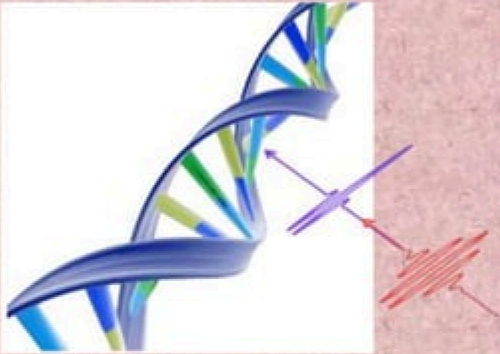


Module 1/3

BIOMOLECULES

Agitha R. Menon
PGT
AECS, Indore

The major complex biomolecules of cells

Biomolecule	Building block	Major functions
Protein	Amino acid	Basic structure and function of cell
DNA	Deoxyribonucleotide	Hereditary information
RNA	Ribonucleotide	Protein synthesis
Polysaccharide	Monosaccharide	Storage form of energy
Lipids	Fatty acids & glycerol	Storage form of energy to meet long term demands

Carbohydrates

- generally ***produced by plants***
- Most have a general formula, $C_x(H_2O)_y$ (were known as hydrates of carbon)
- Ex.Glucose ($C_6H_{12}O_6$) fits into the formula $C_6(H_2O)_6$.
- ***Definition:*** the carbohydrates are optically active polyhydroxy aldehydes/ ketones **or** the compounds which produce such units on hydrolysis.

How are Carbohydrates classified?

- On their behavior towards hydrolysis,they are divided into
  - Monosaccharides - simple sugars with multiple OH groups. Based on number of carbons (3, 4, 5, 6), a monosaccharide is a triose, tetrose, pentose or hexose.
  - Disaccharides - 2 monosaccharides covalently linked.
  - Oligosaccharides - a few monosaccharides covalently linked.
  - Polysaccharides - polymers consisting of chains of monosaccharide or disaccharide units.

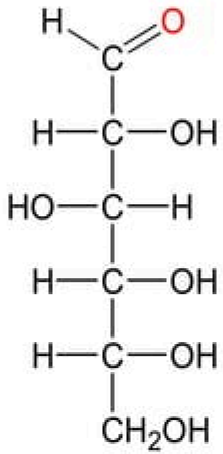
According to the functional group present

- Aldose – If the carbohydrate contains an aldehyde. **Aldotriose** – containing three carbon atoms(*Ex. Glyceraldehyde*), **aldotetrose**, **aldopentose** (Ex. Ribose), **aldohexose** (*Ex. Glucose*)
- Ketose - If the carbohydrate contains a ketone. **Ketotriose, ketotetrose, ketopentose, ketohexose**(*Ex. Fructose*)

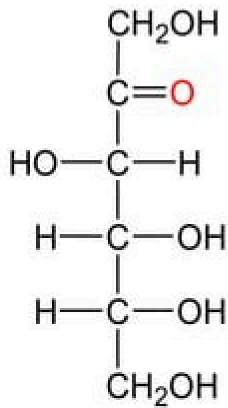
Monosaccharides

Aldoses (e.g., glucose) have an aldehyde group at one end.

Ketoses (e.g., fructose) have a keto group, usually at C2.



D-glucose

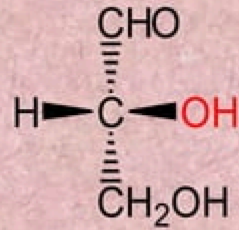


D-fructose

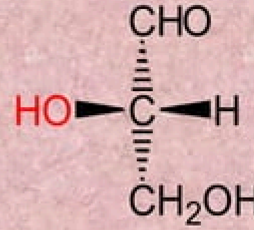
D vs L Designation

D & L designations are based on the configuration about the single asymmetric C in glyceraldehyde.

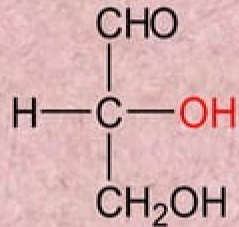
The lower representations are Fischer Projections.



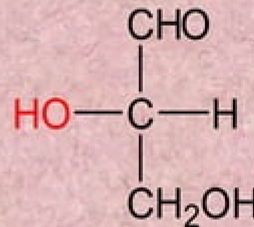
D-glyceraldehyde



L-glyceraldehyde



D-glyceraldehyde

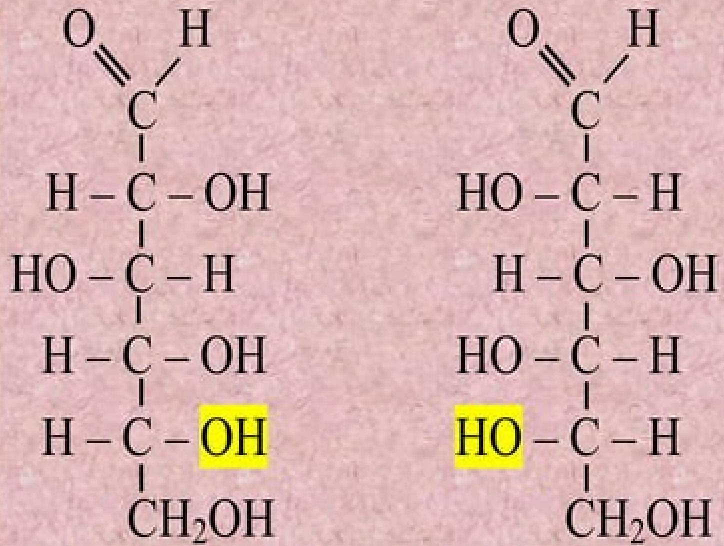


L-glyceraldehyde

Sugar Nomenclature

For sugars with more than one chiral center, **D** or **L** refers to the asymmetric **Carbon** farthest from the aldehyde or keto group.

Most naturally occurring sugars are D isomers.



D-glucose L-glucose

As reducing or non reducing sugars

-

- All those carbohydrates **which reduce Fehling's solution and Tollens' reagent are referred to as reducing sugars**.
- In disaccharides, if the reducing groups of monosaccharides i.e., aldehydic or ketonic groups are bonded, these are **non-reducing sugars e.g. sucrose**. On the other hand, **sugars in which these functional groups are free, are called reducing sugars, for example, maltose and lactose**.

Glucose

- ***Source***: It is present in **sweet fruits and honey**.
- **Ripe grapes** also contain glucose in large amounts.

Preparation of Glucose:

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{HCl} C_6H_{12}O_6 + C_6H_{12}O_6$$

Sucrose → D-Glucose + D fructose

$[\alpha]_D = +66.5^o$ (Sucrose); $[\alpha]_D = 52.5^o$ (D-Glucose); $[\alpha]_D = -92.4^o$ (D fructose)

$$(C_6H_{12}O_5)_n + nH_2O \xrightarrow[393\ k,\ 2-3\ bars]{H^+} nC_6H_{12}O_6$$

Starch or cellulose → glu cose

Structure of Glucose

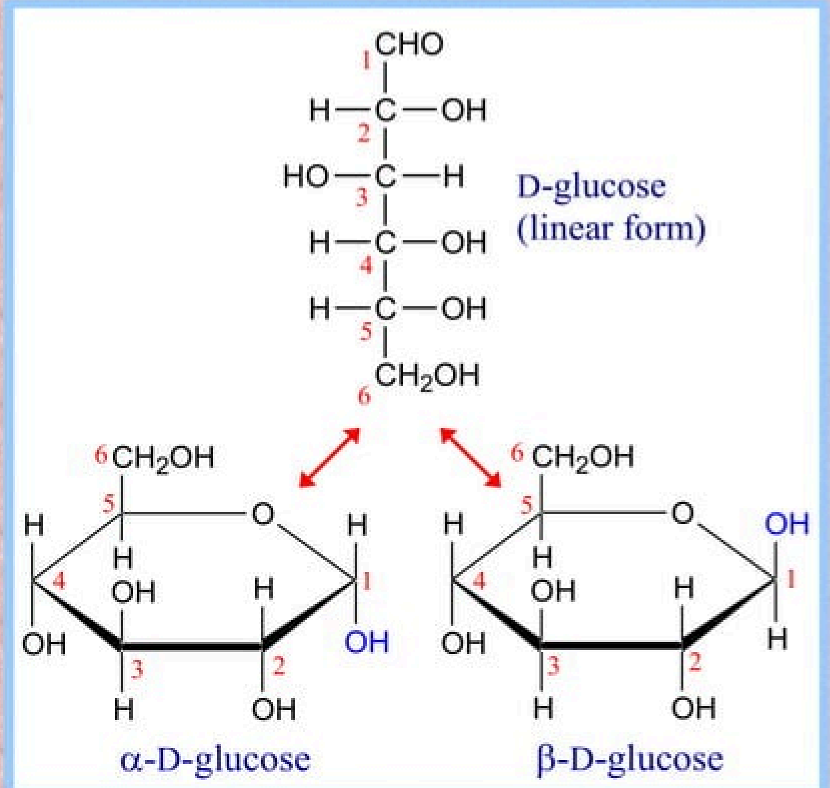
Molecular formula $C_6H_{12}O_6$				
Glucose	Reaction	Reagent	Products	Proves that
$CHO-(CHOH)_4-CH_2OH$	On prolonged heating ***with HI***, it forms n-hexane	$\xrightarrow{HI,\ \Delta}$	$CH_3-CH_2-CH_2-CH_2-CH_2-CH_3$ (*n*-Hexane)	all the six carbon atoms are linked in **a straight chain.**
	Glucose reacts with ***hydroxylamine*** to form an oxime and adds a molecule of ***hydrogen cyanide*** to give cyanohydrin.	$\xrightarrow{NH_2OH}$	$CH=N-OH$ – $(CHOH)_4$ – CH_2OH	These reactions confirm the **presence of a carbonyl group (>C = O)** in glucose.
		$\xrightarrow{HCN}$	$CH(CN)(OH)$ – $(CHOH)_4$ – CH_2OH	

Molecular formula, $C_6H_{12}O_6$

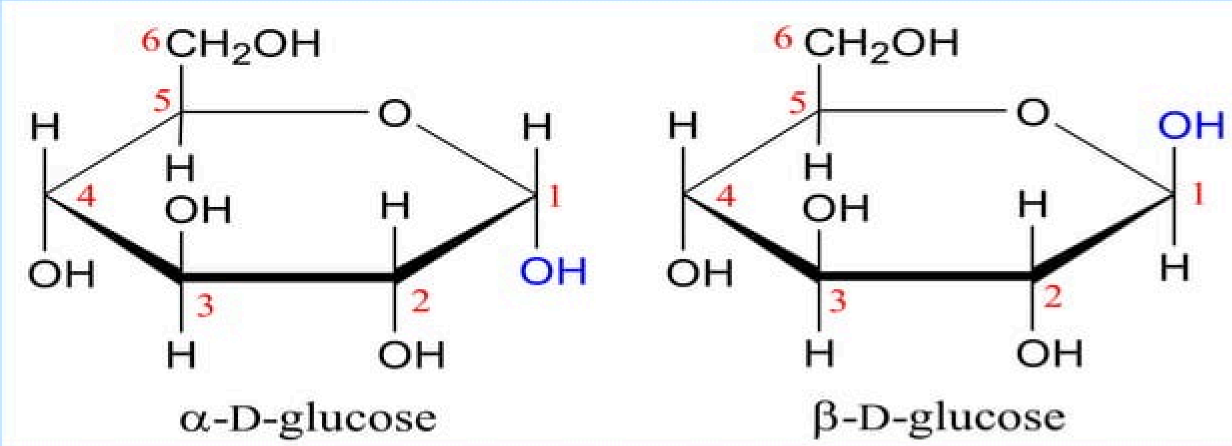
Glucose	Reaction	Reagent	Products	Proves that
CHO | $(CHOH)_4$ | CH_2OH	Glucose gets oxidised to six carbon carboxylic acid (gluconic acid) on reaction with a mild ***oxidising agent like bromine water.***	$\xrightarrow{Br_2\ water}$	$COOH$ | $(CHOH)_4$ | CH_2OH Gluconic acid	the carbonyl group is present as an **aldehydic group**.
	Acetylation of glucose ***with acetic anhydride*** gives glucose pentaacetate	$\xrightarrow{Acetic\ anhydride}$	CHO | $(CH{-}O{-}\overset{O}{\overset{\Vert}{C}}{-}CH_3)_4$ | $CH_2{-}O{-}\overset{O}{\overset{\Vert}{C}}{-}CH_3$	which confirms the presence of **five –OH groups attached to different carbon atoms.**
	On ***oxidation with nitric acid***, glucose as well as gluconic acid both yield a dicarboxylic acid, saccharic acid.	$\xrightarrow{Oxidation}$	$COOH$, $(CHOH)_4$, $COOH$ (Saccharic acid) $\xleftarrow{Oxidation}$ $COOH$, $(CHOH)_4$, CH_2OH (Gluconic acid)	This indicates the presence **of a primary alcoholic (–OH) group** in glucose.

Pentoses and hexoses can cyclize as the ketone or aldehyde reacts with a distal OH.

Glucose forms an intra-molecular hemiacetal, as the C1 aldehyde & C5 OH react, to form a 6-member pyranose ring, named after pyran.



These representations of the cyclic sugars are called Haworth projections.



Cyclization of glucose produces a new asymmetric center at C1. The 2 stereoisomers are called anomers, α & β.

Haworth projections represent the cyclic sugars as having essentially planar rings, with the OH at the anomeric C1:

- α (OH below the ring)
- β (OH above the ring).

Reactions and facts about glucose which <u>cannot</u> be explained by its open chain structure

- Despite having the aldehyde group, glucose ***does not give Schiff's test*** and it ***does not form the hydrogensulphite addition product with $NaHSO_3$***.

- The pentaacetate of glucose **does not react with hydroxylamine** <u>indicating the absence of free —CHO group</u>.

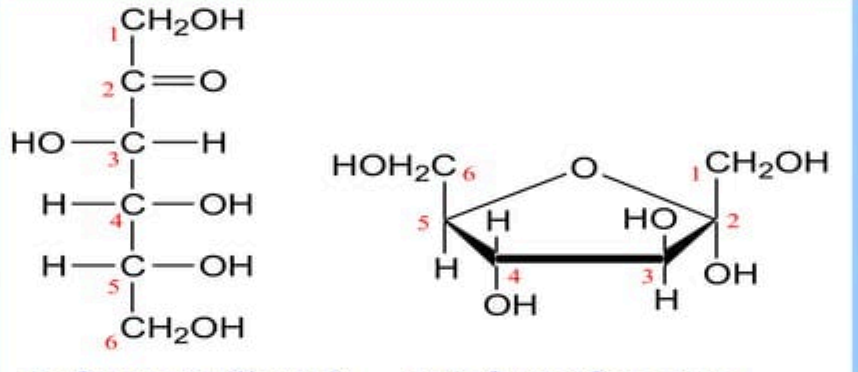
- Glucose is found to **exist in 2 different crystalline forms which - α and β**. The α-form of glucose (m.p. 419 K) is obtained by crystallisation from concentrated solution of glucose at 303 K while the β-form (m.p. 423 K) is obtained by crystallisation from hot and saturated aqueous solution at 371 K.

This behaviour could not be explained by the open chain structure.

Fructose

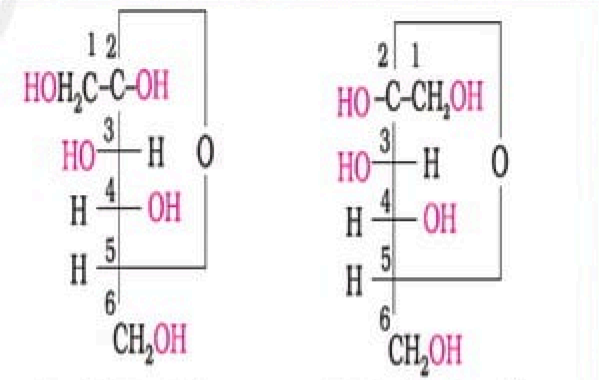
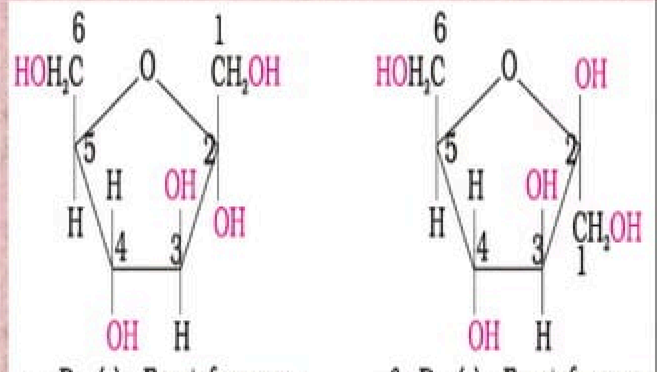
Fructose is an important **ketohexose.**

It is obtained along with glucose by the hydrolysis of sucrose.



D-fructose (linear) α-D-fructofuranose

Fructose forms a 5-member furanose ring, by reaction of the C2 keto group with the OH on C5.

Its two cyclic forms, **α and β,** are obtained by the addition of -OH at C5 to the (>C=O) group. The ring, thus formed, is a 5 membered furanose ring.	The cyclic structures of two **anomers** of fructose are represented by Haworth structures as given.
 *α*-D-(-)-Fructofuranose *β*-D-(-)-Fructofuranose	 *α*-D-(-)-Fructofuranose *β*-D-(-)-Fructofuranose

References:

1. NCERT Class XII Chemistry Vol 2
2. Google images