

Chemistry of Carbohydrates

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Competencies

- 1) Define carbohydrates
- 2) Classify carbohydrates with examples of each class
- 3) Describe monosaccharides, disaccharides and polysaccharides as an energy source
- 4) Describe the biological importance of disaccharides with examples
- 5) Describe polysaccharides like glycogen as a storage form in human body with examples
- 6) Describe polysaccharides like glycosaminoglycans as structural elements in the human body
- Differentiate monosaccharides, disaccharides and polysaccharides as an energy source in the human body, with examples



- 9) Explain the importance of resistant starch in diet
- 10) Identify food items with high and low glycemic index
- 11) explain the importance of food items in the diet with high and low glycemic index
- 12) Explain the clinical importance of dextrans

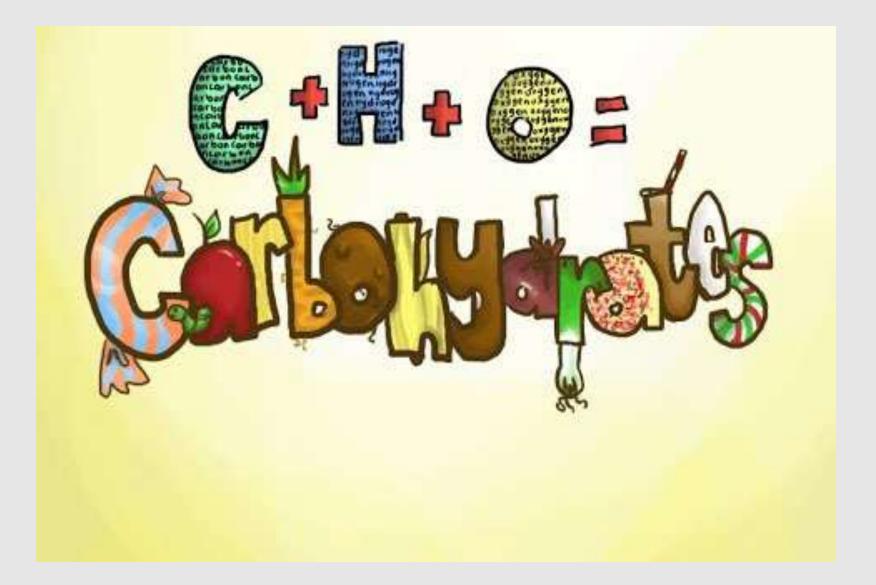


Biomolecule – a general term referring to organic compounds essential to life

 Biochemistry – a study of the compounds and processes associated with living organisms

Definition

- The general molecular formula of carbohydrates is $Cn(H_2O)n$.
- For example, glucose has the molecular formula $C_6H_{12}O_6$.
- CARBOHYDRATES IN GENERAL ARE POLYHYDROXY ALDEHYDES OR KETONES OR COMPOUNDS WHICH YIELD THESE ON HYDROLYSIS.



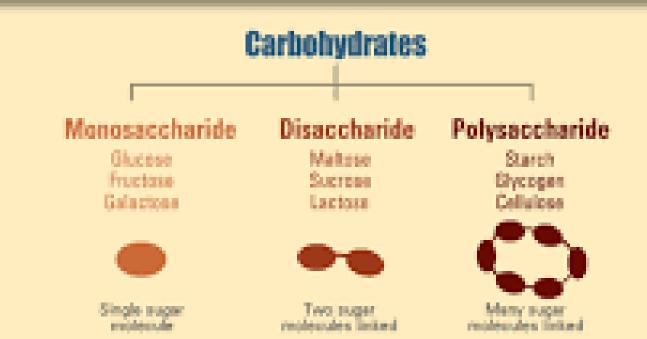
Simple

Simple carbohydrates are found in foods such as fruits, milk, and vegetables

Cake, candy, and other refined sugar products are simple sugars which also provide energy but lack vitamins, minerals, and fiber



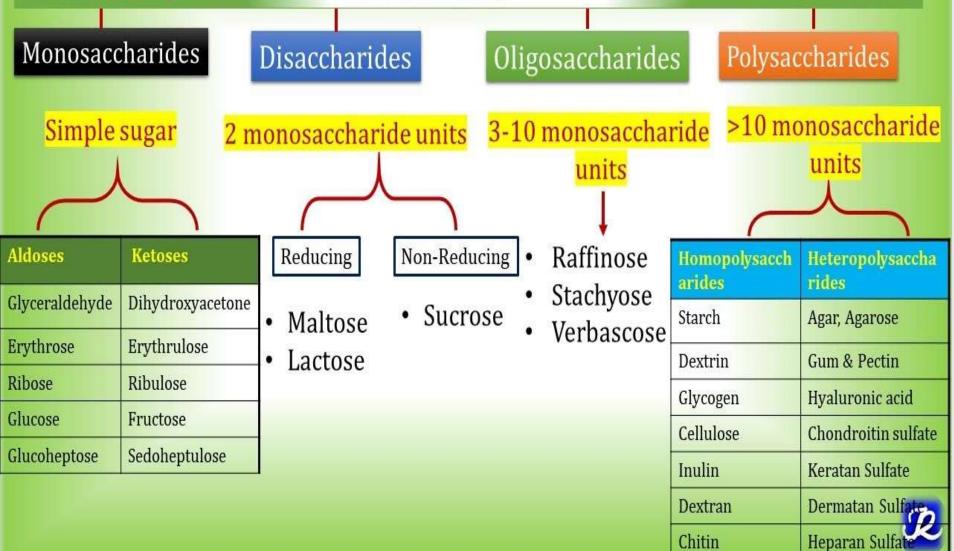
Carbohydrates Classification



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Carbohydrate Chemistry-1

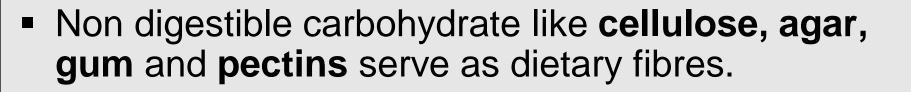
Carbohydrates: Definition, Classification, Functions



IMPORTANT FUNCTIONS OF CARBOHYDRATES

- Carbohydrates are the main sources of energy in the body.
- Brain cells and RBCs are almost wholly dependent on carbohydrates as the energy source.
- Energy production from carbohydrates will be 4 kcal / g.
- Storage from of energy (starch and glycogen)
- Excess carbohydrate is converted as **fat**.
- Riboses and D-oxyriboses are components of nucleic acids and co-enzymes.

- Glycoproteins and glycolipids are components of cell membranes and receptors. They participate in biological transport, cell-cell recognition during developement, activation of growth factors, modulation of the immune system
- Structural basis of many organisms
- ✓ Cellulose of plants
- ✓ exoskeleton of insects
- ✓ cell wall of micro-organisms
- mucopolysaccharides as ground substance in higher organisms.



 Acts as intermediates in the biosynthesis of other basic biochemical entities (fats and proteins)



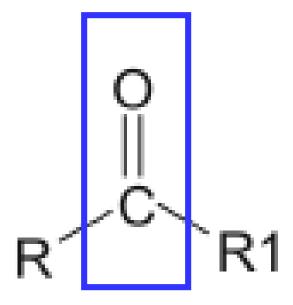
- Carbohydrates are also involved in detoxification e,g, glucuronic acid
- Carbohydrates are utilised as raw material for several industries e.g. paper, plastis, textile, alcohol,etc.

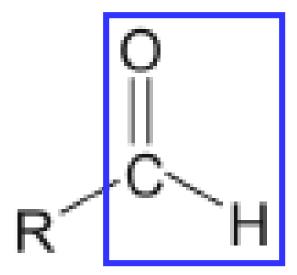
But this is not true due to

- 1. All sugars cannot be represented by this general formula. E.g. Deoxy Ribose $-C_5H_{10}O_4$.
- 2. All compounds having H and O in ratio of 2:1 are not carbohydrates

E.g. Acetic acid $-C_2(H_2O)_2$ Lactic acid $-C_3(H_2O)_3$

Apart from C, H & O, many sugars contain N, S, P etc.
 E.g. Aminosugars, Phosphosugars etc

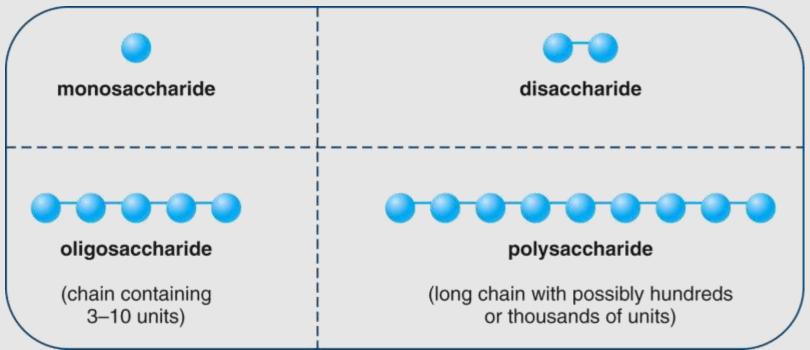




Keto group

Aldehyde group

- **Carbohydrates** are classified according to size:
 - Monosaccharide a single polyhydroxy aldehyde or ketone unit
 - **Disaccharide** composed of two **monosaccharide** units
 - Polysaccharide very long chains of linked monosaccharide units



- Sugars which yield 2 sugar units on hydrolysis. Monosaccharide unit may be the same or different.
- Biologically important disaccharides are
 Sucrose → Glucose + Fructose
 Maltose → Glucose + Glucose
 Lactose → Glucose + Galactose

Depending on whether a disaccharide contains a free functional group or not, classified to

- Reducing disaccharides Lactose, Maltose
- Non-reducing disaccharides Sucrose, Trehalose

Oligosacchrides

- Sugars on hydrolysis yield 3-10 sugar units
- Rhamnose, Raffinose
- Carbohydrate moiety of glycoproteins
- Carbohydrate moiety of Proteoglycans

What are Isomers ?

- Definition: Compounds having the same molecular formula, but differ in chemical and physical properties.
- Phenomenon is called Isomerism.
- 2 Types of Isomerism :
- Structural (Positional)
- Stereo

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• Structural Isomers – Same molecular formula but differ in structure

CH CH₂CH₃

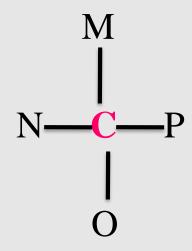
- Eg. C_5H_{12}
- nPentane $CH_3CH_2CH_2CH_2CH_3$

 CH_3

• IsoPentane CH₃



- Optical isomers (Configurational) differ from disposition of various atoms or groups in space around an asymmetric Carbon atom (Chiral center)
- An asymmetric Carbon atom is a Carbon atom the four valences of which is attached to four different atoms or groups of atoms.

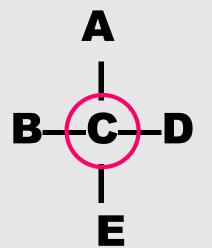


Stereoisomers



Compounds having same structural formula, but differ in spatial configuration are known as stereoisomers.

Asymmetric carbon means that four different groups are attached to the same carbon.



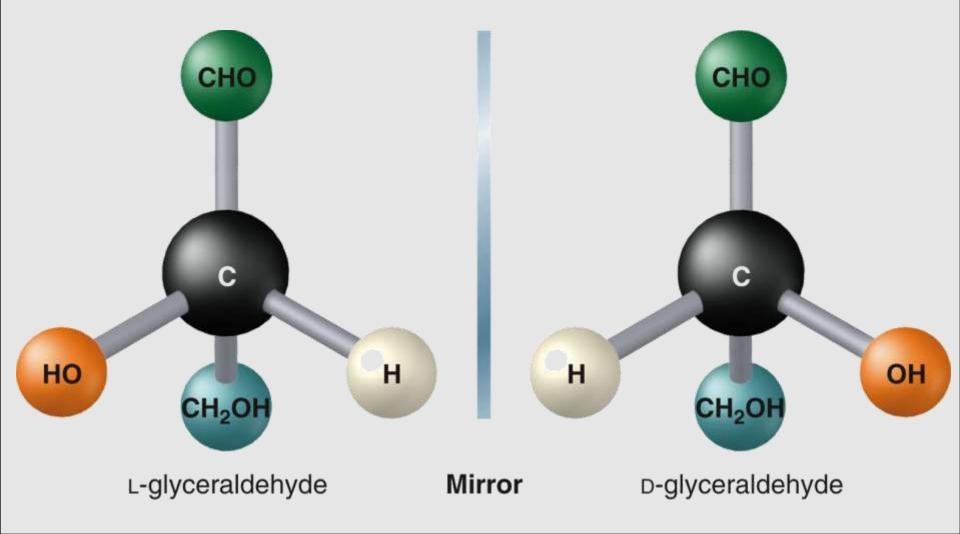


H—C = O
I
I
I
CH2—OH
I
CH2—OH

- D-glyceraldehyde L-glyceraldehyde
- The reference molecule is glyceraldehyde which has a single asymmetric carbon atom.

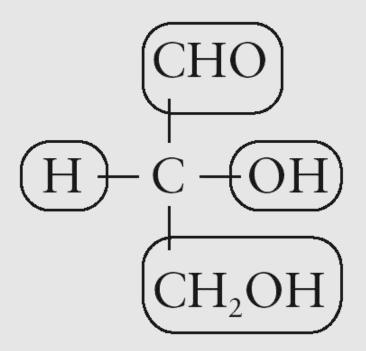
STEREOCHEMISTRY

• Many **carbohydrates** exist as **enantiomers** (stereoisomers that are mirror images).



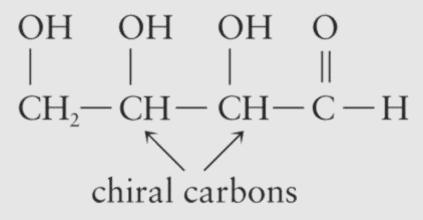
STEREOCHEMISTRY (continued)

- A chiral object cannot be superimposed on its mirror image.
- A chiral carbon is one that has four different groups attached to it.

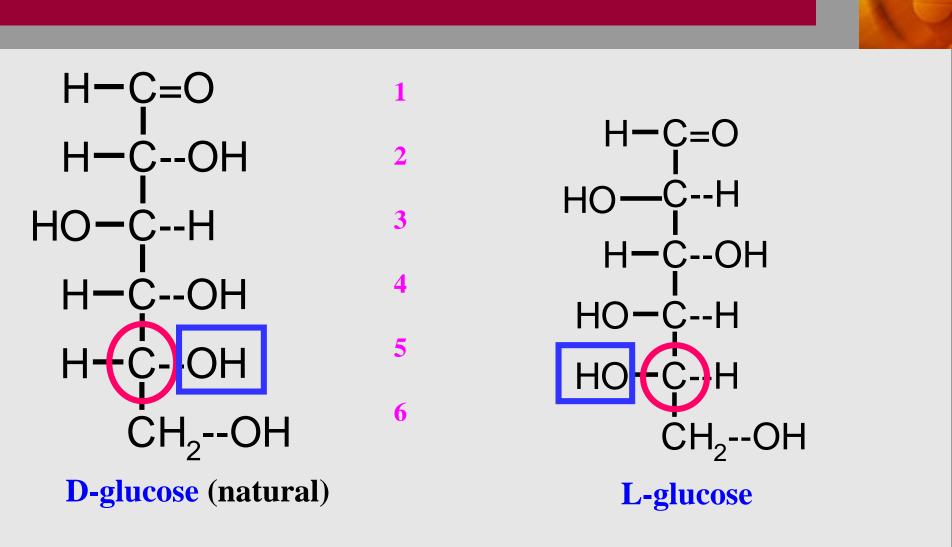


STEREOCHEMISTRY (continued)

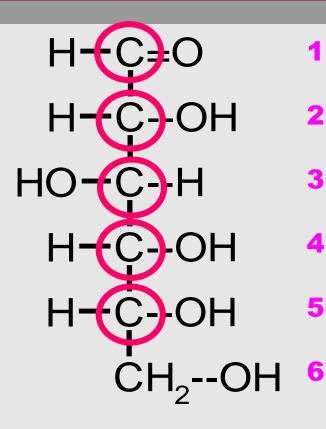
• Compounds can have more than one chiral carbon:



- The maximum number of stereoisomers is 2ⁿ where n= number of chiral carbon atoms.
- Therefore, this compound with two chiral carbon atoms has 2² or 4 stereoisomers.
- The compound on the previous slide with four chiral carbon atoms has 2⁴ or 16 stereoisomers.



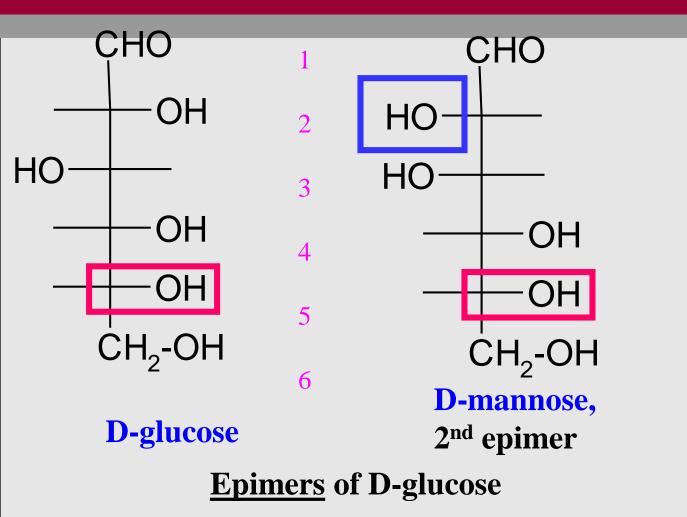
Penultimate (reference) carbon atom

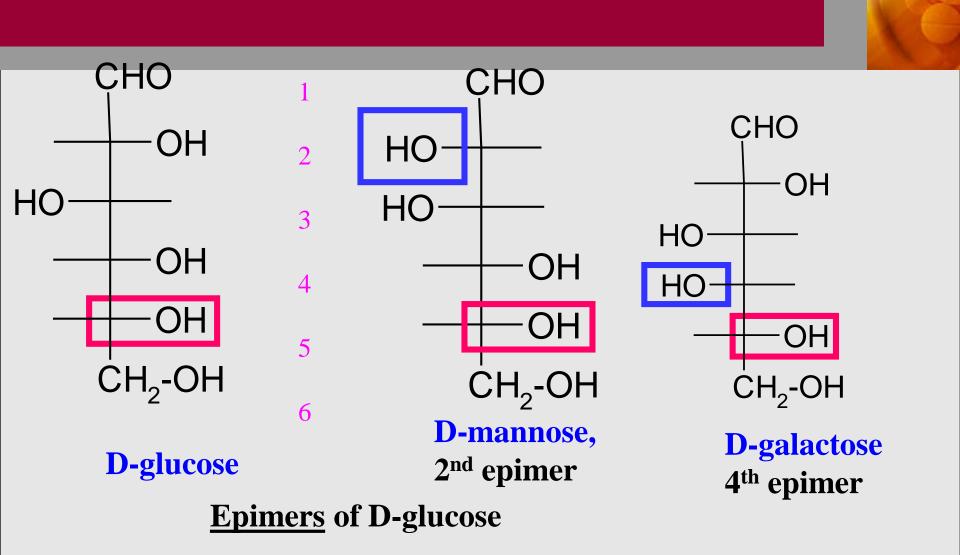


number of possible stereoisomers

formula 2ⁿ where n is the number of asymmetric carbon atoms.

 $2^4 = 16$

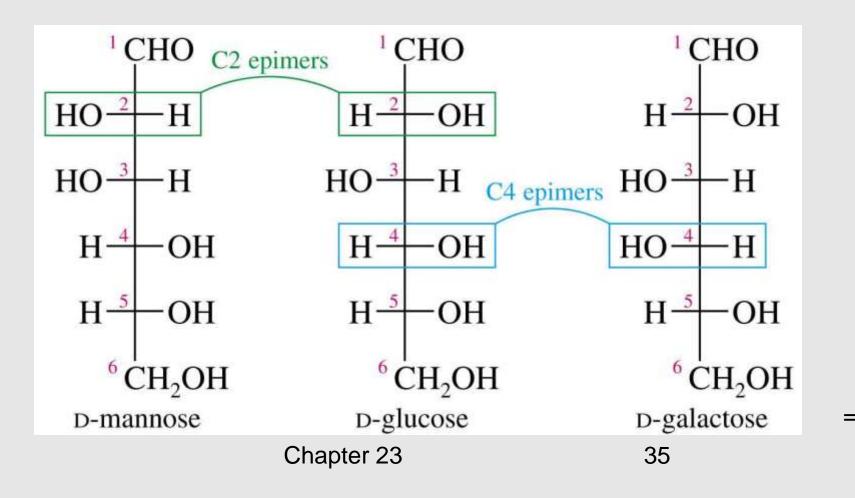




Galactose and mannose are not epimers but diastereo-isomers

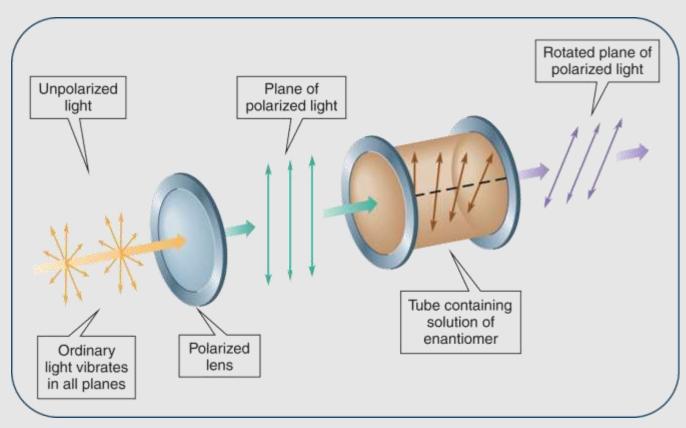
Epimers

Sugars that differ only in their stereochemistry at a single carbon.



ENANTIOMER PROPERTIES

- The physical properties of D and L enantiomers are generally the same.
- D and L enantiomers rotate polarized light in equal, but opposite directions.



ENANTIOMER PROPERTIES (continued)

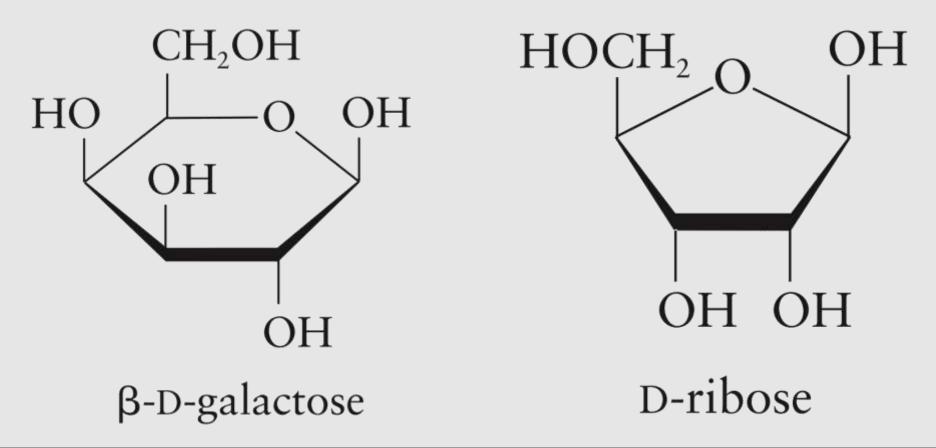
- The enantiomer that rotates polarized light to the left is the levorotatory or (-) enantiomer.
- The enantiomer that rotates it to the right is the dextrorotatory or (+) enantiomer.
- The D and L designations do not represent **dextrorotatory** and **levorotatory**.
- The property of rotating the plane of polarized light is called optical activity, and the molecules with this property are said to be **optically active**.
- Measurements of optical activity are useful for differentiating between **enantiomers**.

ENANTIOMER PROPERTIES (continued)

- In some instances, only the D or L enantiomers are found in nature.
- If both D and L forms are found in nature, they are rarely found together in the same biological system.
- For example:
 - Carbohydrates and amino acids are chiral.
 - Humans can only metabolize the D-isomers of monosaccharides.
 - Most animals are only able to utilize the L-isomers of amino acids to synthesize proteins.

MONOSACCHARIDE REACTIONS

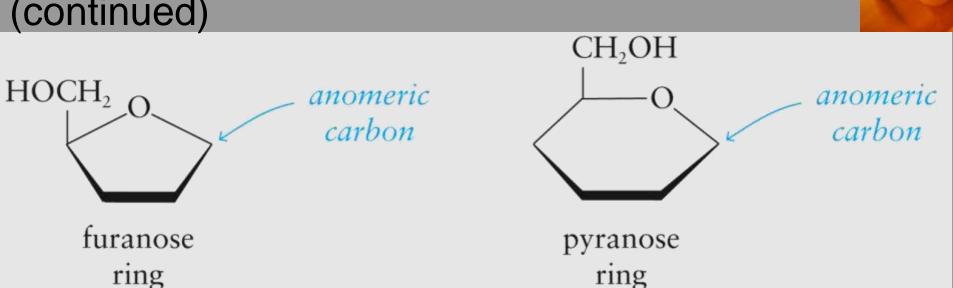
- All **monosaccharides** with at least five carbon atoms exist predominantly as cyclic hemiacetals and hemiketals.
- A **Haworth structure** can be used to depict the threedimensional cyclic **carbohydrate** structures.



CYCLIZATION OF MONOSACCHARIDES

- The open-chain structure is numbered starting at the end closest to the carbonyl carbon atom.
- The alcohol group on the next to the last carbon atom adds to the carbonyl group.
- In the case of glucose, the alcohol group on carbon 5 adds to the aldehyde group on carbon 1 and a pyranose (sixmembered ring containing an oxygen atom) forms.
- In the case of fructose, the alcohol group on carbon 5 adds to the ketone group on carbon 2 and a furanose (fivemembered ring containing an oxygen atom) forms.
- The former carbonyl carbon atom is now chiral and called the anomeric carbon atom.

CYCLIZATION OF **MONOSACCHARIDES** (continued)



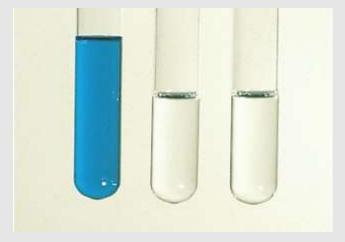
- Because the **anomeric carbon** atom is **chiral**, two possible stereoisomers can be formed during cyclization.
 - An α anomer (-OH on the anomeric carbon pointing down)
 - A β anomer (-OH on the anomeric carbon pointing up)
- Anomers are stereoisomers that differ in the 3-D arrangement of groups at the anomeric carbon of an acetal, ketal, hemiacetal, or hemiketal group.



REACTIONS OF MONOSACCHARIDES

MONOSACCHARIDE REACTIONS (continued)

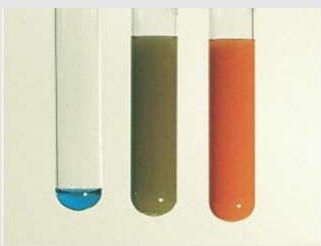
- A reducing sugar can be easily oxidized.
- All monosaccharides are reducing sugars.
- Benedict's reagent tests for reducing sugars: Reducing sugar + Cu²⁺ → oxidized compound + Cu₂O



blue

From left to right, three test tubes containing Benedict's reagent, 0.5% glucose solution, and 2.0% glucose solution

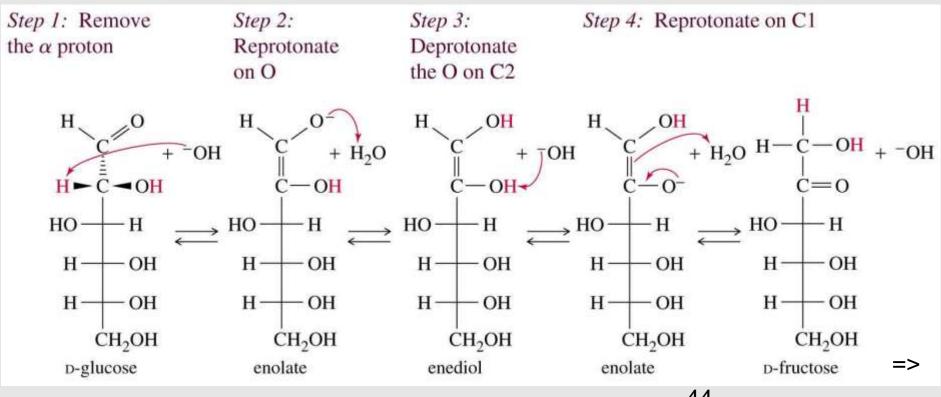
orange-red precipitate



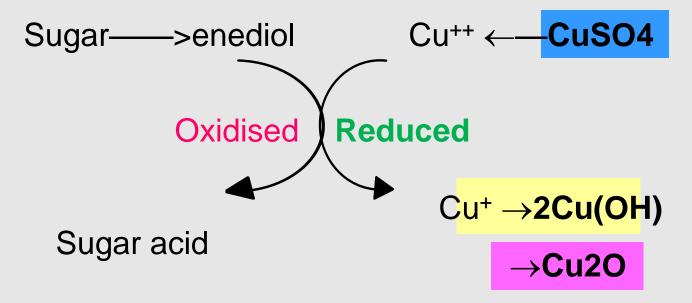
The addition of Benedict's reagent produces colors (due to the red Cu_2O) that indicate the amount of glucose present.

Enediol Formation

In base, the position of the C=O can shift. Chemists use acidic or neutral solutions of sugars to preserve their identity.



Benedict's Reaction

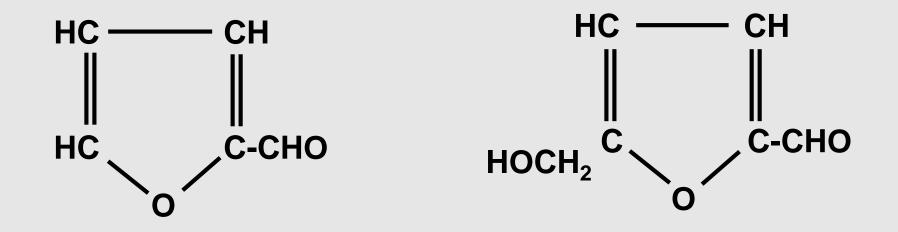


Glucose is a Reducing sugar

Semi-quantitative test

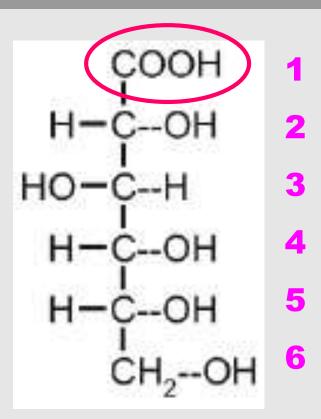
- When treated with strong alkali, sugars are enolised and the double bond will shift from 1:2 to 2:3, 3:4 or 4:5 to form the corresponding enediols and gets fragmented.
- The fragmented molecules will polymerize to form a yellow resinous material called Caramel.

- Dilute acids
 - Aldoses in general are relatively stable. Ketoses degraded.
- Concentrated acids Dehydrated to cyclical derivatives
 Pentoses: Furfural
 Hexoses : Hydroxy methyl furfural
- Ketoses are more susceptible to the action of acids



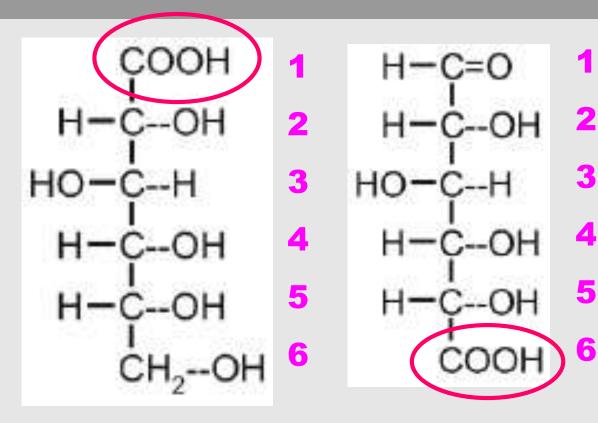
Furfural

Hydroxymethyl Furfural



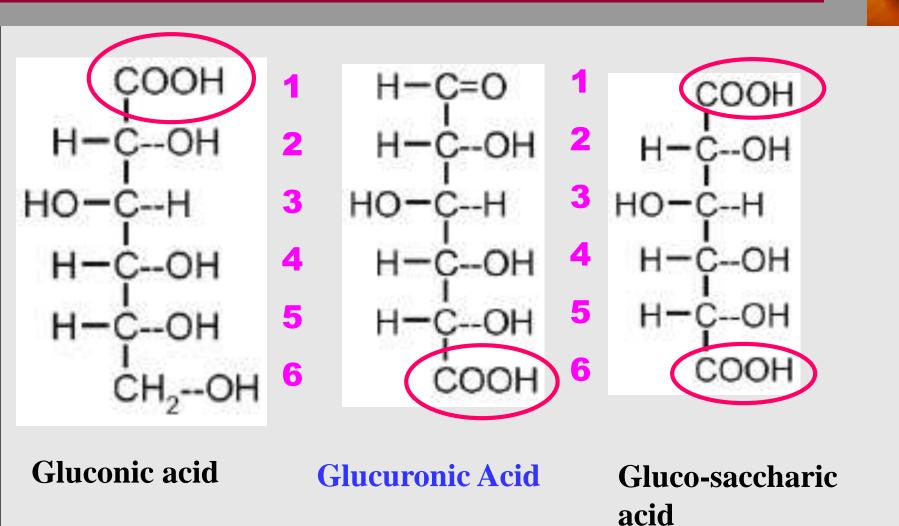
Oxidation

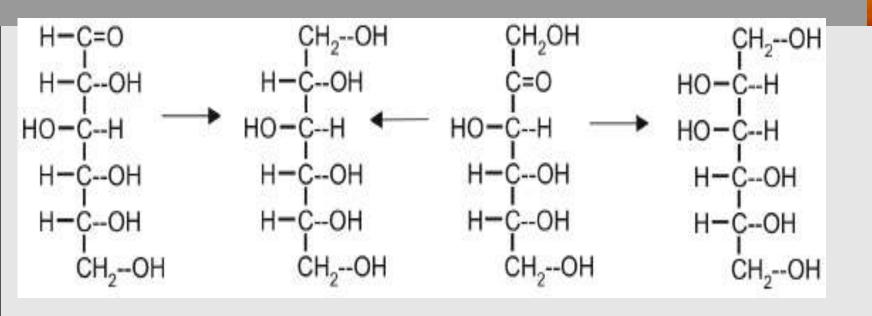
Gluconic acid



Gluconic acid

Glucuronic Acid Used for conjugation with insoluble molecules





Glucose

<u>Sorbitol</u>

Fructose

Mannitol

Reduction

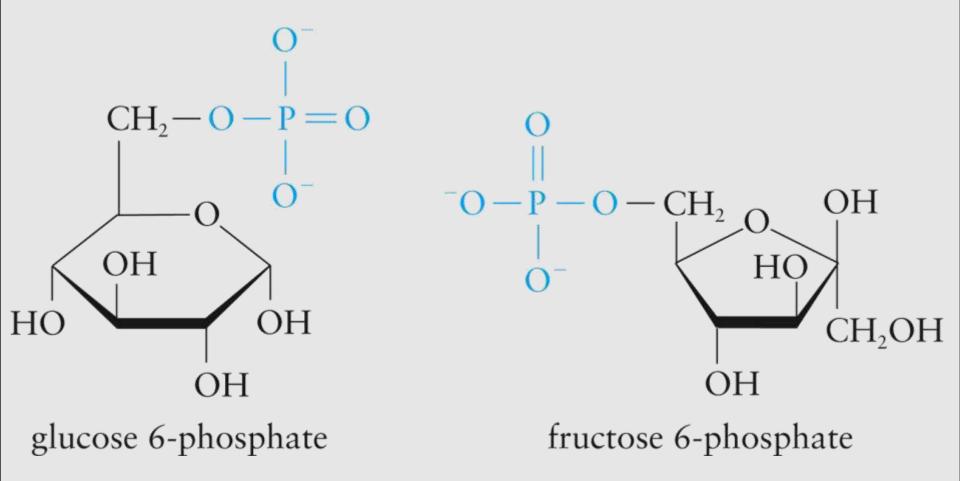
Glucose is reduced to sorbitol, Mannose to mannitol Fructose to sorbitol and mannitol. Galactose is reduced to dulcitol

Sorbitol, mannitol and dulcitol are used to identify bacterial colonies. Mannitol is also used to reduce intracranial tension by forced diuresis.

The osmotic effect of sorbitol and dulcitol produces changes in tissues when they accumulate in abnormal amounts, e.g. cataract of lens.

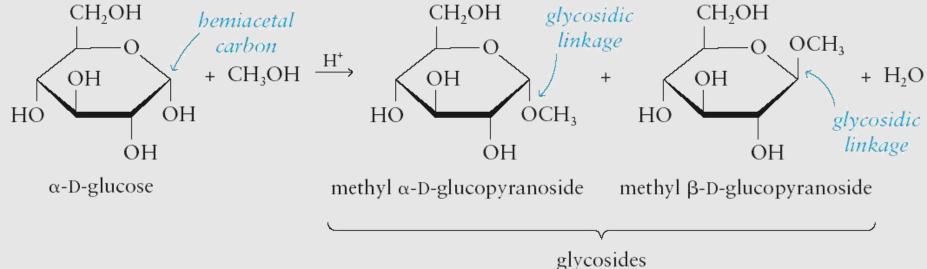
MONOSACCHARIDE REACTIONS (continued)

 The –OH groups of monosaccharides can behave as alcohols and react with acids (especially phosphoric acid) to form esters.



GLYCOSIDES

 Cyclic monosaccharide hemiacetals and hemiketals react with alcohols to form acetals and ketals, referred to as glycosides.



- The new carbon-oxygen-carbon linkage that joins the components of the glycoside is called a glycosidic linkage.
- Glycosides do not exhibit open-chain forms.
- Glycosides are not reducing sugars.

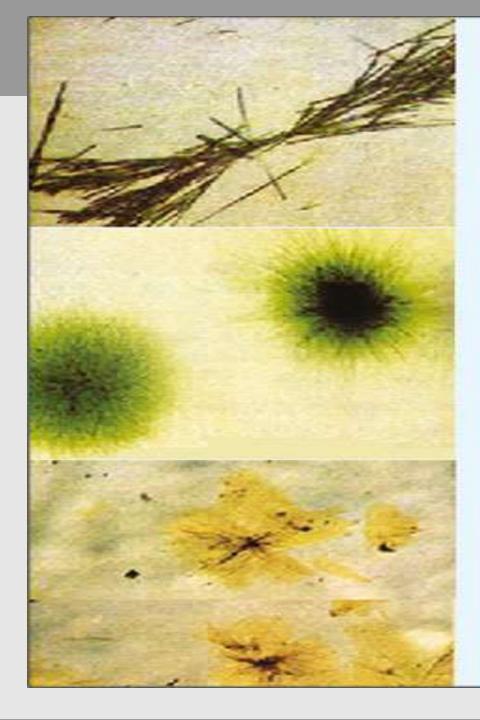
 Some glycosides have medical importance e.g. Digitonin (leaves of foxglove) is a cardiac stimulant.

- Phlorizin (rosebark) is used to produce renal damage in experimental animals.
- Plant indican present in leaves of indigofera used as stain.

Osazone Formation

All reducing sugars will form osazones with excess of phenylhydrazine when kept at boiling temperature.

Osazones are insoluble. Each sugar will have characteristic crystal form of osazones.



Needle shaped crystals arranged like a broom Glucososazone

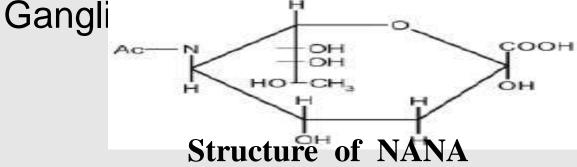
Hedgehog or "pincushion with pins" or flower of "touch-me-not-plant" Lactososazone

Sunflower shaped or petal shaped crystals of Maltosazone Aminosugar : non reducing nature

 Sialic acids: Naturally occurring N-acetyl derivatives

E.g. N acetyl Neuraminic acid – NANA

- **Glucosamine in** hyaluronic acid and blood group substances.
- N-acetyl-galactoseamine present in Glycoproteins, cell membrane antigen and



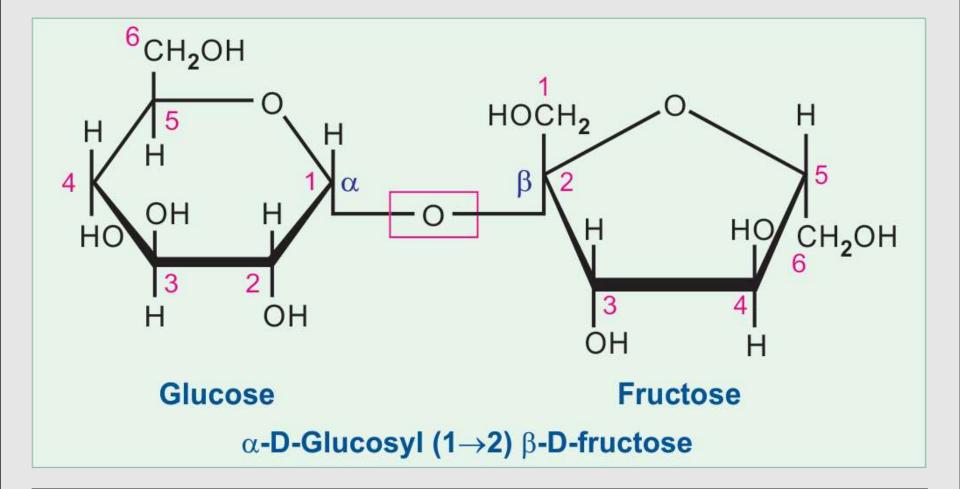
Disaccharides

When two monosaccharides are combined together by glycosidic_linkage, a disaccharide is formed.

Important disaccharides

- 1. Sucrose
- 2. Maltose
- 3. Lactose

Sucrose



Sucrose is the **sweetening agent** known as cane sugar.

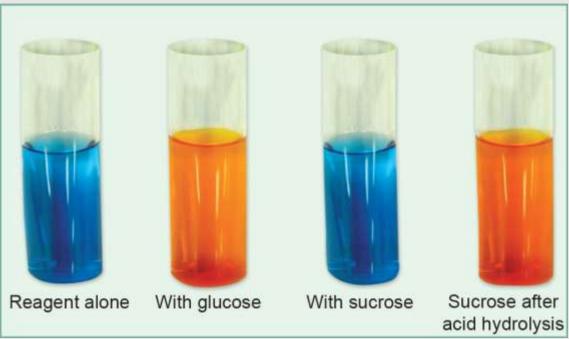
It is present in sugarcane and various fruits.

Sucrose is **not a reducing sugar**; and it will not form osazone.

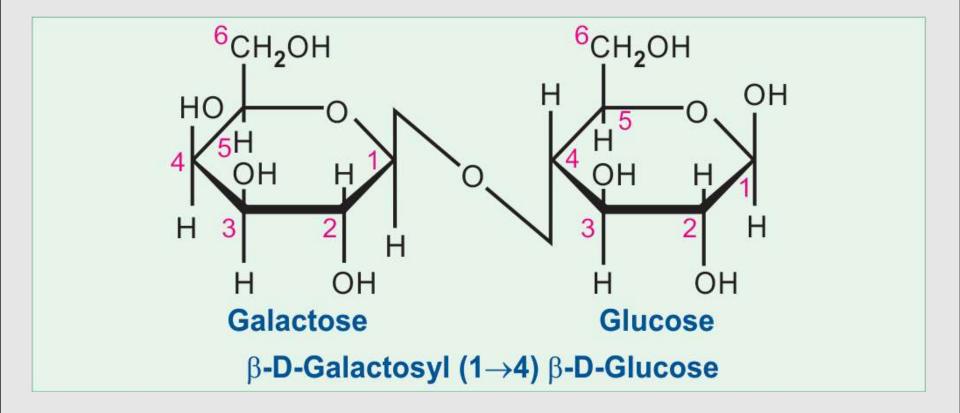
This is because the linkage involves first carbon of glucose and second carbon of fructose, and free sugar groups are not available.

When sucrose is hydrolysed, the products have reducing action.

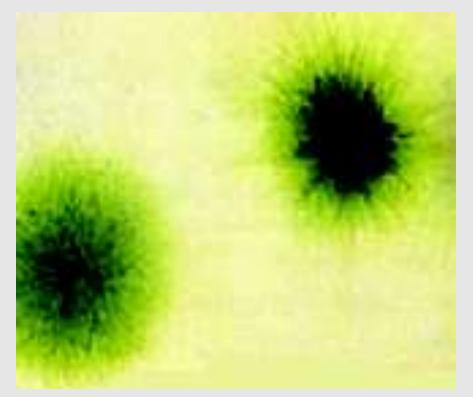
A sugar solution which is originally nonreducing, but becomes reducing after hydrolysis, is inferred as sucrose (**specific sucrose test**).



Lactose

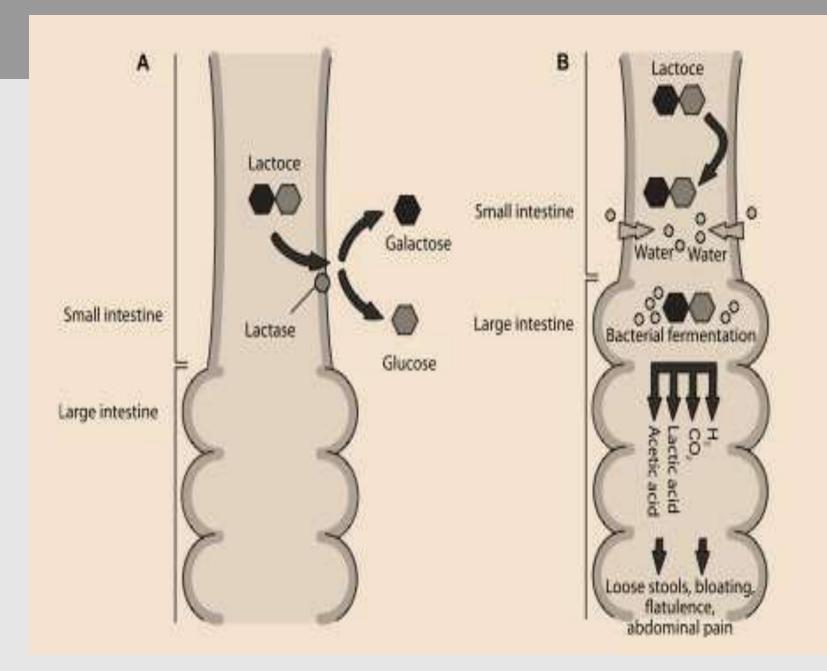


Lactose is the sugar present in milk. It is a reducing disaccharide.



Lactose forms osazone which resembles "pincushion with pins" or "hedgehog" or flower of "touch-me-not" plant.

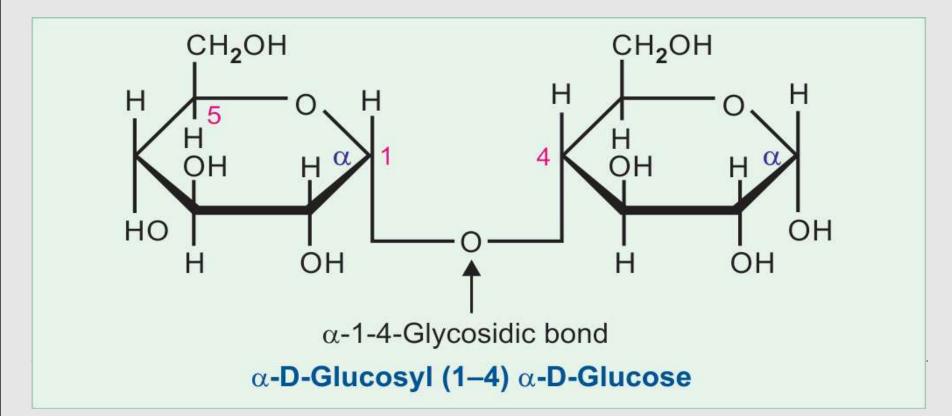
Lactose is hydrolyzed to its monosaccharide components by lactase enzyme in human beings and by ß galactosidase in bacteria. Deficiency of lactase causes Lactose intolerance, manifested by diarrhea, abdominal cramps, bloating and distension.



Maltose

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

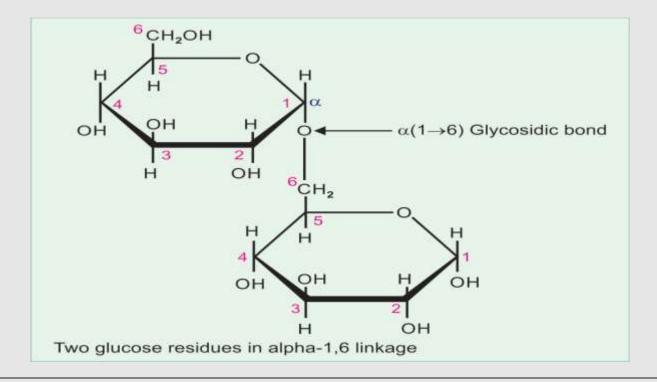
O-α-D-glucopyranosyl-(1->4)- α -D-glucopyranose



-Produced by partial hydrolysis of starch either by Salivary or Pancreatic amylase. -Fermentable sugar. -Used as a nutrient (malt extract; Hordeum vulgare); as a sweetener and as a fermentative reagent -Has a free active group and hence exhibits reducing properties, mutarotation and α - β isomerism.

Isomaltose

Partial hydrolysis of glycogen and starch produces isomaltose.





Polymerised products of many monosaccharide units.

- 1. <u>Homoglycans</u> composed of single kind of monosaccharides, e.g. **starch, glycogen and cellulose**.
- 2. <u>Heteroglycans</u> are composed of two or more different monosaccharides, e.g. **agar**, **hyaluronic acid**, **chondroitin sulphate, glycoproteins**



It is the **reserve carbohydrate** of plant kingdom.

Sources: Potatoes, tapioca, cereals (rice, wheat) and other food grains.

Glucose units with **alpha-1,4 glycosidic linkages** to form a long chain.

Highly branched. The branching points are made by alpha-1,6 linkage.

Starch forms a **blue coloured complex with iodine**; this colour disappears on heating; reappears when cooled. **Sensitive test for starch.**

Starch is **non reducing** because the free sugar groups are **negligible** in number.

When starch is hydrolysed by **mild acid**, smaller and smaller fragments are produced.

Hydrolysis for a short time dextrin which gives violet colour with iodine and is non reducing.

Hydrolysis for a long time : Maltose and glucose (Reducing)



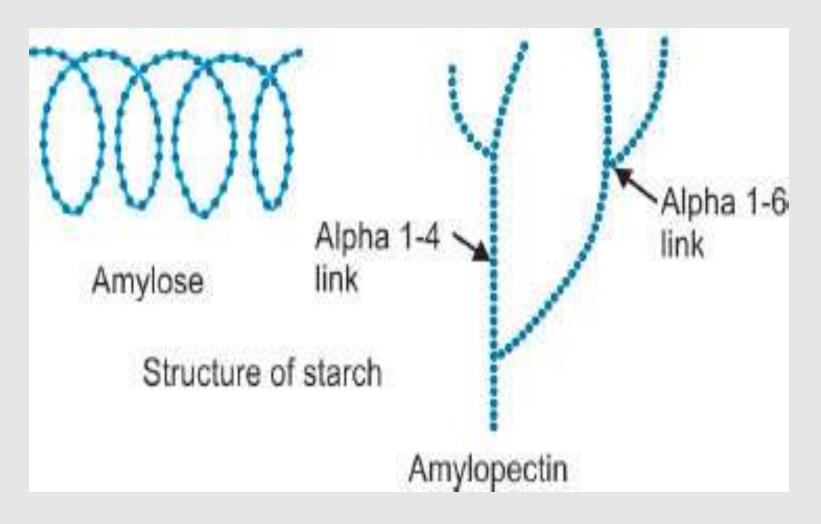
• Amylose:

- Water soluble(15-20%)
- Long unbranched chain with 200-1000 D-glucose units held by α (1-4) glycosidic linkage.

• Amypectin:

- Water insoluble(80-85%)
- Branched chain with 200-1000 D-glucose units held by α (1-6) glycosidic linkage.
- Branching point are present.

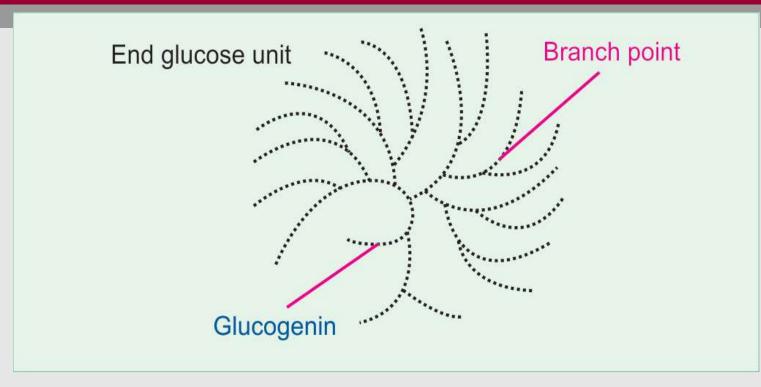




- i) Salivary and pancreatic amylases are alphaamylases, which act at random on alpha-1,4 glycosidic bonds to split starch into smaller units (dextrins), and finally to alpha-maltose.
- **ii)Beta-amylases** are of plant origin. It acts to release, maltose units from the ends of the branches of **amylopectin**.
- iii)The action stops at branching points, leaving a large molecule, called limit **dextrin** or residual dextrin.

Glycogen

- It is the reserve carbohydrate in animals. It is stored in liver and muscle. About 5% of weight of liver is made up by glycogen.
- Glycogen is composed of glucose units joined by alpha-1,4 inkagess in the straight chains. It also have alpha-1,6 glycosidic linkages at the branching points
- **Glycogenin** is protein primer of glycogen synthesis.
- Upto 25,000 glucose units



Exterior branches are composed of 6-7 glucose units and there are about 3-4 units between branches.

Cellulose

Supporting tissues of plants. Cellulose constitutes 99% of cotton, 50% of wood Most abundant organic material in nature.

Made up of glucose units combined with beta-1,4 linkages.

Synthetic fibres, celluloids, nitrocellulose and plastics are made from cellulose.

• Beta-1,4 bridges are hydrolysed by the enzyme **cellobiase.**

This enzyme is absent in animal and human digestive system, and hence **cellulose cannot be digested.**

- It functions as non-digestable fiber in human nutrition and decreases absorption of glucose and cholesterol from intestine with increasing bulk of feces.
- Herbivorous animals have large caecum, which harbor bacteria. These bacteria can hydrolyze cellulose, and the glucose produced is utilized by the animal.

Inulin



Homoglycan Composed of **D-fructose units** with repeating **beta-1,2 linkages**.

It is the reserve carbohydrate present in various **bulbs and tubers** such as **chicory**, **dahlia**, **dandelion**, **onion**, **garlic**.

It is clinically used to find **Renal clearance value** and **Glomerular filtration rate**.



It is present in **exoskeletons of crustacea and insects.**

It is composed of units of N-acetyl-glucosamine combined by beta-1,4 glycosidic linkages.

		Starch		
	Cellulose	Amylose	Amylopectin	Glycogen
Source	Plant	Plant	Plant	Animal
Subunit	β-glucose	α-glucose	a-glucose	a-glucose
Bonds	1-4	1-4	1-4 and 1-6	1-4 and 1-6
Branches	No	No	Yes (~per 20 subunits)	Yes (~per 10 subunits)
Diagram		5-5-5-5	5-5-5 -5	
Shape		2222	HU	

These are polysaccharides containing more than one type of sugar residues.

Agar and Agarose Hyaluronic acid

Heparin and Heparan Sulphate Chondroitin Sulphate

Keratan Sulphate Dermatan Sulphate



Prepared from sea weeds.

Contains galactose, glucose and other sugars.

It is **dissolved in water at 100°C**, which upon cooling sets into a **gel**.

Agar cannot be digested by bacteria and hence used widely as a **supporting agent to culture bacterial colonies**.

Agar

supporting medium for **immuno-diffusion and immuno**electrophoresis.

Agarose

galactose units;

used as matrix for electrophoresis.

<u>MUCOPOLYSACCHARIDES</u> or <u>glycosamino glycans</u> (GAGs) are heteropolysaccharides, containing uronic acid and amino sugars.

GLYCOSAMINOGLYCANS - EXAMPLES



N-Acetyl groups, sulfate and carboxyl groups are also present.

These charged groups attract water molecules; viscous solutions

Mucopolysaccharides in combination with proteins form **Mucoproteins**.

Important GAGs It is present in **connective tissues, tendons, synovial fluid and vitreous humor of eye.**

Lubricant and shock absorber in joints.

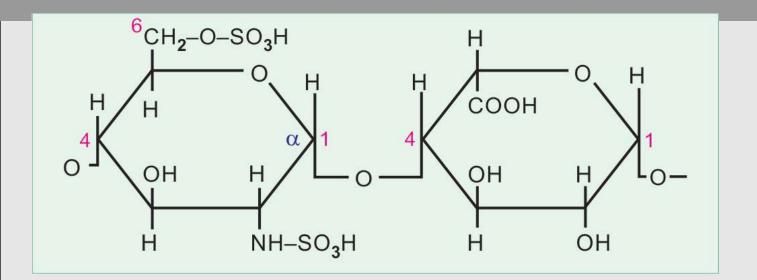
It is composed of repeating units of N-Acetyl-glucosamine \rightarrow Glucuronic acid

Hyaluronidase : plays important role in fertilization Present in testes, seminal fluid and in snake and insect venoms.

Anticoagulant for taking blood. used in vivo to prevent intravascular coagulation.

It activates antithrombin III, which in turn inactivates thrombin, so blood is not clotted.

Heparin is present in liver, lungs, spleen and monocytes.

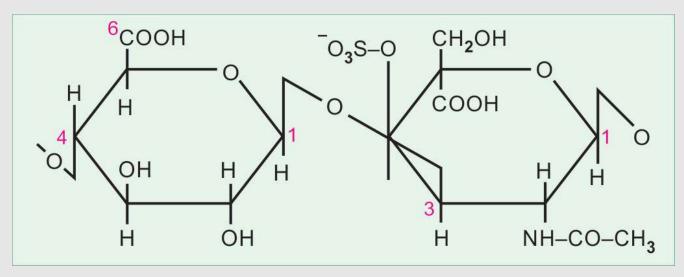


Heparin contains repeating units of sulphated glucosamine \rightarrow alpha-1, 4-L-iduronic acid \rightarrow and so on.

Sulphated heparin or heparan sulfate is also present in tissues.

Chondroitin Sulphate

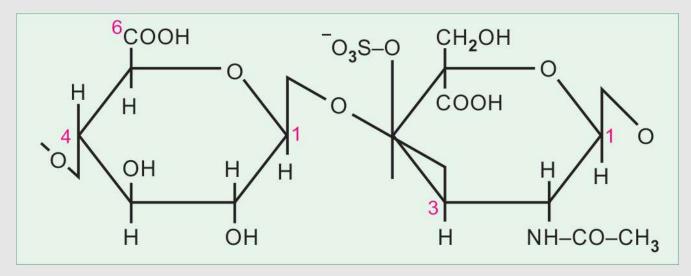
Connective tissues -- in cartilage, bone, tendons, cornea and skin. Structurally same as hyaluronic acid.



Repeating units of glucuronic acid \rightarrow N-acetyl galactosamine 4- sulphate \rightarrow and so on.

Chondroitin Sulphate

Connective tissues -- in cartilage, bone, tendons, cornea and skin.



Repeating units of glucuronic acid \rightarrow N-acetyl galactosamin sulphate \rightarrow and so on.

It is the only GAG which **does not contain any uronic acid.**

The repeating units are **galactose and N-acetyl glucosamine 6-sulphate**

It is found in **cornea and tendons**.

L-iduronic acid and N-acetyl galactosamine in beta -1, 3 linkage.

It is found in skin, blood vessels and heart valves.

Mucopolysaccharides

Hyaluronic acid Heparin Chondroitin Sulphate Keratan Sulphate Dermatan Sulphate

Box 5.6. Repeating Units in Polysaccharides				
Polysaccharide	Repeating units			
Homoglycans				
Inulin	D-fructose, beta-1,2 linkages			
Dextran	Glucose, 1-6, 1-4, 1-3 linkages			
Chitin	N-acetyl glucosamine; beta 1-4 links			
Heteroglycans				
Agar	Galactose, glucose			
Agarose	Galactose, anhydrogalactose			
Hyaluronic acid	N-acetyl glucosamine, glucuronic acid			
Heparin	Sulphated glucosamine, L-iduronic acid			
Chondroitin S	Glucuronic acid, Nacetyl galactos-amine			
Keratan S	Galactose, N-acetyl glucosamine			
Dermatan S	L-iduronic acid, N-acetyl galactos-amine			

Characteristics of GAGs

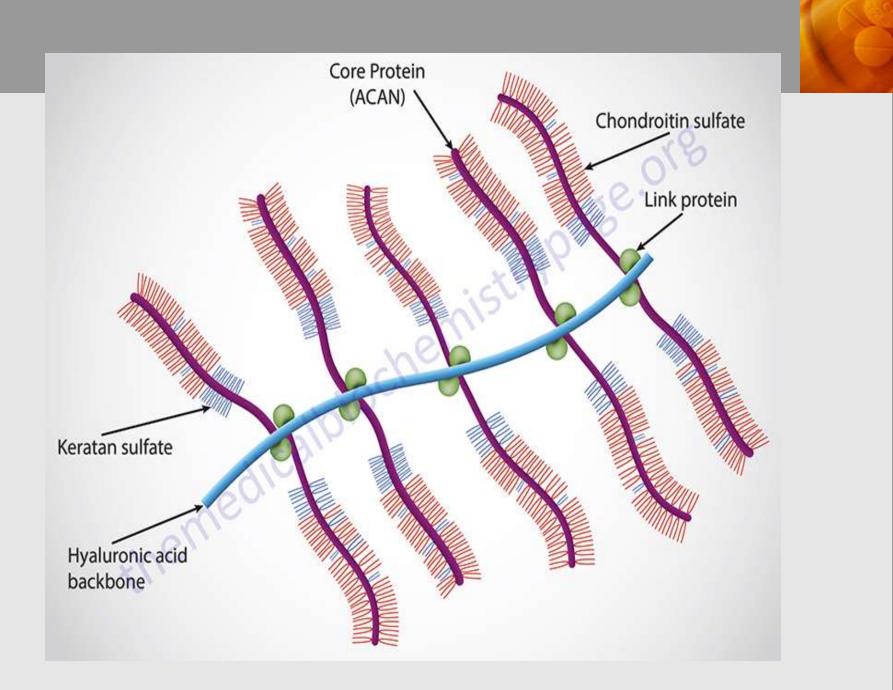
GAG	Localization	Comments
Hyaluronate	synovial fluid, vitreous humor, ECM of loose connective tissue	large polymers, shock absorbing
Chondroitin sulfate	cartilage, bone, heart valves	most abundant GAG
Heparan sulfate	basement membranes, components of cell surfaces	contains higher acetylated glucosamine than heparin
Heparin	component of intracellular granules of mast cells lining the arteries of the lungs, liver and skin	more sulfated than heparan sulfates
Dermatan sulfate	skin, blood vessels, heart valves	
Keratan sulfate	cornea, bone, cartilage aggregated with chondroitin sulfates	

When the **carbohydrate chains** are attached to a **polypeptide** it is called a **proteoglycan**.

If the carbohydrate content is **less than 10%**, it is generally named as a **glycoprotein**.

If the carbohydrate content is more than 10% it is a mucoprotein.

Functions: enzymes, hormones, transport proteins, structural proteins and receptors.



Dietary Fiber

- Dietary fiber is contributed by the **unavailable** carbohydrates in the diet.
- They contribute the bulk and assist in normal bowel movements.
- Cellulose, emicellulose, pectin, alginates, and gums are the usual glycans which form dietary fiber.
- Cellulose is found in **bran**, flour, and tubers.
- Pectins are mixtures of homoglycans found in fruits.
 Gums and alginates are found in legumes and
 oatmeal.



Thank You

