Carbohydrates

Dr. S. K. Maurya Department of Veterinary Physiology & Biochemistry College of Veterinary Sc. & A. H.

ANDUAT, Kumarganj Ayodhya

- Carbohydrates = carbon + hydrates
- hydrogen and oxygen in the same ratio as water (that is 2:1).
- But acetone $(C_2H_4O_2)$, lactic acids $(C_3H_6O_3)$ etc. are not carbohydrates.
- And some certain compounds that do not have hydrogen and oxygen in the same ratio as water but are carbohydrates for example: Rhamnose ($C_6H_{12}O_5$).

Carbohydrates

Carbohydrates are an abundant biomolecule.

– More than 50% of the carbon in organic

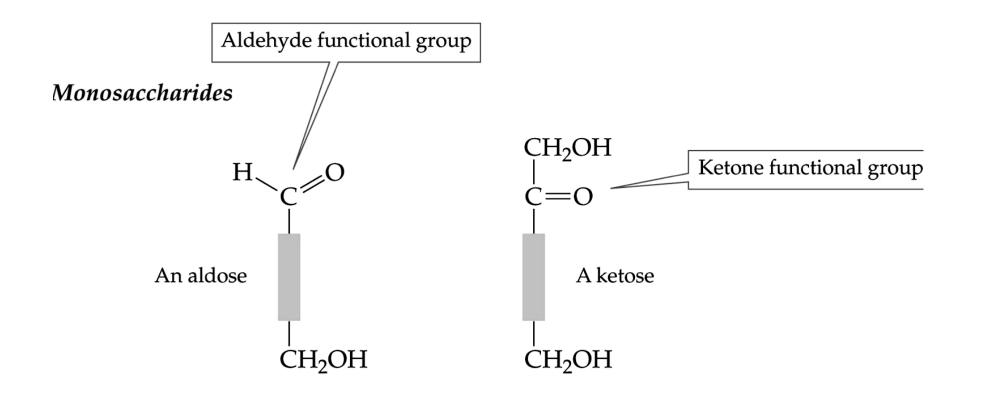
compounds is found in carbohydrates
Most common nutrient on earth
Supplies body with energy
3 Types of Carbohydrates:

Sugars, starches, fibers

Major food sources: plants

Formed during photosynthesis





defined as "polyhydroxy aldehydes or polyhydroxy ketones or their polymerization products that yield such polyhydroxy aldehydes or polyhydroxy ketones on hydrolysis".

Functions

- They are structural components of cells.
- They are main source of energy in the body.
- They are also stored in the body, serving as stored food. In plants, major stored food in carbohydrate.
- They spare oxidation of proteins in body.
- They are needed for proper fat oxidation.
- They are part of nucleic acid and thus function in regulation and control of all metabolic processes.

They are important in cellular recognition process. This means that carbohydrates are important to our immune system. Many antibodies and proteins used in the immune system contain both carbohydrates and protein. Without carbohydrates, these combination protein/carbohydrate molecules cannot form. The carbohydrate component helps the liver know when to degrade the antibody by being cleaved off the proteins making up the immunoglobulin.

- Helps gastro intestinal functions. Carbohydrates play a role in the production of B complex vitamins made by beneficial bacteria in the body. The beneficial bacteria live off the carbohydrates consumed by the GI tract and can then help us in return by producing valuable vitamins we need to function. One of the functions of carbohydrates is to provide fuel for these beneficial bacteria so that they can symbiotically help us in return. Carbohydrates, such as lactate, help the body absorb calcium better, which is good for our bones.
- They also add flavor to diet.

Nomenclature

- Add suffix "ose"
- Aldose
- Ketose
- Suffix "ulose"

Introduction

- Carbohydrates are one of the three major classes of biological molecules.
- Carbohydrates are also the most abundant biological molecules.
- Carbohydrates derive their name from the general formula Cn (H2O).

functions

- Variety of important functions in living systems:
 - nutritional (energy storage, fuels, metabolic intermediates)
 - structural (components of nucleotides, plant and bacterial cell walls, arthropod exoskeletons, animal connective tissue)

- informational (cell surface of eukaryotes -- molecular recognition, cell-cell communication)
- osmotic pressure regulation (bacteria)

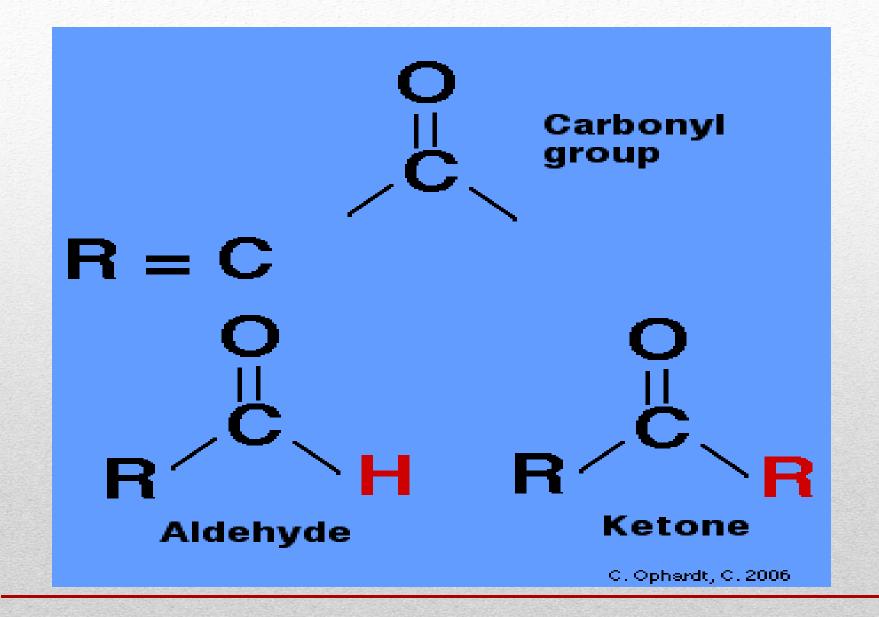
• Carbohydrates are carbon compounds that contain large quantities of hydroxyl groups.

Carbohydrates are chemically characterized as:

• Poly hydroxy aldehydes or

• Poly hydroxy ketones.

- Sugars that contain an aldehyde group are called Aldoses.
- Sugars that contain a keto group are called Ketoses.



Classification Of

Carbohydrates

Classification

BASED ON HYDROLYSIS

All carbohydrates can be classified as either:

- Monosaccharides
- Disaccharides
- oligosaccharides or Polysaccharides.

- Monosaccharides- Mono= 1 Saccharide= Sugar
- one unit of monomeric unit
- Cannot be broken down by mild acid hydrolysis
- Glucose
- Fructose
- Galactose

• Oligosaccharide

- Anywhere from two to ten monosaccharide units
- Disaccharides- Two units.
- Trisaccharides- Three units.
- Tetrasaccharides
- Penta.....hexa.....and so on
- Sucrose
- Trehalose
- Stachyose etc

• Polysaccharides are much larger, containing hundreds of monosaccharide units.

Polysaccharides

TWO TYPES

- **HOMOpolysaccharides** (all 1 type of monomer), e.g., glycogen, starch, cellulose, chitin
- **HETEROpolysaccharides** (different types of monomers), e.g., peptidoglycans, glycosaminoglycans

• OTHER MODES OF CLASSIFYING

- Sugars & Non sugars (Taste)
- Aldose & Ketose (group)
- Reducing & Non reducing (Reducing property)

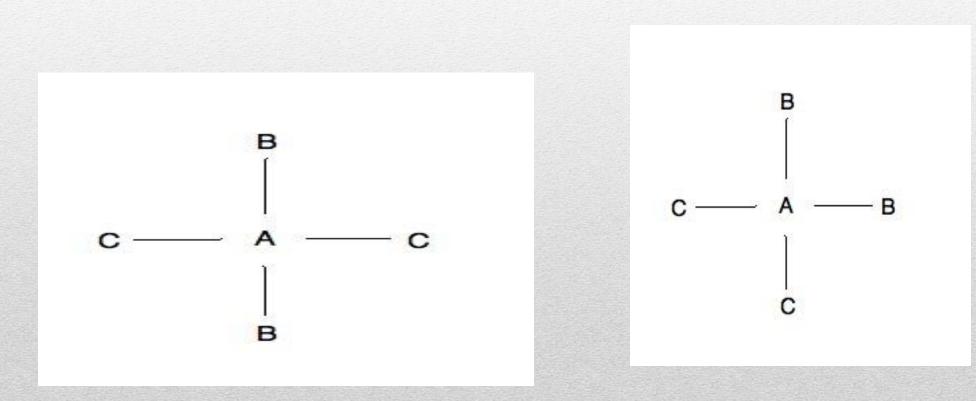
- Carbohydrates also can combine with lipids to form **glycolipids** OR
- With proteins to form glycoproteins.

ISOMERISMIN CARBOHYDRATES

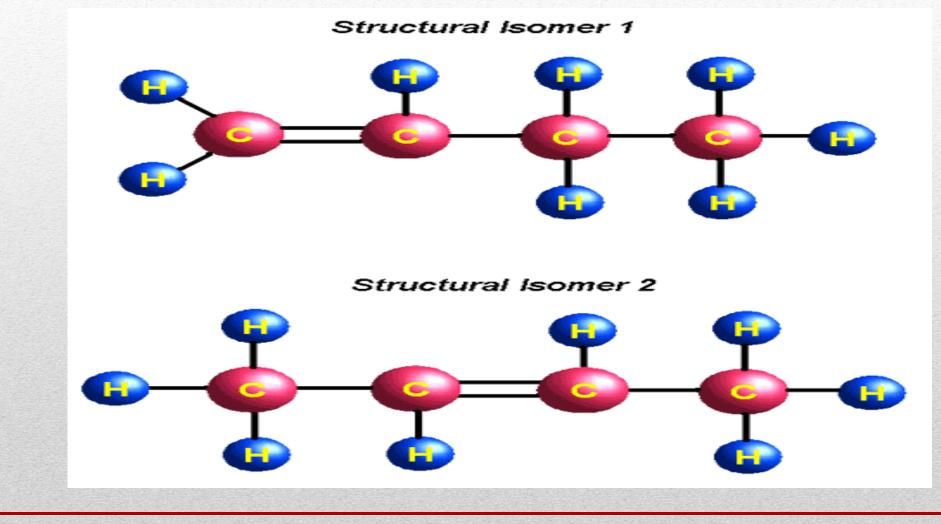
Isomers

- Isomers are molecules that have the same molecular formula, but have a different arrangement of the atoms in space. (different structures).
- For example, a molecule with the formula AB_2C_2 , has two ways it can be drawn:

Isomer 1 Isomer 2



Plane isomerism



Stereoisomerism

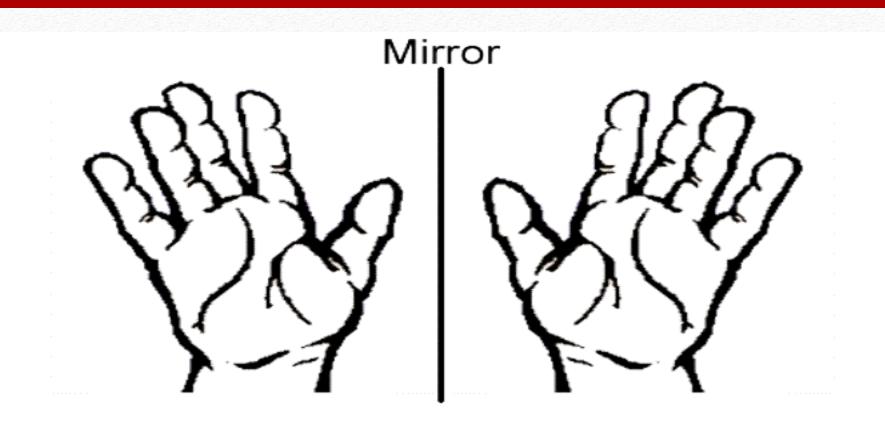
Examples of isomers:

- 1. Glucose
- 2. Fructose
- 3. Galactose
- 4. Mannose

Same chemical formula C6 H12 O6 Cannot be distinguished in one plane Only can be distinguished by writing proper orientation in space or in 3 dimension or in space

Optical Activity

- When a plane polarized light is passed through a solution containing monosaccharides the light will either be rotated towards right or left.
- This rotation is because of the presence of asymmetric carbon atom.
- If it is rotated towards left-levorotatory (-)
- If it is rotated towards **right-dextrorotatory**(+)



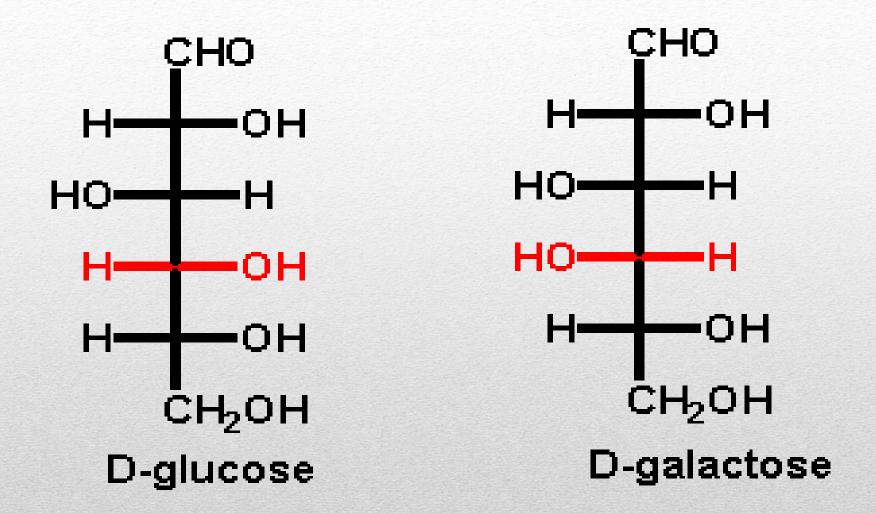
The mirror image of a chiral substance cannot be superimposed on the original image. Hands are chiral, as are sugars and amino acids.

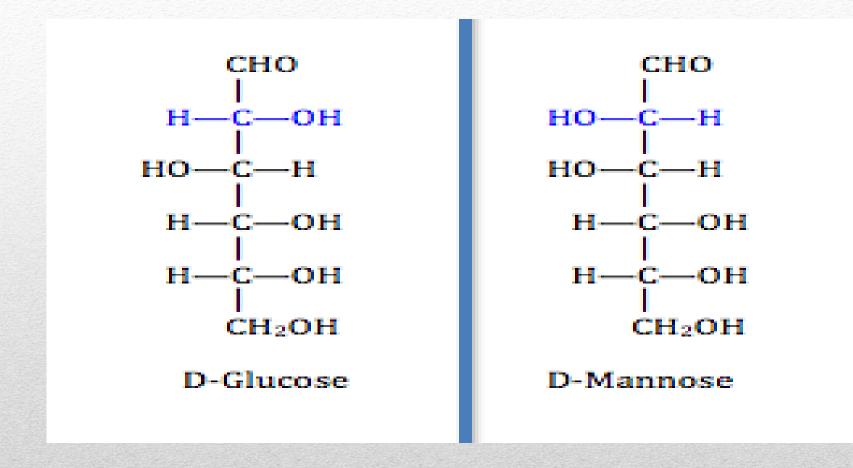
Asymmetric carbon

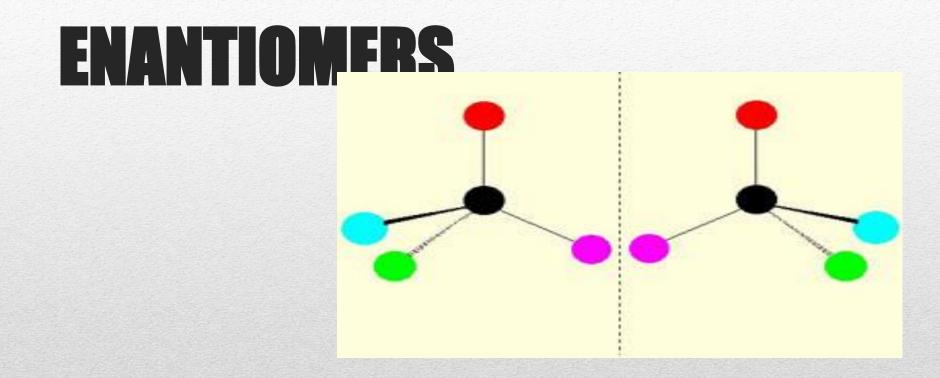
- A carbon linked to four different atoms or groups farthest from the carbonyl carbon
- Also called Chiral carbon
- Isomerism shown by such compounds is call as optical isomerism



- EPIMERS are sugars that differ in configuration at ONLY 1 POSITION.
- Examples of epimers :
 - D-glucose & D-galactose (epimeric at C4)
 - D-glucose & D-mannose (epimeric at C2)
 - D-glucose & L-glucose (epimeric at C5)

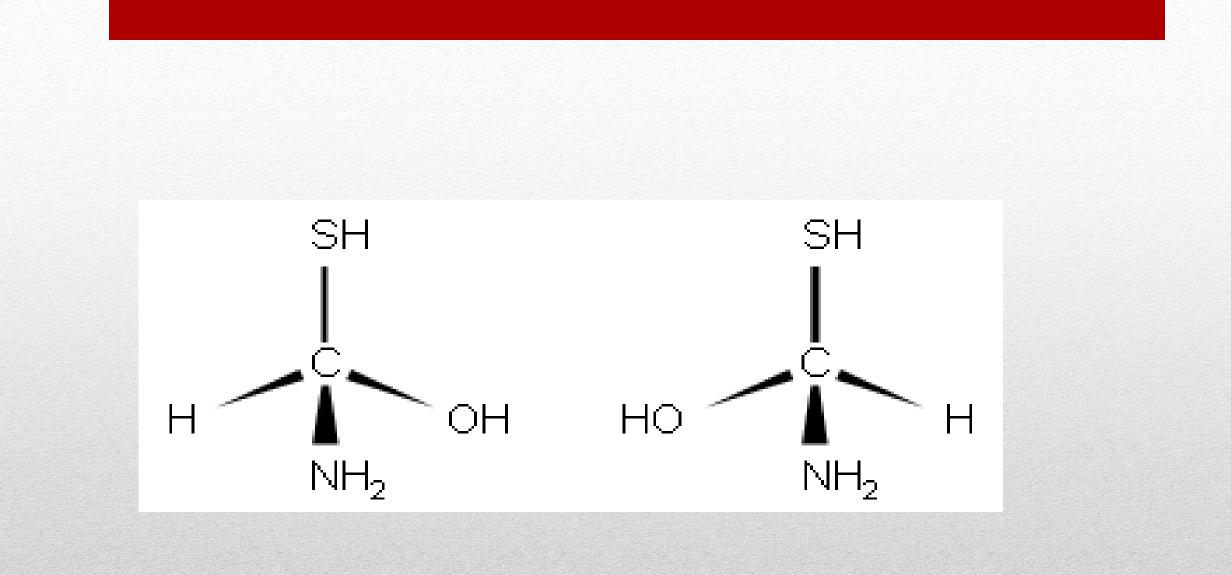


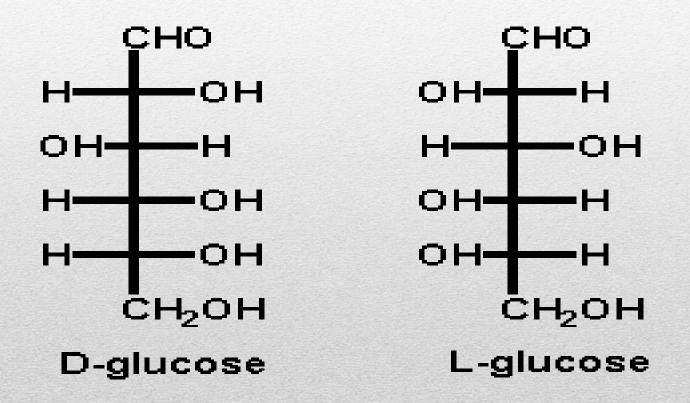


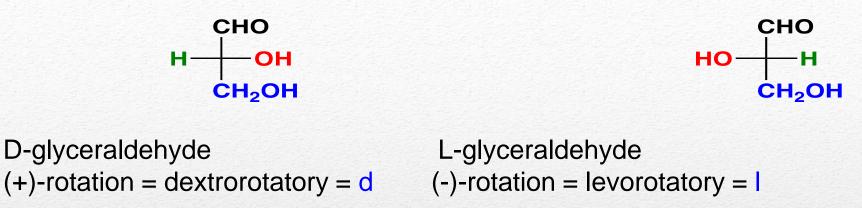


Non-Superimposable *COMPLETE* mirror image (differ in configuration at EVERY CHIRAL CENTER.

- The two members of the pair are designated as **D** and **L** forms.
- In **D** form the OH group on the asymmetric carbon is on the **right**.
- In L form the OH group is on the left side.
- D-glucose and L-glucose are **enantiomers**:







- D-carbohydrates have the -OH group of the highest numbered chiral carbon pointing to the right
- For carbohydrates, the convention is to arrange the Fischer projection with the carbonyl group at the top for aldoses and closest to the top for ketoses. The carbons are numbered from top to bottom.

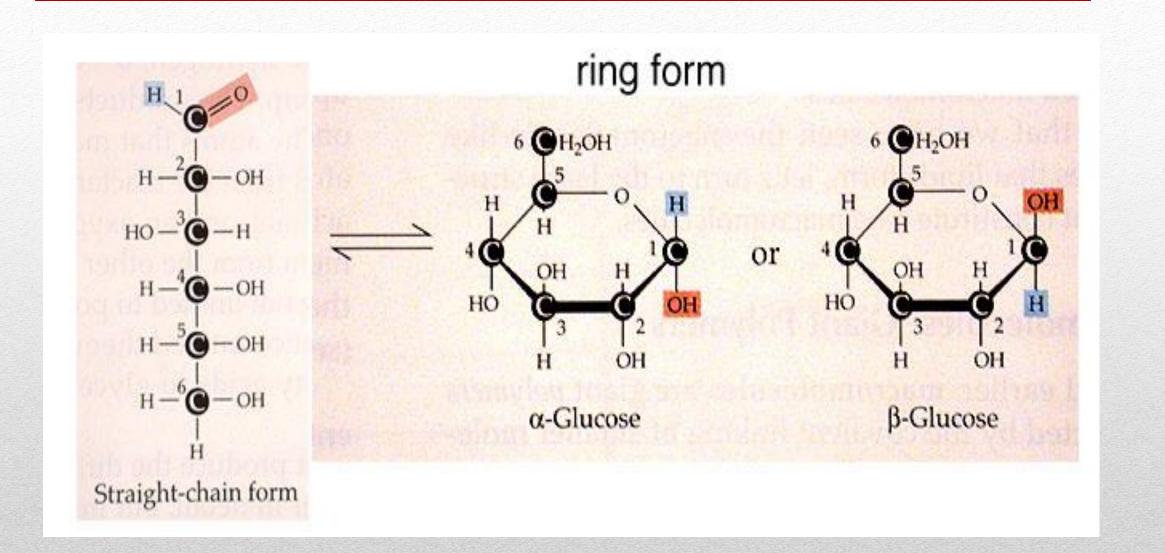
- Carbohydrates are designated as D- or L- according to the stereochemistry of the highest numbered chiral carbon of the Fischer projection. If the hydroxyl group of the highest numbered chiral carbon is pointing to the right, the sugar is designated as D (<u>Dextro</u>: Latin for on the right side).
- 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.

Cyclization & anomerism

- Less then 1% of CHO exist in an open chain form.
- Predominantly found in ring form.
- involving reaction of C-5 OH group with the C-1 aldehyde group or C-2 of keto group.

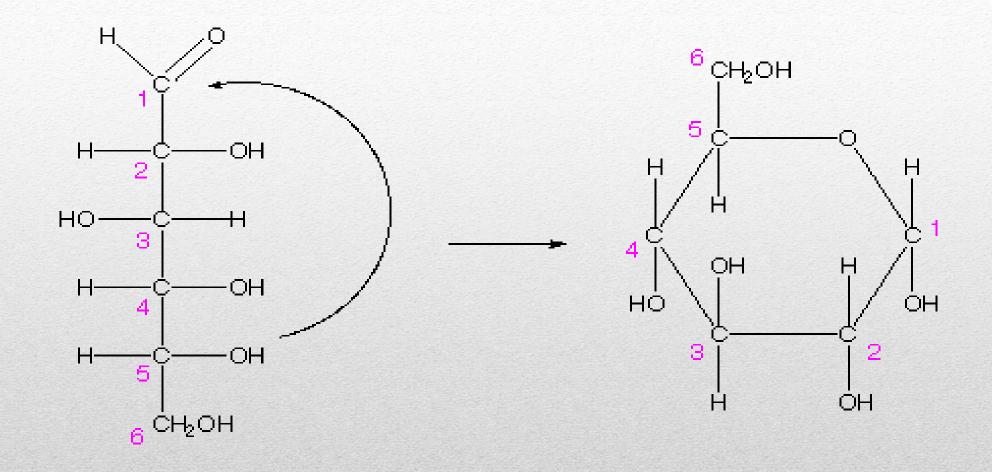
• Six membered ring structures are called **Pyranoses**.

• five membered ring structures are called **Furanoses** .

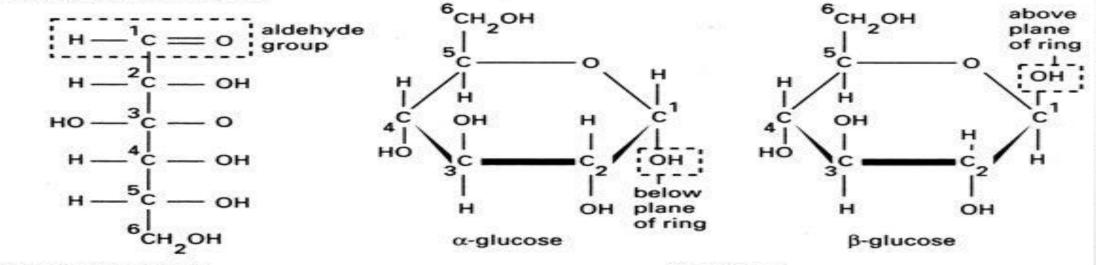


Anomeric carbon

- The carbonyl carbon after cyclization becomes the anomeric carbon.
- This creates α and β configuration.
- In α configuration the OH is on the same of the ring in fischer projection. In Haworths it is on the trans side of CH2OH.



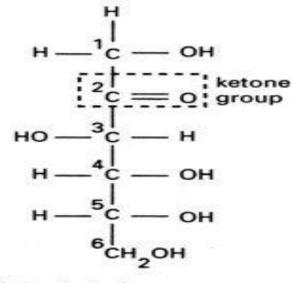
Glucose (an aldohexose)



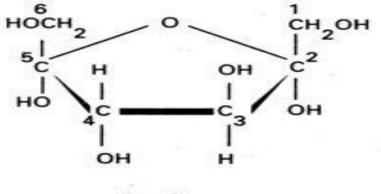
straight-chain form

ring forms

Fructose (a ketohexose)



straight-chain form



ring form

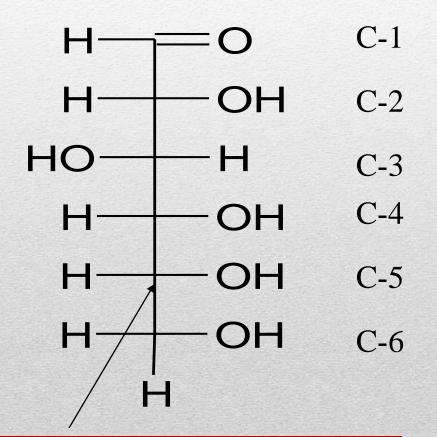
• Such α and β configuration are called diastereomers and they are not mirror images.

Enzymes can distinguished between these two forms:

- Glycogen is synthesized from α-D glucopyranose
- Cellulose is synthesized from **β** -**D** glucopyranose

Glucose

- Fisher projection
- D-series sugars are built on Dglyceraldehyde
- 3 additional chiral carbons
- 2³ D-series sugars (and 2³ L-series based on L-glyceraldehyde)



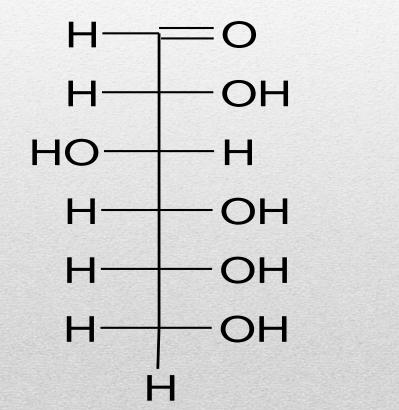
Original D-glyceraldehyde carbon

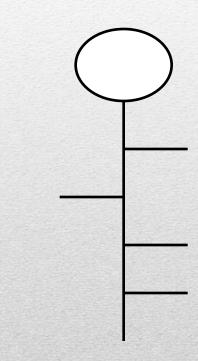
D-Fructose

- A ketose sugar
- One less chiral carbon than the corresponding aldose
- Sweetest known sugar

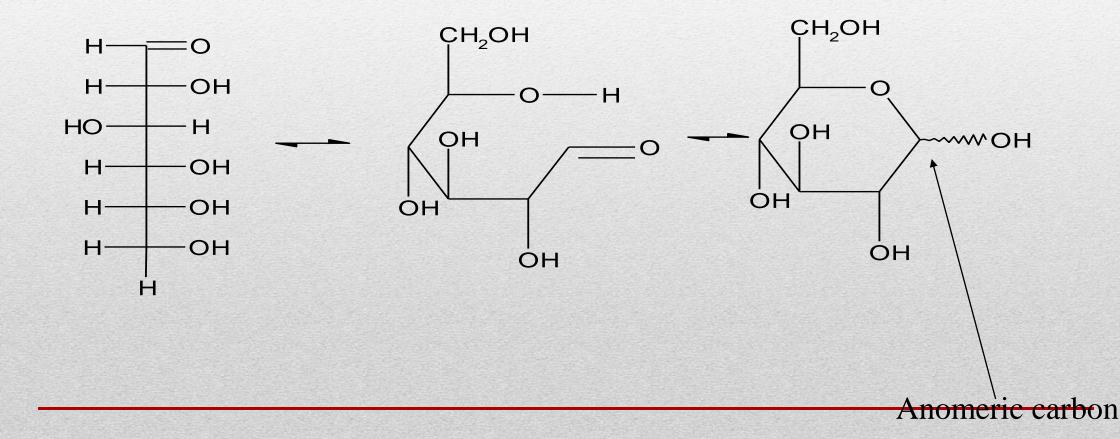
 H_2C-CH_3 -ĊΗ HO HÇ-OH HC - OHC - OH H_2

The Rosanoff Projection





Ring Formation

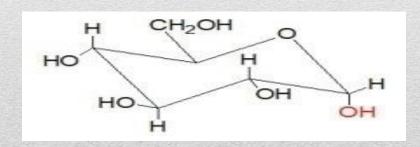


Ring Formation

Haworth formula

- Intramolecular reaction between alcohol and carbonyl to form a ring
 - 6-membered rings are **pyranose**
 - 5-membered are **furanose**
- Generates a new a-carbon and two additional anomers (α and β -)

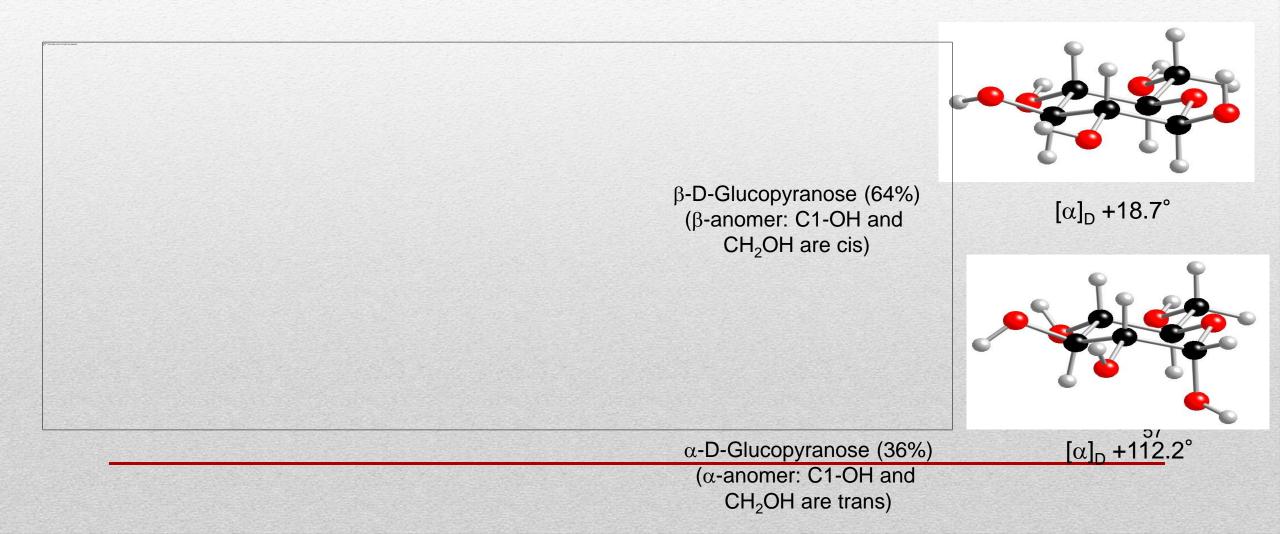
CHAIR & BOAT

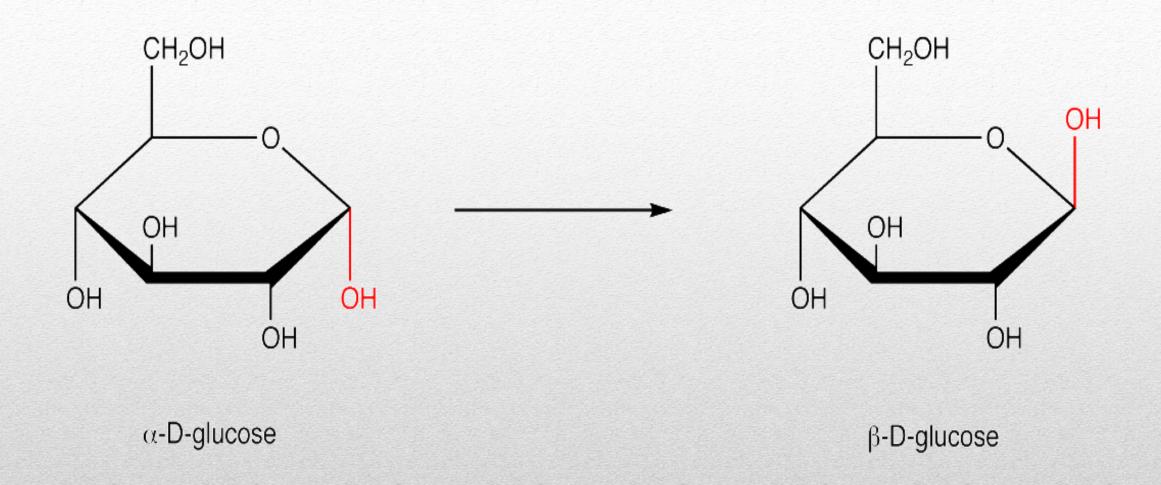


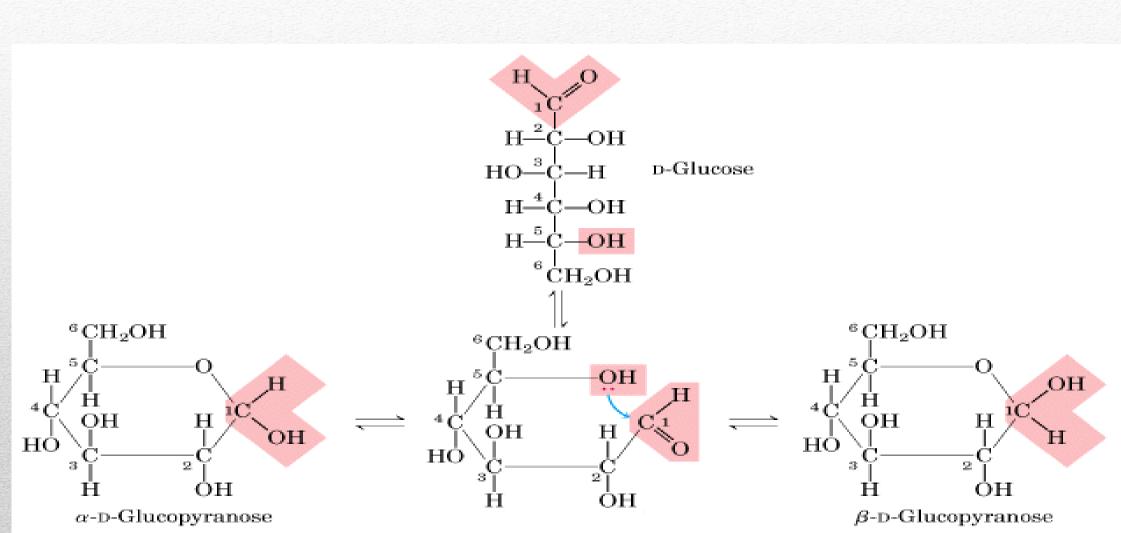
MUTAROTATION

- Unlike the other stereoisomeric forms, α and β anomers spontaneously interconvert in solution.
- This is called mutarotation.

Mutar otation. The α - and β -anomers are in equilibrium, and interconvert through the open form. The pure anomers can be isolated by crystallization. When the pure anomers are dissolved in water they undergo mutarotation, the process by which they return to an equilibrium mixture of the anomer.







PROPERTIES OF MONOSACCHARIDES

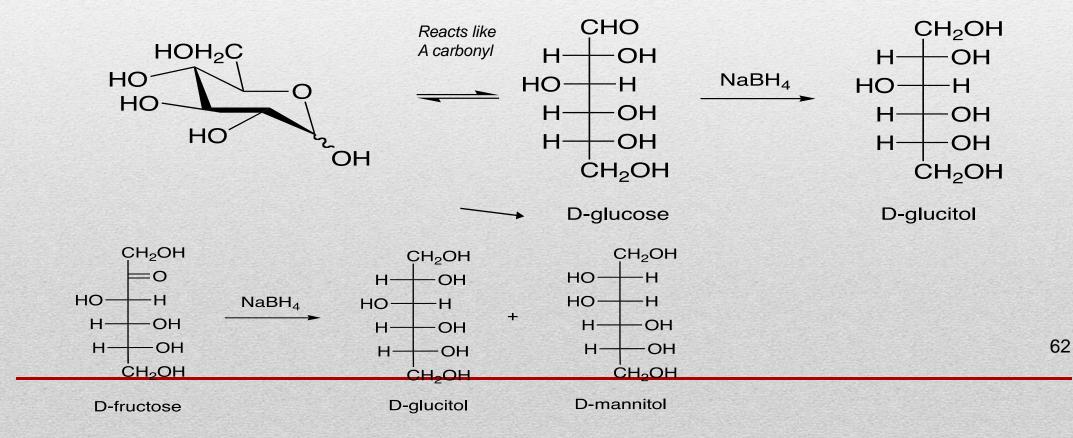
• PHYSICAL PROPERTIES—

- Carbohydrates are colourless, crystalline, solid, neutral and generally sweet in taste.
- All are water soluble, low soluble in alcohol and insoluble in benzene.
- Mostly they are optically active. All naturally occurring monosaccharides are optically active.
- Mostly they show mutarotation.
- On heating they become charred without melting.

Chemical Properties

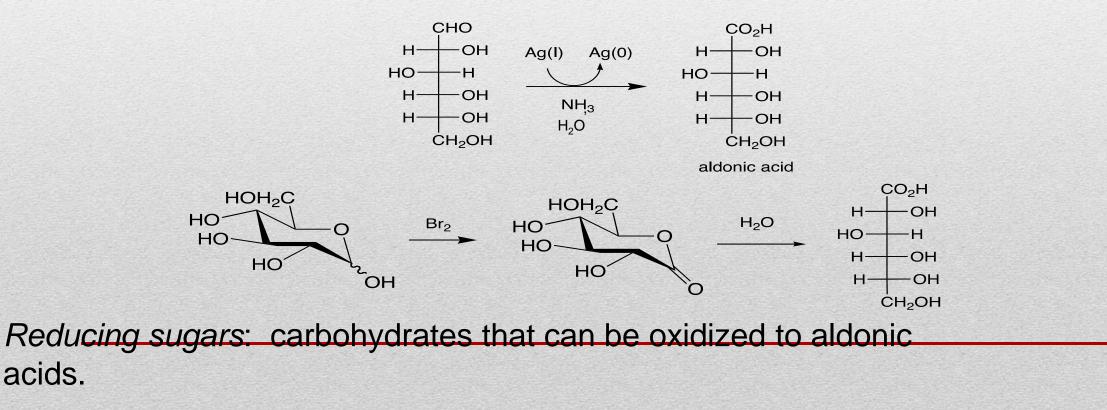
1. Reduction:

- produce poly hydroxy alcohols
- C1 of aldoses are reduced with sodium borohydride to the 1° alcohol (*alditols*). All aldoses produce single kind of alcohol: Sorbitol (glucitol)
- Ketoses produce a mixture of sorbitol & mannitol



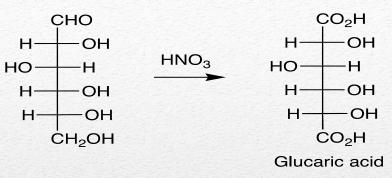
2. Oxidation:

- C1 of aldoses can be selectively oxidized to the carboxylic acid
- Oxidation product depends on oxidising agent
- With weak agents like Br₂ or Ag(I) they produce aldonic acids

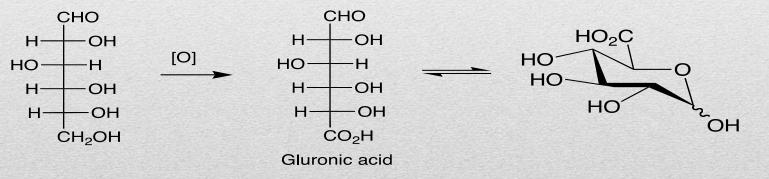


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Oxidation of aldoses to *aldaric acids* with HNO₃.



Uronic Acid: Carbohydrate in which only the terminal $-CH_2OH$ is oxidized to a carboxylic acid.

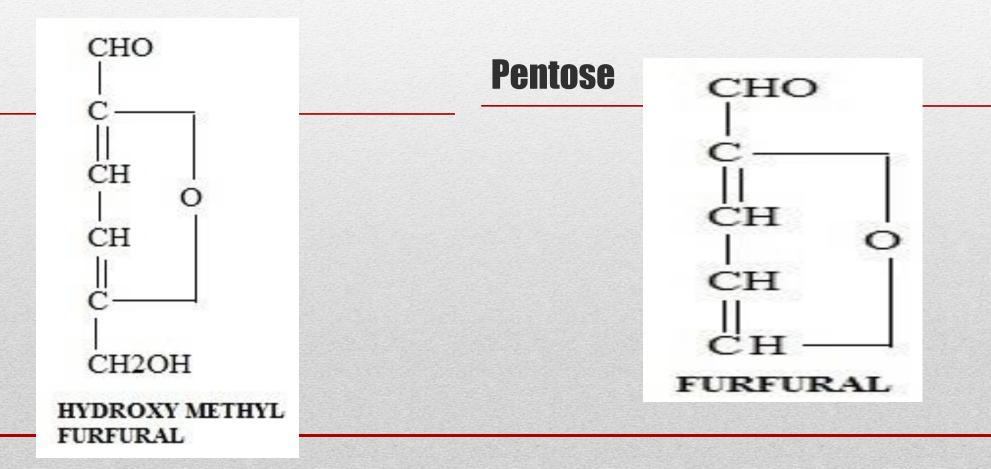


Oxidation of ketoses produce simple acids either with weak or strong agents. 64

Action of strong non oxidizing acids

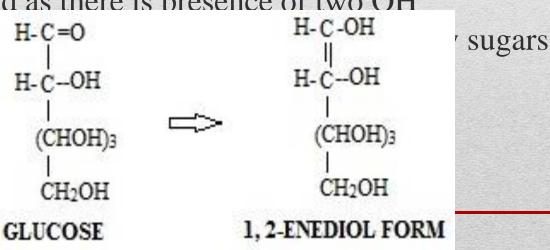
- Dehydrated by the action of strong acids like sulphuric acid.
- a hydrocarbon skeleton is left with a carbonyl group and/ or primary alcohol group.
- the dehydrated skeleton left is in a cyclic form: an anhydride cyclic aldehyde.
- It is called as furfural in cases of pentoses where there is only a carbonyl group left without primary alcohol group.
- The cyclic anhydride aldehyde obtained from hexoses have a primary alcohol also, and thus are called hydroxymethyl furfural.

Hexose



Action of alkalies

- With weak alkalies: monosaccharides undergoe tautomerization,
- In this there is migration of double bond of carbonyl group to C atom.
- C=O is converted to C=C and there is presence of OH group at the both ends.
- This is known as enol (ene + ol) and as there is presence of two OH (alcohol/ol) group at both ends of a $\begin{array}{c} H-C=0 \\ H-C-OH \end{array}$ $\begin{array}{c} H-C-OH \\ H-C-OH \end{array}$ sugars
- also called as enolization.



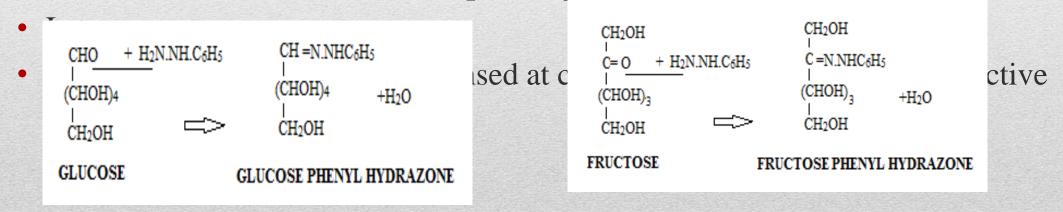
- With strong alkalies: Enolization occur not only between C-1 and C-2 position; but also between C-2 & C-3 and C-3 & C-4 positions.
- Thus it produces a visible change in the sugars called as **caramelization**

Reducing Property • Sugars in which the oxygen of the anomeric carbon is free and not

- Sugars in which the oxygen of the anomeric carbon is free and not attached to any other structure, such sugars can act as reducing agents and are called reducing sugars.
- Sugars oxidized
- Reducing sugars when treated with alkaline copper sulphate have the property of reducing cupric ions into cuprous ions. The cuprous (Cu⁺) combines with OH to form cuprous hydroxide which is yellow, but upon heating is converted to cuprous oxide (Cu₂O) which is red.
- Actually, in alkaline solution sugars undergo enolization and enediol form is more reactive. The cupric ions (Cu⁺⁺) take electrons from the enediols and oxidize them to sugar acids and are in turn reduced to cuprous ions (Cu⁺).

OSAZONE FORMATION

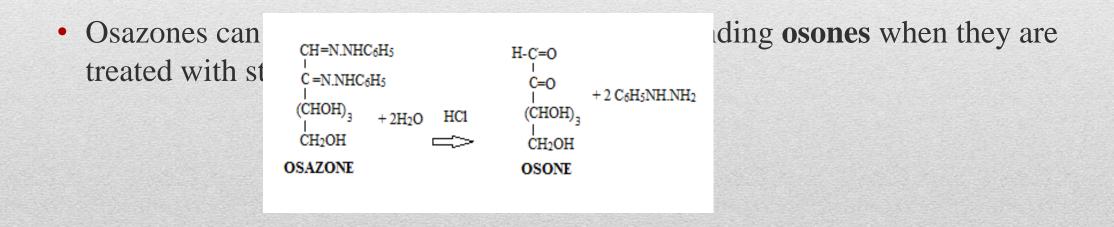
• react with phenyl hydrazine (NH_2 . $NH.C_{e}H_{z}$) and produce osazones

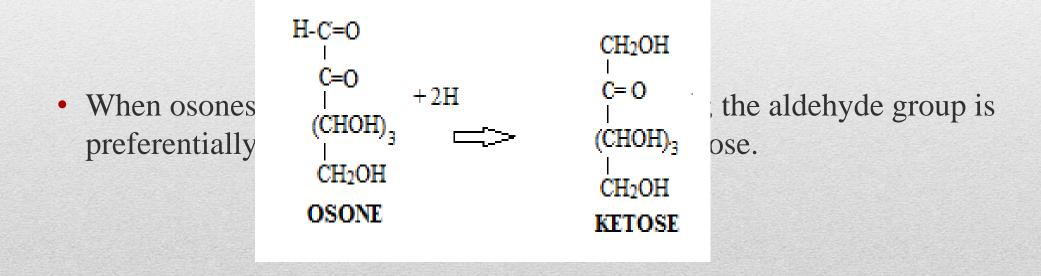


• In the next instance of reaction, another molecule of phenyl hydrazine condenses and forms a compound that has two molecules of phenyl hydrazine attached essentially at C-1 and C-2. This substance is an **OSAZONE**

```
CH=N.NHC6H5
C=N.NHC6H5
(CHOH)3
CH2OH
OSAZONE
```

• hydrazones are soluble and difficult to isolate but on the contrary, the osazones are insoluble and crystallize i





SOME IMPORTANT CARBOHYDRATES

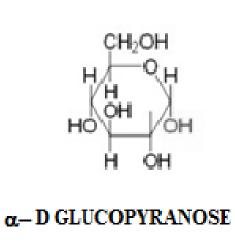
• MONOSACCHARIDES

HEXOSES: Glucose

- . Found in fruit
- "blood sugar"
- . Called Dextro

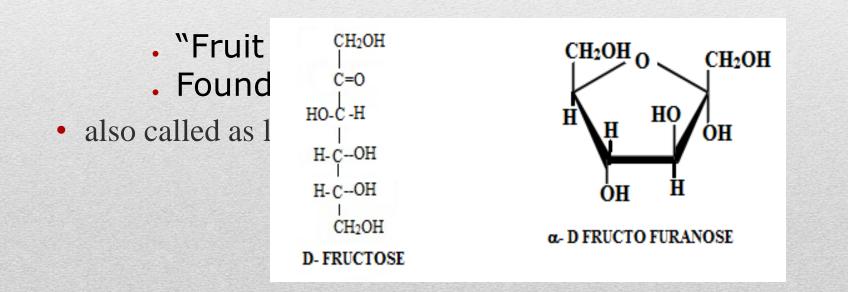
H-C=0
H-C-OH
но-с-н
H-COH
H-C-OH
CH ₂ OH
GLUCOSE

 $\Pi \cap - \cap$



D. GLUCOSE

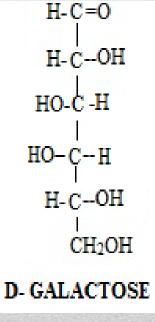
Fructose

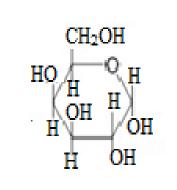


Galactose

rarely present in Found as particular

hydrolysis

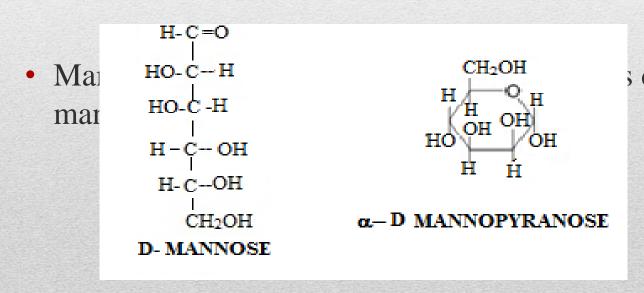




a-D GALACTO PYRANOSE

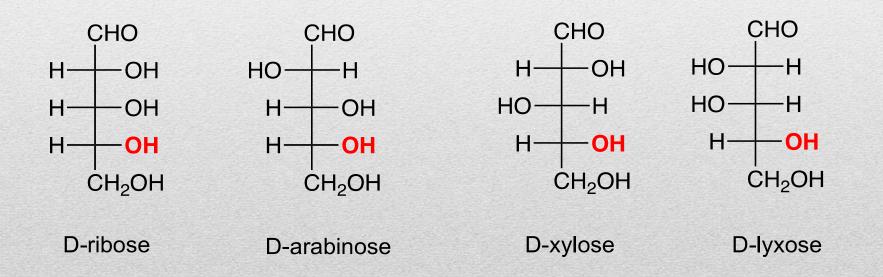
nervous tissue. m lactose after

Mannose



s distributed in combination with

PENTOSES



Ribose & Deoxyribose

- Ribose and deoxyril of nucleic acid.
- Ribose is also part of

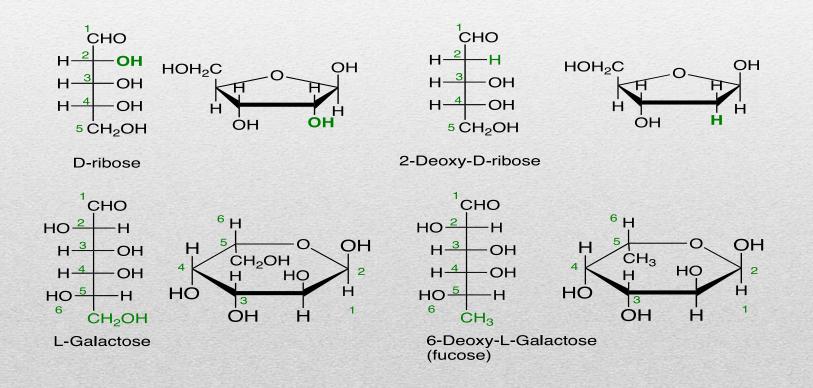
H-C=0	H-C=O
H-C-OH	н-сн
н-с-он	н-с-он
H-C-OH	H-COH
CH ₂ OH	CH ₂ OH
D- RIBOSE	2- DEOXYRIBOSE

rtant as they are constituents

ymes.

- Xylulose is similar to ribose, except that it has a ketone group.
- The L- Xylulose is metabolite of glucuronic acid and is excreted in urine in persons suffering from pentosuria.
- Ribulose, the ketonic equivalent of ribose is intermediate compound formed during pentose phosphate pathway.

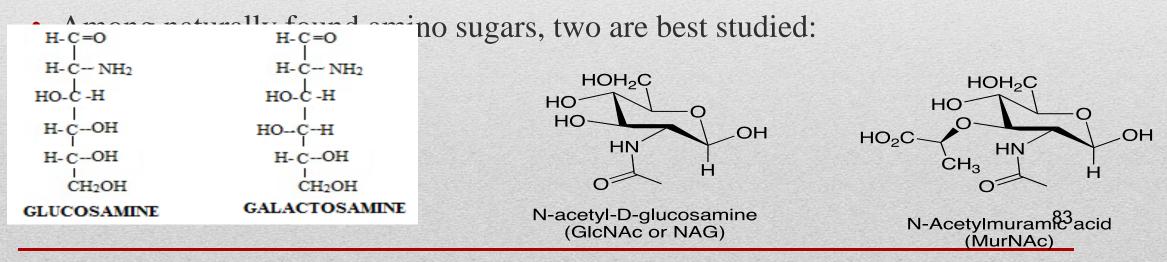
Deoxy Sugars. Carbohydrates that are missing a hydroxy group. Most important is Deoxyribose



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Amino Sugars

• Carbohydrates in which a hydroxyl group is replaced with an -NH₂ or -NHAc group



Glucosamine

- 2, amino, 2-deoxy D- glucose.
- Main constituent of mucopolysaccharides and mucoproteins like hyaluronic acid, heparin and blood group substances.
- It is chief organic component of cell wall of fungi and crustaceans where it occurs as chitin; so it is also known as **chitosamine**.

Galactosamine

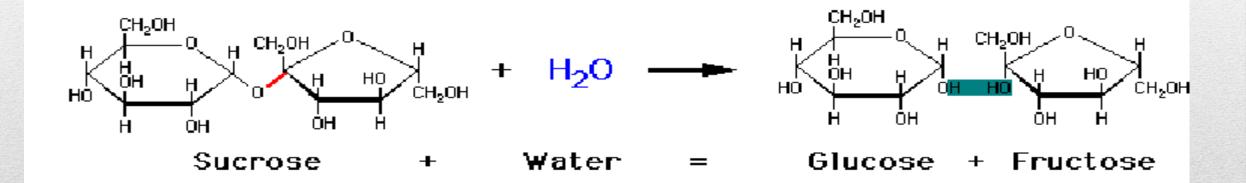
- 2, Amino, 2, deoxy D- galactose
- It occurs as N- Acetylated form in a group of complex sulfated mucopolysaccharides present in chondroproteins found in cartilages, bones, tendons, cornea, skin, heart valves etc.
- Upon hydrolysis, chondroproteins produce protein and chondroitin sulfate.
- As the galactosamines are chief constituents of chondroitin sulfate, it is also known as **chondrosamine**.

DISACCHARIDES: The Double Sugars

Sucrose

- . glucose + fructose
 - "Table sugar"
 - Made from sugar cane and sugar beets
 - glucose and fructose through an α -(1,2)- β -glycosidic bond.
 - Non reducing sugar

Hydrolysis of a Sucrose

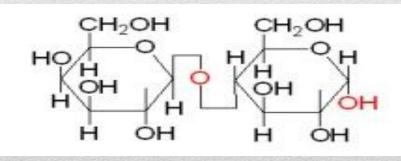


Inversion

- Hydrolysis of sucrose by dilute acid or by the enzyme "invertase" or "sucrase" produces one molecule of glucose and one molecule of fructose.
- This solution makes a change in optical rotation from positive to negative because fructose is more laevorotatory than glucose is dextrorotatory.
- The specific rotation of sucrose is +66.5° and of glucose and fructose if + 52.5° and -92° respectively.
- Thus, due to hydrolysis of sucrose, there is inversion of signs of optical rotation; thus this process is also known as "inversion".
- Thus a mixture of glucose and fructose is referred as "invert sugar".

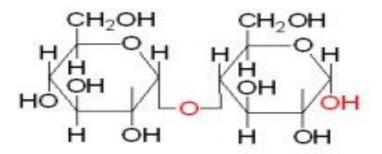
Lactose

- glucose + galactose
 - "Milk sugar"
 - Found in milk and dairy products
 - β -(1,4) glycosidic bond



Maltose

- . glucose + glucose
 - Found in germinating cereal grains
 - Product of starch breakdown
 - α -(1,4) glycosidic bond
 - also called as "malt sugar".
 - It is a reducing sugar and thus shows osazone formation.

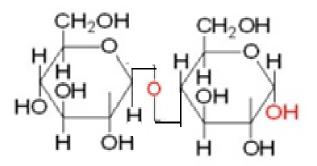


Isomaltose

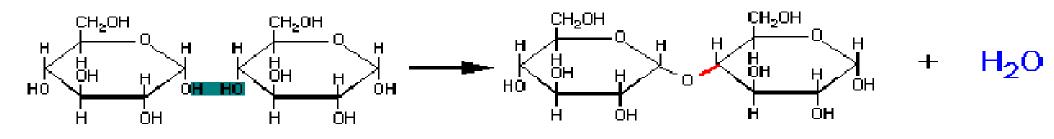
- another product of starch digestion and is similar to maltose in that it is also composed of 2 glucose monomers
- but they are linked in an a-(1,6) glycosidic bond.
- maltose is the result of breakdown of linear amylase of starch, whereas, isomaltose is formed due to hydrolysis of branched amylopectins of starch.

CELLOBIOSE

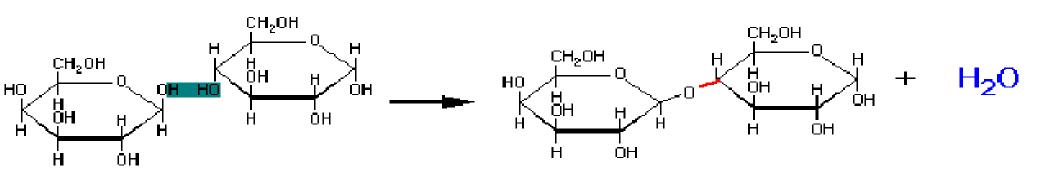
- does not occur freely in nature.
- obtained as a product of incomplete hydrolysis of cellulose.
- composed of two glucose monomers but in an β -(1,4) glycosidic bond.
- It is a reducing sugar and thus shows osazone formation



Formation of Disaccharides



Glucose + Glucose = Maltose +



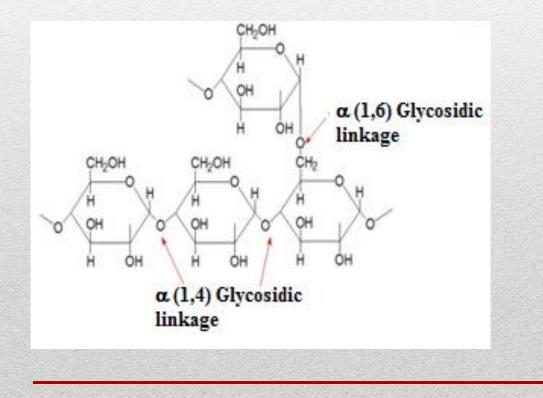
Water

Galactose + Glucose = Lactose + Water

POLYSACCHARIDES

• HOMO POLYSACCHARIDES

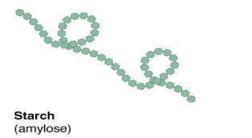
Starch & Glycogen

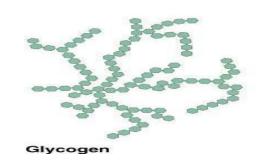


- Consists of glucose subunits
- Plant energy storage molecule
- Glycogen is a very similar molecule in animals.
- Starch and glycogen can be digested by animals.

Starch

- Great source of calories
- Long chains of glucose units (sugar molecules)
 - Amylose—straight chains
 - Amylopectin—branched chains





Glycogen

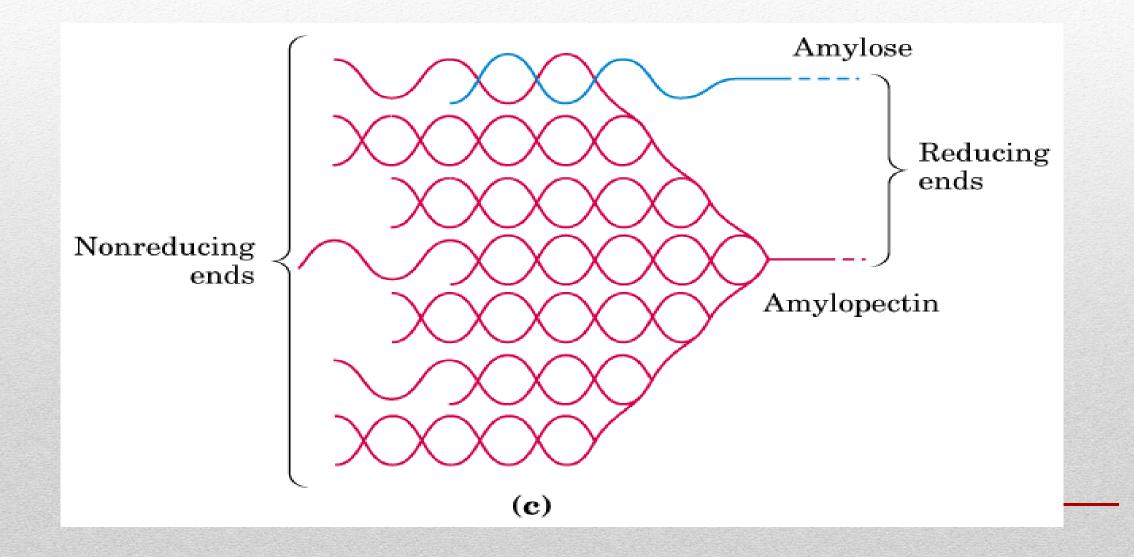
- Highly branched chains of glucose units
- . Body's storage form of carbohydrate
- Good food sources include: bread, cereal, dried peas & beans & some vegetables (corn and potatoes

- Starch and glycogen
 - Function: glucose storage
 - Starch -- 2 forms:
 - **amylose**: *linear* polymer of **a(1-> 4)** linked **glucose** residues
 - amylopectin: *branched* polymer of a(1-> 4) linked glucose residues with a(1-> 6) linked branches

• Glycogen:

- *branched* polymer of a(1-> 4) linked glucose residues with a(1-> 6) linked branches
- like amylopectin but even more highly branched and more compact
- branches increase H₂O-solubility
- Branched structures: many nonreducing ends, but only ONE REDUCING END (only 1 free anomeric C, not tied up in glycosidic bond)

- Each molecule, including all the branches, has only **ONE free anomeric C**
 - single free anomeric C = "reducing end" of polymer
 - the only end capable of equilibrating with straight chain form of its sugar residue, which has **free carbonyl C.**



DGXTAINSpounds in partial hydrolysis of starch or glycogen.

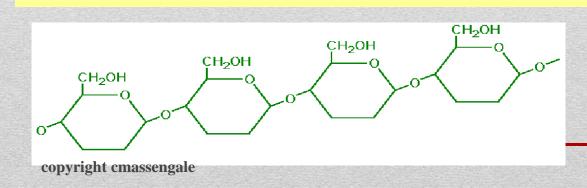
- are low molecular weight polysaccharides than starch and glycogen.
- present in honey, leaves of plants (as intermediate in starch synthesis).
- Generally, they are straight chain glucose polymer joined by α -1,4 or α -1,6 linkages.
- They do not form gels and are soluble in water.
- used in various industrial applications like
 - as water-soluble glues,
 - in remoistable envelope adhesives,
 - as additives in the mining industry,
 - as green strength additives in in the foundry industry,
 - as binders in paint, leather industry, pharmaceuticals etc.

Dextrans

- polysaccharide made from dextrose, also known as glucan.
- differs from dextrins in having a complex branched structure,
- In dextrans, the straight chain consists of α -1,6 glycosidic linkages between glucose molecules, while branches begin from α -1,3 linkages.
- used in pharmaceutical industry as antithrombotic agents to decrease vascular thrombosis, as volume expanders in intra venous fluids etc.

Important Polysaccharides: Cellulose

- Composed of glucose subunits
- Different bond formed than starch
- Structural component in plants
- Cannot be digested by animals
- homopolymer, b(1-> 4) linked glucose residues



Inulin

- polymer of D- fructose, thus also known as fructans.
- present as reserve carbohydrate in the tubers, bulbs of onion and garlic.
- easily hydrolyzed by acids, but cannot be hydrolyzed by any of the enzymes present in the gastro intestinal tract and thus is not utilized as food.
- The momomeric fructose units are linked in a β -(1,2) linkage.
- Most plants that synthesize and store inulin do not store other forms of carbohydrate such as starch.
- In medicine, inulin is more commonly used to measure kidney function by estimating glomerular filtration rate (GFR).

Heteropolysaccharides

Hemicelluloses

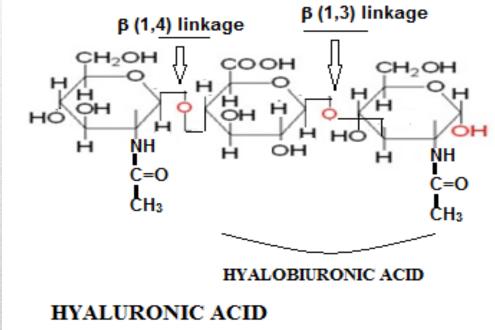
- are a group of several hetero polysaccharides.
- accompany celluloses in leafy and woody structures.
- On hydrolysis with dilute acids, they produce hexoses, pentoses and uronic acid. They are less resistant to chemical agents than celluloses.

MUCOPOLYSACCHARIDES/ Glycosaminoglycans (gag)

- are repeating units of a disaccharide
- also contain an amino sugar and a uronic acid
- Generally they are linear unbranched polymer.
- These mucopolysaccharides include: hyaluronic acid, heparin, chondroitin sulfate etc.
- Component of extracellular matrix in CT

· is n**Hyaluronjic** acid

- also found in skin, umbilical cord etc.
- serve as an integral part of gel like ground substance of connective tissue and other tissues, where it act as lubricant and shock absorbent in joints.
- It is considered as a polymer of "hyalubiuronic acid" which is a disaccharide of D- glucuronic acid and Dglucosamine joined in β-(1,3) linkage.
- The hyalubiuronic acids are in turn joined in a β-(1,4) linkage.





- acts as anticoagulant and is present in liver, lung, thymus, spleen and blood.
- It is a polymer of D-glucuronic acid and D-glucosamine.
- Amino group of some of the OH groups are sulfated otherwise, it is structurally similar to hyaluronic acid.

Chondroitin sulfate

• is similar to hyaluronic acid except that it contains **D**- galactosamine in place of glucosamine and is sulfated at C-6. This compound is present in cartilages, tendons and bones.

Sialic acid

- represents a group of substances widely distributed in mucin and blood group substances.
- are acetyl derivative of a 9 carbon 3 deoxy 5 amino sugar acid, commonly known as "Neuraminic acid" in which the amino group is acetylated and in some cases a hydroxyl group is also acetylated.
- In humans the brain has the highest sialic acid concentration, where they play an important role in nerve impulse transmission and ganglioside structure.
- It is also component of cell surface features like lipopolysaccharide and capsule of cell wall of many bacteria, which helps them evade the innate immune response of the host.