CARBOHYDRATES: STRUCTURE AND FUNCTION

By Dr. Sumbul Fatma

Objectives

To understand:

- The structure of carbohydrates of physiological significance
- The main role of carbohydrates in providing and storing of energy
- The structure and function of glycosaminoglycans

OVERVIEW

- **Carbohydrates:**
- The most abundant organic molecules in nature The empiric formula is (CH₂O)n, "hydrates of carbon"
- **Carbohydrates:**

provide important part of energy in diet Act as the storage form of energy in the body are structural component of cell membranes

OVERVIEW



Many diseases associated with disorders of carbohydrate metabolism including:

Diabetes mellitus

Galactosemia

Glycogen storage diseases

Lactose intolerance

CLASSIFICATION

Monosaccharides: Simple sugar

- Disaccharides: 2 monosaccharide units
- Oligosaccharides: 3-10 monosaccharide units
- Polysaccharides: more than 10 sugar units
 Homopolysaccharides & heteropolysaccharides

Monosaccharides

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Further classified based on:

1. No. of carbon atoms

| Generic | names | Exa |
|-------------------|----------|-------|
| 3 carbons: | trioses | Glyce |
| 4 carbons: | tetroses | Eryth |
| 5 carbons: | pentoses | Ribo |
| 6 carbons: | hexoses | Gluc |
| | | |

- 7 carbons: heptoses
- 9 carbons: nonoses

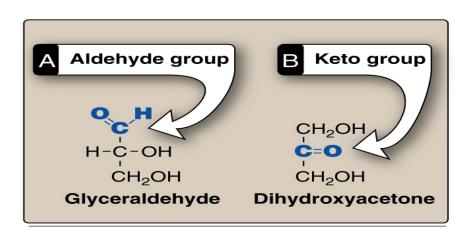
amples

eraldehyde

- rose
- se
- ose
- Sedoheptulose
- Neuraminic acid

2. Functional sugar group: Aldehyde group – aldoses

Keto group – ketoses



Monosaccharides

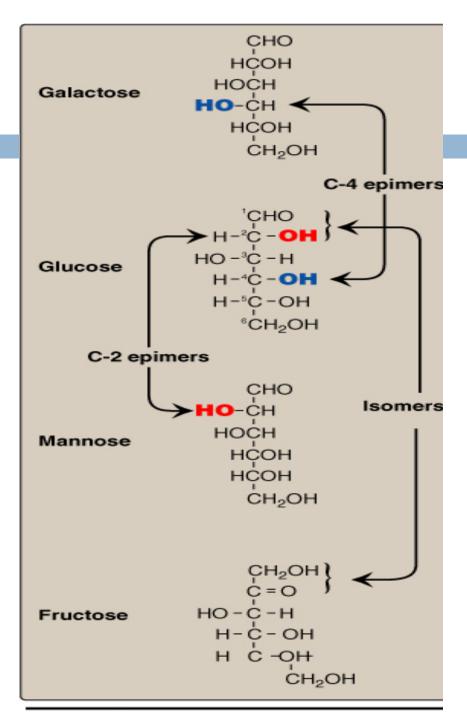
CONT'D

| | Aldose | Ketose |
|---------|----------------|------------------|
| Triose | Glyceraldehyde | Dihydroxyacetone |
| Pentose | Ribose | Ribulose |
| Hexose | Glucose | Fructose |

Isomerism

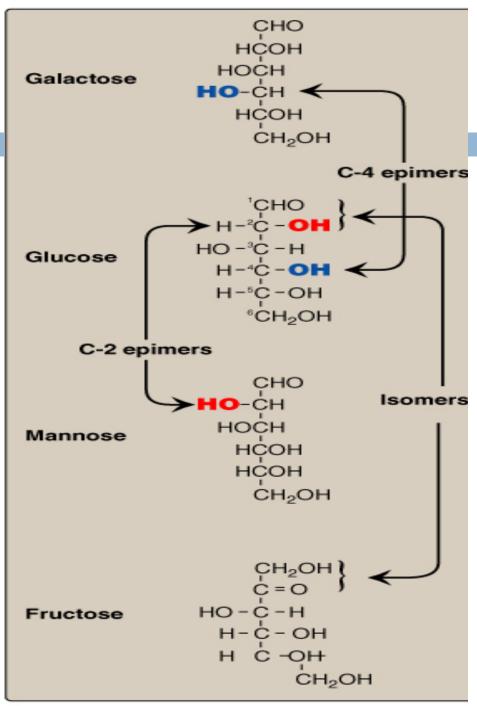
Isomers

Compounds having same chemical formula but different structural formula



Aldo-Keto Isomers

Example: Glucose (Aldose) and Fructose (Ketose)

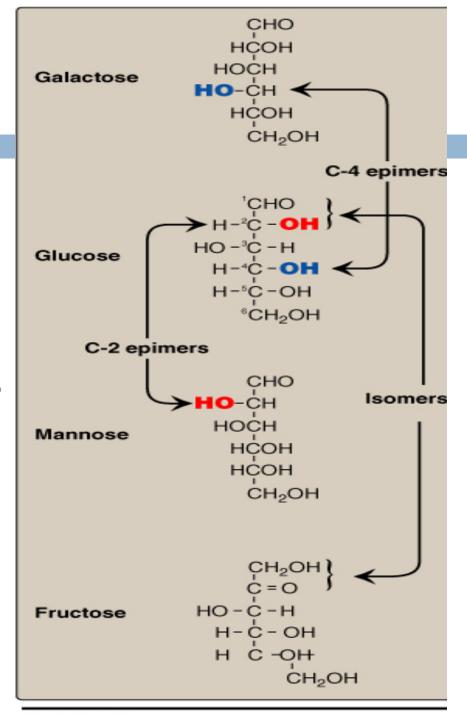




Epimers

CHO dimers that differ in configuration around only one specific carbon atom -Glucose and galactose, C4 -Glucose and Mannose, C2

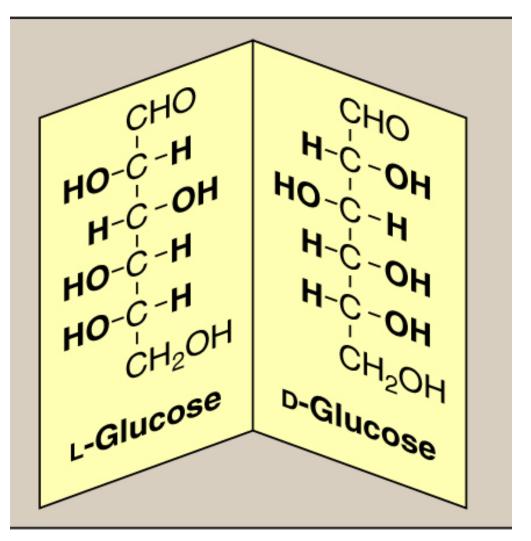
Galactose and mannose are not epimers



Enantiomers (D- and L-Forms)

Structures that are **mirror images** of each other and are designated as D- and L- sugars based on the position of –OH grp on the **asymmetric carbon farthest from the carbonyl carbon**

Majority of sugars in humans are **D-sugars**



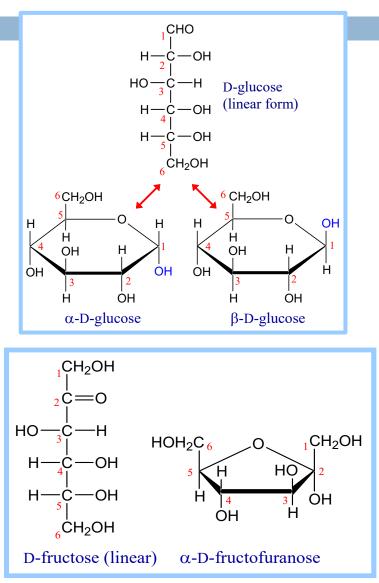
α- and β-Forms

Cyclization of Monosaccharides

Monosaccharides with 5 or more carbon are predominantly found in the ring form

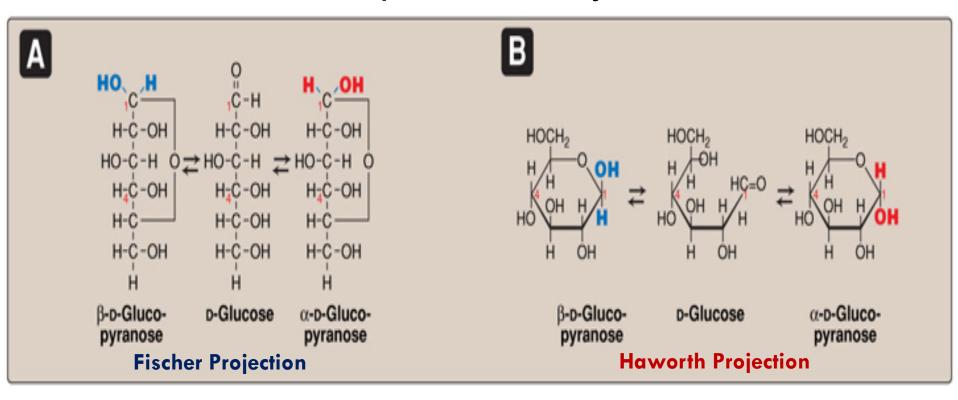
-The aldehyde or ketone grp reacts with the –OH grp on the same sugar

-Cyclization creates an **anomeric carbon** (former carbonyl carbon) generating the α and β configurations



Mutarotation

In solution, the cyclic α and β anomers of a sugar are in equilibrium with each other, and can be interconverted spontaneously





- 1. Aldo-keto
- 2. Epimers
- **3.** D- and L-Forms
- **4.** α- and β-anomers

Disaccharides

Joining of 2 monosaccharides by O-glycosidic bond:

Maltose (α -1, 4)= glucose + glucose

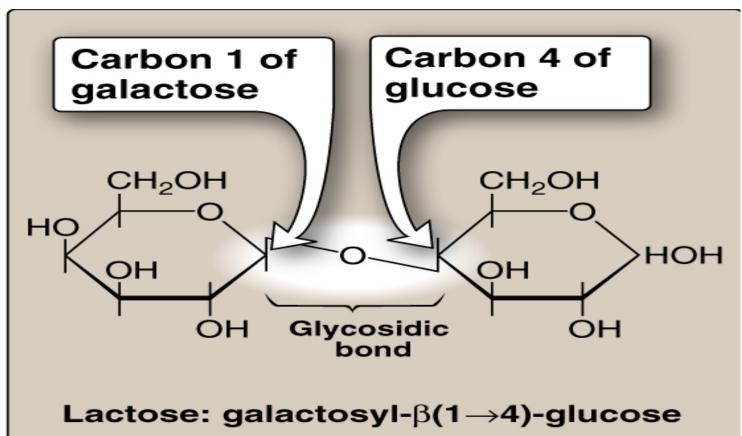
Sucrose $(\alpha - 1, 2) = glucose + fructose$

Lactose (β -1,4) = glucose + galactose

Disaccharides

CONT'D

Lactose



Polysaccharides

Homopolysaccharides: **Branched**: Glycogen and starch (α -glycosidic polymer) **Unbranched**: Cellulose (β -glycosidic polymer) Heteropolysaccharides:

e.g., glycosaminoglycans (GAGs)

Reducing Sugars

- If the O on the anomeric C of a sugar is not attached to any other structure (Free), that sugar can act as a reducing agent
- Reducing sugars reduce chromogenic agents like Benedict's reagent or Fehling's solution to give a colored precipitate
- Urine is tested for the presence of reducing sugars using these colorimetric tests

Reducing Sugars

CONT'D

Examples: Monosaccharides

Maltose and Lactose

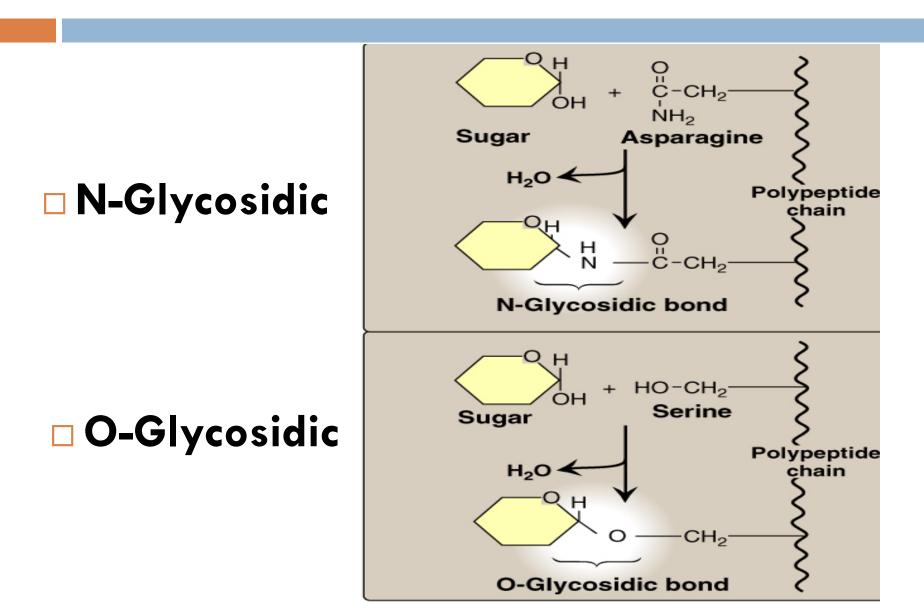
Sucrose is non-reducing, Why?

Complex Carbohydrates

Carbohydrates attached to non-carbohydrate structures by glycosidic bonds (O- or N-type) e.g.,

- 1. Purine and pyrimidine bases in nucleic acids
- 2. Bilirubin
- 3. Proteins in glycoproteins and proteoglycans
- 4. Lipids found in glycolipids

Glycosidic Bonds



Glycosaminoglycans (GAGs)

- Glycosaminoglycans (GAGs) are large complexes of negatively charged heteropolysaccharide chains
- are associated with a small amount of protein, forming proteoglycans, which consist of over 95 percent carbohydrate
- bind with large amounts of water, producing the gellike matrix that forms body's ground substance
- The viscous, lubricating properties of mucous secretions also result from GAGs, which led to the original naming of these compounds as mucopolysaccharides

Glycosaminoglycans (GAGs)

GAGs are linear polymers of repeating disaccharide units

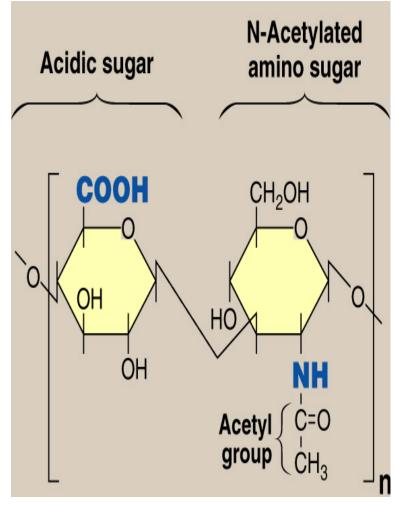
[acidic sugar-amino sugar]n

The amino sugar (usually sulfated) is either D-glucosamine or D-galactosamine

□ The acidic sugar is either

D-glucuronic acid or L-iduronic acid

 GAGs are strongly negatively-charged: carboxyl groups of acidic sugars
 Sulfate groups



Resilience of GAGs

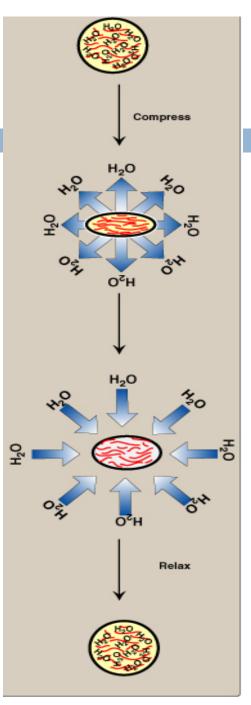
Relationship between glycosaminoglycan structure and function

Because of negative charges, the GAG chains tend to be extended in solution and repel each other and when brought together, they "slip" past each other

This produces the <u>"slippery" consistency of mucous</u> <u>secretions and synovial fluid</u>

When a solution of GAGs is compressed, the water is "squeezed out" and the GAGs are forced to occupy a smaller volume. When the compression is released, the GAGs spring back to their original, hydrated volume because of the repulsion of their negative charges

This property contributes to the **resilience of synovial fluid and the vitreous humor of the eye**



Members of GAGs

Examples of GAGs are:

- 1. Chondroitin sulfates: Most abundant GAG
- 2. Keratan sulfates: Most heterogeneous GAGs
- **3. Hyaluronic acid:** Compared to other GAGs, it is unsulfated and not covalently attached to protein
- 4. Heparin: Unlike other GAGs, Unlike other GAGs that are extracellular, heparin is intracellular and serves as an anticoagulant

Take home Message

Structure and function of carbohydrates

- Mono-, Di-, and Poly-saccharides
- Sugar Isomers: Aldo-keto, epimers, D- and L-, αand β-anomers
- Complex carbohydrates:

e.g., Glycosaminoglycans and proteoglycans

- Structure and function of GAGs
- Examples of GAGs: chondroitin sulfate, keratin sulfate, hyaluronic acid and heparin



Lippincott's Illustrated reviews- Biochemistry, 6th Edition, pages- 83-86 and 157-159