

CARBOHYDRATES: STRUCTURE AND FUNCTION

By

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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 $(\text{CH}_2\text{O})_n$, “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

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- **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

Further classified based on:

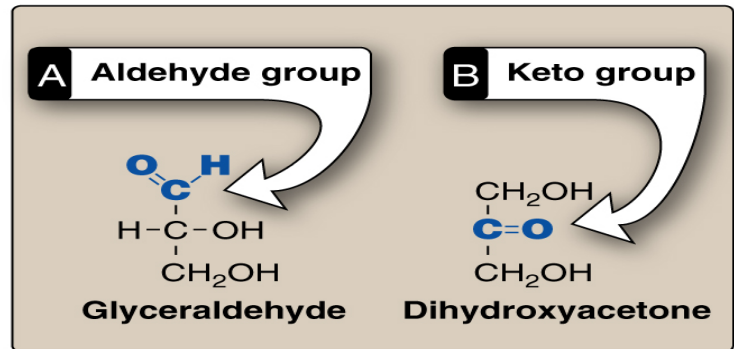
1. No. of carbon atoms

<u>Generic names</u>	<u>Examples</u>
3 carbons: trioses	Glyceraldehyde
4 carbons: tetroses	Erythrose
5 carbons: pentoses	Ribose
6 carbons: hexoses	Glucose
7 carbons: heptoses	Sedoheptulose
9 carbons: nonoses	Neuraminic acid

2. Functional sugar group:

Aldehyde group –
aldoses

Keto group – **ketoses**



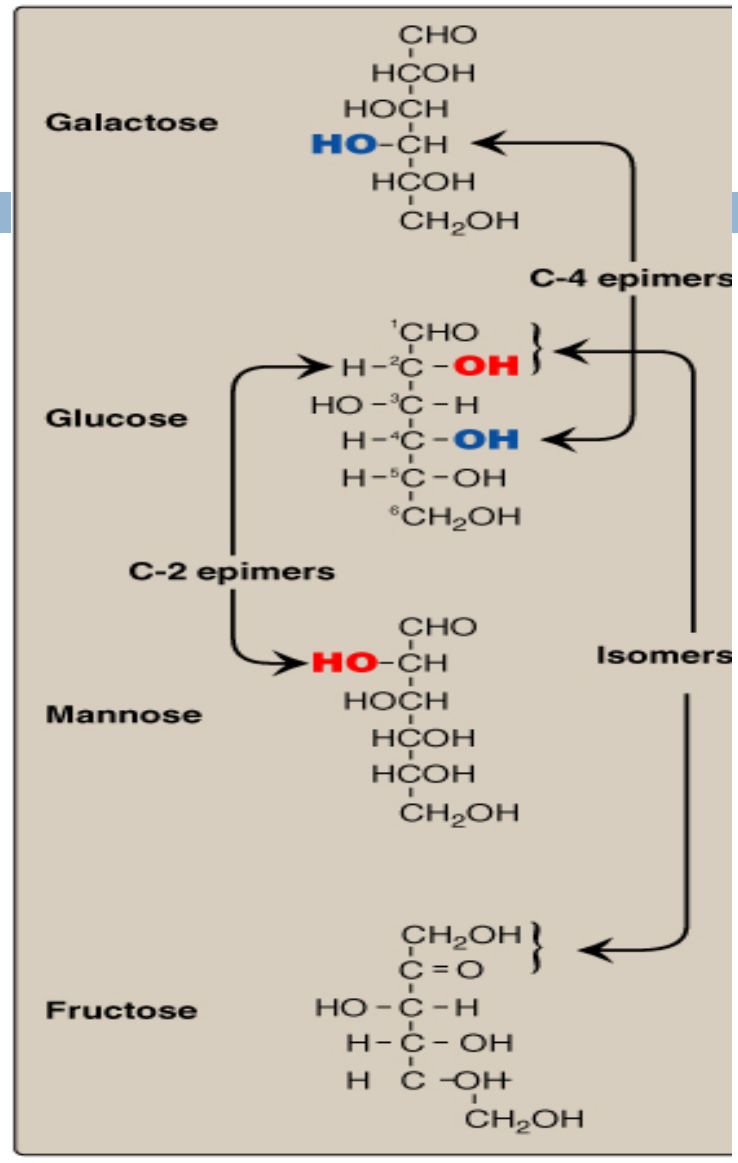
Monosaccharides

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	Aldose	Ketose
Triose	Glyceraldehyde	Dihydroxyacetone
Pentose	Ribose	Ribulose
Hexose	Glucose	Fructose

Isomerism

- **Isomers**
Compounds having same chemical formula but different structural formula



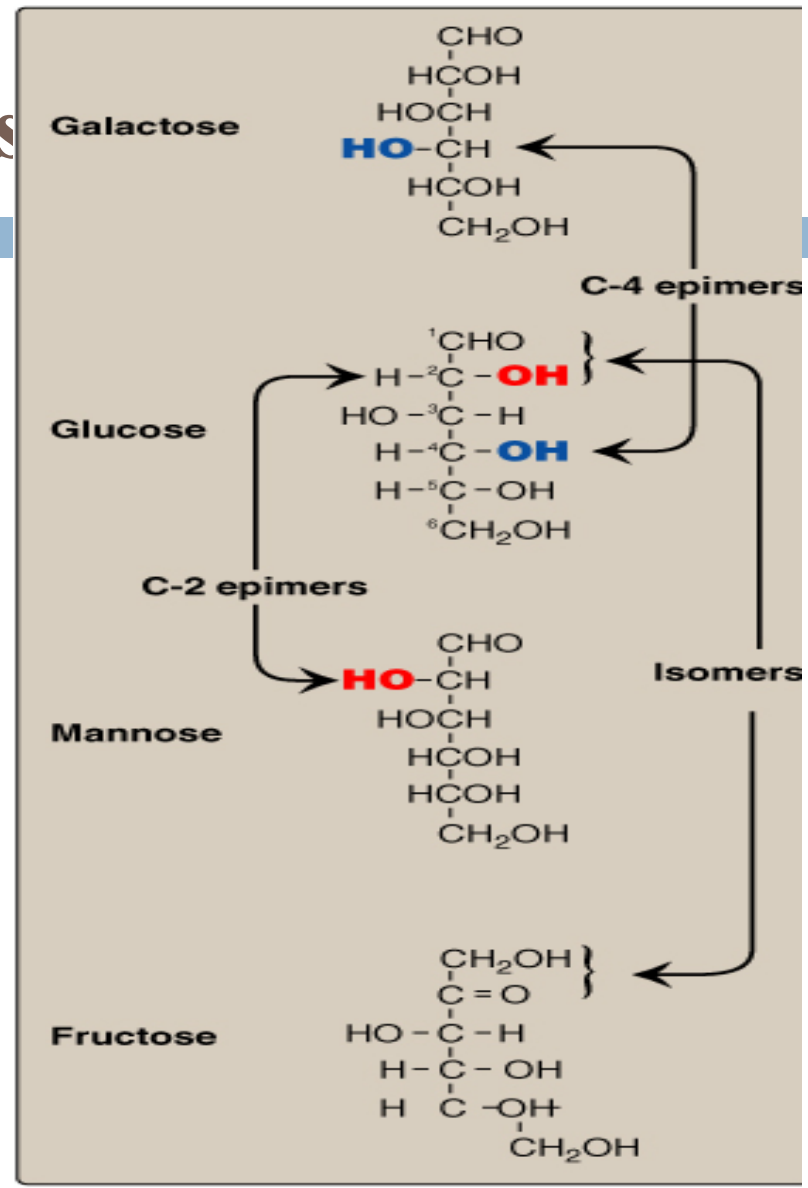
Aldo-Keto Isomers

Example:

Glucose (Aldose)

and

Fructose (Ketose)



Epimers

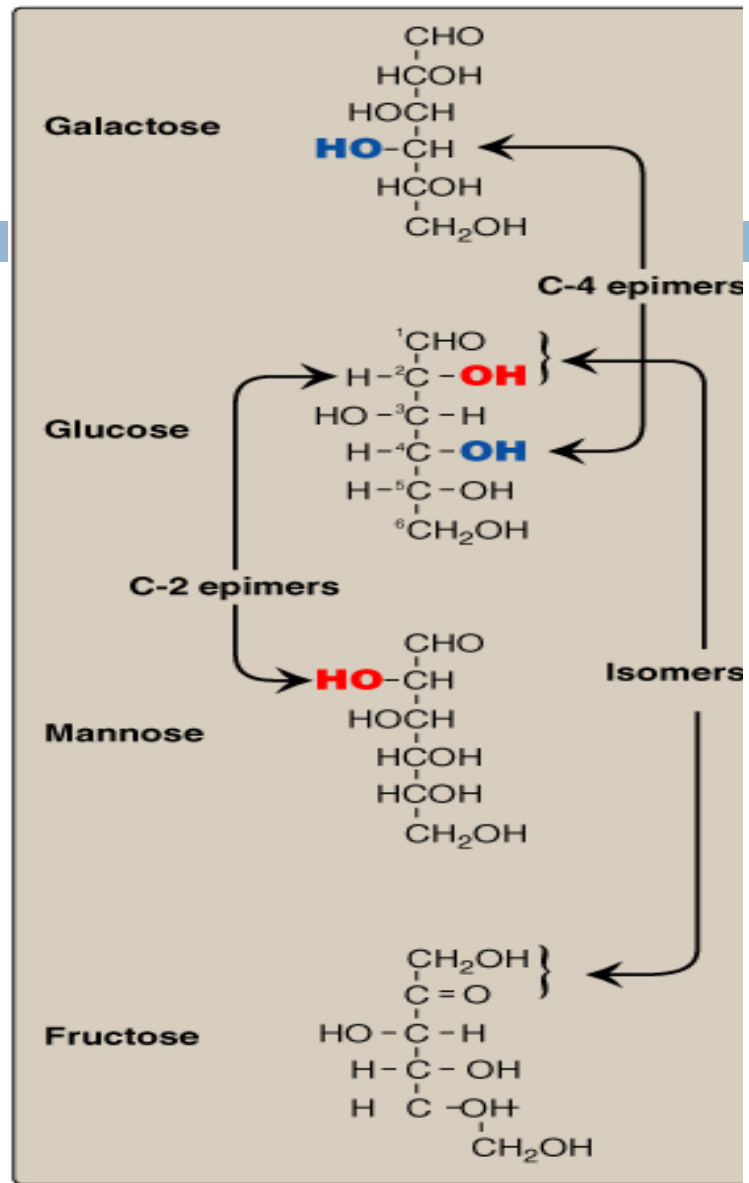
Epimers

CHO dimers that differ in configuration around only one specific carbon atom

-Glucose and galactose, C4

-Glucose and Mannose, C2

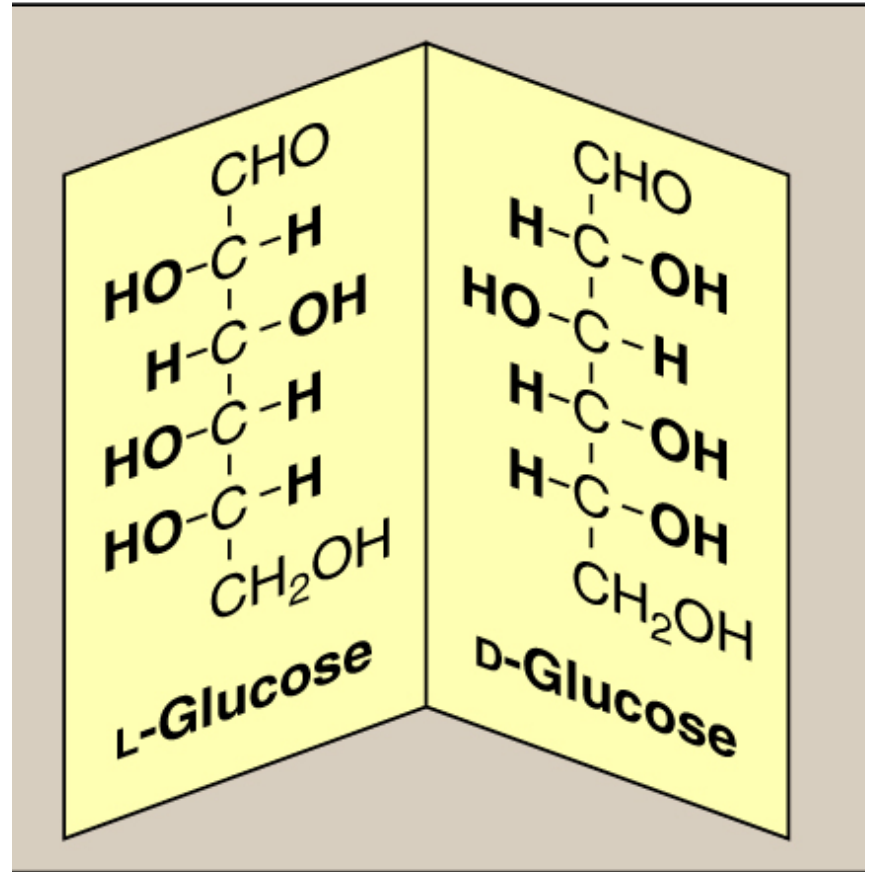
Galactose and mannose **are not** epimers



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**

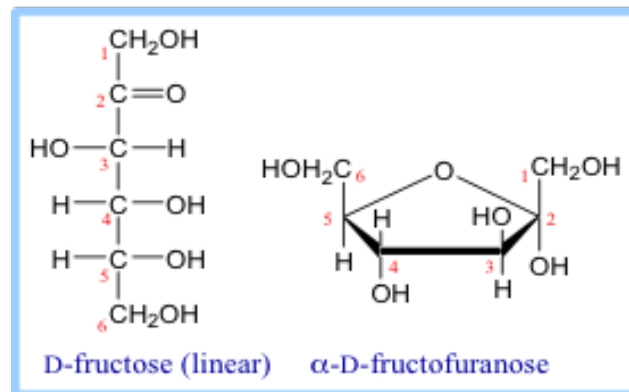
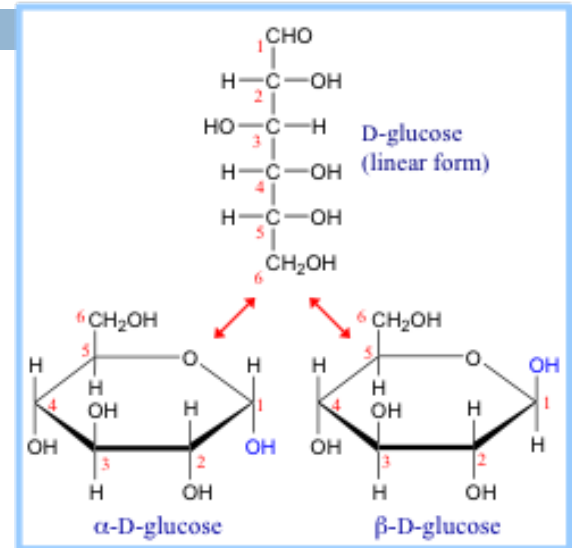


α - and β -Forms

- **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

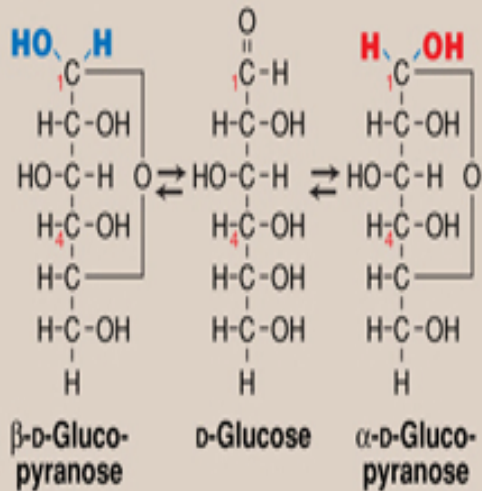
- Cyclization creates an **anomeric carbon** (former carbonyl carbon) generating the α and β configurations



Mutarotation

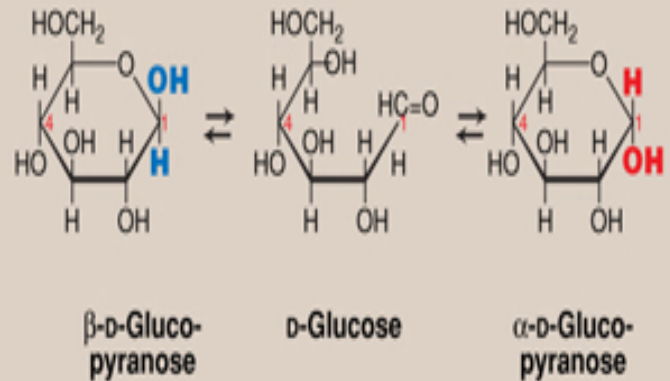
In solution, the cyclic α and β anomers of a sugar are in equilibrium with each other, and can be interconverted spontaneously

A



**Fischer
Projection**

B



**Haworth
Projection**

Sugar Isomers

- **Aldo-keto**
- **Epimers**
- **D- and L-Forms**
- **α - and β -anomers**

Disaccharides

- **Joining of 2 monosaccharides
by O-glycosidic bond:**

Maltose (α -1, 4) = glucose + glucose

Sucrose (α -1,2) = glucose + fructose

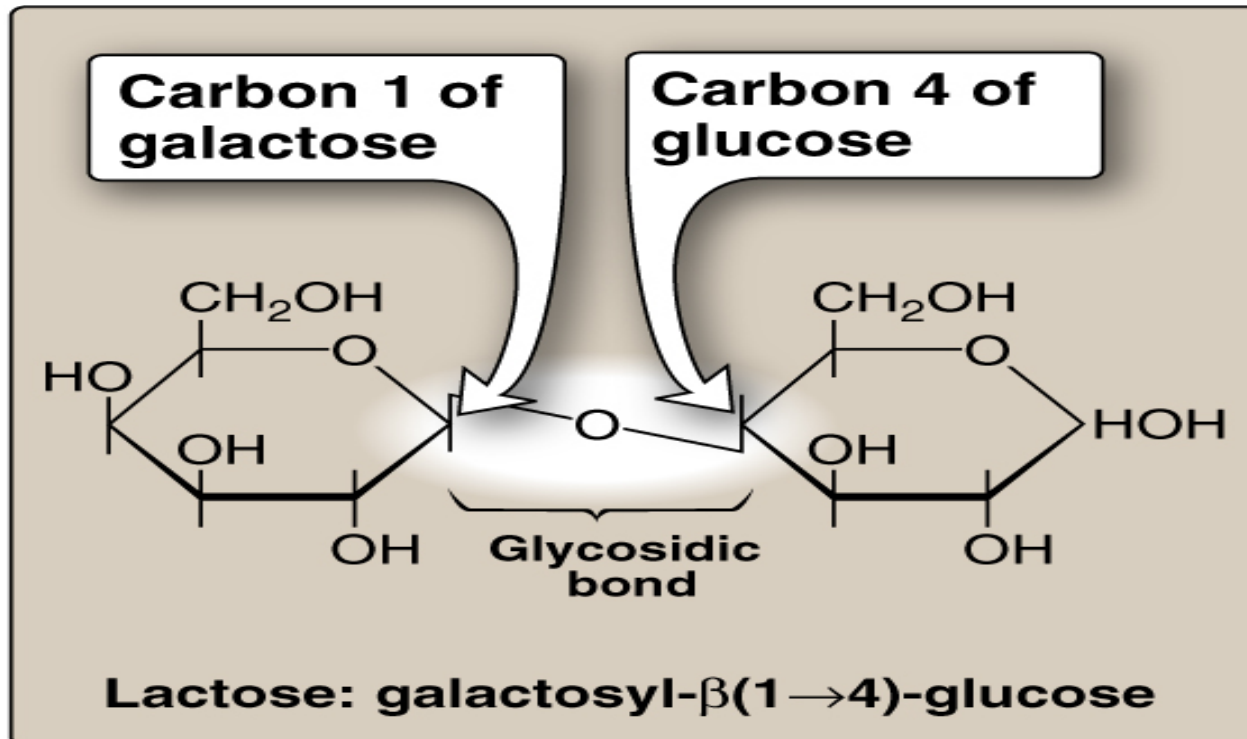
Lactose (β -1,4) = glucose + galactose

Disaccharides

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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
- **R**educing sugars reduce chromogenic agents like Benedict's reagent or Fehling's solution to give a colored precipitate
- **U**rine is tested for the presence of reducing sugars using these colorimetric tests

Reducing Sugars

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- **Examples:**

Monosaccharides

Maltose and Lactose

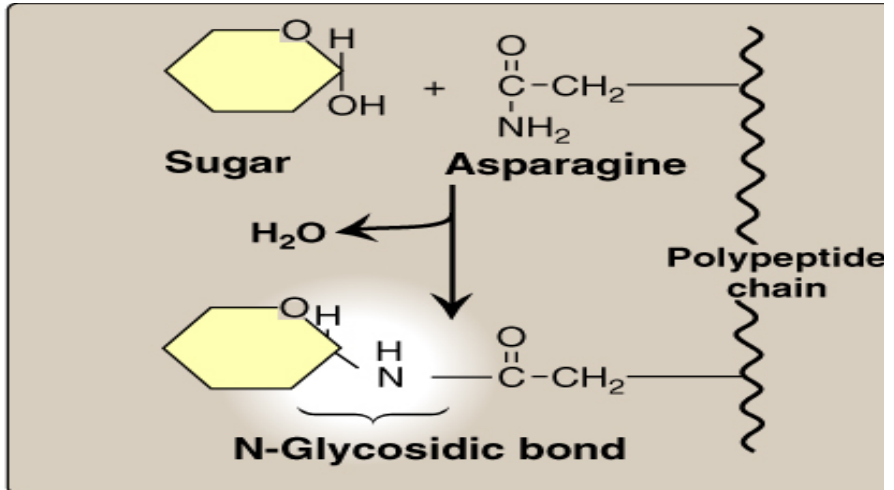
Sucrose is non-reducing, Why?

Complex Carbohydrates

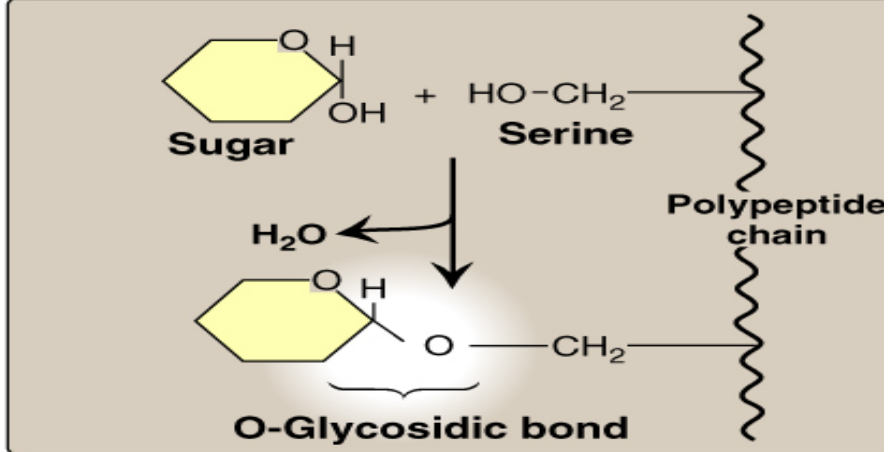
- **Carbohydrates attached to non-carbohydrate structures by glycosidic bonds (O- or N-type) e.g.,**
 1. **Purine and pyrimidine bases** in nucleic acids
 2. **Bilirubin**
 3. **Proteins** in glycoproteins and proteoglycans
 4. **Lipids** found in glycolipids

Glycosidic Bonds

- **N-Glycosidic**



- **O-Glycosidic**

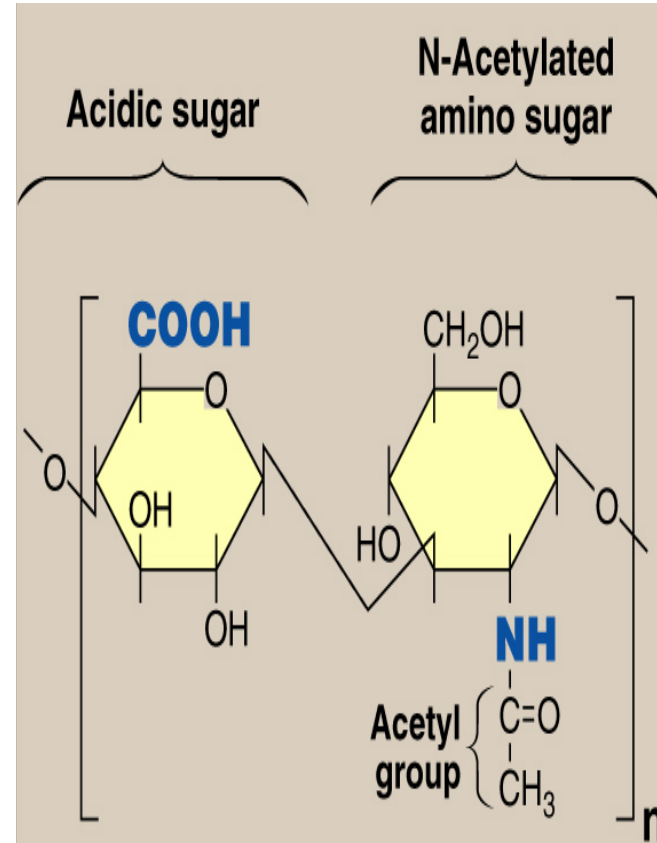


Glycosaminoglycans (GAGs)

- 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 gel-like 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

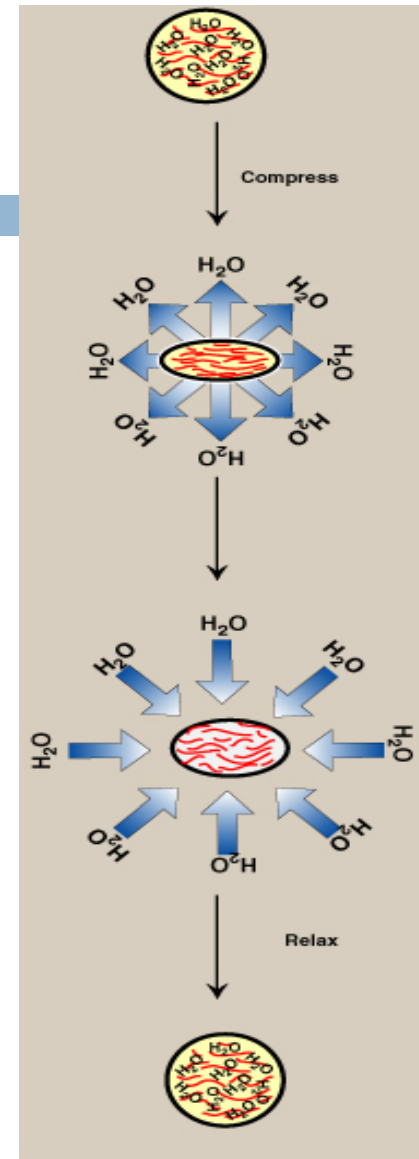
Relationship between glycosaminoglycan structure and function

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 "slippery" consistency of mucous secretions and synovial fluid

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:

Chondroitin sulfates: Most abundant GAG

Keratan sulfates: Most heterogeneous GAGs

Hyaluronic acid: Compared to other GAGs, it is unsulfated and not covalently attached to protein

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-, α - and 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

Reference

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