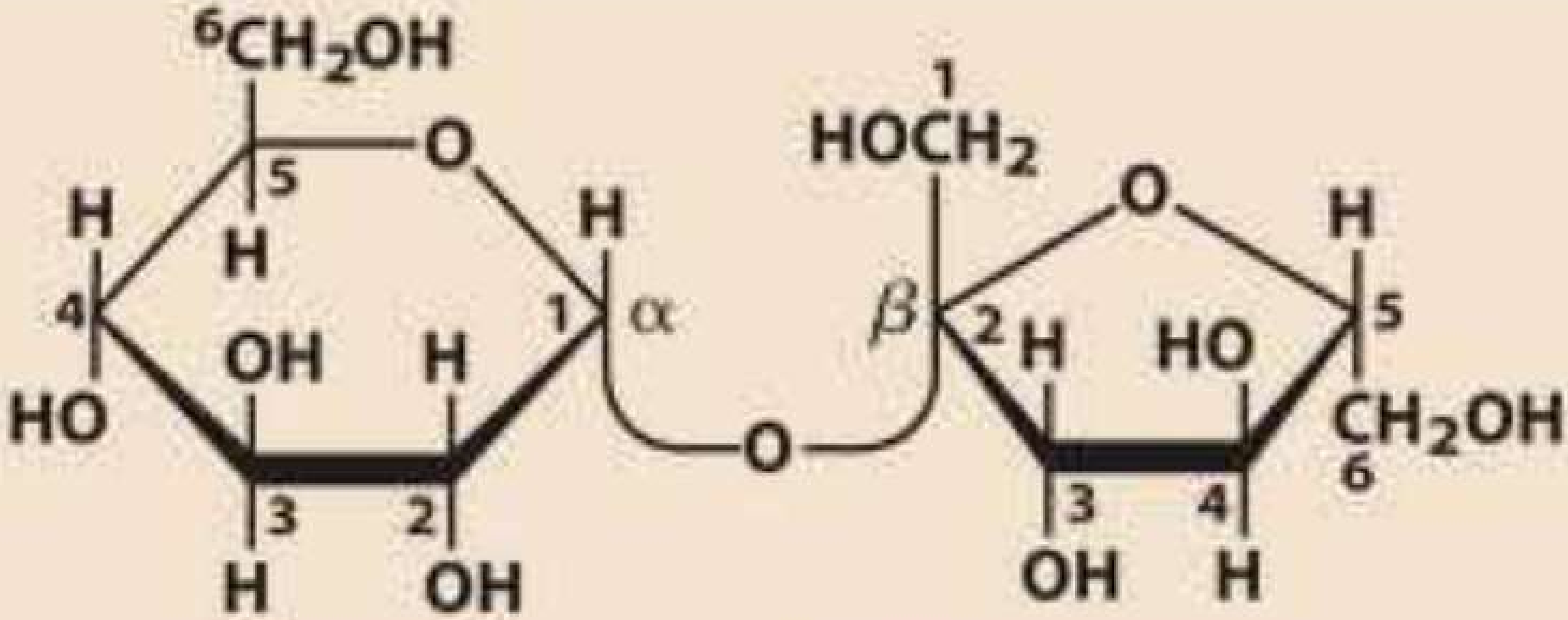
- Has a free active group and hence exhibits reducing properties, mutarotation and α-β isomerism.

Uses-

- Fermentable sugar.

- Used as a nutrient (malt extract; Hordeum vulgare); as a sweetener and as a fermentative reagent

SUCROSE (TABLE SUGAR)

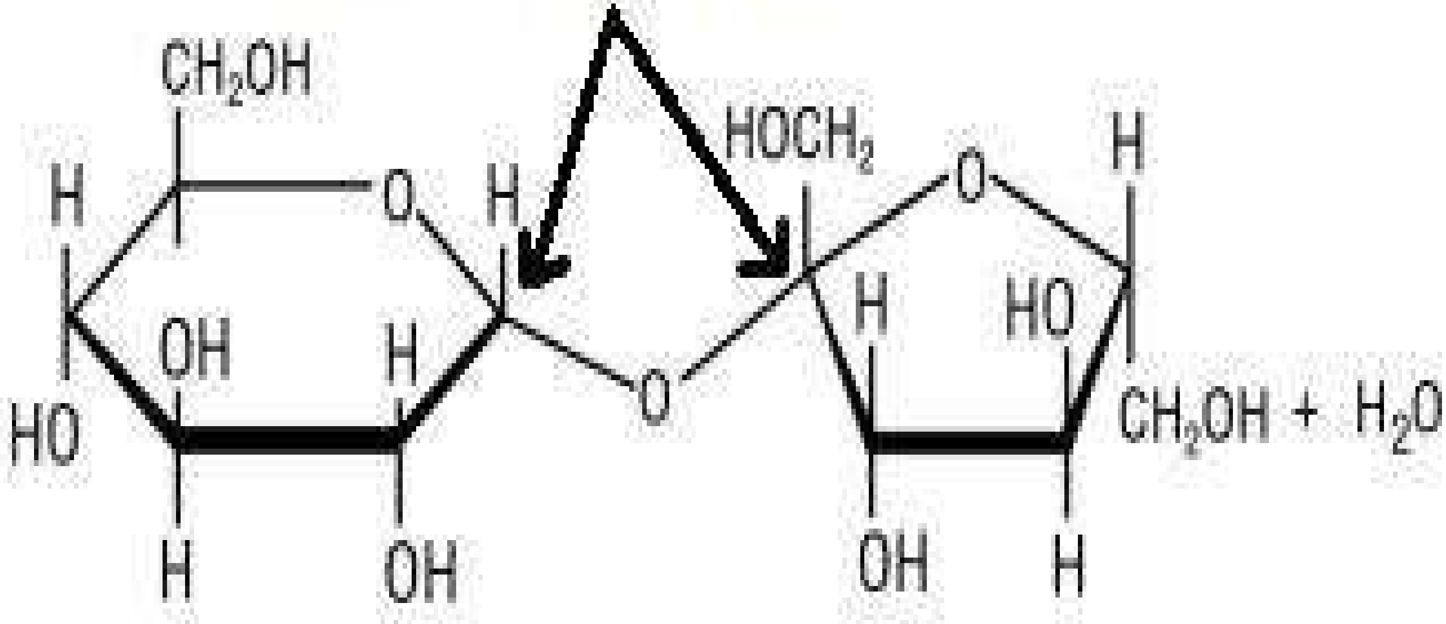


Sucrose

α-D-glucopyranosyl β-D-fructofuranoside

Glc(α1$\leftrightarrow$2β)Fru

Both anomeric carbons are involved in the O-glycosidic bond



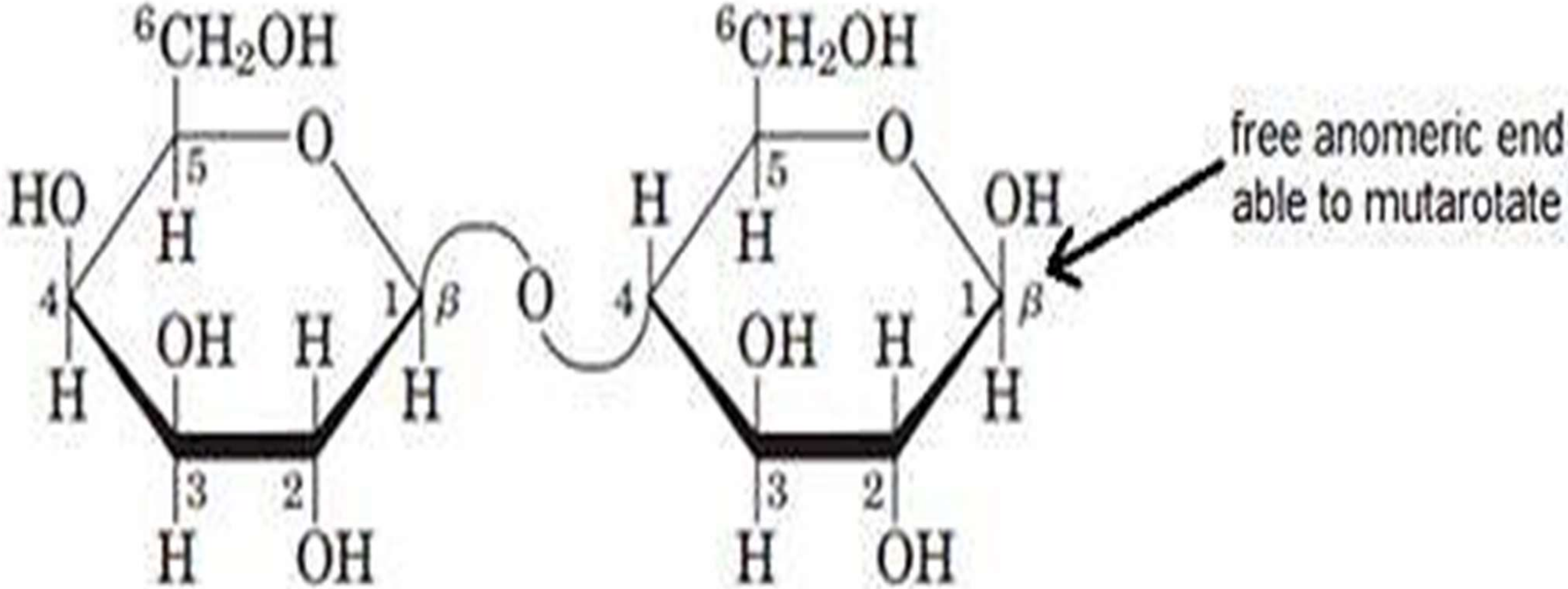
Sucrose

- Sucrose has no free reactive group because the anomeric carbons of both monosaccharides units are involved in the glycosidic bond.

- Thus, sucrose neither shows reducing properties nor mutarotation characters.

- Hydrolytic product of Sucrose is called invert sugar because the optical activity of sucrose (dextrorotatory) is inverted after hydrolysis [by an acid or an enzyme (invertase or sucrase)] into equimolar mixture of its two components glucose (+52.5) and fructose (-92.5) and the optical activity of the mixture becomes levorotatory.

LACTOSE (MILK SUGAR)



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

- Lactose is the only sugar of milk -

  Synthesized by mammary glands during lactation.

  Milk contains the α and β-anomers in a 2:3 ratio.

  β -lactose is sweeter and more soluble than ordinary α – lactose.

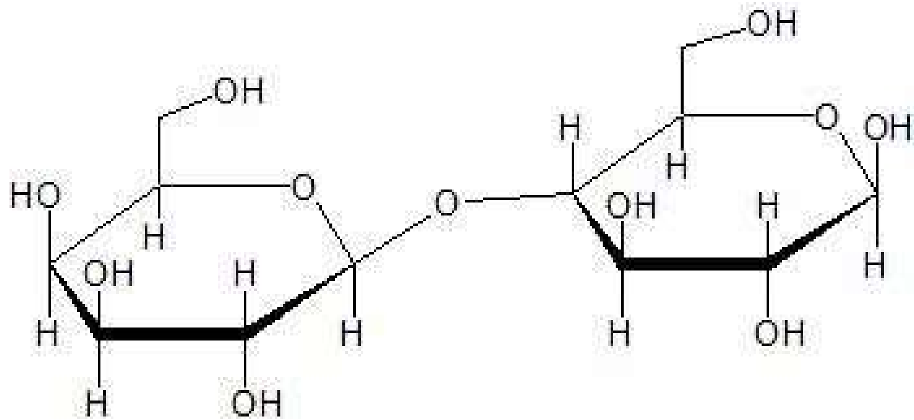
  used in infant formulations, medium for penicillin production and as a diluent in pharmaceuticals.

OLIGOSACCHARIDES

- Trisaccharide: Raffinose (glucose + galactose + fructose)
- Tetrasaccharide: Stachyose (2 galactose + glucose + fructose)
- Pentasaccharide: Verbascose (3 galactose + glucose + fructose)
- Hexasaccharide: Ajugose (4 galactose + glucose + fructose)

Sample question

(01) Some people cannot digest the disaccharide lactose. The term for this is known as lactose intolerance. Lactose is shown below. Answer the following questions.



I. What is the name of the enzyme that would be required for someone to be able to digest lactose?
II. Classify lactose as a mono-, di-, oligo-, or polysaccharide.
III. Label anomeric carbons by circling them. Is lactose a reducing sugar?
IV. Draw an arrow pointing to the glycosidic bond. Is the glycosidic bond connected to both anomeric carbons?
V. Classify the glycosidic bonds using the alpha or beta-(#,#) format.
VI. If the glycosidic bond is hydrolyzed, what are the names of the monosaccharides produced. Remember to include the alpha or beta classification for the anomeric carbon.