بسم الله الرحمن الرحيم

Basic Principles and Perspectives in Medical Chemistry and Biochemistry

Chemistry of Carbohydrates

Part-1- Monosaccharides & Disaccharides

Medical and Biochemistry (BIQC-101) Lecture

by

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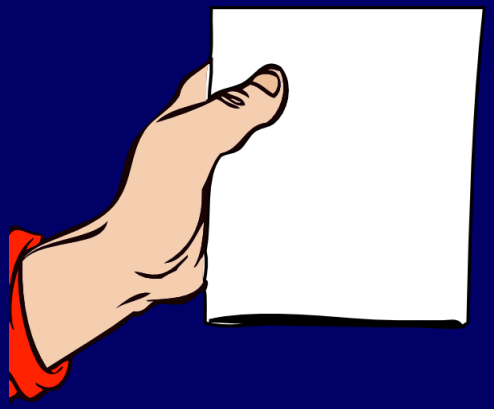
Carbohydrates Chemistry

Learning Objectives

1. Define carbohydrate and the groups of saccharides
2. Know the chemical structure of the common sugars .
3. Understand the concepts of and isomerism in simple sugars anomers.
4. Glycosides, sugar alcohols, sugar acids, phosphate esters, deoxy sugars and amino sugars.
5. Understand the role saccharides play in biology
6. Know the biochemical functions and differences between the various heteropolysaccharides
7. Be able to recognize the N and O linked polysaccharides
8. Know how dietary polysaccharides are digested by humans



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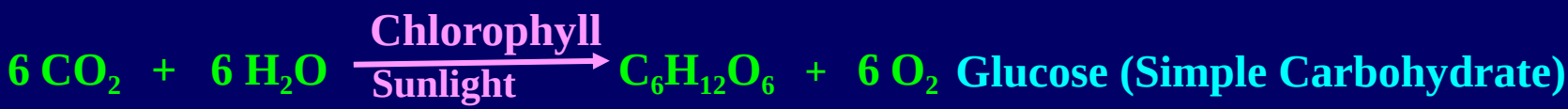
Introduction

- Carbohydrates are organic biomolecules abundantly present in the nature, found in the cells of plants and animals.
- Carbohydrates are predominantly biosynthesized by plants through **photosynthesis**. Glucose is synthesized in plants from CO_2, H_2O, and solar energy from the sun.



- Animals and human beings cannot biosynthesize carbohydrates predominantly. Thus carbohydrates are chief constituents of human food.
- However in a critical condition when cells are deprived of glucose, Human body biosynthesizes glucose using the non carbohydrate precursors present in body via **Gluconeogenesis**

The Functions of Carbohydrates in the Body

1. Carbohydrates serve as primary source of energy/Fuel of body (Metabolic role). Glucose $\xrightarrow{\text{Oxidation}}$ $CO_2 + H_2O + ATP$.
2. Carbohydrates provide skeletal framework to cells ,tissues, and organs of body. (Structural role)
3. Building Macromolecules: Ribose and deoxyribose are essential building blocks of RNA, DNA, and ATP.
4. Carbohydrates are associated to many other roles with human beings.

- **Sparing Protein**: Glucose is synthesized from amino acids. The presence of adequate glucose basically spares the breakdown of proteins from being used to make glucose needed by the body.
- **Lipid Metabolism**: As blood-glucose levels rise, the use of lipids as an energy source is inhibited. Thus, glucose additionally has a "fat-sparing" effect. This is because an increase in blood glucose stimulates release of the hormone insulin, which tells cells to use glucose (instead of lipids) to make energy.

Classification of Carbohydrates

Carbohydrates

1.Monosaccharide
1 Monosaccharide Unit

- Functional group
  - Aldoses
    e.g Glucose
    have an aldehyde
  - Ketoses
    e.g Fructose
    have a ketone
- Number of carbon atoms
  - Trioses
  - Tetroses
  - Pentoses
  - Hexoses

2. Disaccharide
2 Monosaccharide Units

- Reducing
  - Maltose
  - Lactose
- Non-Reducing
  - Sucrose

3.Oligosaccharides
3-10 Monosaccharide units

3 units Maltotriose (Glu-Glu-Glu)
4 units Stachyose (Glu-Fru-2Gal
5 units Verbascose (Glu-Fru-3Gal)

4. Polysaccharide
10-100 Saccharide Units

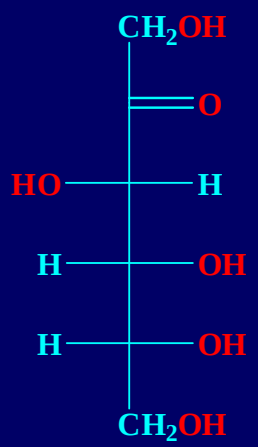
- Homopoly-saccharide
  - Starch
  - Dextrin
  - Glycogen
  - Cellulose
- Hetropoly-saccharide
  - Hyaluronic acid
  - Heparin

Monosaccharides

- Simple carbohydrates has many hydroxyl groups (polyhydroxy).
- Simple carbohydrates has carbonyl/ functional groups as aldehyde or ketone.
- Simple carbohydrates (glucose/fructose) repeatedly linked to form its condensed complex carbohydrates for ex starch, inulin.
- Monosaccharides are sub classified on the basis of:

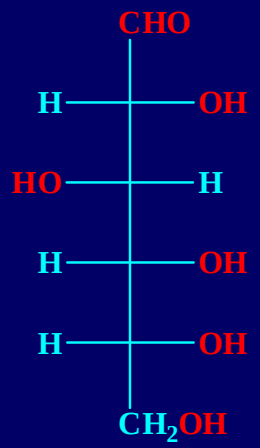
1. Functional Group
   - Aldoses (CHO)
   - Ketoses (C=O)
2. Number of Carbon atoms.
   - Trioses (3C)
   - Tetroses (4
   - Pentoses (5C)
   - Hexoses (6C)

Hexoses



Ketose

(e.g., Fructose) have a ketone group, usually at C2.



Aldose

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

Number of Carbon Atoms	Aldoses (Aldehyde-CHO)	Ketoses (Ketone -C=O)
3 Triose	Aldo Triose Glyceraldehyde	Keto Triose Di HydroxyAcetone
4 Tetrose	Aldo Tetrose Erythrose	Keto Tetrose Erythrulose
5 Pentose	Aldo Pentose Ribose, Xylose, Arabinose	Keto Pentulose Ribulose, Xylulose
6 Hexose	Aldo Hexose Glucose, Galactose ,Mannose	Keto Hexose Fructose
7 Heptose	Aldo Heptose SedoHeptose	Keto Heptulose SedoHeptulose

Properties of Monosaccharides

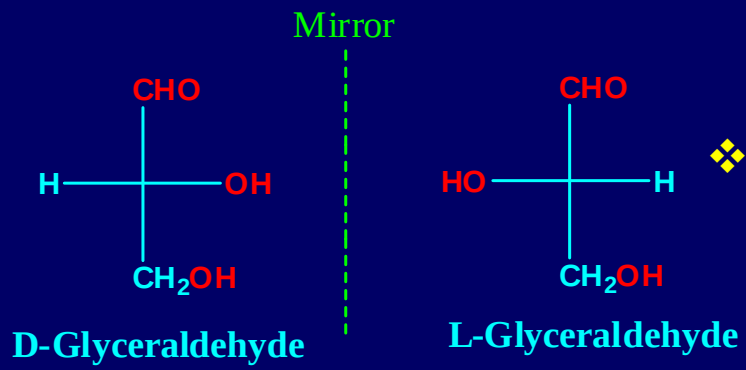
- They are composed of one saccharide unit.
- Monosaccharides cannot be further hydrolyzed.
- Monosaccharides are building blocks/monomeric units of higher forms of carbohydrates.
- All monosaccharides except di hydroxy acetone (DHA) possess **asymmetric carbon** atoms in their structure.
- Presence of **asymmetric carbon** atoms confer two properties:

1. Stereoisomerism.
2. Optical Activity

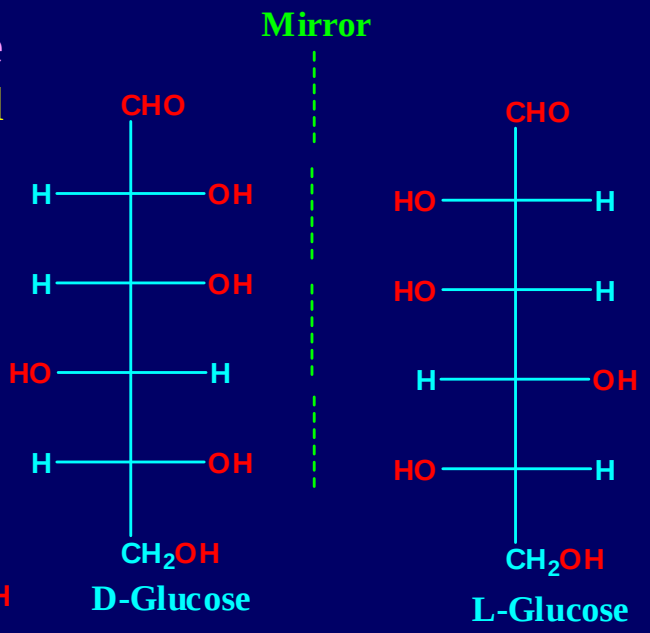
Stereoisomerism

- Stereoisomerism, or spatial isomerism, is a form of isomerism in which molecules have the same molecular formula and sequence of bonded atoms (constitution), but differ in the three-dimensional orientations of their atoms in space.
- Enantiomers, also known as optical isomers, are two stereoisomers that are related to each other by a reflection: they are mirror images of each other that are non-superposable. Human hands are a macroscopic analog of this.
- Every stereogenic center in one has the opposite configuration in the other. Two compounds that are enantiomers of each other have the same physical properties, except for the direction in which they rotate polarized light
- As a result, different enantiomers of a compound may have substantially different biological effects.
- Asymmetric centers or chiral centers: a carbon atom with four different constituents, allow the formation of stereoisomerism.

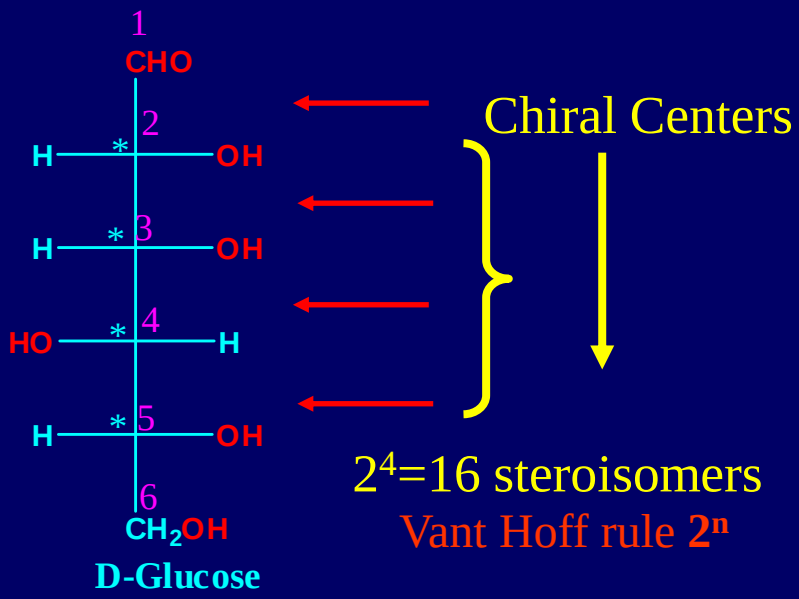
D & L Notation

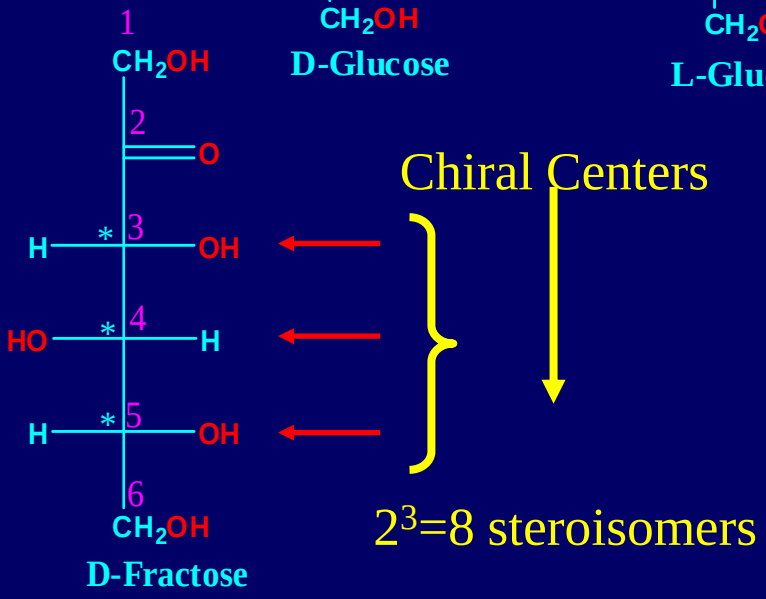


- L-carbohydrates have the -OH group of the highest chiral carbon number pointing to the lift in the Fischer projection. in L-(-)glyceraldhyde
- Enzyme Racemase interconvert '**D**' and '**L**' isomers.



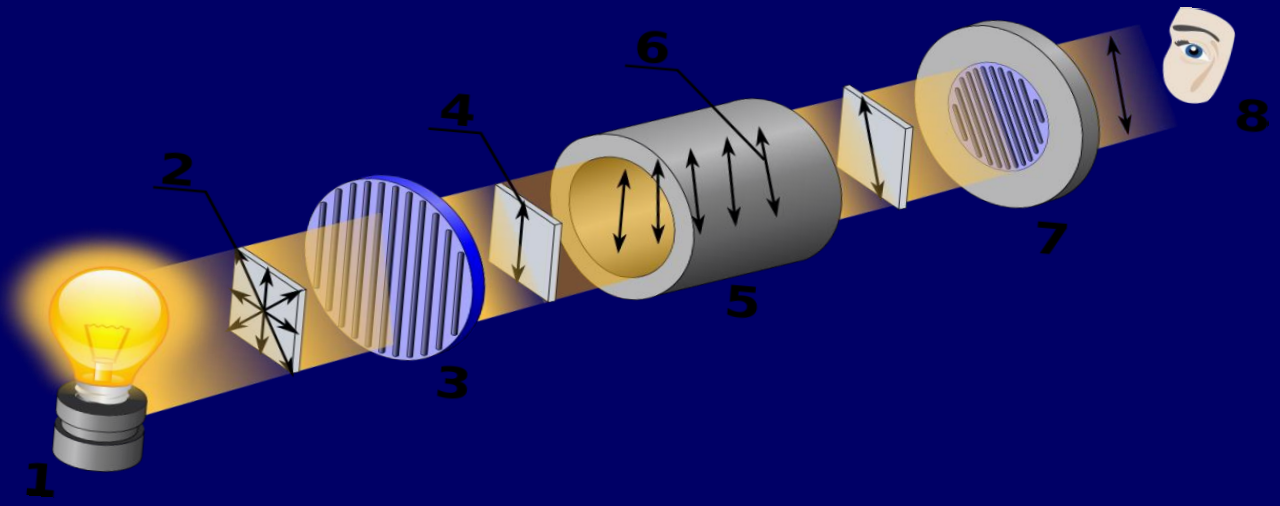
- D-carbohydrates have the -OH group of the highest chiral carbon number pointing to the right in the Fischer projection as in D-(+)-glyceraldhyde, **Sugars** present in **human body** are of **'D' series.**





Optical Activity

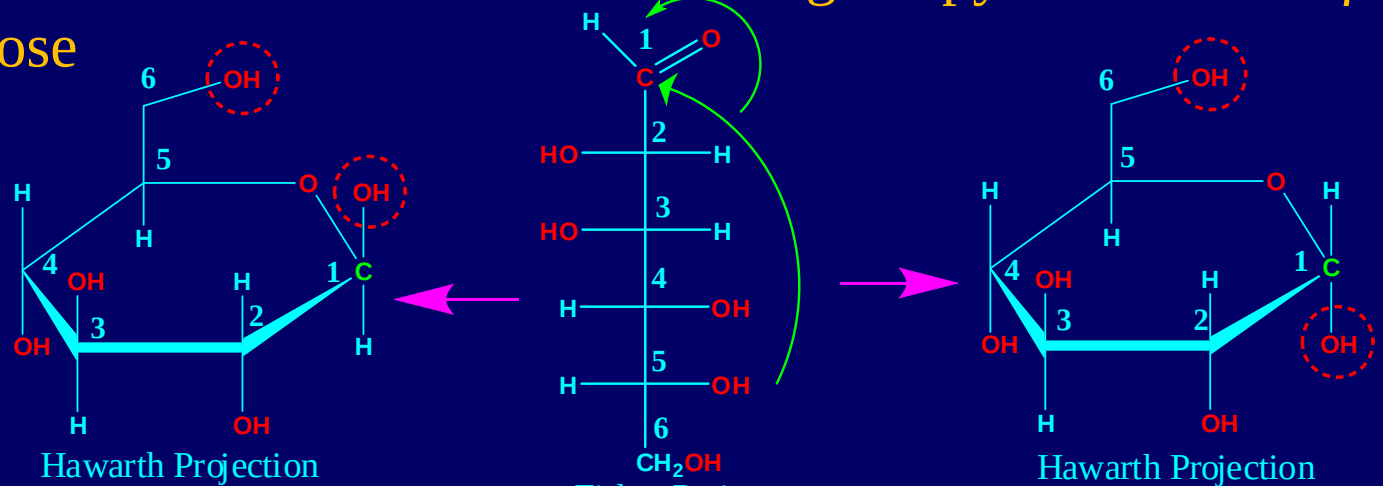
- Optical activity is the capacity of a substance to rotate the plane polarized light passing through it.
- **D** enantiomer mean dextrorotatory (d) (+) rotate to right (clockwise) direction.
- **L** enantiomer mean levorotatory (l) (-) rotate to left (anticlockwise) direction.
- When equal amount of D and L isomers are present, that mixture is said to be **recemic mixture**



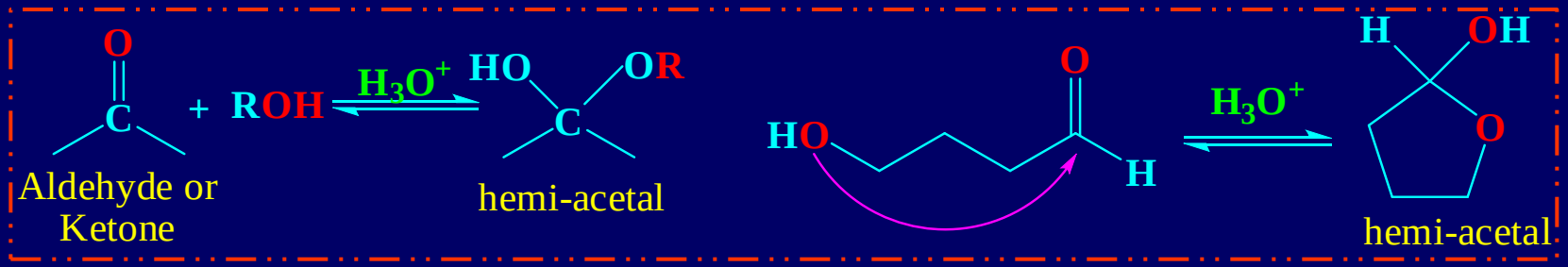
Glucose

- Grape sugar, chief blood sugar, main sugar of body cells, also termed as Dextrose.
- Glucose chemically aldo hexose, molecular formula-$C_6H_{12}O_6$
- In solution glucose predominantly exist as closed chain structure, because of cyclization of sugar, an additional asymmetric center is created at C-1 (anomeric carbon).
- This leads to formation of two isomers α- D-glucopyranose and β- D-glucopyranose

Cyclic sugars show mutarotation as α and β anomeric forms interconvert through the open chain

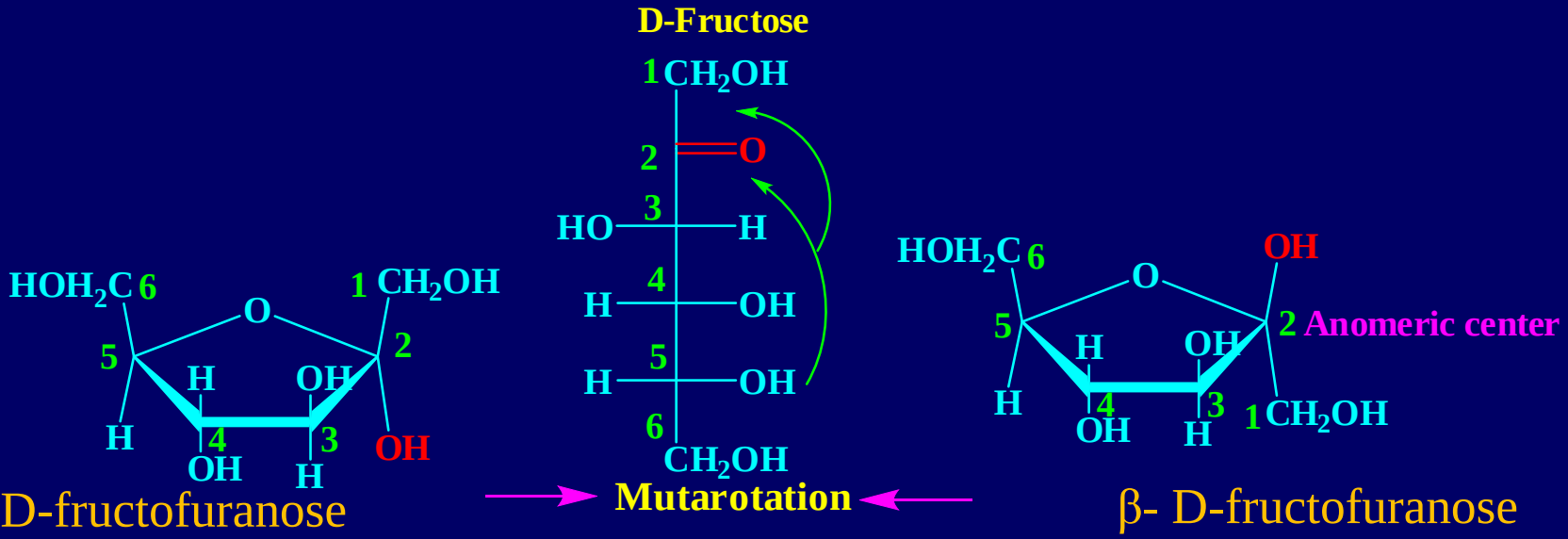


- At equilibrium: D-glucose is a mixture of the β anomer (63.6%) and the *a* anomer (36.4%)



Fructose

Fructose $C_6H_{12}O_6$ is sweetest sugar. Fructose is a keto hexose. It's found in fruits, honey, body, semen. In liver fructose is transformed to glucose and metabolized. Fructose present in semen serves as nutrient for sperms. C2 is anomeric carbon of fructose

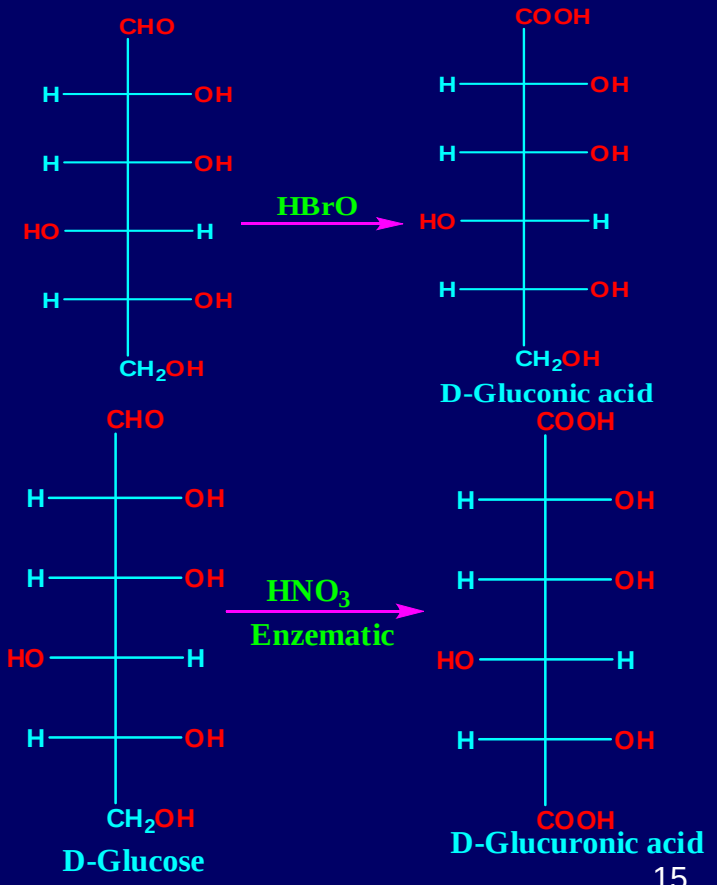


Monosaccharides Oxidation

When glucose oxidizes under proper conditions the sugars may form:

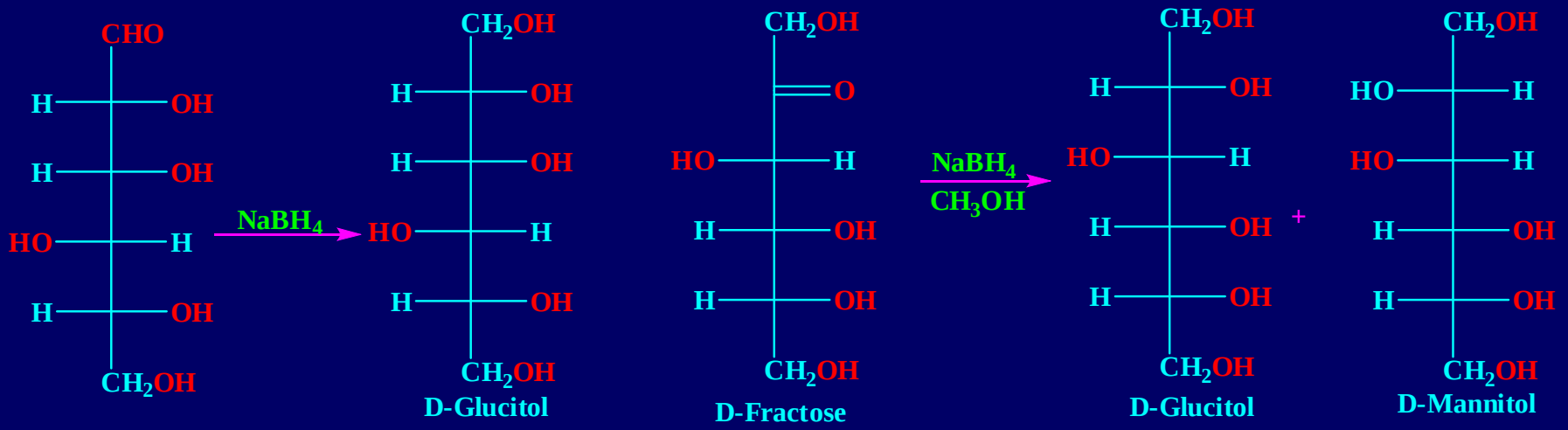
1. Monobasic aldonic Acid: oxidation with hydrobromous acid .
2. Dibasic saccharic acids or alderic acid**:** oxidation with (HNO_3).

- **Calcium gluconate (gluconic acid)** used as source of calcium. These are given I.V. fluids rise the calcium levels.
- **Glucuronic acid** produced in the liver of humans. It is a highly soluble compound that can bind to substances such as hormones, drugs, and toxins to facilitate their transport around the body. In this way glucuronic acid is largely responsible for the elimination of poisonous substances.



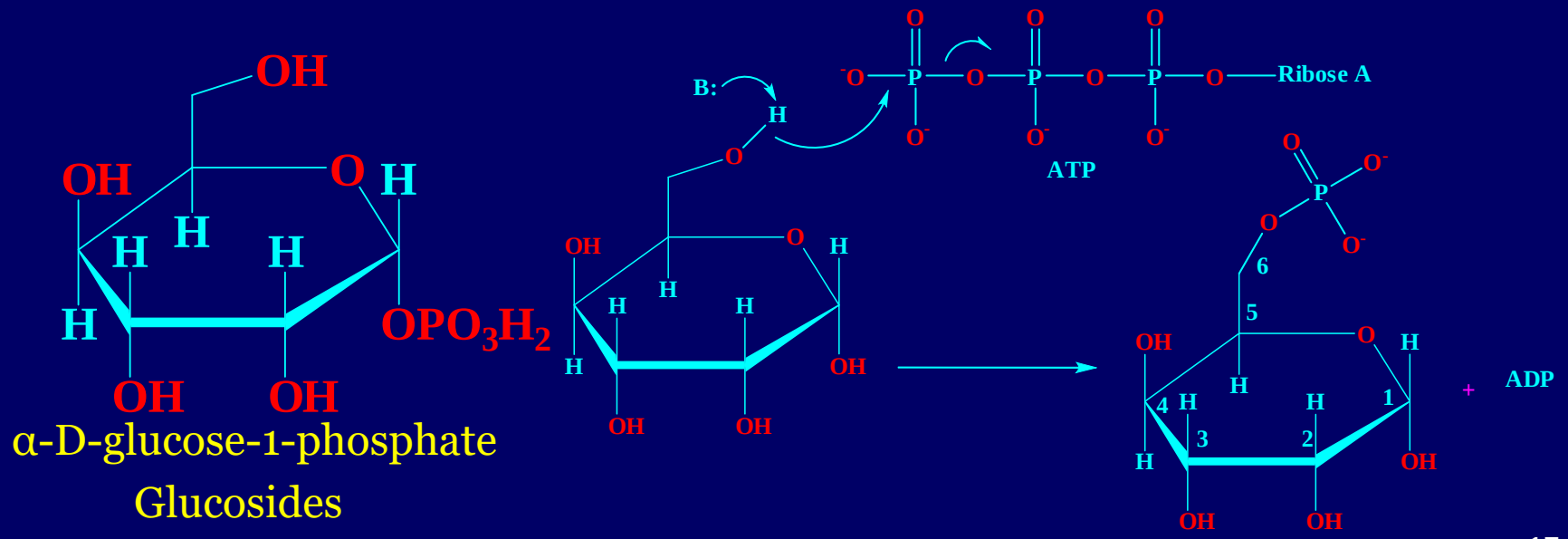
Monosaccharides Reduction

- The reduction of monosaccharides involves the carbonyl group.
- Produces sugar alcohols called ***alditols or sugar alcohols***, such as D-glucose gives **D-glucitol** also called **sorbitol**.
- Sorbitol is a sugar alcohol found in fruits and plants with diuretic, laxative and cathartic property.
- Excess blood glucose in diabetics, get reduced to Sorbitol which further deposits in the lens of eye and forms Cataract.
- sorbitol has one-third fewer calories and 60 % the sweetening activity of sucrose and is used as a sugar replacement in diabetes.



Biological Ester Formation: Phosphorylation

- ✓ A number of important antibiotics are glycosides; among the best known are streptomycin and erythromycin.
- ✓ Glucosides formed from glucose—in which the anomeric carbon atom (at position 1) has phosphoric acid linked to it, are extremely important biological compounds for example α-D-glucose-1-phosphate .
- ✓ For example, α-D-glucose-6-phosphate is an intermediate product in the biosynthesis of cellulose, starch and glycogen



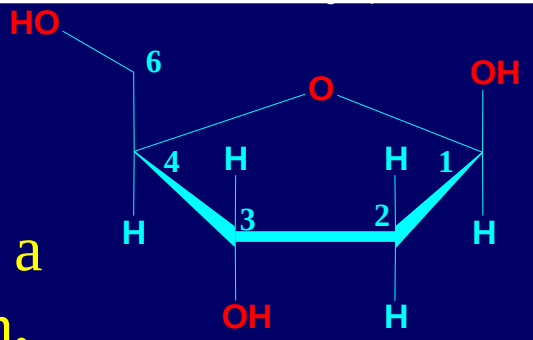
α-D-glucose-1-phosphate

Glucosides

Monosaccharide derivatives

1. Deoxy Sugars

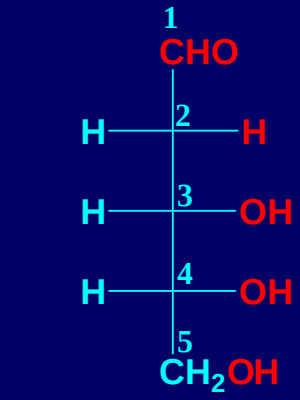
- Deoxy sugars are sugars that have had a hydroxyl group replaced with a hydrogen atom.
- Deoxyribose, or 2-deoxy-D-ribose, a constituent of DNA. Deoxyribose is synthesized through the reduction of ribose.

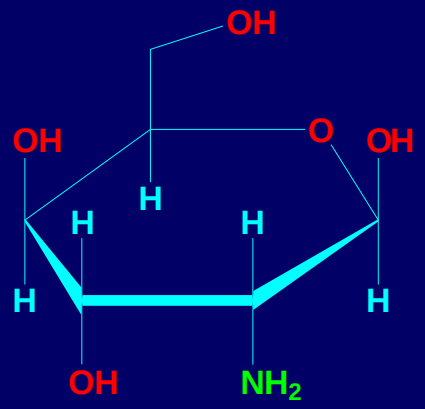


α-deoxy-D-ribose

2. Amino Sugars

- In organic chemistry, an amino sugar (or more technically a 2-amino-2-deoxysugar) is a sugar molecule in which a hydroxyl group has been replaced with an amine group.
- One of the most abundant being **β** -D-glucose amine, which is help in rebuild cartilage , joint function and connective tissue.





β -D-glucose amine

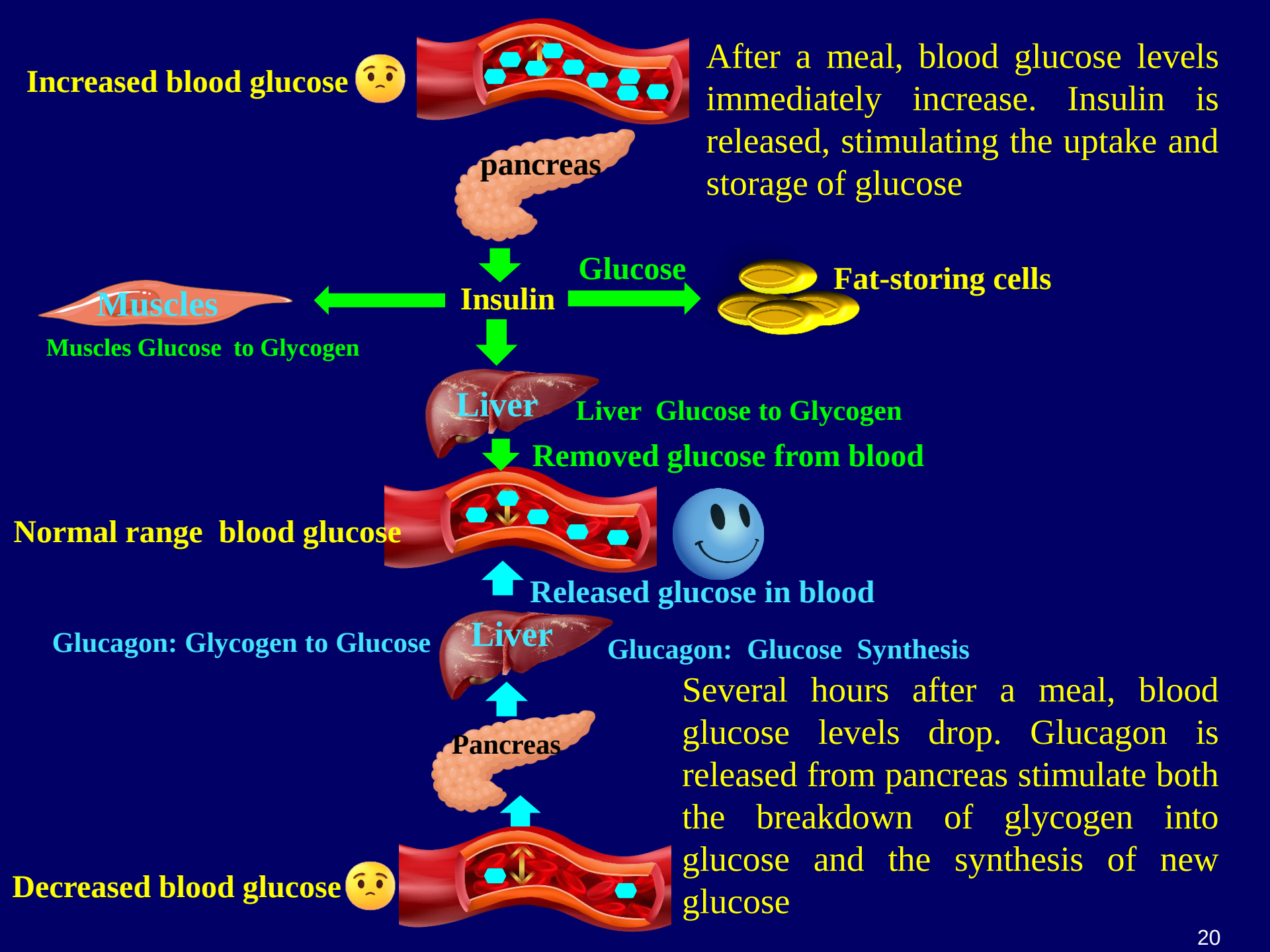
Source of glucose in the body

1. **Glycogenolysis:** Process by which glycogen, the primary carbohydrate stored in the liver and muscle, is broken down into glucose to provide immediate energy and to maintain blood glucose levels during fasting. Glycogenolysis occurs primarily in the liver and is stimulated by the hormones glucagon and epinephrine (adrenaline).
2. **Gluconeogenesis:** Is a metabolic pathway that results in the generation of glucose from non-carbohydrate carbon substrates such as pyruvate , lactate , glycerol and glucogenic amino acids.

Maintaining glucose homeostasis

Blood glucose homeostasis is regulated mainly by two hormones:

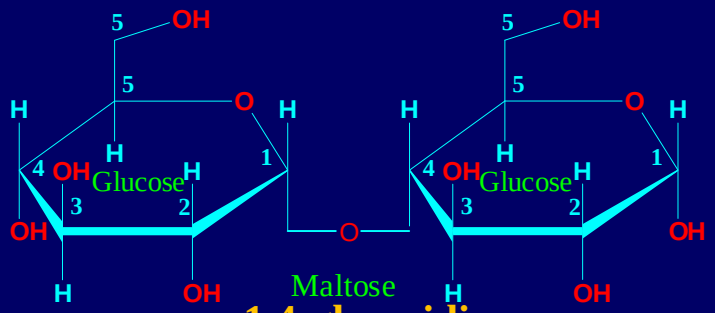
1. Insulin: secreted when blood glucose is high. Controls transport of glucose from blood to muscle and fat cells to storage the excess.
2. Glucagon: secreted when blood glucose is low. Helps in release of glucose from storage.


Increased blood glucose
pancreas
After a meal, blood glucose levels immediately increase. Insulin is released, stimulating the uptake and storage of glucose
Glucose
Insulin
Muscles
Fat-storing cells
Muscles Glucose to Glycogen
Liver
Liver Glucose to Glycogen
Removed glucose from blood
Normal range blood glucose
Released glucose in blood
Glucagon: Glycogen to Glucose
Liver
Glucagon: Glucose Synthesis
Several hours after a meal, blood glucose levels drop. Glucagon is released from pancreas stimulate both the breakdown of glycogen into glucose and the synthesis of new glucose
Pancreas
Decreased blood glucose

Disaccharide

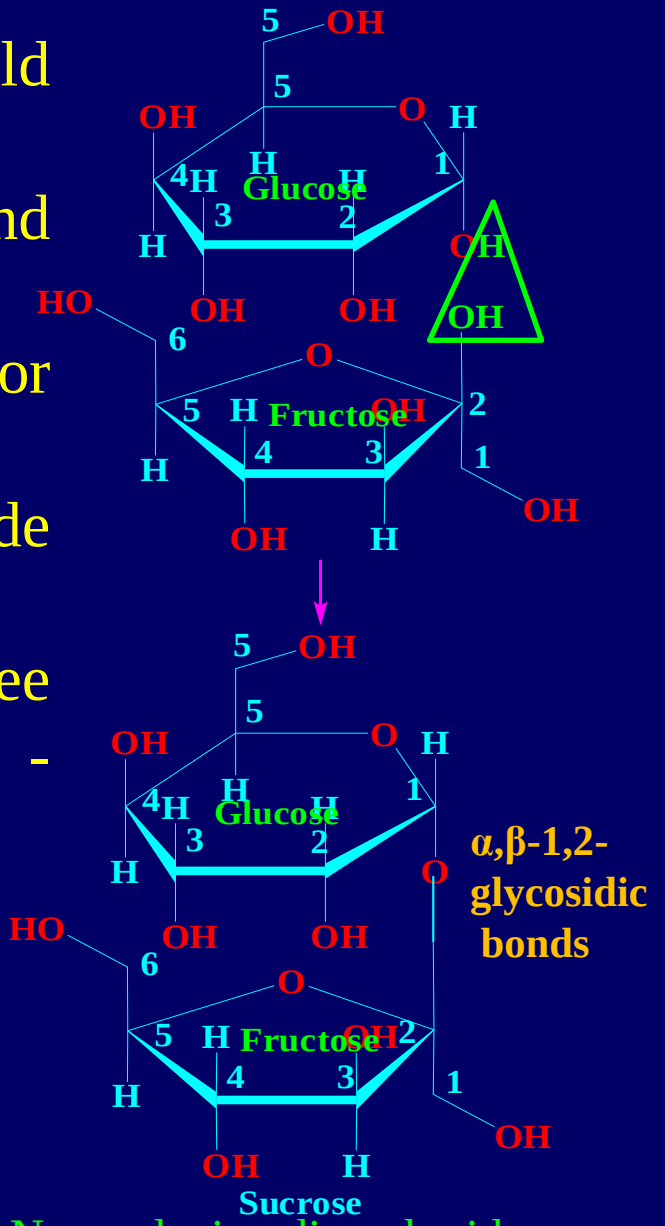
- Consists of two monosaccharide units held by **glycosidic bond.**
- They are crystalline, water soluble, and sweet taste.
- They subdivide based on presence or absence of free reducing group into…

1. Reducing disaccharides with free aldehyde or ketone group ex: Maltose and Lactose
2. Non reducing disaccharide without free aldehyde or ketone group example - Sucrose



α-1,4-glycosidic bonds

Reducing disaccharides



α,β-1,2-glycosidic bonds

Non reducing disaccharide

Reducing Sugar Vis Non Reducing Sugars

	Reducing Sugar	Non Reducing Sugars
Structure	Possessing free or potential (reactive) aldehyde or ketone group	Not possessing free or potential aldehyde or ketone group
Reaction	Reducing property efficiently in alkaline medium and reduces certain metallic ions as- Cu^{++};Bi^{++};Fe^{+++}	Does not show reducing property and do not reduce metallic ions
Chemical test	Reducing Sugars answer following tests positive :- Benedict's Test, Fehling's test Nylander's Test, Form Osazones.	Non reducing sugars give following reducing tests negative: Benedict's Test Fehling's test, Nylander's Test Do not form Osazones
Mutarotation	Reducing shows Mutarotation	Do not exhibit Mutarotation
Optical activity	Change in Optical activity	Change in optical activity
Examples	Monosaccharides : Ribose, Glucose, Galactose, Fructose Disaccharides : Lactose, Maltose	Disaccharides: Sucrose , Trehalose Polysaccharides/Complex Carbohydrates are Non reducing

Thank You For Your Attention