

Polysaccharides

- Monosaccharides can undergo a series of condensation reactions, adding one unit after another to the chain until very large molecules (polysaccharides) are formed. This is called condensation **polymerisation**, and the building blocks are called **monomers**.
- The majority of carbohydrate material in nature occurs in the form of polysaccharides (also known as glycans). Other molecules that contain polysaccharide structures are also referred to as polysaccharides.
 - **Homopolysaccharide**. A polysaccharide whose monosaccharide units are identical.
 - **Heteropolysaccharide**. A polysaccharide made up of different monosaccharides
- The most common constituent of polysaccharides is D-Glucose
- Homopolysaccharides composed of **glucose** are called **glucans**; Those composed of mannose are called **mannans**; etc.
- Glycosidic linkages involve only one anomeric carbon (keto or aldehyde) per monosaccharide. However, there are several potential hydroxyl acceptor groups on a given monosaccharide. Thus, polysaccharides can be branched as well as linear.
 - The characterization of polysaccharides includes their length, the type of monosaccharide units, the linkages and branched nature
 - **Starch** is a **glucan** that has two polysaccharide forms: one is a linear molecule with α -1-4 linkages called **amylose**. The other is a branched form of **amylose**, where the branches have α -1-6 linkages, called **amylopectin**.
- The properties of a polysaccharide molecule depend on:
 - i. Its length (though they are usually very long)
 - ii. The extent of any branching (addition of units to the side of the chain rather than one of its ends)
 - iii. Any folding which results in a more compact molecule
 - iv. Whether the chain is 'straight' or 'coiled'
- **Starch, Glycogen** and **Cellulose** are all polymers of **glucose**. They differ in the type of glucose present and the bonds which link thru glucose monomers together, whereas **Insulin** is the polymer of glucose and fructose
- **Starch** and **Glycogen** are made from **alpha-glucose**. This is an isomer of glucose in which the **hydroxyl** (-OH) group attached to carbon number 1 is **below** the plane of the ring. Whereas **Cellulose** are β -glucose monomer.
- The major form of storage polysaccharide in **animals** is **glycogen** (found in the liver and skeletal muscle).
- The most common storage polysaccharide in **plants** is **starch**.
- **Yeast** and **bacteria** make dextran as a storage polysaccharide. It is composed of α -1-6 linkages of Dglucose, with branched chains (1-2, 1-3 or 1-4 linkages between glucose units). Important component of dental plaque (from bacteria).

Properties of Carbohydrates

- General properties of carbohydrates

Carbohydrates act as energy reserves, also stores fuels, and metabolic intermediates.

- ✓ Ribose and deoxyribose sugars forms the structural frame of the genetic material, RNA and DNA.
- ✓ Polysaccharides like cellulose are the structural elements in the cell walls of bacteria and plants.
- ✓ Carbohydrates are linked to proteins and lipids that play important roles in cell interactions.
- ✓ Carbohydrates are organic compounds; they are aldehydes or ketones with many hydroxyl groups.

- Physical Properties of Carbohydrates

- ✓ **Stereoisomerism**: Compound having same structural formula, but they differ in spatial configuration. Example: Glucose has two isomers with respect to penultimate carbon atom. They are D-glucose and L-glucose.
- ✓ **Optical Activity**: It is the rotation of plane polarized light forming (+) glucose and (-) glucose.
- ✓ **Diastereoisomers**: It the configurational changes with regard to C₂, C₃, or C₄ in glucose. Example: Mannose, galactose.
- ✓ **Anomerism**: It is the spatial configuration with respect to the first carbon atom in aldoses and second carbon atom in ketoses.

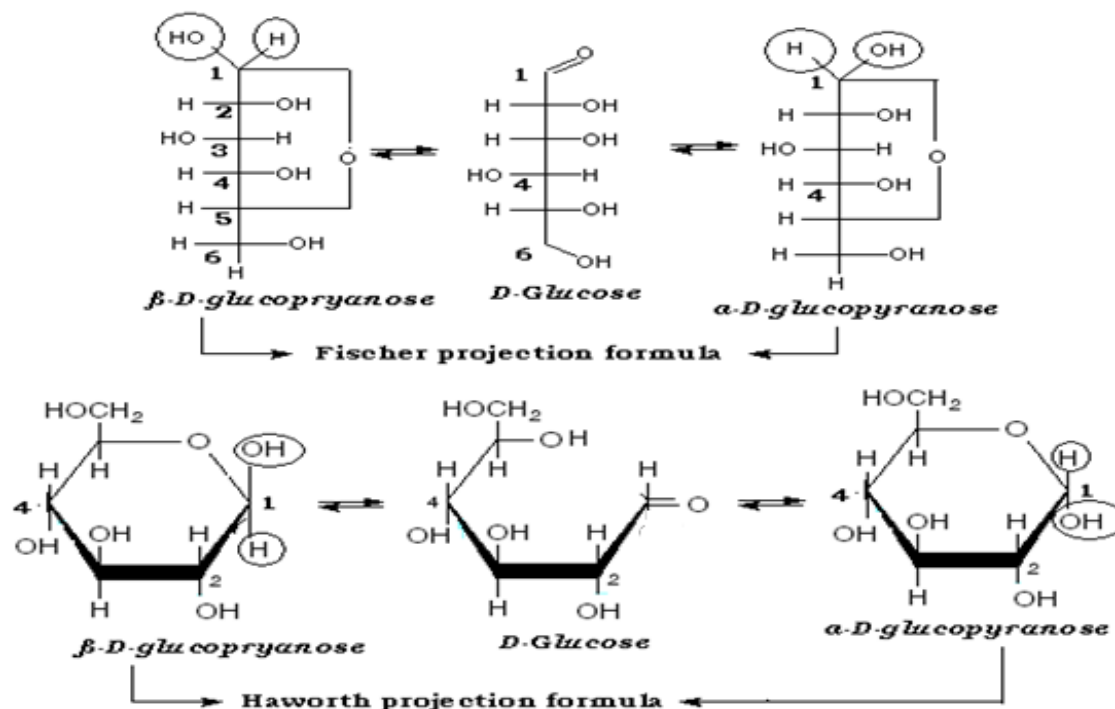
Chemical Properties of Carbohydrates

- ✓ Osazone formation with phenylhydrazine.
- ✓ Benedict's test.
- ✓ Oxidation
- ✓ Reduction to alcohols

Structure of Carbohydrates

There are three types of structural representations of carbohydrates:

- (i) Open chain structure.
- (ii) Hemi-acetal structure.
- (iii) Haworth structure.



Difference between Starch, Glycogen & Cellulose			
Characters	Starch	Glycogen	Cellulose
Monomer	α-glucose <i>Amylose</i> : (60 to 300 α-glucose Unit) <i>Amylopectine</i> : (300 to 6000 α-glucose Unit)	α-glucose (6000 to 30,000 α-glucose Unit)	β-glucose (300 to 2500 β-glucose Unit)
Type of bond between monomers	α(1→4) glycosidic bond (<i>Amylose</i>) + α(1→4) and α(1→6) glycosidic bond (<i>Amylopectin</i>)	α(1→4) and α(1→6) glycosidic bonds	β(1→4) glycosidic bond
Nature of chain	<i>Amylose</i> is coiled unbranched <i>Amylopectin</i> is long branched chains, some coiling	Short many branched chains, some coiling	Straight, long unbranched chains form H-bonds, with adjacent chains
Occurrence	In plants	In animals and fungi	In plants
Function	Carbohydrate energy store	Carbohydrate energy store	Structural
General form	Grains	Small granules	Fibres
Chemical Test or Iodine test	Deep Blue-Violet color	Reddish brown color	Negative test

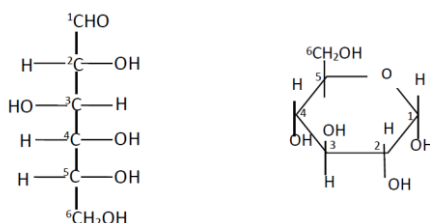
Functions of Carbohydrates

- ✓ Carbohydrates are chief energy source, in many animals; they are instant source of energy. Glucose is broken down by glycolysis/ kreb's cycle to yield ATP.
- ✓ Glucose is the source of storage of energy. It is stored as glycogen in animals and starch in plants.
- ✓ Stored carbohydrates act as energy source instead of proteins.
- ✓ Carbohydrates are intermediates in biosynthesis of fats and proteins.
- ✓ Carbohydrates aid in regulation of nerve tissue and are the energy source for brain.
- ✓ Carbohydrates get associated with lipids and proteins to form surface antigens, receptor molecules, vitamins and antibiotics.
- ✓ They form structural and protective components, like in cell wall of plants and microorganisms.
- ✓ In animals they are important constituent of connective tissues.
- ✓ They participate in biological transport, cell-cell communication, and activation of growth factors.
- ✓ Carbohydrates those are rich in fiber content help to prevent constipation.
- ✓ Also, they help in modulation of immune system.
 - **Example of Carbohydrates**
 - *Monosaccharides*: Glucose, galactose, glycerose, erythrose, ribose, ribulose, fructose.
 - *Oligosaccharides*: Maltose, lactose, sucrose, raffinose, stachyose.
 - *Polysaccharides*: Starch, glycogen, cellulose, pectin, inulin, hyaluonic acid.
- ✓ Food's rich in carbohydrates are referred to as strachy foods. They are found in legumes, starchy vegetables, whole-grain breads and cereals. They also occur naturally with vitamins and minerals in foods like milk, fruits, and milk products. They are also found in refined and processed products like candy, carbonated beverages, and table sugar.
 - **Examples of Polysaccharides**

Name of the Polysaccharide	Composition	Occurrence	Functions
Starch	Polymer of glucose containing a straight chain of glucose molecules (amylose) and a branched chain of glucose molecules (amylopectin)	In several plant species as main storage carbohydrate	storage of reserve food
Glycogen	Polymer of glucose	Animals (equivalent of starch)	Storage of reserve food
Inulin	Polymer of fructose	In roots and tubers (like Dahlia)	Storage of reserve food
Cellulose	Polymer of glucose	Plant cell wall	Cell wall matrix
Pectin	Polymer of galactose and its derivatives	Plant cell wall	Cell wall matrix
Hemi cellulose	Polymer of pentoses and sugar acids	Plant cell wall	Cell wall matrix
Lignin	Polymer of glucose	Plant cell wall (dead cells like sclerenchyma)	Cell wall matrix
Chitin	Polymer of glucose	Bodywall of arthropods. In some fungi also	Exoskeleton Impermeable to water
Murein	Polysaccharide cross linked with amino acids	Cell wall of prokaryotic cells	Structural protection
Hyaluronic acid	Polymer of sugar acids	Connective tissue matrix, Outer coat of mammalian eggs	Ground substance, protection
Heparin	Closely related to chondroitin	Connective tissue cells	Anticoagulant
Gums and mucilage's	Polymers of sugars and sugar acids	Gums - bark or trees. Mucilage's - flower	Retain water in dry seasons

Properties of food carbohydrates

- Monosaccharide exists in both as straight chain structure and cyclic structure. Sugars with five membered rings and with six membered rings are most stable. Cyclic structures are the result of hemiacetal formation by intermolecular reaction between carbonyl group and a hydroxyl group.

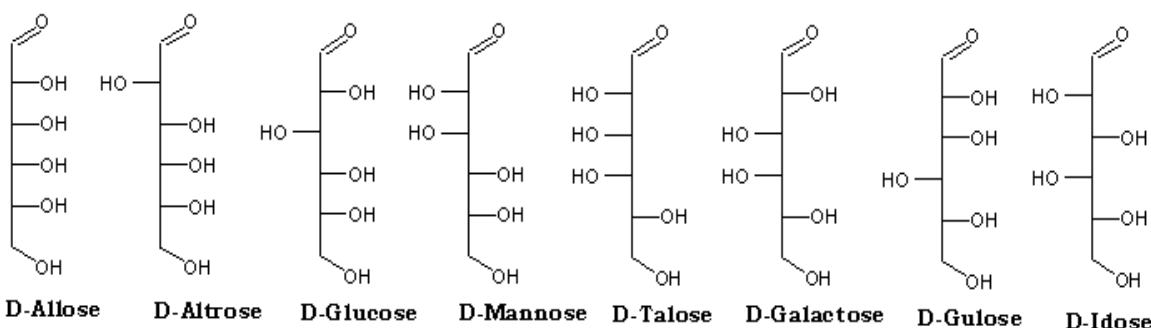
Structure of α -D-glucose:

A. Straight chain

B. Cyclic form

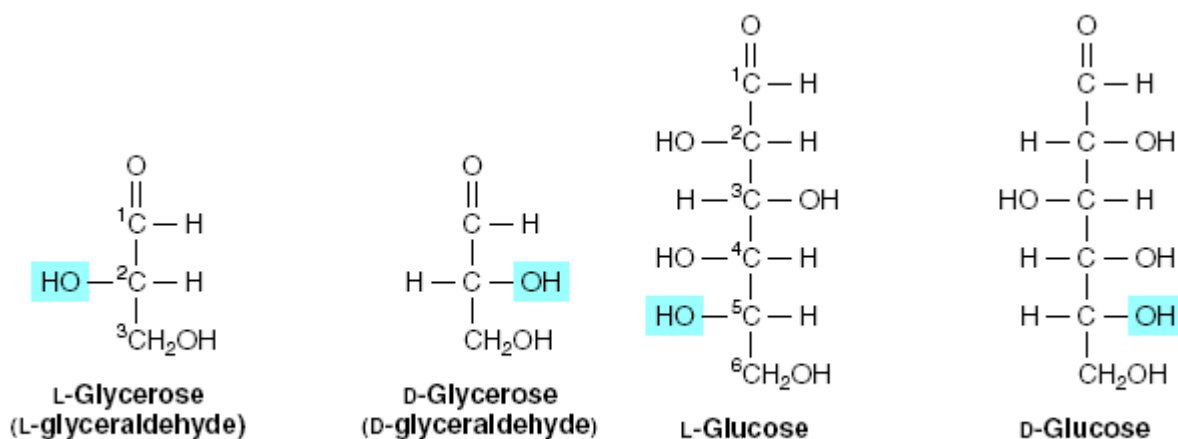
(i) Chiral centre

All monosaccharide except dihydroxy acetone contain one or more asymmetric (chiral) carbon atoms thus are optically active isomers (enantiomers). A molecule with n chiral centres can have 2^n stereoisomers. Glyceraldehyde with one chiral centre has $2^1=2$ and glucose with four chiral centres, have $2^4=16$ stereoisomers.



(ii) D and L isomerism

- The designation of a sugar isomer as the D form or of its mirror image as the L form.
- The L and D forms of the sugar depends on the orientation of the **-H** and **-OH** groups around the carbon atom adjacent to the **terminal primary alcohol carbon** (carbon 5 in glucose) determines whether the sugar belongs to the D or L series.
- When the **-OH** group on this carbon is on the right, then sugar is the **D-isomer**; when it is on the left, then it is the **L-isomer**.



D- and L-isomerism of glycerose and glucose

- Most of the monosaccharide occurring in mammals is D sugars, and the enzymes responsible for their metabolism are specific for this configuration. In solution, glucose is dextrorotatory—hence the alternative name **dextrose**.
- The presence of asymmetric carbon atoms also confers **optical activity** on the compound. When a beam of plane-polarized light is passed through a solution of an **optical isomer**, it will be rotated either to the right,