CHEMISTRY OF CARBOHYDRATES

- Carbohydrates are organic substances with C, H and O in the ratio of 1:2:1. ($C_6H_{12}O_6$)
- Defined as polyhydroxy aldehyde or ketone derivatives.

1] Monosaccharides.

Simple sugars & cannot be hydrolysed further. They are further classified on the basis of number of carbon atoms present as well as on the presence of functional groups.

Carbon atoms	Examples	Functional groups
Trioses (3 carbon)	Glyceraldehyde	Aldehyde (aldotriose)
	Dihydroxy acetone	Ketone (Ketotriose)
Tetroses (4 carbon)	Erythrose	Aldehyde (aldotetrose)
Pentoses (5 carbon)	Ribose	Aldehyde(Aldopentose)
	Xylose	Aldehyde(Aldopentose)
	Xylulose	Ketone (Ketopentose)
Hexoses (6 carbons)	Glucose	Aldehyde (Aldohexose)
	Galactose	Aldehyde (Aldohexose)
	Fructose	Ketone (Ketohexose)

2] Disaccharides.

Contain two molecules of same or different monosaccharide units.

On hydrolysis they give two monosaccharide units.

Monosaccharide units are joined by **glycosidic bond.**

Examples	Product formed Upon hydrolysis	Glycosidic Linkage	Sources
Maltose	glucose + glucose	α 1-4	Malt
Lactose	galactose + glucose	β 1-4	Milk
Sucrose	glucose + Fructose	β 1-2	Sugar cane
Isomaltose	glucose + glucose	α 1-6	Digestion of amylopectin

3] Oligosaccharides

Contain 3 - 10 molecules of monosaccharide units.

E.g. Maltotriose. (Glucose + Glucose + Glucose)

4] Polysaccharides

Contain more than ten molecules of monosaccharide units

They are further classified into homopolysaccharides and heteropolysaccharides

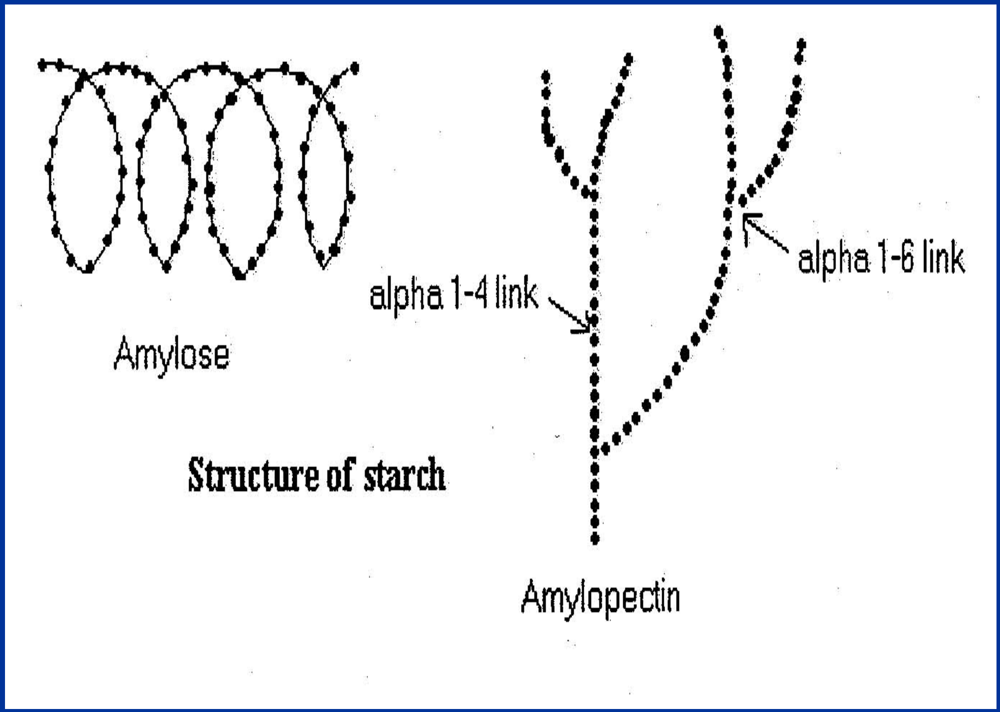
a) Homopolysaccharide:

Polymer of same monosacchraide units

	Examples	Monosaccharide Unit	Sources
▪	Starch	Glucose	Plant, rice
▪	Dextrin	Glucose	from starch hydrolysis
▪	Glycogen	Glucose	liver, muscle
▪	Cellulose	Glucose	Plant fibers
▪	Inulin	Fructose	dahlia roots
▪	Chitin	N-acetyl glucosamine	Shells of arthropod

Starch:

- Is a mixture of two polysaccharides, 1) Amylose and 2) Amylopectin.



Difference between amylose and amylopectin are:

	Amylose	Amylopectin
1.Amount present in starch	15-20%	80-85%
2. Structure	Unbranched, linear	Highly branched.
3.Molecular Weight	60 kDa	500 kDa
4.Linkage	250 to 300 glucose residues joined by α 1-4 glycosidic link	glucose residues joined by by α 1-4 linkages Branch point occurs by α-1-6 glycosidic link.
5.Reaction with Iodine solution	Blue color forms because the iodine molecules are trapped inside the helical structure. Color disappears upon heating. Reappears upon cooling!	Reddish violet color

Glycogen

Stored in liver and muscle.

Polymer of glucose units.

Also called as animal starch.

Similar to the amylopectin component of starch.

It has more branches than starch. There are 11 to 18 glucose residues between any branch points.

Dextrin

These are partially hydrolyzed product of starch.

Cellulose

Made up of β-D glucose joined by β 1-4 glycosidic bonds

Digested by cellulase enzyme in animals which is absent in human body.

Acts as dietary fiber and adds bulk to the food and helps in peristalsis.

Inulin

Consists of a small number of β D-fructose joined by β 2-1 glycosidic linkages

It is used to measure the glomerular filtration rate, a test to assess the function of kidney.

b) Heteropolysaccharide

They are polymer of different monosaccharide units or their derivatives

E.g. Mucopolysaccharides (MPS) and blood group substances

Mucopolysaccharides (MPS) are Hyaluronic acid, Chondroitin sulfate, Heparin, keratan sulfate, Heparan sulfate and dermatan sulfate

Mucopolysaccharides are **heteropolysaccharides**
Proteoglycan – protein = MPS
MPS are also known as glycosaminoglycans

Biomedical importance of MPS

They are the components of ground substances throughout the extracellular space.

They are attached to proteins and form proteoglycans.

- **Hyaluronic acid acts as a barrier in tissues against the penetration of bacteria.**
- **Heparin acts as anticoagulant in vitro as well as in vivo. It inhibits thrombin.**

ISOMERISM IN CARBOHYDRATES

- The presence of asymmetric carbon atoms (A carbon atom to which four different atoms or groups attached is known as asymmetric carbon) in a compound produces following effect;
- It gives rise to the formation of sterioisomerism of that compound
- It also confers optical activity to the compound.

1. Sterioisomerism

Compounds which are identical in composition and structural formula but differ in spatial configuration are called as sterioisomers. These include

a. **Enantiomer:**

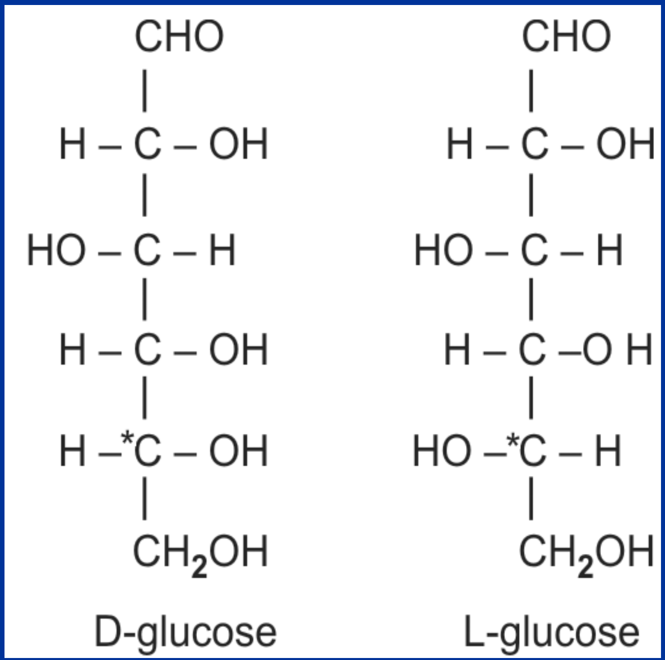
D and L-sugars are referred to as enantiomers. Their structures are mirror images of each other.

Only D-glucose or D- sugars are utilized by humans.

D and L-glucose are termed D and L form depending on the arrangement of H and OH on the penultimate carbon atom.

When the sugar has OH group on right, is D isomer.

If OH group is on left side then it is L – isomer.



B. Anomerism

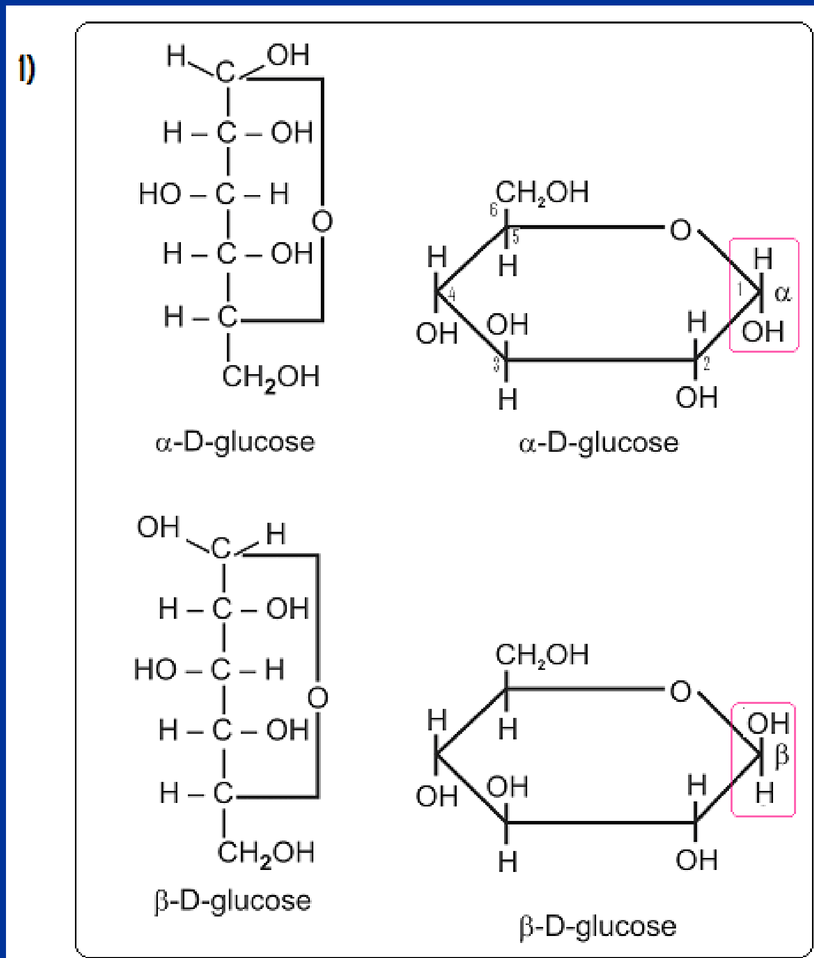
Sugars in solution exist in ring form and not in straight chain form.

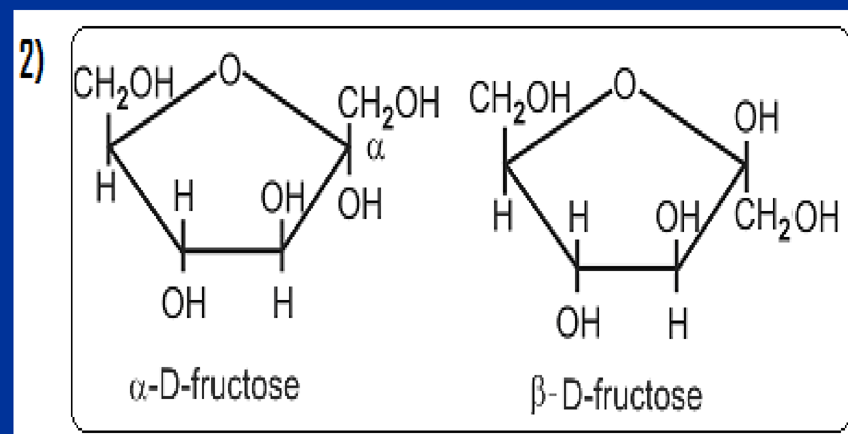
Aldosugar form mainly pyranose ring and ketosugar form furanose ring structure

Carbon 1, after ring formation becomes asymmetric and it is called as anomeric carbon atom. If the two sugars which differ in the configuration at only C1 in case of aldoses and C2 in ketoses are known as anomers and represented as alpha and beta sugars.

E.g. α-D glucose and β-D-glucose

α-D fructose and β-D-fructose


1)
H C OH
H – C – OH
HO – C – H
O
H – C – OH
H – C
CH₂OH
α-D-glucose
CH₂OH
O
H
α
OH
H
H
OH
OH
H
H
OH
α-D-glucose
OH C H
H – C – OH
HO – C – H
O
H – C – OH
H – C
CH₂OH
β-D-glucose
CH₂OH
O
OH
β
H
H
H
OH
OH
H
H
OH
β-D-glucose

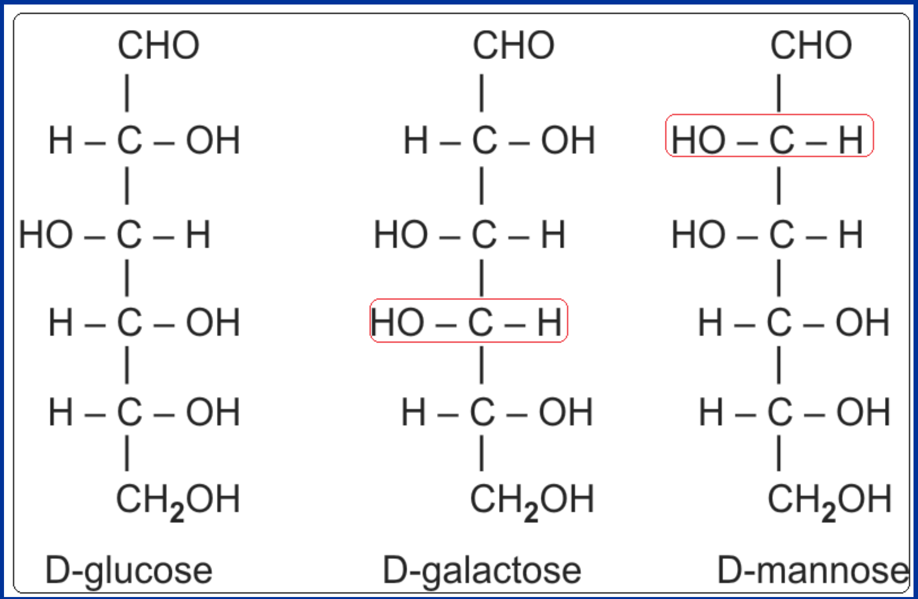

2)
CH₂OH
O
CH₂OH
α
OH
H
H
OH
OH
H
α-D-fructose
CH₂OH
O
OH
CH₂OH
H
H
OH
OH
H
β- D-fructose

- **Epimerism:**

  The isomers formed due to variations in the configuration of –H and –OH around a single carbon atom in a sugar molecule is called as epimers.

  Mannose is 2 – epimer of glucose because these two have different configuration only around C2.

  Galactose is 4-epimer of glucose [at C4]



2. Optical activity

The compounds having asymmetric carbon atoms can rotate the beam of plane polarized light and are said to be optically active.

An isomer which can rotate the plane of polarized light to the right is called as dextrorotatory and is designated as (d) or (+)

Example: D- (d)-glucose or it is also known as dextrose.

While the isomer which rotates the plane of polarized light to left is known as levorotatory, and is identified as (l) or (-).

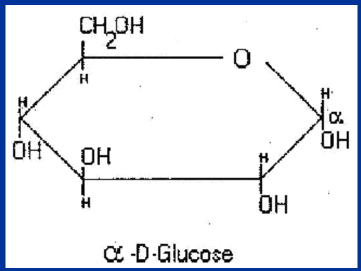
Example: D-(l)-fructose.

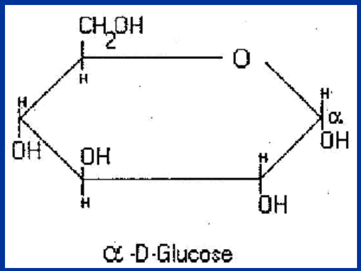
A compound with D- configuration can be dextrorotatory (D+) or levorotatory (D-).

E.g. D + glucose and D- fructose.

- **Glycosidic bond**

  It is the linkage formed between **OH** group of **anomeric carbon** of one sugar with any **OH** group of another sugar (or alcohol) resulting in the loss of a water molecule. This linkage is involved in the formation of disaccharide and polysaccharides.





- **Reduction tests**

Due to the presence of a free aldehyde or ketone group, carbohydrates are readily oxidised and behave as the reducing agents. These sugars have the capacity to reduce cupric ion (Cu^{2+}) to cuprous ion (Cu^{+}). Therefore the **reducing sugar** like **glucose** will give positive Benedicts reactions.

Non-reducing sugars like **sucrose** will respond to these tests provided it is first hydrolysed into its reducing components glucose and fructose.

Functions of carbohydrates

1. Most abundant dietary source of energy (4Cal/g)
2. They are precursors for many organic compounds (fats, amino acids)
3. Carbohydrates (glycoprotein, glycolipids) participate in the structure of cell membrane and cellular functions
4. Structural components of many organisms. These include the fibers (cellulose) of plant, exoskeleton of some insects and the cell wall of microorganisms.
5. Serve as the storage form of energy (glycogen) to meet the immediate energy demands of the body.

Reference: Essentials of Biochemistry by Dr S Nayak