

INTRODUCTION TO BIOCHEMISTRY

Definition

The science that is concerned with the structures, interactions, and transformations of biological molecules. The chemistry of life

Biochemistry can be subdivided three principal areas

- Structural chemistry
- Metabolism
- The chemistry of processes and substances that store and transmit biological information (molecular genetics)

Biochemistry and Life

The cell is the fundamental unit of life

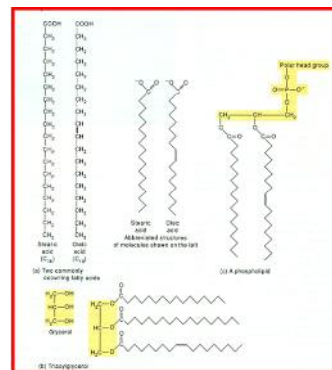
- Prokaryotes and eukaryotes
- Eukaryotic cells
- animal cells
- plant cells (chloroplasts and cell walls)

Cells are composed of:

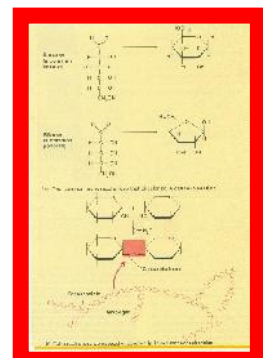
- Small molecules
- Macromolecules
- Organelles

Except for water, most of the molecules found in the cell are macromolecules, can be classified into four different categories:

- Lipids
- Carbohydrates
- Proteins
- Nucleic acids
- Lipids are primarily hydrocarbon structures



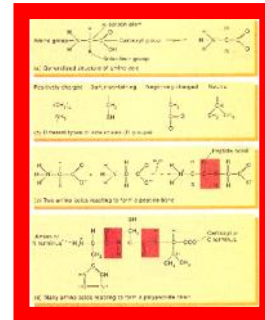
- Carbohydrates, like lipids, contain a carbon backbone, but they also contain many polar hydroxyl (-OH) groups and therefore very soluble in water.



- Proteins are the most complex macromolecules in the cell.
- They are composed of linear polymers called polypeptides, which contain amino acids connected by peptide bonds

Each amino acid contains a central carbon atom attached to four substituents

- A carboxyl group
- An amino group
- A hydrogen atom
- An R group



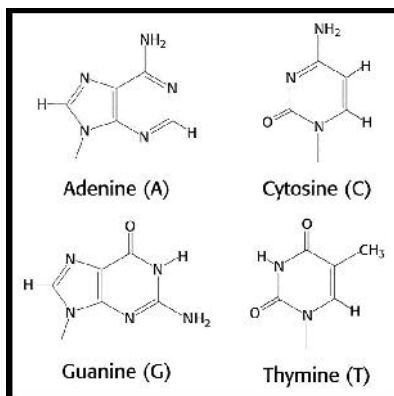
Nucleic acids are the large macromolecules in the cells.

They are very long linear polymers, called polynucleotides, composed of nucleotides

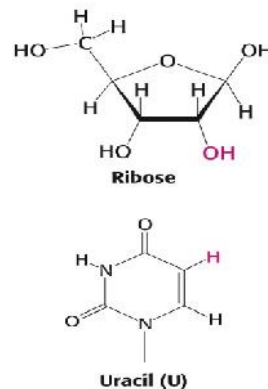
A nucleotide contains:

- A five-carbon sugar molecules
- One or more phosphate groups
- A nitrogenous base
- DNA: A, T, G, C
- RNA: A, U, G, C

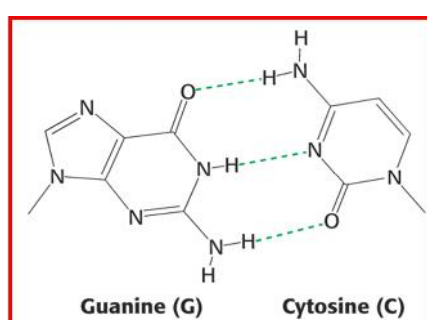
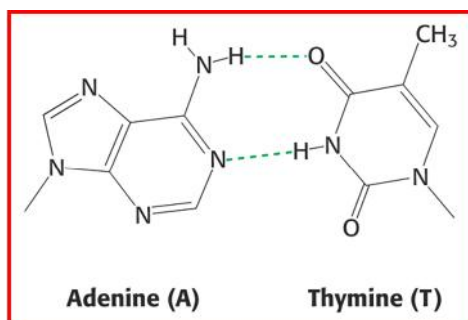
DNA Contain Four Bases



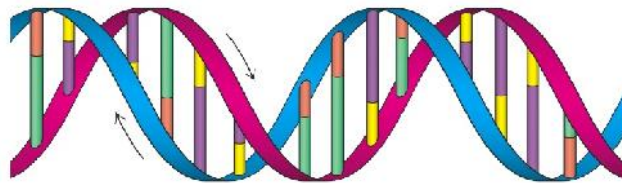
RNA



Watson-Crick base pairs



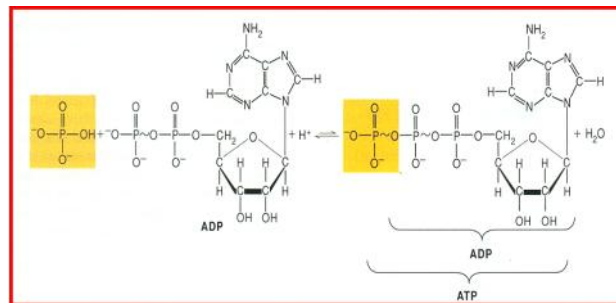
The Double Helix



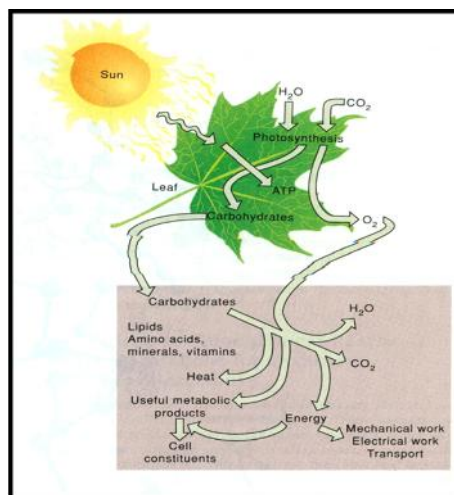
Biochemical Energy

- All cellular functions require energy.
- The most-important chemical form of energy in most cells is ATP, *adenosine 5'-triphosphate*.
- $\text{ATP} \longrightarrow \text{ADP} + \text{P}_i$
- Most ATP synthesis occurs in chloroplasts and mitochondria

ADP and ATP Structures



Energy Transfer



Transfer of Information from DNA to Protein



CARBOHYDRATES

Occurrences

Carbohydrates are the most abundant organic compounds in the plant world. They act as storehouses of chemical energy (glucose, starch, glycogen); are the components of supportive structures in plants (cellulose), crustacean shells (chitin) and connective tissues in animals (acidic polysaccharides) and are essential components of nucleic acids (D-ribose and 2-deoxy-D-ribose). Carbohydrates make up about three fourths of the dry weight of plants.

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

Carbohydrates are usually defined as

Polyhydroxy aldehydes or ketones, or substances that hydrolyze to yield polyhydroxy aldehydes or ketones". (Or) Aldehyde or Ketone derivatives of polyhydroxy alcohols

Carbohydrates are aldehyde or ketone compounds with multiple hydroxyl groups

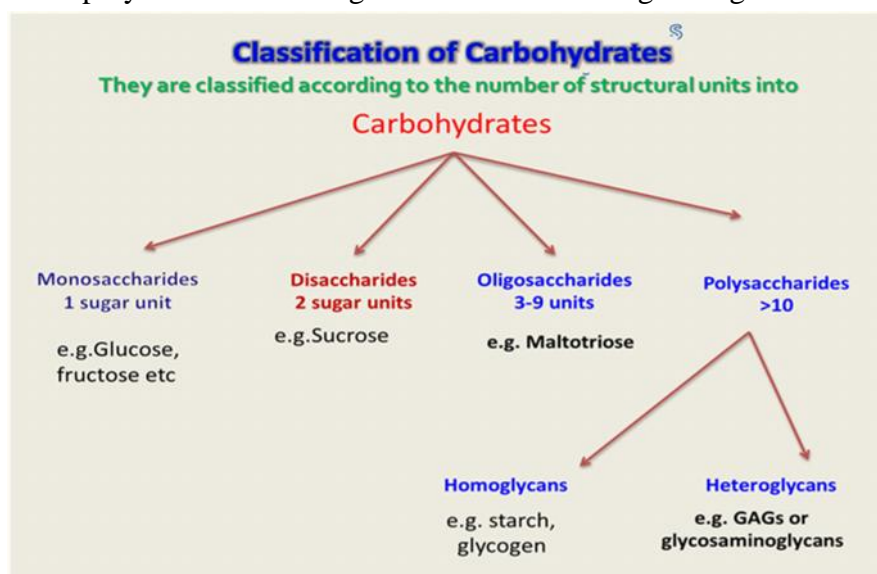
General molecular formula $C_n (H_2O)_n$

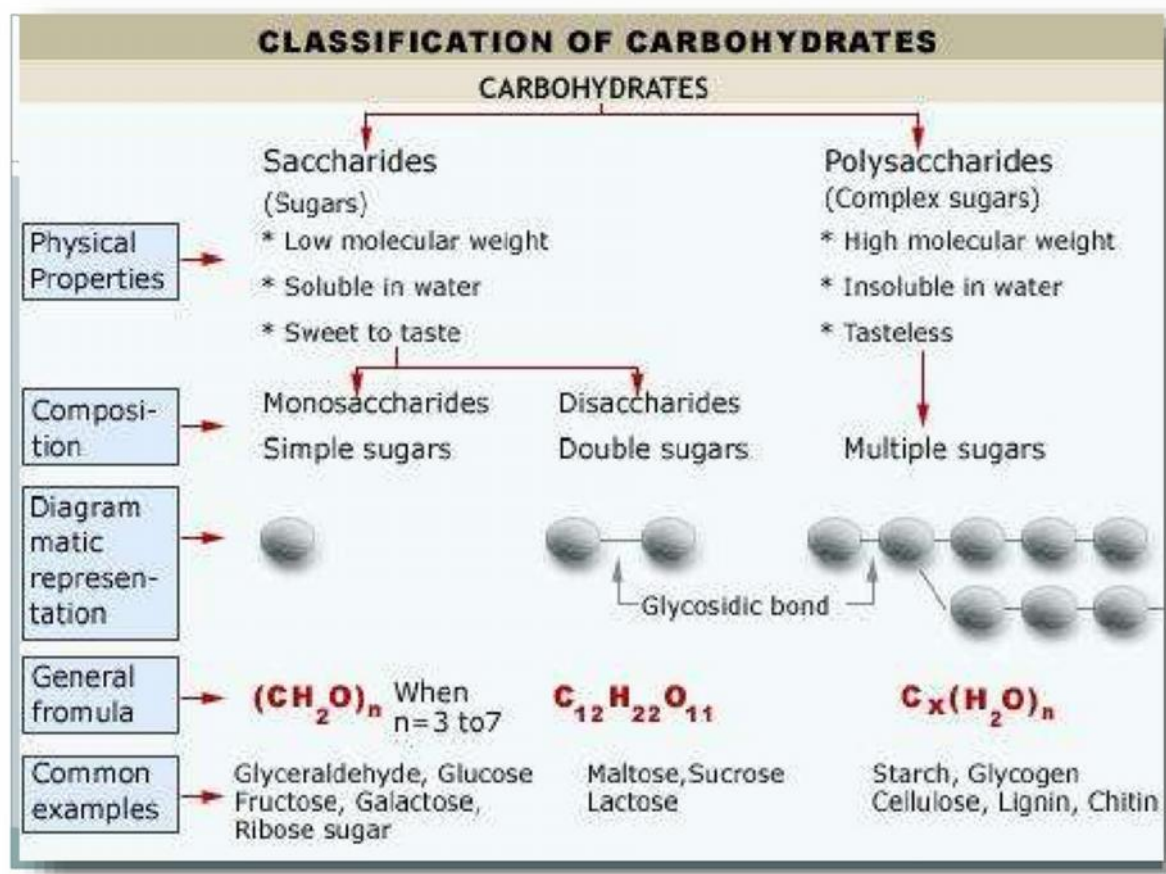
The term carbohydrate comes from the observation that when you heat sugars, you get carbon and water (hence, hydrate of carbon).

Functions of carbohydrates

Main sources of ENERGY in body (4kcal/g)

- RBCs and Brain cells have an absolute requirement of carbohydrates
- Storage form of energy (starch and glycogen)
- Excess carbohydrate is converted to fat.
- Glycoproteins and glycolipids are components of cell membranes and receptors.
- Structural basis of many organisms.e.g. Cellulose in plants,
- exoskeleton of insects, cell wall of microbes,
- Mucopolysaccharides and ground substance in higher organisms.





MONOSACCHARIDES

Def : They are the simplest carbohydrate units which cannot be hydrolysed to a simpler form
They are classified into a) simple monosaccharides b) derived monosaccharides

Simple monosaccharides sub classified according to

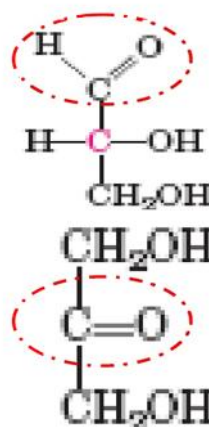
- 1-The number of carbon atoms present in their molecule and,
- 2- The type of carbonyl group they contain.

Derived monosaccharides include the derivatives of simple monosaccharides such as oxidation products, reduction products, substitution products and esters

* Nomenclature:

• 1- According to active group in the sugar:

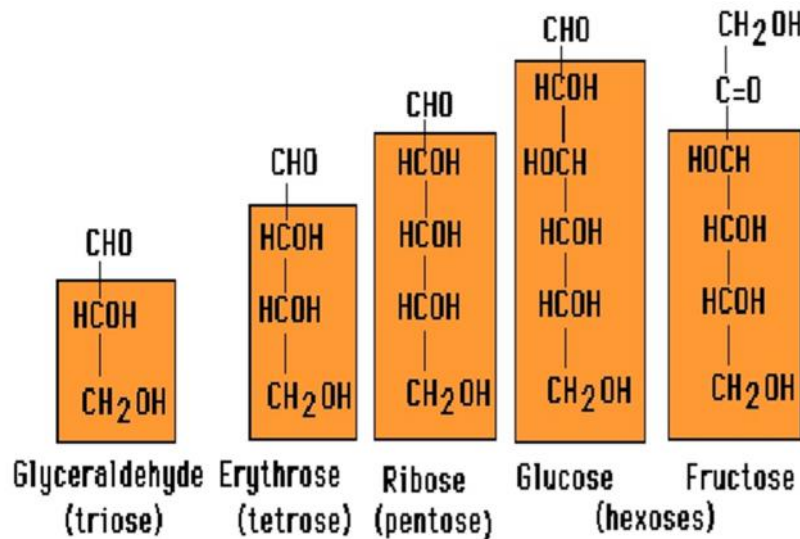
- If monosaccharide contains aldehyde group (CHO) → it's called **aldose**.
- And if contain ketone group (C=O) → it's called **ketose**.



2.- According to the number of carbon atoms (n):

If sugar contains

3 carbons it's called triose, 4c tetroses 5c pentose 6c hexose 7c heptoses

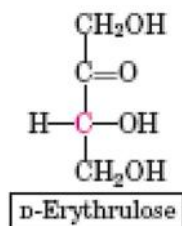
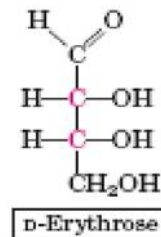
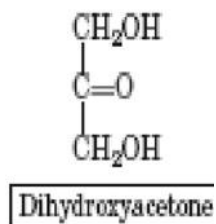
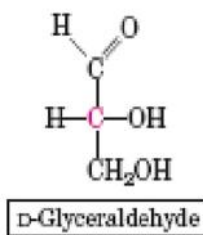


3- By combining the two methods, we find that

3c-Aldotriose	ketotriose
4c-Aldotetrose	Ketotetrose
5c-Aldopentose	Ketppentose
6c-Aldohexose	Ketohexose

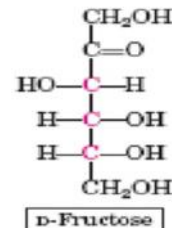
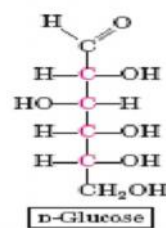
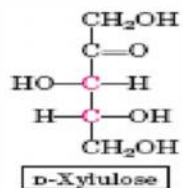
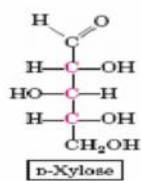
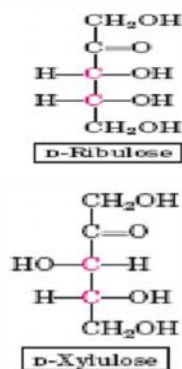
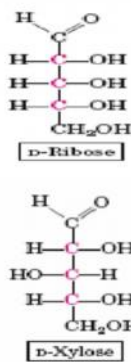
Three Carbon

Four Carbon



Five Carbon

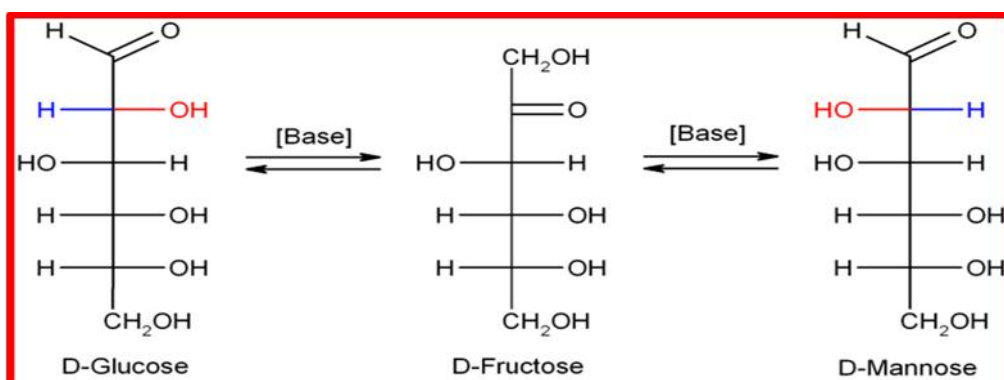
Six Carbon



Glucose **Fructose**
Galactose **Mannose**

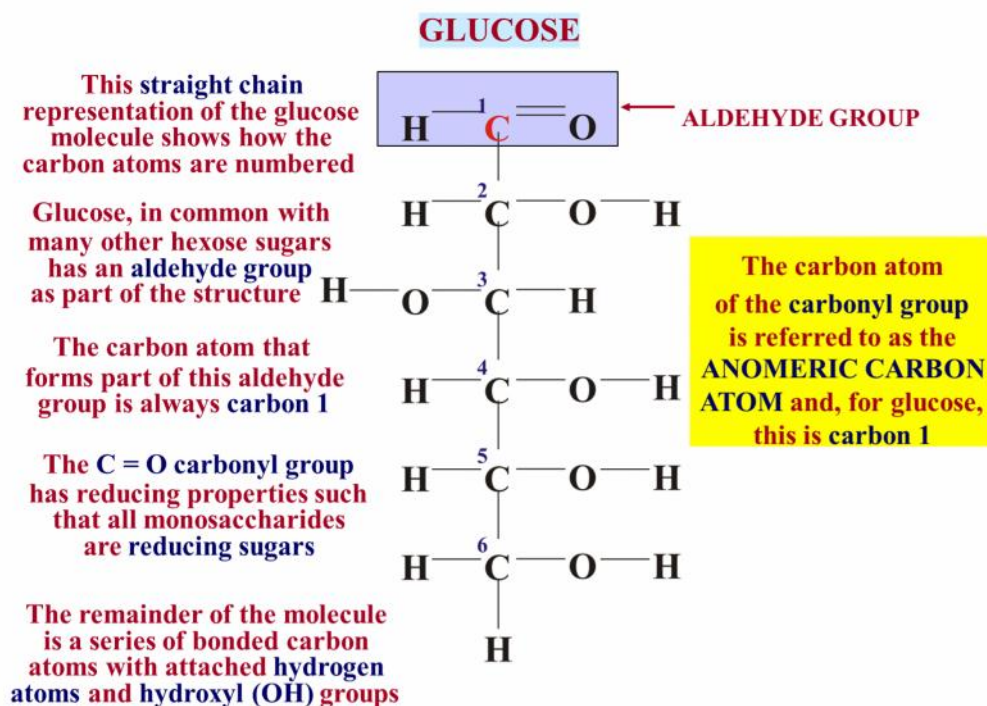
Monosaccharides	No. of carbon atoms	Aldose	Ketose	Occurrence
Simple				
Triose	3	D-Glycerose	Dihydroxy acetone	Intermediary metabolites in glucose metabolism
Tetrose	4	D-Erythrose	D-Erythrulose	
Pentose	5	D-Ribose	D-Ribulose	Ribose is a constituent of nucleic acid
		L-Arabinose	-	Occurs in oligosaccharides
		D-Xylose	D-Xylulose	Gum arabic, cherry gums, wood gums, proteoglycans
Hexose	6	D-Glucose	D-Fructose	Fruit juices and cane sugar

		D-Galactose	-	Lactose, constituent of lipids
		D-Mannose	-	Plant mannosans and glycoproteins
Heptose	7	-	D-Sedoheptulose	Intermediate in carbohydrate metabolism



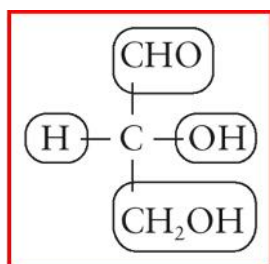
Derived				
Deoxysugar	5	2-Deoxyribose	-	DNA
	6	L-Rhamnose	-	Component of cell wall
Aminosugar	6	D-Glucosamine	-	A major component of polysaccharide found in insects and crustaceans (chitin)
Polyol	6	Sorbitol	-	Berries
	6	Mannitol	-	Commercially prepared from mannose and fructose
Aldonic acid	6	Gluconic acid	-	-
Uronic acid	6	Glucuronic acid	-	Constituent of chondroitin sulfate
	6	Galacturonic acid	-	Constituent of pectin
Aldaric acid (Saccharic acid)	6	Glucaric acid	-	Oxidation product of glucose
	6	Mucic acid	-	Oxidation product of galactose

GLUCOSE



MONOSACCHARIDE STRUCTURES

The simplest monosaccharide that possesses a hydroxyl group and a carbonyl group with an asymmetric carbon atom is the aldotriose -glyceraldehyde.(Reference carbohydrate) (A carbon is said to be asymmetric if four different groups or atoms are attached to it. The carbon is also called as a chiral center). Glyceraldehyde is considered as a reference compound and it exists in two optically active forms, D and L. A chiral object cannot be superimposed on its mirror image. A chiral carbon (Asymmetric carbon) is one that has four different groups attached to it.

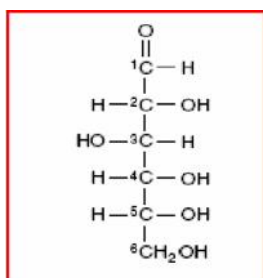


1. The straight – chain (open chain) structural formula

Aldohexose- an account for some of the properties of glucose, but cannot explain some

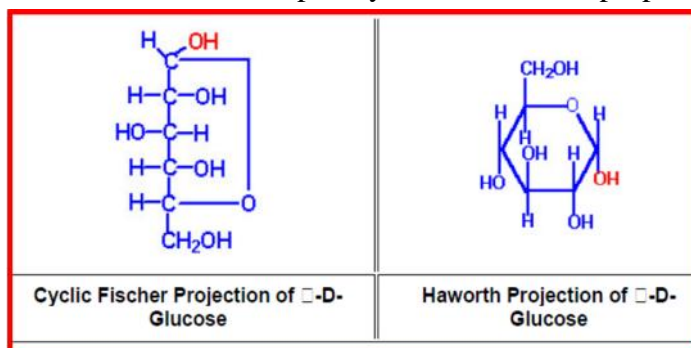
Reaction

D-glucose

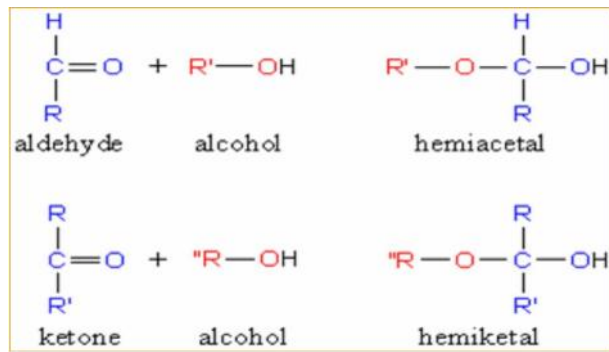


2. Cyclic structure

When an aldehyde or a ketone group is present in a molecule that also possesses hydroxyl groups, an intramolecular arrangement may occur to form a hemiacetal or a hemiketal, respectively. This intramolecular hemiacetal or hemiketal is the basis for the cyclic structure of the sugars .Hence, Haworth (an English chemist) proposed a cyclic hemiacetal structure that accounts completely for its chemical properties

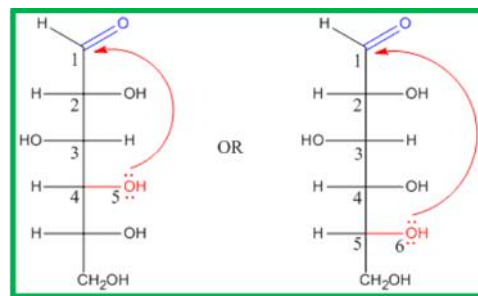


Hemiacetals or Hemiketals



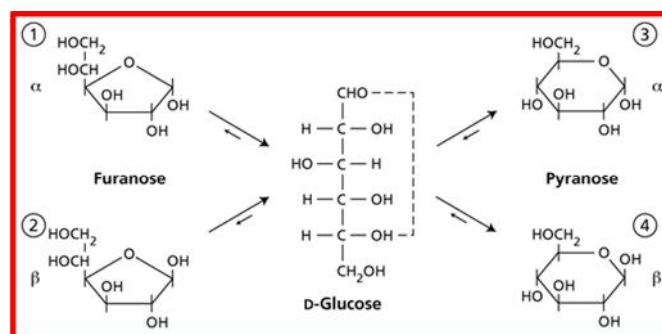
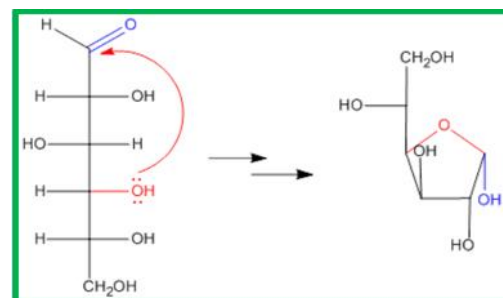
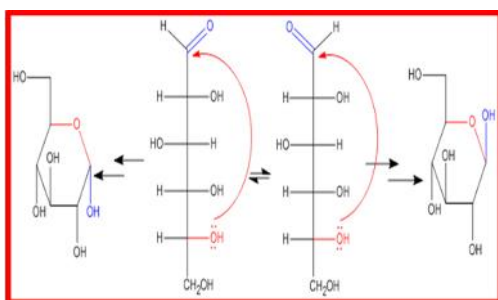
An aldehyde or ketone can react with an alcohol in a 1:1 ratio to yield a hemiacetal or hemiketal, respectively, creating a new chiral center at the carbonyl carbon

Two types of ring structures are possible, the five-membered furanose and the six membered pyranose ring if the carbonyl group interact with hydroxyl group. These names are derived from the parent compounds 'furan' and 'pyran'. The most common ring structure for aldohexoses is the pyranose ring structure that involves the first carbonyl carbon and the hydroxyl group attached to the fifth carbon. The furanose ring structure is formed by interaction of carbonyl carbon with the hydroxyl group attached to the fourth carbon. This furanose form is less stable than the pyranose structure and is not very common among Aldohexose



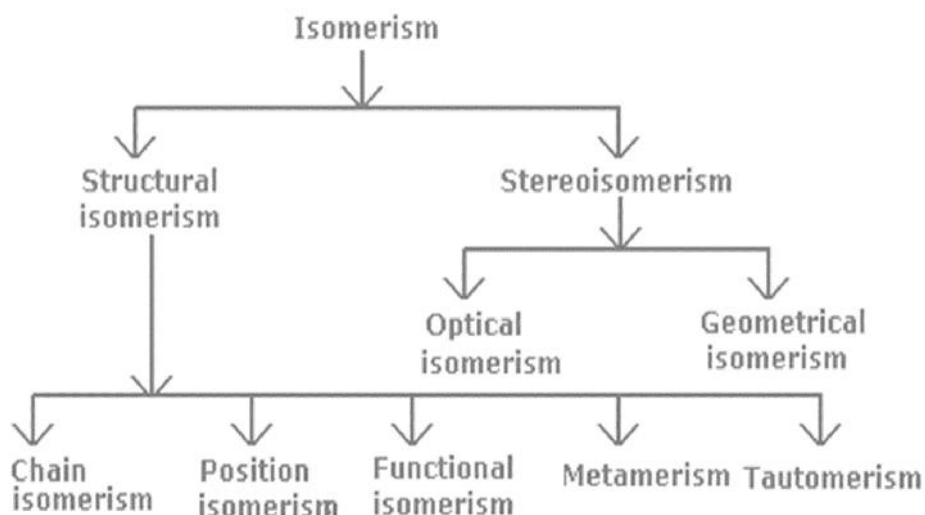
Six membered pyranose ring

Five membered furanose ring



Isomerism

Isomers are different compounds that have the same molecular formula. Different compounds means that they have different physical properties (melting point, boiling point etc.). They may also have very different chemical properties depending on the type of isomerism present. It was coined by J.J. Berzelius for different compounds with same molecular formula

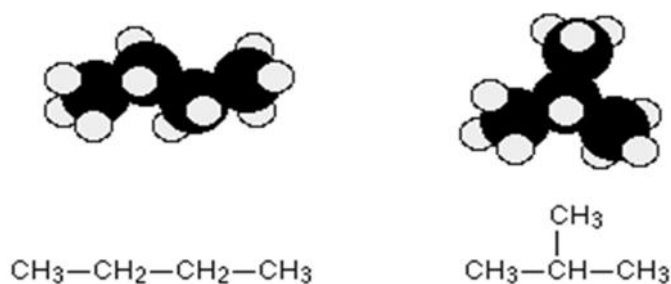


Structural isomers, in which the atoms are joined in a different order, so that they have different structural formulae

Types of structural isomerism

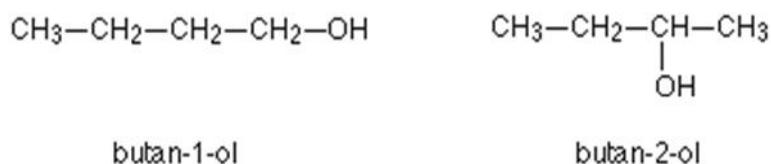
Chain isomerism

These isomers arise because of the possibility of branching in carbon chains. For example, there are two isomers of butane, C_4H_{10} . In one of them, the carbon atoms lie in a "straight chain" whereas in the other the chain is branched.



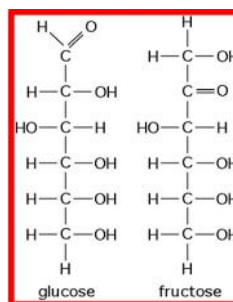
Position isomerism

In position isomerism, the basic carbon skeleton remains unchanged, but important groups are moved around on that skeleton.



Functional Isomers

D-glucose and D-fructose differ in the position of carbonyl group (aldehyde and ketone group). These two compounds are functional isomers.



Stereoisomerism or constitutional isomers

Another type of isomerism exhibited by compounds possessing asymmetric carbon atom like monosaccharides, is stereoisomerism. These stereoisomers differ in the spatial arrangement of atoms or groups. There are two types of stereoisomerisms - geometrical and optical isomerism.

Van't Hoff's 2ⁿ rule

When a molecule has more than one chiral carbon, each carbon can possibly be arranged in either the right-hand or left-hand form, thus if there are n chiral carbons, there are 2^n possible stereoisomers.

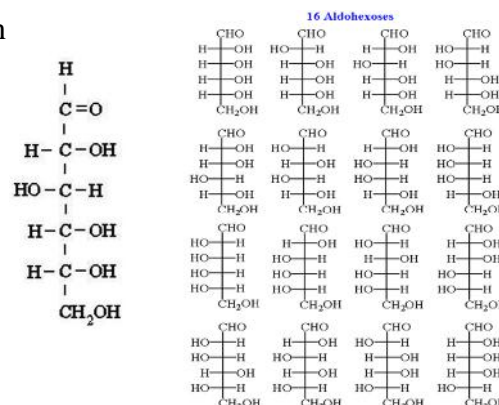
$$\text{Maximum number of possible stereoisomers} = 2^n$$

Geometric Isomerism

Geometric isomers (also called cis/trans isomers) are a type of stereoisomer resulting from a double bond or a ring structure. The double bond or ring in the structure means that not all bonds are free to rotate, giving rise to geometric isomers whose shapes cannot interconvert. Geometrical isomerism is not noticed among carbohydrates.

Optical isomerism

Optical isomers differ in the arrangement of atoms around an asymmetric carbon atom. The number of possible optical isomers can be calculated using the formula 2^n where n = number of asymmetric carbon atoms. For example, glucose contains four asymmetric carbon atoms and the possible optical isomers of glucose are $2^4 = 16$. Optical isomers are named like this because of their effect on plane polarised light.



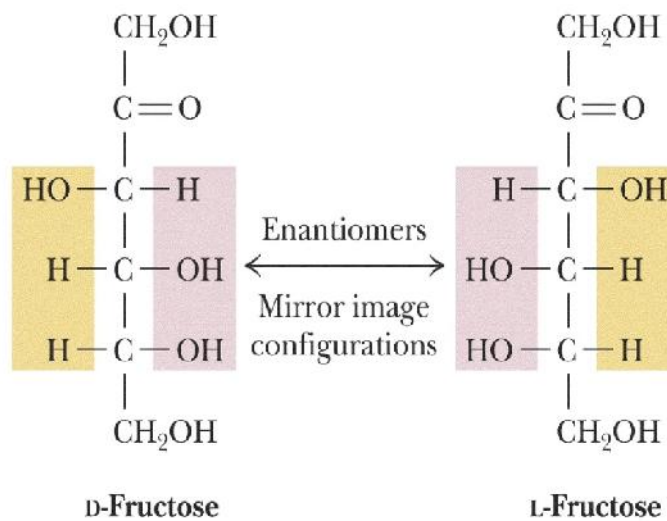
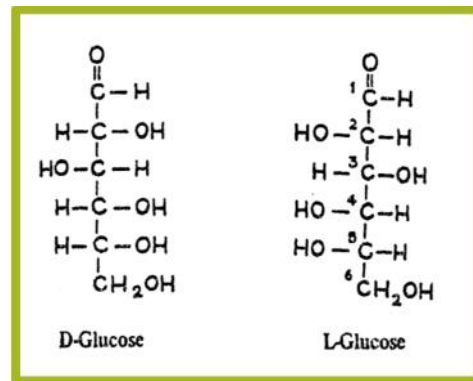
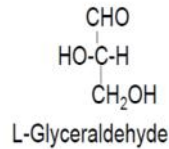
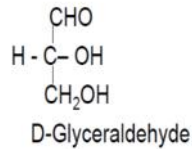
Enantiomers

Enantiomers are non-superimposable mirror images of each other. They differ in the ability to rotate the plane polarized light. A solution of one enantiomer rotates the plane of such light to the right, and a solution of the other to the left. D-glucose and L-glucose are examples of enantiomers.

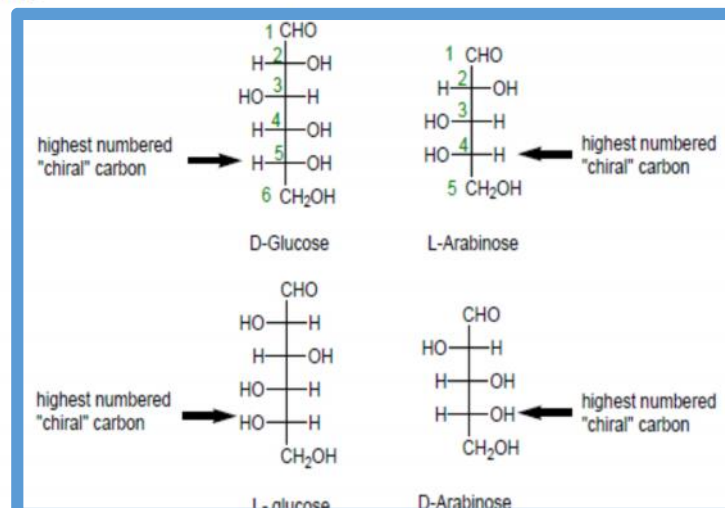
D and L isomers (Enantiomers)

Enantiomers :

They are the **mirror image** of each others.

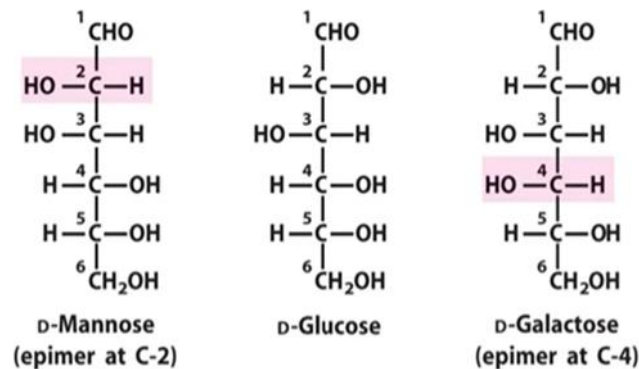


Carbohydrates are designated as D- or L- according to the stereochemistry of the highest numbered chiral carbon of the Fischer projection. If the hydroxyl group of the **highest numbered chiral carbon** is pointing to the right, the sugar is designated as **D** (*Dextro*: Latin for *on the right side*). If the hydroxyl group is pointing to the left, the sugar is designated as **L** (*Levo*: Latin for *on the left side*). Most naturally occurring carbohydrates are of the D-configuration.



Epimers

Epimers are monosaccharides differing in configuration around a single carbon atom other than the carbonyl carbon. e.g. Mannose and glucose are epimers with respect to carbon 2. Galactose and glucose are epimers with respect to carbon 4.

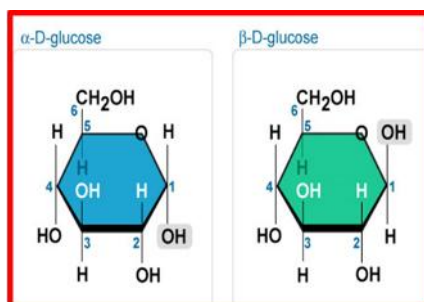
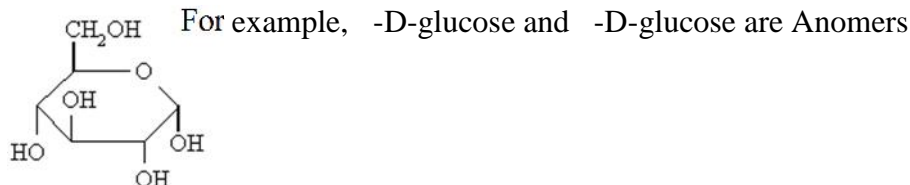


D-Galactose is an epimer of D-glucose because the two sugars differ only in the configuration at C-4. D-Mannose is an epimer of D-glucose because the two sugars differ only in the configuration at C-2.

Anomers

When a molecule such as glucose converts to a cyclic form, it generates a new chiral centre at C-1.

The carbon atom that generates the new chiral centre (C-1) is called the anomeric carbon. Anomers are special cases — they are epimers that differ in configuration only at the anomeric carbon



The α form has the anomeric OH group at C-1 on the opposite side of the ring from the CH₂OH group at C-5.

The β form has the anomeric OH group on the same side as the CH₂OH

Diastereomers

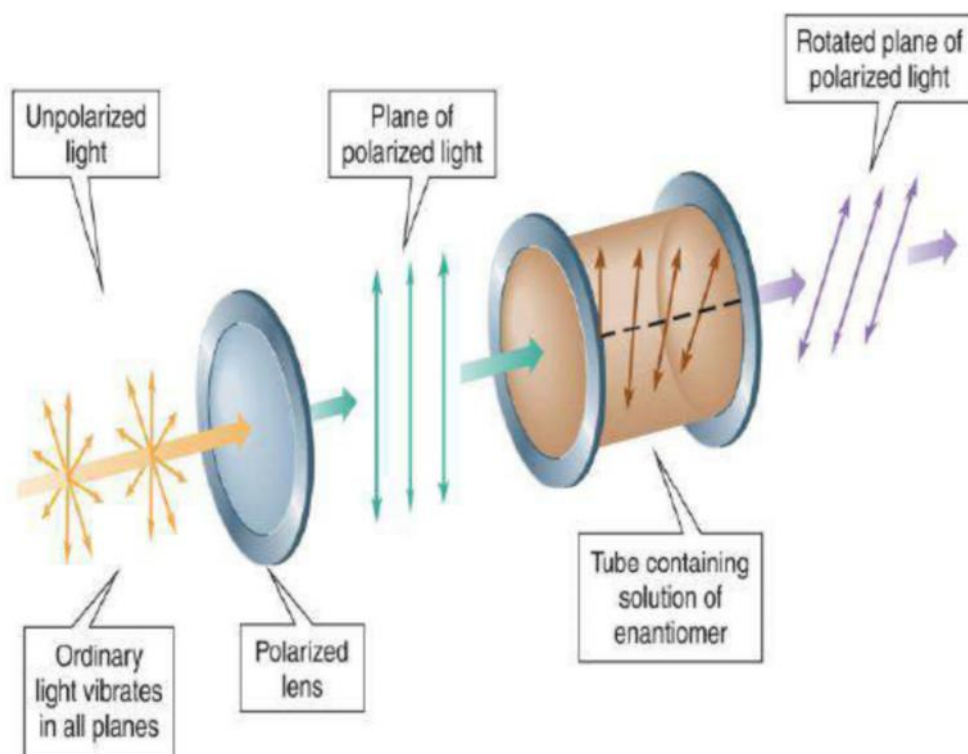
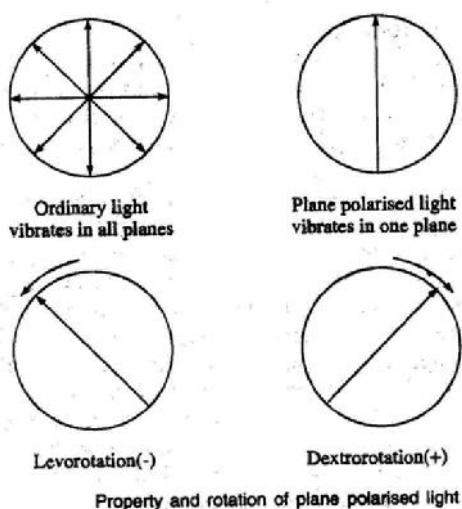
Diastereomers are stereoisomers that are not mirror images of each other. D-glucose, D-mannose, D-galactose and other members of aldohexose are diastereoisomers.

Stereoisomers with two or more stereocenters can be diastereomers. It is sometimes difficult to determine whether or not two molecules are diastereomers.

Optical activity

Molecules that are chiral can rotate the plane of polarized light. The property of rotating the plane of polarized light is called optical activity. A ray of ordinary light vibrates in all directions at right angles to the direction in which the ray is travelling. When this light is passed through a Nicol prism, the emerged light vibrates in only one direction and such light is called as a 'plane polarized light

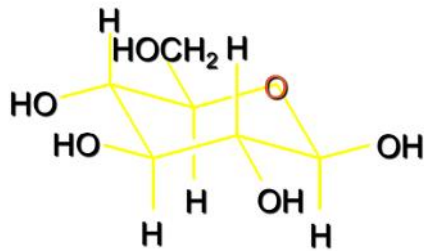
When a beam of plane polarized light is passed through a sugar solution, that is optically active, the plane-polarized light will be rotated either to the right (clockwise) or to the left (anticlockwise). When the plane polarized light is rotated to the right, the compound is dextrorotatory and is written as (+). • If the plane polarized light is rotated to the left, the compound is levorotatory (-)



Mutarotation

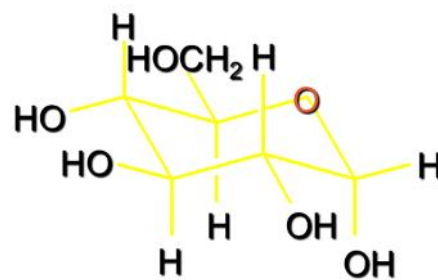
Mutarotation is a term given to the change in the observed optical rotation of a substance with time. Glucose, for example, can be obtained in either its α or β -pyranose form. The two forms have different physical properties such as melting point and optical rotation. When either form is dissolved in water, its initial rotation changes with time. Eventually both solutions have the same rotation. In Glucose solution, $2/3$ of sugar exist as β form, & $1/3$ as α form. Inter conversion of α & β forms is called MUTAROTATION

Mutarotation of D-Glucose



β -D-Glucopyranose

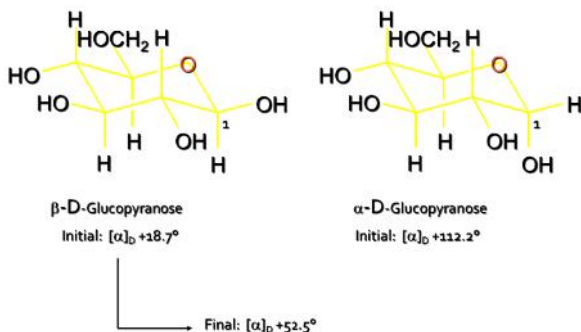
Initial: $[\alpha]_D +18.7^\circ$



α -D-Glucopyranose

Initial: $[\alpha]_D +112.2^\circ$

Mutarotation of β -D-Glucose

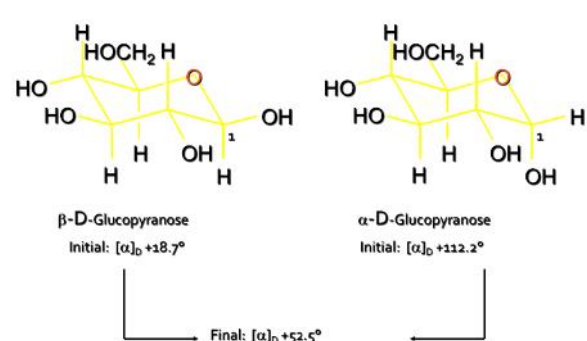


β -D-Glucopyranose
Initial: $[\alpha]_D +18.7^\circ$

α -D-Glucopyranose
Initial: $[\alpha]_D +112.2^\circ$

Final: $[\alpha]_D +52.5^\circ$

Mutarotation of α -D-Glucose

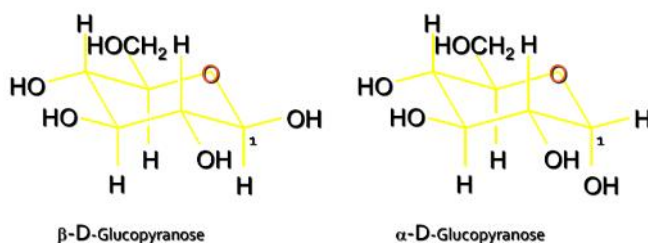


β -D-Glucopyranose
Initial: $[\alpha]_D +18.7^\circ$

α -D-Glucopyranose
Initial: $[\alpha]_D +112.2^\circ$

Final: $[\alpha]_D +52.5^\circ$

Mutarotation of β -D-Glucose

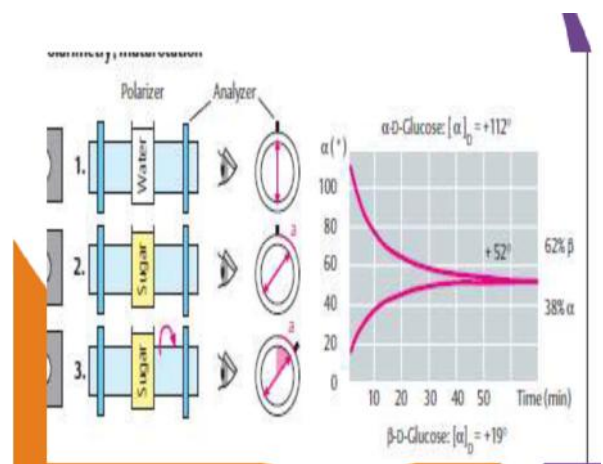


β -D-Glucopyranose

α -D-Glucopyranose

•Explanation: After being dissolved in water, the α and β forms slowly interconvert via the open-chain form.

• An equilibrium state is reached that contains 64% β and 36% α .



Oligosaccharides

These consist of 2 and up to 10 molecules of simple sugars and are hydrolysable. They are sub classified into di-, tri- and tetrasaccharides etc..., according to the number of molecules of simple sugars they yield on hydrolysis

Disaccharides

Disaccharides are sugars composed of two monosaccharides covalently bonded together by a glycosidic linkage. The most abundant disaccharides are sucrose, lactose and maltose. The disaccharides can be classified into homo disaccharides and hetero disaccharides

A) Homo disaccharides: are formed of the same monosaccharide units maltose, isomaltose, cellobiose and trehalose

B) Hetero disaccharides: are formed of different monosaccharide and include: sucrose, lactose

- Maltose, also known as malt sugar, is formed from two glucose molecules
- Lactose, or milk sugar, is a disaccharide formed when the monosaccharides glucose and galactose are joined
- Sucrose is common household sugar and is formed when the monosaccharides glucose and fructose bond

MALTOSE = GLUCOSE + GLUCOSE

LACTOSE = GLUCOSE + GALACTOSE

SUCROSE = GLUCOSE + FRUCTOSE

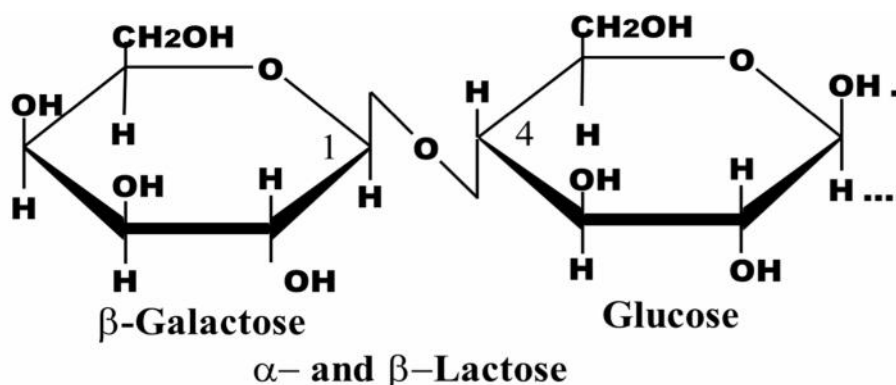
Lactose:

It is formed of β -galactose and α -glucose linked by β -1,4-glycosidic linkage

Contain free anomeric carbon so reducing sugar

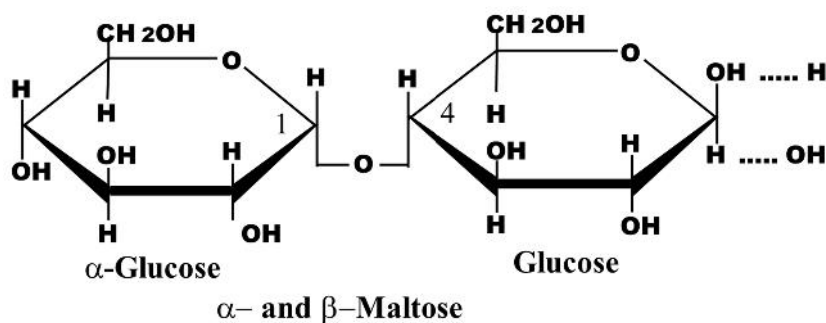
Lactose is a reducing disaccharide found only in milk.

It is made up of galactose at the non-reducing end and glucose at the reducing end.

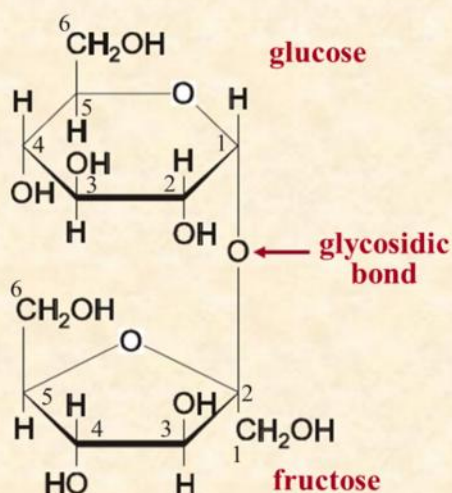


Maltose (malt sugar):

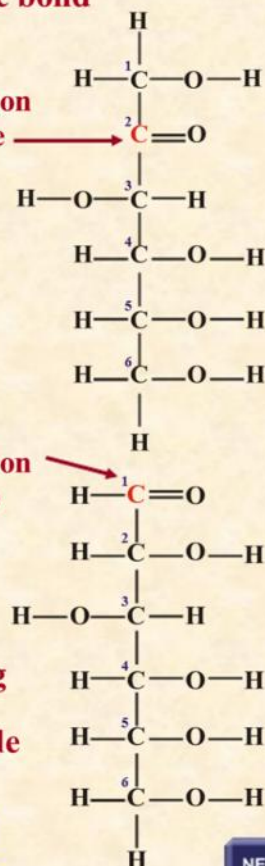
Maltose is a disaccharide made up of two glucose residue joined by a glycosidic linkage between C-1 of one glucose residue and C-4 of the other. The anomeric carbon atom of the second glucose is free and therefore maltose is a reducing sugar.



Sucrose is formed when glucose forms a glycosidic bond with fructose



The anomeric carbon atom for fructose is carbon 2



The anomeric carbon atom for glucose is carbon 1

As both the anomeric carbon atoms are involved in forming the glycosidic bond when glucose and fructose join, there are no potentially free anomeric carbon atoms available to reduce Benedict's solution

SUCROSE IS A NON-REDUCING SUGAR

NEXT

Sucrose, a sugar of commercial importance, is widely distributed in higher plants. Sugarcane and sugar beet are the sole commercial sources. It is made up of glucose and fructose. The anomeric carbon atom of glucose (C-1) and fructose (C-2) are involved in linkage and is therefore a non-reducing disaccharide. Sucrose is a major intermediate product of photosynthesis and it is the principal form in which sugar is transported from the leaves to other portions of plants via their vascular systems.

Invert sugar

The hydrolysis of sucrose when followed Polarimetrically the optical rotation changes from positive (dextro-) to negative (levo-). The dextrorotatory sucrose on hydrolysis yield levorotatory mixture of glucose and fructose. The levorotation is due to the presence of fructose

which is by itself more levorotatory (-92) than dextrorotatory glucose (+52.2). This phenomenon is called inversion and the mixture of glucose and fructose is called invert sugar. This reaction is catalysed by the enzyme invertase. Invert sugar is sweeter than sucrose. Honey contains plenty of invert sugar and therefore is very sweet.

Polysaccharides

Polysaccharides are large polymers of the monosaccharides. Unlike monosaccharides and disaccharides, polysaccharides are either insoluble or form colloidal suspensions. The polysaccharides found in nature either serve a structural function (structural polysaccharides) or play a role as a stored form of energy (storage polysaccharides).

Storage polysaccharides (digestible polysaccharides)

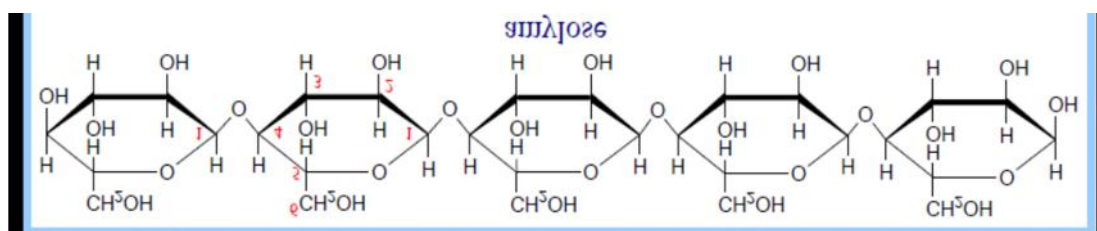
The principal storage polysaccharides are STARCH AND GLYCOGEN. Starch is a polymer of alpha glucose and is, in fact, a mixture of two different polysaccharides – AMYLOSE AND AMYLOPECTIN

Starch

The principal food-reserve polysaccharide in the plant kingdom is starch. It forms the major source of carbohydrate in the human diet. Starch has been found in some protozoa, bacteria and algae. But the major source is plants where it occurs in the seeds, fruits, leaves, tubers and bulbs in varying amount from a few percent to over 74%. Starch is an alpha-glucan that has structurally distinct components called amylose and amylopectin. A third component referred as the intermediate fraction has also been identified in some starches. Starch molecules are organized into quasicrystalline macromolecular aggregates called granules. The shape of the granules are characteristics of the source of the starch. The two components, amylose and amylopectin, vary in amount among the different sources from less than 2% of amylose in waxy rice or waxy maize to about 80% amylose in amylo maize. The majority of starches contain 15 to 35% of amylose.



AMYLOSE



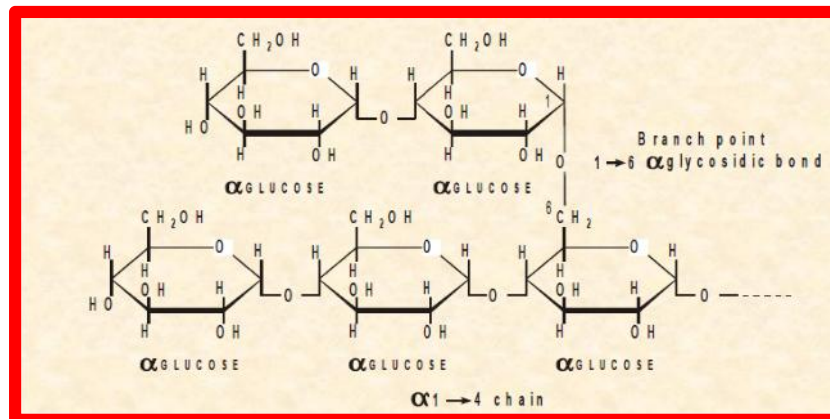
Amylose is formed by a series of condensation reactions that bond alpha glucose molecules together into a long chain forming many glycosidic bonds

Amylose is made up of D-glucose units linked mostly in a linear way by 1-4 linkages

It has a molecular weight of 150,000 to 1,000,000 depending on its biological origin. It consists of a mixture of linear molecules with limited, long-chain branching involving 1-6 Linkages. Amylose gives a characteristic blue color with iodine due to the ability of the iodine to occupy a position in the interior of a helical coil of glucose units

Amylopectin

Amylopectin consists of a straight chain of alpha glucose units with branch points occurring at approximately every twelfth glucose unit along the straight chain. The branch points form when carbon 6 of a glucose molecule in the straight chain forms a glycosidic bond with carbon 1 of a glucose molecule positioned above the chain.



This highly branched amylopectin molecule is wrapped around the amylose to make up the final starch molecule. This large insoluble molecule with branch points that allow for easy access for enzymes when breaking down the molecule, makes starch an ideal food storage compound. Amylopectin is a branched, water-insoluble polymer comprised of thousands of D-glucose residues. It contains 94-96% 1-4 and 4-6% 1-6 linkages. The molecular weight of amylopectin is in the order of $10^7 - 10^8$. The amylopectin molecule is 100 - 150 A in diameter and 1200-4000 A long.

REACTION BETWEEN STARCH AND IODINE SOLUTION

When iodine solution is added to a suspension of starch, the iodine molecules pack inside the amylose helix to give a blue-black colour

When iodine reacts with the starch in a piece of bread, the bread itself develops the blue-black colour

N.B. Iodine is virtually insoluble in water - 'Iodine Solution' is really iodine dissolved in an aqueous solution of Potassium Iodide (KI)

NEXT

GLYCOGEN

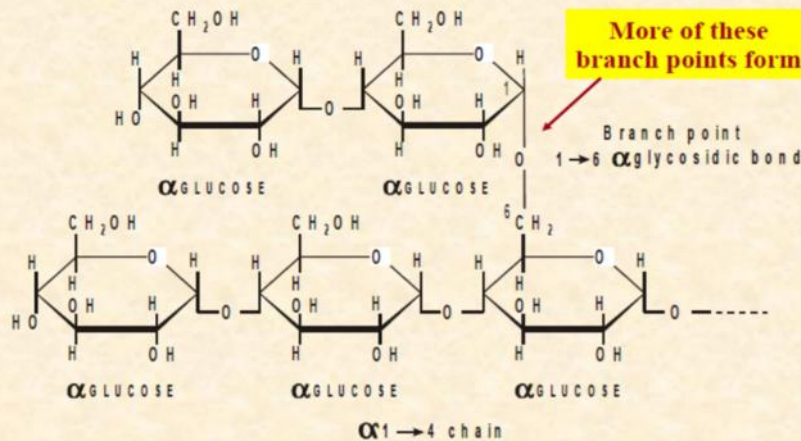
GLUCOSE IS STORED AS GLYCOGEN IN LARGE AMOUNTS IN BOTH THE LIVER AND SKELETAL MUSCLES



GLYCOGEN

Glycogen is often referred to as animal starch

Glycogen has the same overall structure as amylopectin but there is significantly more branching in this molecule



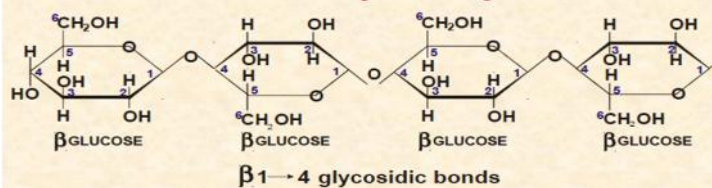
Inulin

Inulin is a non-digestible fructosyl oligosaccharide found naturally in more than 36000 types of plants. It is a storage polysaccharide found in onion, garlic, chicory, artichoke, asparagus, banana, wheat and rye. It consists of mainly, if not exclusively, of - 2->1 fructosyl-fructose links. A starting glucose moiety can be present, but is not necessary. Inulin is a soluble fibre that helps maintain normal bowel function, decreases constipation, lowers cholesterol and triglycerides. It is used for fat replacement and fibre enrichment in processed foods

STRUCTURAL POYSACCHARIDES (indigestible polysaccharides)

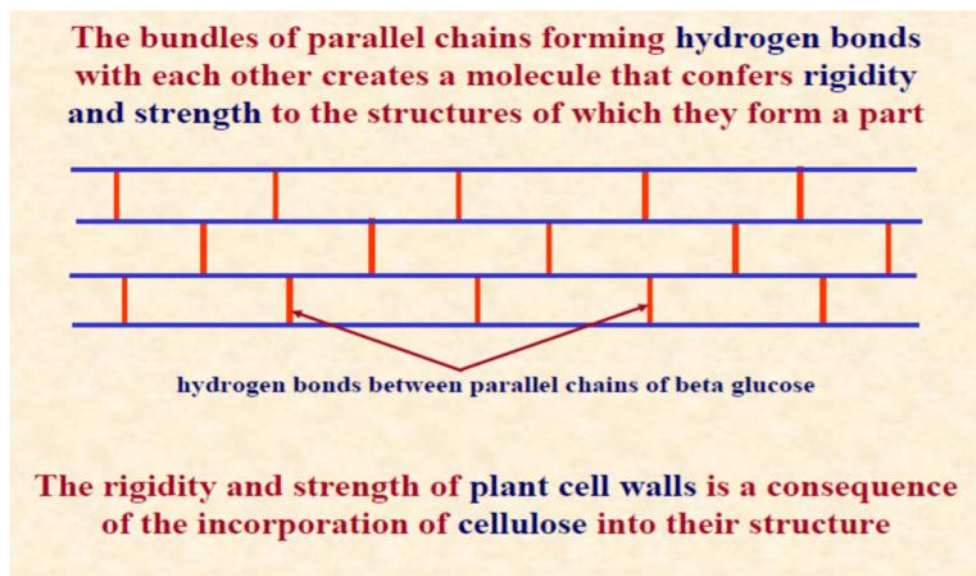
Cellulose is one of the most important structural polysaccharides as it is the major component of plant cell walls

Cellulose is a polymer of beta glucose units where each glucose molecule is inverted with respect to its neighbour



The orientation of the beta glucose units places many hydroxyl (OH) groups on each side of the molecule

Many parallel chains of beta glucose units form and each chain forms hydrogen bonds between the OH groups of adjacent chains



Cellulose is the most abundant organic substance found in nature. It is the principal constituent of cell walls in higher plants. It occurs in almost pure form (98%) in cotton fibres and to a lesser extent in flax (80%), jute (60-70%), wood (40-50%) and cereal straws (30-43%). It is linear, unbranched homoglycan of 10,000 to 15,000 D-glucose units joined by 1-4 linkages. The structure of cellulose can be represented as a series of glucopyranose rings in the chair conformation.

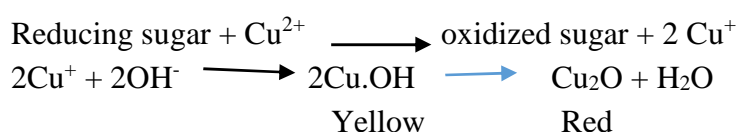
Pectin- It is in fruits of many plants. The constituent monosaccharide is -D – galactouronic acid

Chitin- Most abundant in nature after cellulose, found in fungi and anthropods. The constituent monosaccharides are N- Acetyl- D- glucosamine. It is non- reducing sugar

Properties of carbohydrate

Monosaccharides

- 1. Reaction with alcohol** – The Glycosidic OH group of mutarotating sugars reacts with alcohol to form and glycosides or acetals. Thus glucose form glucosides and fructose from fructosides
- 2. Reaction with acetic anhydride-** The Glycosidic and alcoholic OH group of monosaccharides and disaccharides react with acetylating agents to form acetate derivatives called esters
- 3. Oxidation with acids-** Only the aldehydes group of sugar is oxidized to produce monocarboxylic acid with bromine water, while with nitric acid both aldoses and ketoses react to form dicarboxylic acid
- 4. Oxidation with metal hydroxides-** Metal hydroxides like copper hydroxide oxidize free aldehydes or keto group of mutarotating monosaccharides and at the same time they themselves reduce to free metal



This sugar is active ingredient in Fehling's, Benedict's and Barfoed's reagent

5. **Reduction**- The sugars undergo reduction with sodium amalgam to form corresponding alcohols. Glucose yields sorbitol and fructose yields mixture of sorbitol and mannitol. With strong acids, it undergo reduction to form levulinic acid.

6. **Reaction with hydrogen cyanide**- (Kiliani synthesis). It forms cyanohydrins

7. Reaction with **alanine**– The aldehydes group of carbohydrate condenses with the amino group of alanine to form Schiff's base.

8. **Reaction with Phenyl hydrazine** – reaction of monosaccharides with phenyl hydrazine yields osazone

9. **Fermentation**- Monosaccharides are readily fermented by yeast to form alcohol

Disaccharides

1. Sucrose- it is dextrorotatory, a non- reducing sugar, does not exhibit mutarotation, does not form osazone and fermentable
2. Lactose- It is dextrorotatory, a reducing sugar, exhibit mutarotation, form osazone and non-fermentable
3. Maltose- It is dextrorotatory, a reducing sugar, exhibit mutarotation, form osazone and fermentable
4. Cellobiose- It is a reducing sugar, exhibit mutarotation

Polysaccharides

1. Starch- It is made up of amylose and amylopectin. Amylose gives blue colour with iodine, amylopectin gives purple with iodine and dextrorotatory,
2. Glycogen- It is a non-reducing sugar, gives red colour with iodine, white powder, fairly stable in hot alkali
3. Cellulose- It gives no colour with iodine, fibrous, tough, white solid
4. Inulin- It is a non-reducing sugar, gives no colour with iodine
- 5) Chitin- It is non-reducing sugar

Physical Properties of Carbohydrates

a) Monosaccharides

- 1) Crystalline compound
- 2) Sweet to taste
- 3) Soluble in water
- 4) Need to be digested before absorbed in blood stream

b) Disaccharides

- 1) Crystalline compound
- 2) Sweet to taste
- 3) Soluble in water
- 4) Need to be digested before absorbed in blood stream

c) Polysaccharides

- 1) Amorphous compound
- 2) Not soluble in water
- 3) No sweet taste
- 4) Form colloidal suspension and need to be digested before absorbed

Reducing property of sugars

Sugars are classified as either reducing or non-reducing depending upon the presence of potentially free aldehyde or keto groups. The reducing property is mainly due to the ability of these sugars to reduce metal ions such as copper or silver to form insoluble cuprous oxide, under alkaline condition



Any carbohydrate which is capable of being oxidized and causes the reduction of other substances without having to be hydrolyzed first is known as reducing sugar. The aldehyde group of aldoses is oxidized to carboxylic acid. This reducing property is the basis for qualitative (Fehling's, Benedict's, Barfoed's tests) and quantitative reactions. All monosaccharides are reducing. In the case of oligosaccharides, if the molecule possesses a free aldehyde or ketone group it belongs to reducing sugar (maltose and lactose). The carbohydrates which are unable to be oxidized and do not reduce other substances are known as non-reducing sugars. If the reducing groups are involved in the formation of glycosidic linkage, the sugar belongs to the non-reducing group (trehalose, sucrose, raffinose and stachyose). The reason that sucrose is a non-reducing sugar is that it has no free aldehyde or keto group. Additionally, its anomeric carbon is not free and can't easily open up its structure to react with other molecules.

Reaction with acids

Monosaccharides are generally stable to hot dilute mineral acids though ketoses are appreciably decomposed by prolonged action. Heating a solution of hexoses in a strong non-oxidising acidic conditions, hydroxyl methyl furfural is formed. The hydroxymethyl furfural from hexose is usually oxidized further to other products. When phenolic compounds such as resorcinol, naphthol or anthrone are added, mixture of coloured compounds are formed. The Molisch test used for detecting carbohydrate in solution is based on this principle. When conc. H_2SO_4 is added slowly to a carbohydrate solution containing naphthol, a pink color is produced at the juncture

Reaction with alkali

Dilute alkali

Sugars in weak alkaline solutions undergo isomerization to form 1,2-enediols followed by the formation of a mixture of sugars.

Strong alkali

Under strong alkaline conditions sugar undergo caramelization reactions