

LECTURE NOTE

On

BCH

By

Prof. (Mrs.) E. A. BALOGUN

CHEMISTRY OF CARBOHYDRATE

Carbohydrate may be defined as polyhydroxy aldehydes or ketones or as substances that yield one of these compounds on hydrolysis. They are widely distributed in plants – cellulose and starch and animals – glucose, glycogen.

Carbohydrates are classified into;

Monosaccharides

Disaccharides

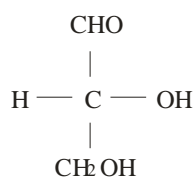
Polysaccharides

Monosaccharides – Are simple sugars that cannot be hydrolyzed into simpler sugars or CHO. Have the formula $(CH_2O)_n$ can be classified into trioses, tetroses, pentoses, hexoses depending on the no of C atoms and as aldoses or ketoses depending on the presence of aldehyde or ketone group

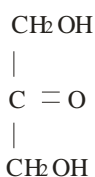
Trioses Glyceraldehyde

All the simple monosaccharides are white crystalline solids that are soluble in water but insoluble in nonpolar solvents. Most have a sweet taste

	Aldose	Ketone
Tetroses	Erythrone	Erythrulose
Pentoses	Ribose	Ribulose
Hexoses	Glucose	fructose



D – Glyceraldehyde



D-hydroxyacetone

Glucose is the most important because all others are converted to it in mammals.

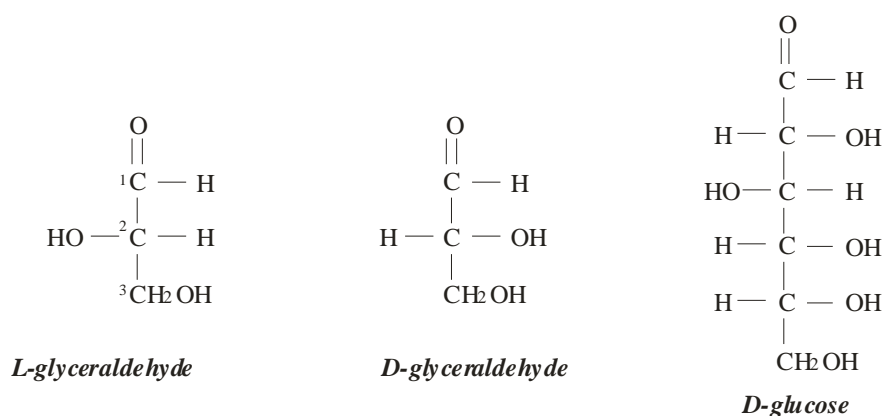
ISOMERISM

Stereoisomers are compounds that have the same structural formula but differ in spatial configuration

Most common ones with monosaccharides or glucose are ;

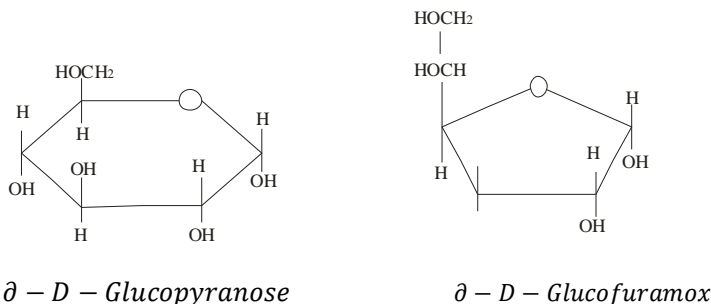
1. **DL Isomer:** This is determined by its special relationship to the parent compound of the CHO family- glyceraldehyde. The orientation of the – H and OH groups around the penultimate C i.e. aC⁵ for glucose determine this. When the OH is to the right it is D series, if it is to the left = L series.

The presence of asymmetric C atoms also consider optical activity on the compound when a beam of plane-polarized light is passed this a solution of an optical isomers it will be rotated other to the right- dextrorotatory (+) or to the left levorotating (–) when equal anti of D & L isomers are present, the resulting mixture has no optical activity, since the achievements of each isomer cancel one another. It is used to be a racemic or DL mixture

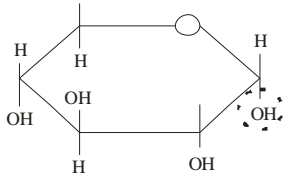


2. **Pyranose and furanose ring structures**

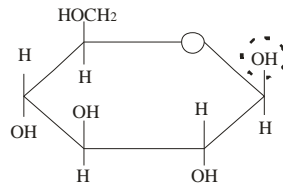
The stable ring structures of monosaccharide are similar to the ring structures of either pyran or furan.



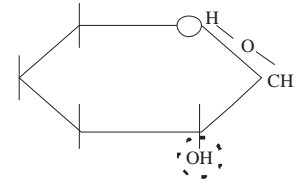
3. **α and β anomers:** When isomerism takes place about position 1 the carbonyl or anomeric C atom, α or β forms of isomers are produced.



α-D-Glycopyranose

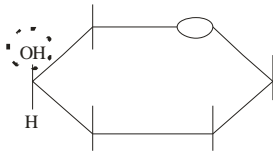


β - D - glycopyranose

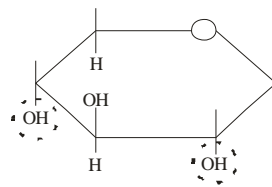


Mutarotation of glucose α and β forms exists making the chain to open

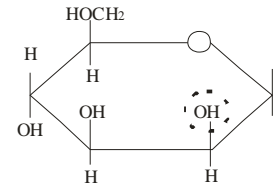
4. **Epimers:** isomers differing as a result of variation in configuration of the -OH and H on A atoms 2, 3, and 4 of glucose are known as epimers. Mannose differ from glucose in C 2 while galactose in C4.



α-D-Galactose



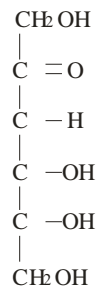
Glucose



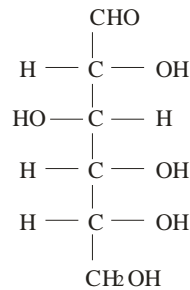
α-D-Mannose

5. **Aldose - Ketose isomerism:** - Aldose sugar has an aldehyde group in position the anomeric C while ketose sugars keto group in equation 2.

e.g.



D-fructose (ketose)



D-glucose

Hexoses of physiological

Glucose – fruit juices, starch, cane sugar, maltose, Lachine, forbid sugar

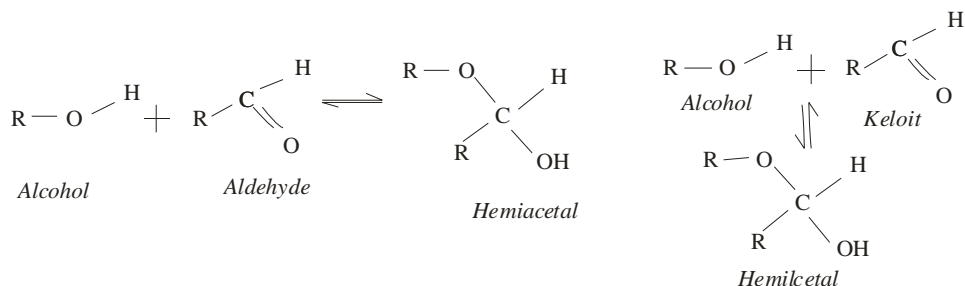
Fructose- fruit juices, honey, hydrolysis of cane sugar

Gala chine – hydrolysis of lactose change to glucose in the lactose also a constituting glycolyds, glycopotium

Maltose- hydrolysis of manners and gums-consistent of glycoprotein

Properties of Monosacchandes:

1. when monosacchandes react with alcohol, hemketal or hemacetal are formed.



2. *Glycosides formation:* Formed by Condensation between the hydroxyl gp of the anomeric carbon of a monosacchande and a second compound that may or may not be another monosacchande. They form glycosides or acetals. Glucose forms glucosides, galactine – galactoside the bond between the 2 sugars is called Pentoses – Ribose, Ribulose, Arabinose, Xylulone etc Hexoses – Glucose, Fructose, Galactine, Manmore.

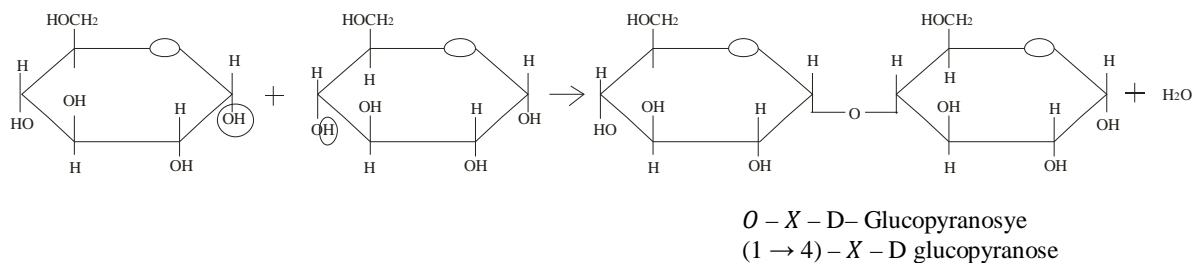
Glycosidic bond, Glycosides are found in many drugs and spices. Caidacglycosides, antibiotics such as streptonyan are very input in medicine.

3. *Ester Formation:* e.g. When X – D – glucopyranoside is heated with acetic anhydride all the hydroxyl functions are acetylated to yield the penta – O – acetyl glucose. Important ones are phosphate esters – when CHO react with ATP in the presence of appropriate enzyme Glucine + ATP = GbP.

4. *Oxidation:* Aldoses are oxidized at the ealdehydric C atom by weak oxidizing agent or specific enzymes to form corresponding sugar acids or carboxylic acies e.g. glucore form gluconic acid oxidized at c₁. If stronger oxidizy agent is used (e.g. HN₀3) aldane acids are formed – glucose form glucaric acide. When oxidized at c₁ and c₆ It can further form glucuronic acid when oxidijed at c₆ by enzyme.

5.*Disacchande formation:* Condensation of 2 monosacchandes give a disacchande while H₂O is eliminated .

Glucose + Glucose = Maltose



6. *Reduction:* Monosaccharides may be reduced to their corresponding alcohols by reducing agents such as sodium amalgam or enzymes, Glucose yields sorbitol, mannose – mannitol.

7. *Reducing sugar:* Sugars are classified as reducing or non reducing sugars. They act as reducing agents because free or potentially free aldehyde and ketone groups are present in the molecule. They reduce metal was such as Cu, Ag in allcaho solution.

Benedict solution of refilling solution is the reagent for defecting reducing sugars. They cu^{2t} α reduced to cu^f forming a brick red precipitate.

8. *Action of Acids and Bases:* Monosace are stable to hot dilute mineral acides conc acids came dehychation of sugars to yield furfurals. Furfurals condense with phenols e.g. orcenol to give characteristic cilored products often used for colorimetric analysis of sugars.

b. Dilute aqueous bases at room temp cause rearrangement about the anomie C and its adjacent C atom. At high temp they undergo further rearrangement or polymerization.

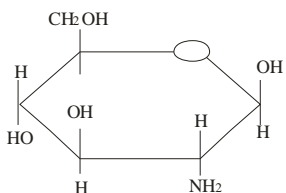
Formation of phenylosazones: Monosacchades in slightly acid solution at 1000C reat with excess phenylhydrgine to form phenylosazones which are insoluble in water and are easily crystallized. Glu, Fruc and Manna form the see osazone but galactine form a deft crystal i.e. used to identify galactine.

Derivatives of Monosacchandees:

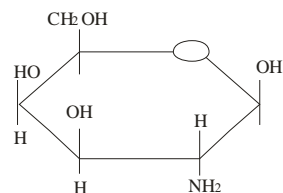
1. *Deoxy sugars:* Are throne in which a hydrocyl gp attached to the ring structure has been replaced by a H gp e.g. DNA.

2. *Lodo Compd:* An aldose heated with conic hydriodic acid (H1) loses all of its oxygen and is converted unto an lodo compd. (glucose to iodohepane $C_6 H_{12} O_6 f Hi \rightarrow C_6 H_{13}^1$

3. *Amino sugars* e.g. 2 amino sugars of wide distribution are D – glucosamine and D galactosamine in which the OH gp at C atom 2 is replaced by an amino gp



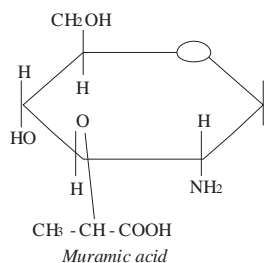
β - D glucosamine



β - D – Galactosamine

Several antibiotics (e.g) erythromycin contain amino sugar

4. *Muramic and Neuramic acid*: They are components of polysaccharides of higher organisms and bacteria cell wall. They are glucosamines linked to 3C acids at the C – 1 or C – 3 positions.



Sugar acids, sugar alcohols, sugar esters are also derivatives of monosaccharides.

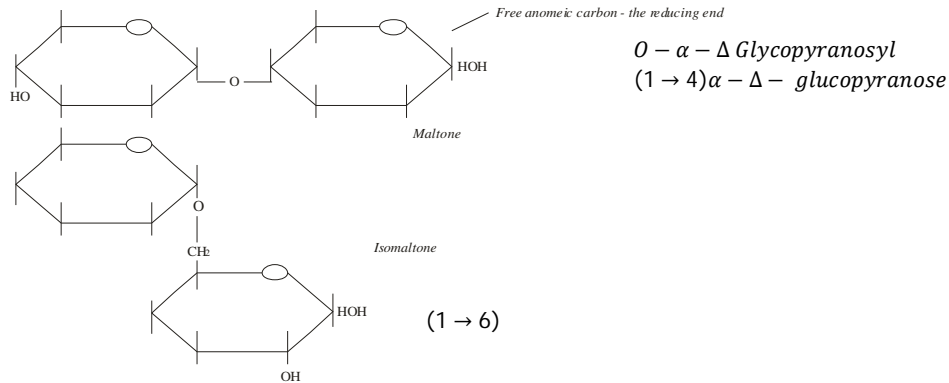
5. *O-methyl derivatives*: The OH gp of monosaccharides can be methylated esp the OH gp on the anomeric C reacts with methanol in the presence of acid to yield methyl glycosides which are acetals.
6. *Honey*: Bees Processing of honey consists of (1) reducing the water content of the nectar (2) hydrolysing the sucrose in nectar to glucose and fructose by the action of the enz invertase (3) producing small amount of gluconic acid from glucose by the action of the enz glucose oxidase. The final product is sucrose 1%, fructose 38%, glucose 31% by wt.

DISSACCHARIDES:

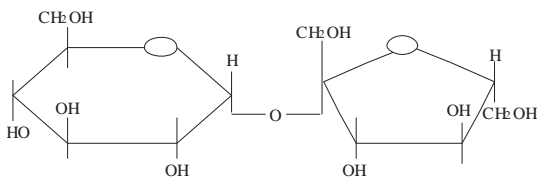
2 Monosacchande musts looked by a glycosidic bond. The most common are succour, maltore and laclose. Each is a reducing agent except succore became of the presence of one free anomeic C atom.

Maltone: Is produced from starch by the action of anylase enz and is a component of malt (a substance obtained by allowing grain (esp barley) to soften in water and germinate, the enz diastase produced during the germination process hydrolye starch to maltose). The glucose units are 1→4 linked.

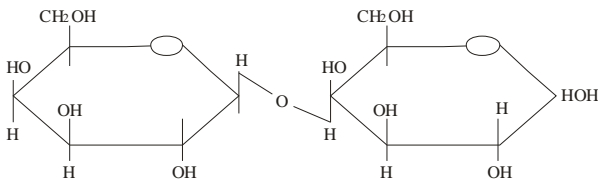
Isomaltore is obtained in the hydrolyen of dextrain but the glycoside bond is 1 → 6 and the configuration is α .



Sucoree: known as table sugar. It is confirmed of fructose and glucose. It is hydrolyzed by the enzyine invertase of science in the intestine. It is non reducing sugar because of the absence of free anomeric C i.e. has no free OH gp both anomie C are substituted and cannot be converted to the aldehydic configuration nor participate in the oxidation – reduction reaction as in other reducing sugars.



Lactose: $O - \beta - D -$ Galactopyranosyl $(1 \rightarrow 4) p - D -$ glucopynanose



Carbohydrate in milk. Hydrolyzed by lactase to galactose and glucose with β (1 \rightarrow 4) link. Has a free anomeric C i.e. 4 is a reducing sugar some that cannot tolerate lactose has diarrhoea and intestinal pain when they consume milk.

Trehalose – is a non reducing disaccharide found in insect blood (hemolymph).

Oligosaccharides: Yield 2 – 10 monosaccharides units on hydrolysis e.g. stachyose is found in peas, beans bran and whole grains they are not affected by digestive enzymes but are metabolized by bacteria. This is the source of the flatulence often accompany consumption of such foods.

POLYSACCHARIDES

Also called glycans. If it contains only one kind of monosaccharide. It is called homopolysaccharides where it contains more than one kind = heteropolysaccharides.

<u>Storage</u>	<u>Polysac</u> : - provide stores of energy
Starch	storage polysac in plants

Exists as <u>α - anylose</u>	and	<u>amylopectin</u>
15 – 20%		50 – 55%

Storage Polysaccharides e.g. Starch in plants, glycogen in animals are deposited in the form of large granules in the cytoplasm of cells.

Starch: Exists in 2 forms α anylose and amylopectin – yields only glucose in hydrolysis. It is the most important food source of CHO and is found in cereals, potatoes legumes and other vegetables α - anylose (15 – 20% of starch) it consists of long unbranched chains (linear) in which all the glucose units are bound in α (1 \rightarrow 4) linkages it is poorly soluble in water. It reacts with iodine to give a blue color.

Amylopectin: Is a highly branched chain of glucose units. The backbone glycoside linkage is α (1 \rightarrow 4) but the branch points are α (1 \rightarrow 6) linkages. Its reaction with iodine to produce a red violet color.

Anylose may be hydrolyzed by α amylase which is present in pancreatic juice saliva participate in the digestion of starch in the GIT it hydrolyses it to glucose and maltose Amylase may be hydrolyzed by α - amylase an enzyme present in malt.

Amylopectin is also hydrolyzed by α and α amylases. The intermediate Polysaccharide formed during amylase action is called DEXTRIN starch is stored in plants in the form of

granules in the stroma of plastids of 2 types – the chloroplasts (where photosynthesis takes place) and amyloplasts that are specialised starch accumulation bodies. When the starch is to be mobilized & used by the plant it is split into its monosaccharide by starch phosphorylase (1 → 4) cleavase for form GIP in amylopectin the (1 → 6) bond is attacked by α (1 → 6) glucosidase → to give GIP.

Glycogen: It is a polysaccharide of glucose an α (1 → 4) (1 → 6) linkages. Major form of storage polysaccharide in animals. It is found mainly in the liver and skeletal muscle it yields a red violet colour with iodine. It can be hydrolysed by both α and β amylases yields glucose and maltose and by glycogen phosphorylase to release glucose 1 – P. It is non reducing and highly branched like amylopectin.

Dextrans: They are α (1 → 6) linked polysaccharides of D – glucose with branched chains found in yeast and bacteria. The repeating unit is isomaltose Gluc α 1 → 6 Glucose. The branch points may be 1 → 2, 1 → 3, 1 → 4 in various species.

Bacteria growing on the surface of teeth produce accumulation of dextrans an inpt composed of dental plaque. Bacterial dextrans are also used as support medium in column chromatography e.g. Sephadex, Biogel etc.

Fructans: Cont. D – fructose units.

Inulins: Starch found in tubers and roots of dahlias, dandelions etc. It is a fructosan.

STRUCTURAL POLYSACCHARIDES

Cellulose: It is the most abundant natural polymer in the world. Found in cell walls of plants it provides physical structure and strength. Wood and bark of trees are formed from cellulose and lignin. Cotton is pure cellulose. Cellulose acetates are used in dresses etc.

It is a linear homopolymer of D – glucose units linked by α (1 → 4) glycosidic bonds strengthened by H bonds. It is resistant to hydrolysis whether by acid or amylases in GIT most animals including humans cannot digest it because of the hydrolase that attacks the α linkage but ruminant animals because of the bacteria living in their rumen which secrete cellulase a α – glucosidase hydrolyze it.

Cellulose gives no color with iodine and is not soluble in ordinary solvents strong acid can give glucose but partial hydrolysis yields cellobiose. It is an important source of bulk in the diet.

Chitin:- Similar to cellulose in function and viscous – is a viscous solution of cellulose used in making fibres for cloth structure. It is found in cell walls of fungi and exoskeletons of

crustaceans, insects and spiders. Consist of N – acetyl – glucosamine units joined by α (1 → 4) glycosidic linkages.

Rhamnogalacturonan II is the most complex polysac on earth and is found in red wine court II driff sugar monomers.

Agarose: Polysac isolated fun marne red algae consist of agarose and agaropection Agarose is a chain of alternating D- galactore and 3, 6 – an hydro – C – galaclose with side chains of 6 – methyl D – galaclose.

Agaropectum is similar but cont sulphate ester side chains and D – glucuronic acid.

Aganose and aganopectin readily form gels (used as Sephedex) in purification of macrounilec.

Mucopolysacchandes: (Glycosaminoglycans)

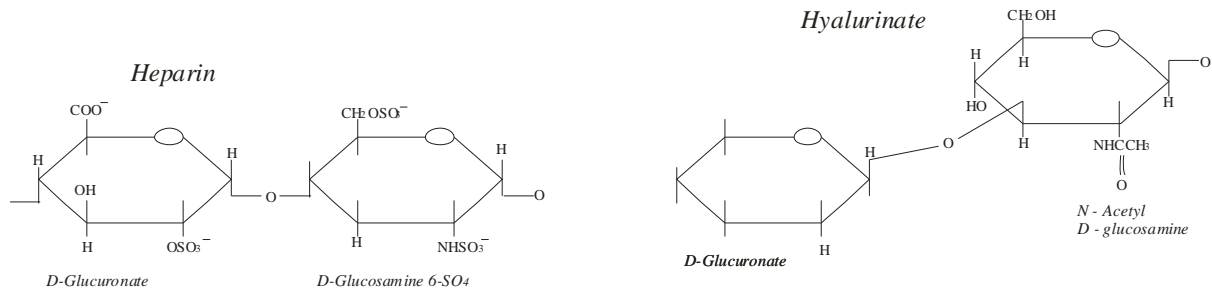
They are heteropolysarchardes. Consist of chains of complex CHO characterised by their contentof amino sugars and uromic acids.

The acid mucopolysacchardes – hyaluronic and, chondronlin sulfales and heparin are found in the connecture tissues of aminds. They gave connective tissues toughness and flecibility.

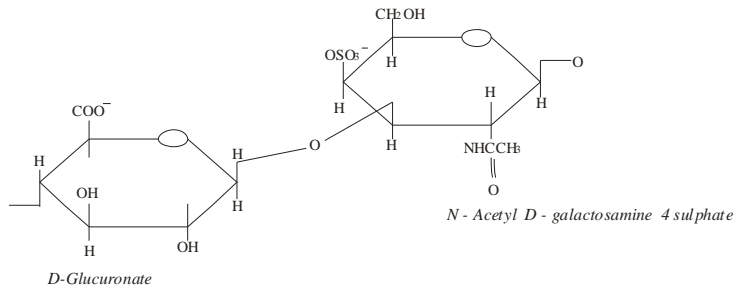
HJeparum – a natural anticoagulant substance the disacchesde contain D – Glucuronate 2 surfate and D – glucosamme 6 – sulphate. It institutes bed clothing.

Hyaluronate are input components of the intreous humour in the eye and synovial fluid the lubricant of the joints in the body. The disacchanda count D – Glucononate ed N – Acetyl/D- glucosamine.

The chondrontuns and Keratan sulphate and found in tendious cartilage and other connecture tissues e.g. chordiunton 4 sulfate count D – Glucumate and N – acetyl D – galactosamme – 4 sulfate. But if chondinlin 6 – supphate subst 6 for 4.



Chondiontion 4 – sulphate



Glycoproteins (mucoproteins) occurrence in many different situations in fluids mucus secretions and tissues including the cell membranes. They are proteins containing carbohydrates in varying amounts. They do not contain uronic acids unlike glycosaminoglycans but contain acetyl + methyl neurone and sialic acids.

Polysaccharides provide strength and rigidity to bacterial cell walls which provide protection for the cellular contents.

Peptidoglycan is the polysaccharide of bacterial cell walls. The backbone is a α (1 \rightarrow 4) linked polymer of alternating N – acetylglucosamine and N – acetylmuramic acid units. It is joined to a tetrapeptide L-Ala-D-Glu-L-Lys-D-Ala. Gram positive bacteria have a thick cell wall but gram negative is thinner.

BIOCHEMISTRY

Biochemistry is the study of biology at the molecular level.

- It is concerned with the molecules that make up the structure of cells and organs
- And also with the function of molecules in carrying out the needs of the cells and organs.
- Now biochem is making an impact on medicine – (i) assays for enz. Activities now play an important role in clinical diagnosis and also a basis for the design of drugs
- Most of the questions that remained unsolved for a long time can now be solved by biochem e.g.
 1. How does a cell give rise to cells as different as those in muscle brain, and the liver
 2. How is the growth of cells controlled?
 3. What is the mechanism of memory
 4. What are the causes of cancer etc.

All these have been solved by Biochemistry today.

Introduction: CHO are widely distributed in both plant and animal tissues

- In plants – cellulose and starch due to photosynthesis

- In animals – glucose and glycogen

Chemistry of Carbohydrates:

Definition: CHO may be defined as polyhydroxy aldehydes or ketones or as substances that yield one of these compounds on hydrolysis

classified into :

- Monosaccharides
- Oligosaccharides
- Polysaccharides

Monosaccharides – formula $C_nH_{2n}O_n$ (n = m or n – 1) simple sugars that cannot be hydrolyzed into smaller units trioses, tetroses, pentoses, hexoses e.g. glyceraldehyde; dihydroxyacetone Oligosaccharides – are hydrolysable polymers of monosaccharides that contain 2 -6 molecules of simple sugars.

Polysaccharides: long chains or polymers of monosaccharides that may be either linear or branched in structure. Tasteless, insoluble compounds with long molecular weight.

Properties of monosaccharides:

1. **Mutarotation:** This is a property exhibited by the hemiacetal and ketal forms of sugars that are free to form the open chain sugar e.g. when glucose is exposed to dilute alkali for several hours the mixture contains both fructose and mannose this is due to enolization of these sugars in the presence of alkali. At higher concentration of alkali; monosaccharides are unstable and undergo oxidation degradation and polymerization.

They are stable in dilute mineral acids even on heating. But when also hexoses are heated with strong mineral acids they are dehydrated and hydroxymethyl furfural is formed.

This dehydration reaction is the basis of cellular qualitative tests for sugars since the furfurals can be reacted with α -naphthol and other aromatic compounds to form characteristic colored products.

2. **Reducing Sugars:** Sugars

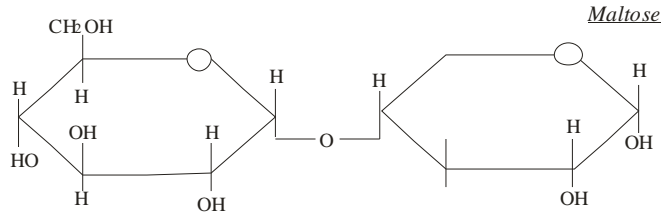
- reducing
- non reducing

Act as Reducing agents because free or potentially free aldehyde and ketone groups are present – the molecule.

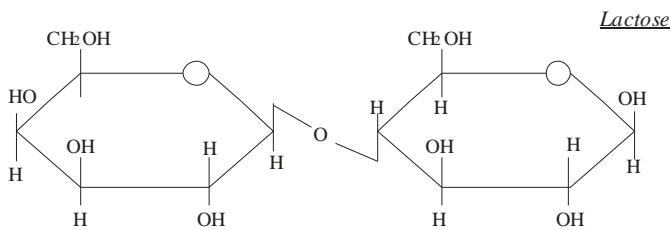
Reduce – metal ions (Cu, Ag in alkaline solution).

Benedict's solution is the reagent for detecting reducing sugars – the Cu^{2+} is reduced to Cu^+ forming a precipitate.

Sucrose is neither a hemiacetal nor hemiketal. It does not undergo mutarotation, it does not react with phenylhydrazine to form osazones and it does not act as a reducing sugar.



$O - \alpha - D - \text{Glucopyranose} (1 \rightarrow 4)$
 $\alpha - D - \text{glucopyranoside}$



$O - \beta - D - \text{Galactopyranosyl} - (1 \rightarrow 4)$
 $\beta - D - \text{glucopyranoside}$

Trisaccharides – e.g. Raffinose- cont. Fructose, glucose and galactose.

Polysaccharides: - Most of the CHO found in nature occur as polysaccharides of high mol wt. On complete hydrolysis with acid or specific enzymes. They yield monosaccharide and/or single monosaccharide derivatives. Glucose is the most prevalent, although polysaccharides of mannose, fructose and galactose are also common.

Polysaccharide differs in the nature of the monosaccharide units in the length of their chains and in the degree of branching.

There are two types

1. Homopolysaccharides e.g. starch consisting of only a single type of monomeric unit
2. Heteropolysaccharides- cont. 2 or more different monomeric units e.g. hyaluronic acid cont. D glucuronic acid and N- acetyl glucosamine

Storage Polysacc: - e.g. starches in plants glycogen in animals are deposited in the form of large granules in the cytoplasm of cells.

Starch: -- It is a homopolymer called a glucose or glucan found in cereals, potatoes & other vegetables. The 2 chief constituents are α - amylose and amylopectin

α - Amylose: - Not truly soluble in water but forms hydrated micelles, which give a blue color with iodine. It consists of long unbranched chains in which all the glucose units are bound in α linkages.

Amyl pectin is highly branched the backbone glycosidic linkages is α (1 \rightarrow 4), but the branch points are α (1 \rightarrow 6) linkages. It gives a red or red hole colour with iodine. Amylose may be hydrolyzed by α - amylase which is present in pancreatic juice and saliva participates the digestion of starch in the GIT. It hydrolyses it to glucose and maltose. Amylose may be hydrolyzed by β - amylase an enzymes present: - malt.

Amyl pectin is also attacked by the α and β amylases the intermediate polysacc formed during amylase action are called dextrans.

Inulin- starch found in tubers and not of dahlas, dandelions etc, it is fructosan.

Glycogen: - found in animal tissue especially liver and muscle. It is polysaccharides of glucose in α

(1 \rightarrow 4) (1 \rightarrow 6) linkage the branch linkages as same as in amylopectin but it is more highly branched.

It is non reducing and given a red color with iodine.

Other Storage Polysaccharide:-

Dextrans – Glucose units

Linkage – α (1 \rightarrow 6) found in yeast α bacteria they form highly viscous slimy solutions

Fructans – cont D – fructose units

Check small sheet – INULIN etc:

Structural Polysaccharides:-

Cellulose: - Cell walls of plants on hydrolysis with strong acids yields glucose, but partial hydrolysis yields cellobiose. Enzymes cellulases. It gives no color with iodine and is not soluble in ordinary solvents. It consists of straight of β -d- glucopyranose. It is insoluble and consist of β – D – glucopyranose units linked by β (1 \rightarrow 4) bonds to form long st chains strengthened by hydrogen bonds. It cannot be digested by many mammals because of the absence of a hydrolase that attacks the β - linkage. It's an important since of bulk in the diet. In get of herbivores, there are lincolonic that hydrolyses the β linkage.

Mucopolysaccharides

This is used to describe heteropolysaccharides that contain residues of both uronic acid and hexosamine the acidic mucopolysaccharides, hyaluronic acid, the chondroitin surface and

heparin are found in the connection tissues of animals. They give the connective tissues toughness and flexibility.

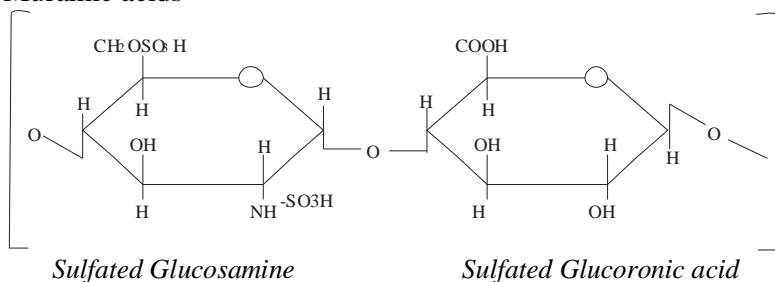
Heparin act as a blood anticoagulant and as an antilipemic agent.

(Other ions of CHO)

Ascorbic acid: - Vitamin C.

Salic acids

Muramic acids



Glycoprotein (Mucoproteins):- Are protein polysaccharide compounds occurring in the tissues especially mucous secretion and fluids. E.g. α 1 and α 2 globulins of plasma. They do not contain uronic the glycosaminoglycans but they contain acetylhexosamines. Hexoses such as mannose or galactose are found, also present. Other e.g. of glycoproteins are

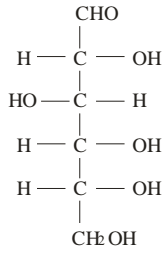
- (1) isoagglutinogens (the blood group substances of the erythrocytes responsible for the major immunologic reactions of blood).
- (2) Hcg and luteinizing hormones.

Quantitative Tests of CHO

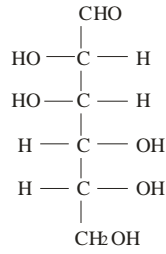
Chitin:- structural polysaccharide in invertebrates –aspect etc consist of N- acetyl- D- glucosamine joined by (1→4) glycoside linkages.

Carbohydrate also occurs in cell membrane as glycoproteins and glycolipids. Also CHO is in lipoprotein as low density lipoproteins (LDL).

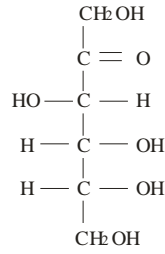
Hexoses Monosac:



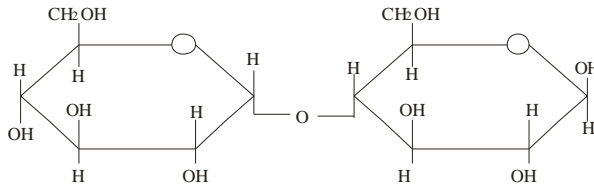
Glucose (aldose)



Mannose (aldose)

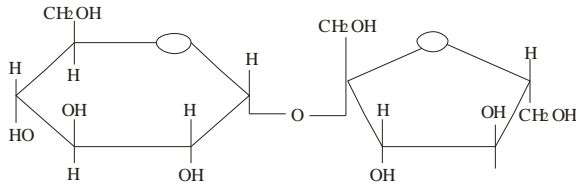
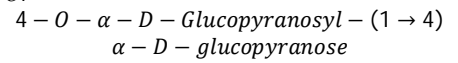


Fructose (ketose)



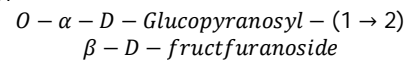
Maltose

Or



Sucrose

Or



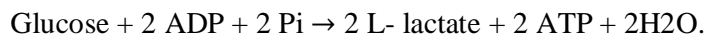
Lactose



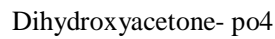
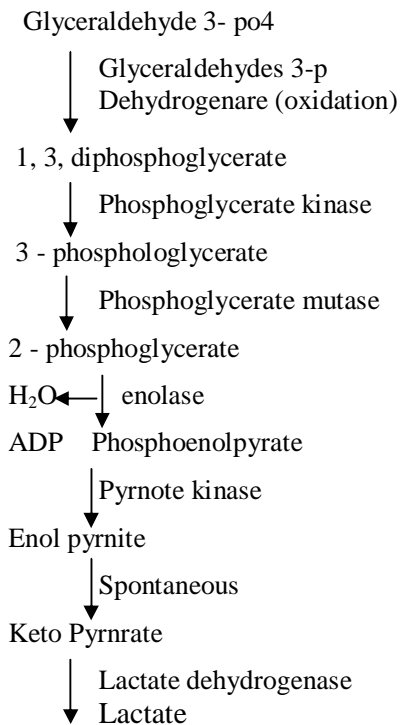
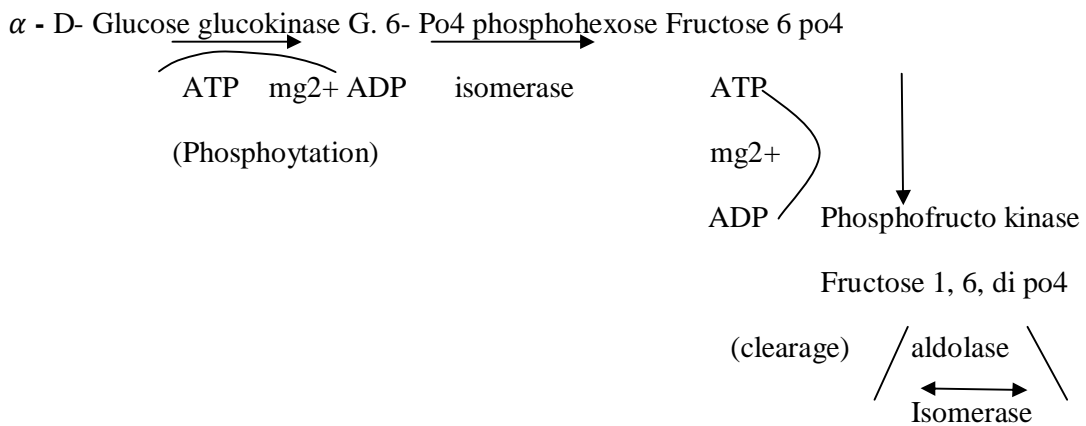
Metabolism of CHO Divided into

1. Glycolysis
2. Glycogenesis
3. Glycogenolysis
4. Oxidation of pyruvate to
5. Hexose monophosphate shunt
6. Gluconeogenesis.

This is the anaerobic oxidation of glucose to lactate in the presence of O_2 , the pathway stops at pyruvic acid intermediate and then proceeds on to the TCA cycle. It occurs in the cytoplasm overall equation outside the units chordia



Sequence of reactions



TCA: - This is the final pathway for the oxidation of glucose, lipids, protein under aerobic condition. Occurs in the unit chindra. It brings about oxidation of oxidation of acetyl residues to CO₂ liberating H equivalents which eventually form water.

CH₃ – CO – S – COA. (Acetyl C OA

Significance: -

1. Oxidation of foodstuffs
2. It is the mechanism by which much of the free energy liberated during the oxidation of CHO etc is made available
3. The intermediate of the cycle are also sources of molecules for anabolic processes in faulty acid, amino acid synthesis & gluconeogenesis