

# Carbohydrates

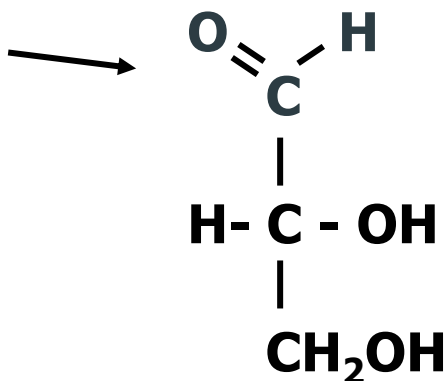
## Structure And Classification

- ▶ Term carbohydrate is derived from the French: **HYDRATE DE CARBONE**
- ▶ compounds composed of C, H, and O
- ▶  $(\text{CH}_2\text{O})_n$  when  $n = 5$  then  $\text{C}_5\text{H}_{10}\text{O}_5$
- ▶ not all carbohydrates have this empirical formula: deoxysugars, aminosugars
- ▶ carbohydrates are the most abundant compounds found in nature (cellulose: 100 billion tons annually)

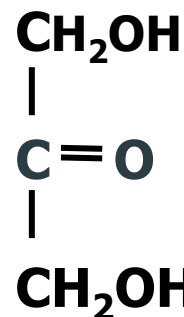
# CARBOHYDRATES

Polyhydroxy aldehydes or ketones,  
or substances that yield these compounds on hydrolysis

Aldehyde  
group



Glyceraldehyde



Dihydroxyacetone

Both can be  
written  
 $C_3H_6O_3$  or  
 $(CH_2O)_3$

Keto  
group

Carbohydrate with an aldehyde group: Aldose

Carbohydrate with a ketone group: Ketose

Empirical formula of many simpler carbohydrates:  $(CH_2O)_n$   
(hence the name hydrate of carbon)

# Characteristic

- ▶ Most carbohydrates are found naturally in bound form rather than as simple sugars
- ▶ Polysaccharides (starch, cellulose, inulin, gums)
- ▶ Glycoproteins and proteoglycans (hormones, blood group substances, antibodies)
- ▶ Glycolipids (cerebrosides, gangliosides)
- ▶ Glycosides
- ▶ Mucopolysaccharides (hyaluronic acid)
- ▶ Nucleic acids

# Function

- ▶ A storage form of energy in the body.
- ▶ Cell surface recognition receptors (by other cells, hormones, viruses)
- ▶ Cell surface antigens, e.g. blood groups.
- ▶ Gastric glycoprotein (mucin) contains more than 60% carbohydrate.
- ▶ A structural component of many organisms:
  - a) cell walls of bacteria
  - b) exoskeleton of insects
  - c) cellulose of plants.
- ▶ intermediates in the biosynthesis of other basic biochemical entities (fats and proteins)
- ▶ associated with other entities such as glycosides, vitamins and antibiotics)
- ▶ participate in biological transport, cell-cell recognition, activation of growth factors, modulation of the immune system, lubrication of skeletal joints

# Classification and Nomenclature of Carbohydrates

- Monosaccharides (monoses or glycoses)
  - ▶ Trioses, tetroses, pentoses, hexoses
- ▶ Oligosaccharides
  - ▶ Di, tri, tetra, penta, up to 9 or 10
  - ▶ Most important are the disaccharides
- ▶ Polysaccharides or glycans
  - ▶ Homo and Heteropolysaccharides
  - ▶ Complex carbohydrates
- ▶ Derived carbohydrate
  - ▶ Oxidation product- Ascorbic acid
  - ▶ Reducing product- glycerol
  - ▶ Amino sugar- glucosamin
  - ▶ Deoxy sugars- deoxyribose

# Monosaccharides

Polyhydroxy aldehydes or ketones that can't easily be further hydrolyzed  
"Simple sugars"

<u>Number of carbons</u>	<u>Name</u>	<u>Example</u>
3	Trioses	Glyceraldehyde
4	Tetroses	Erythrose
5	Pentoses	Ribose
6	Hexoses	Glucose, Fructose
7	Heptoses	Sedoheptulose
9	Nonoses	Neuraminic acid

# Classification According to the Functional Group

a) Aldoses

b) Ketoses



Functional Group	Sugar Class	No of Carbons	Name of Sugar
Aldehyde	Aldose	3 (aldotriose)	<b>Glycerose</b>
		4 (aldotetrose)	<b>Erythrose</b>
		5 (aldopentose)	<b>Ribose</b>
		6 (aldohexose)	<b>Glucose</b>
			<b>Galactose</b>
			<b>Mannose</b>
Ketone	Ketose	3 (ketotriose)	<b>Dihydroxyacetone</b>
		4 (ketotetrose)	<b>Erythrulose</b>
		5 ketopentose)	<b>Xylulose</b>
		6 (ketoheptose)	<b>Fructose</b>
		7 Ketoseptose	<b>Sedoheptulose</b>

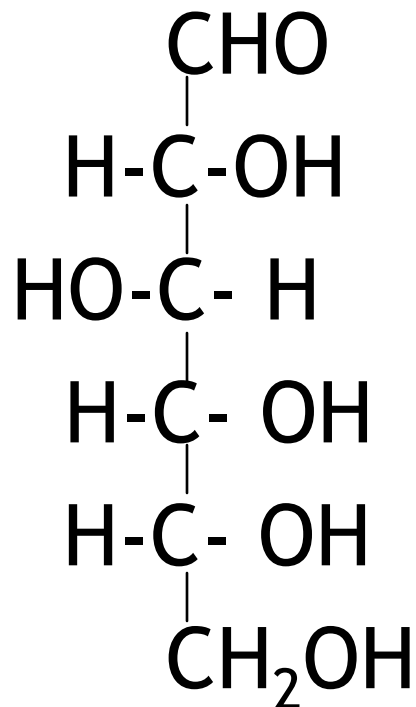
# Examples For Monosaccharide

## Glucose (Dextrose); Grape sugar:

Glucose is the most important carbohydrate in biology

The cell uses it as a source of energy and metabolic intermediate.

Glucose is produced in the process of photosynthesis, and is used in both prokaryotes and eukaryotes.

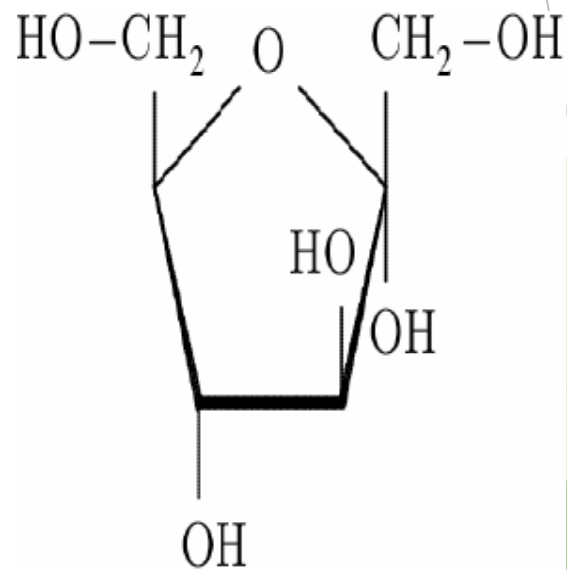
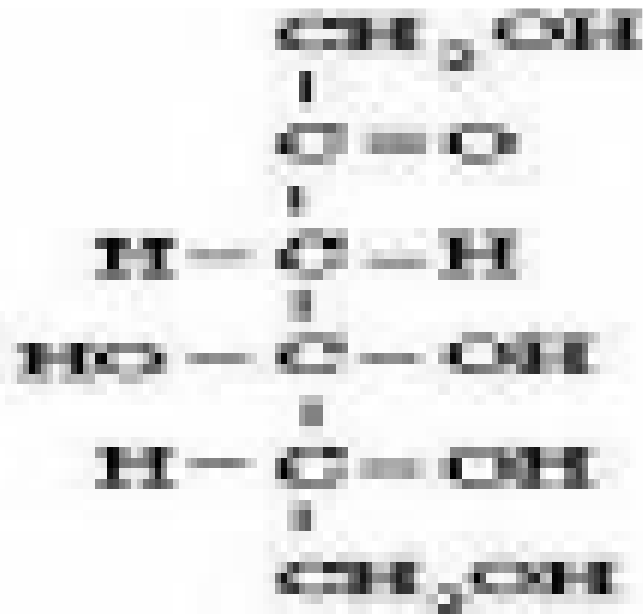


# Fructose (Levulose); Fruit sugar

Found in honey & fruits.

Fructose is produced from the digestion of sucrose (a disaccharide consisting of glucose and fructose).

Fructose is the sweetest naturally occurring sugar, estimated to be twice as sweet as sucrose

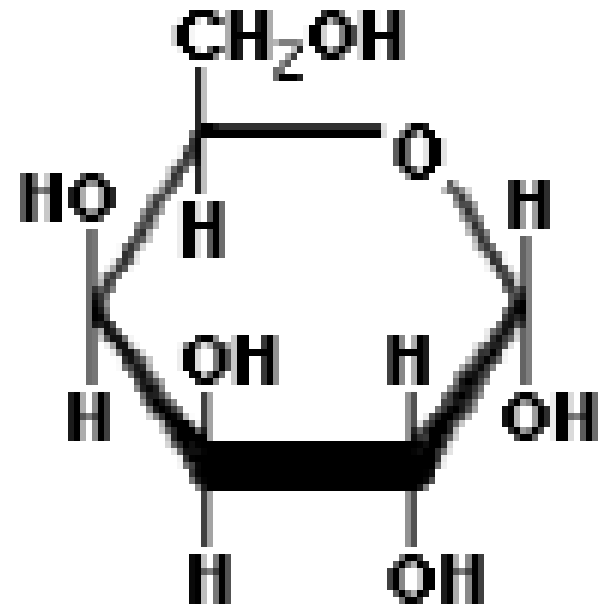
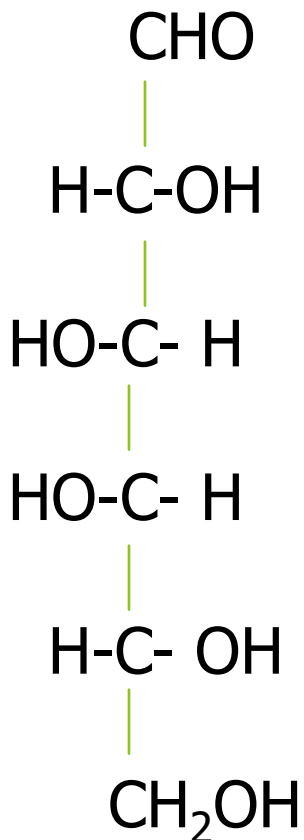


# Galactose

It is a sugar found in dairy products, in the form of Lactose.

It is a disaccharide formed of Glucose & Galactose.

It forms part of glycolipids and glycoproteins in several tissues of the body



# Oligosaccharides

Hydrolyzable polymers of 2-6 monosaccharides

Disaccharides composed of 2 monosaccharides  
Examples: Sucrose, Lactose

# Disaccharides

Disaccharides are produced from the condensation of 2 monosaccharide molecules.

Lactose [milk sugar] is formed in the mammary gland. It is composed of galactose and glucose.

Maltose (Malt sugar) is composed of 2 molecules of glucose.

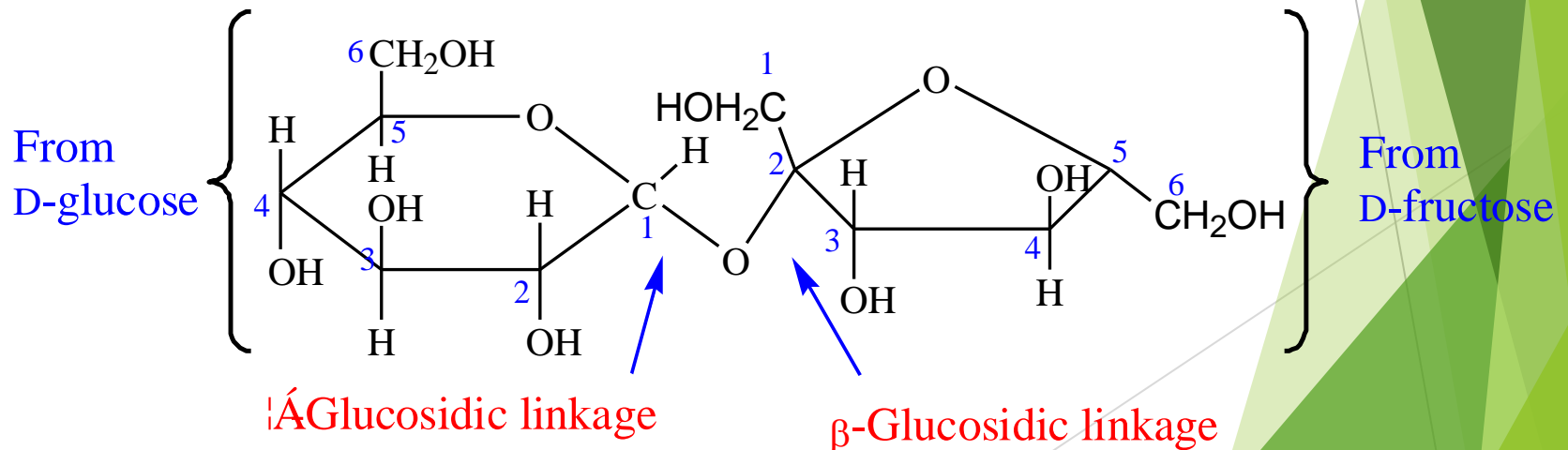
Sucrose (Table sugar, Cane sugar, Beet sugar) is composed of glucose and fructose

# DISACCHARIDES

## SUCROSE

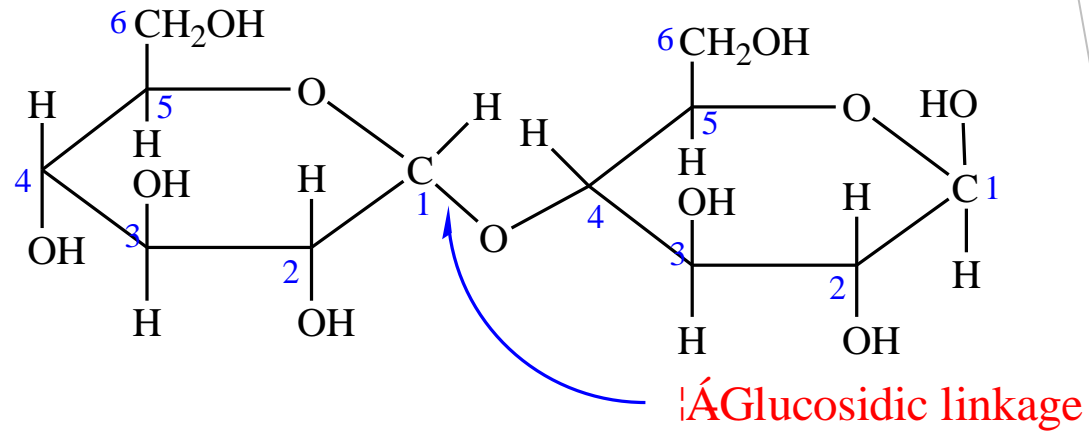
Sucrose: the most widely occurring disaccharide of ordinary table sugar.

Structure:

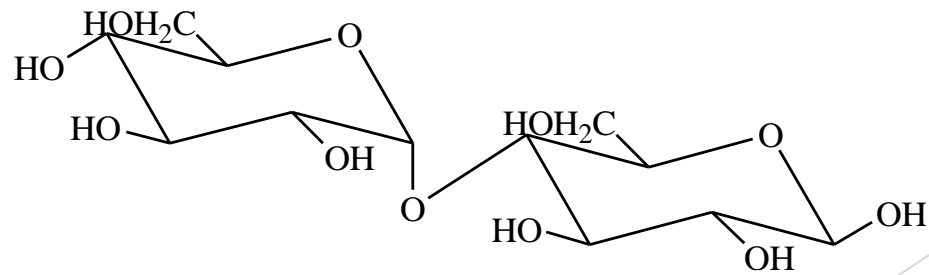


# MALTOSE

Structure:



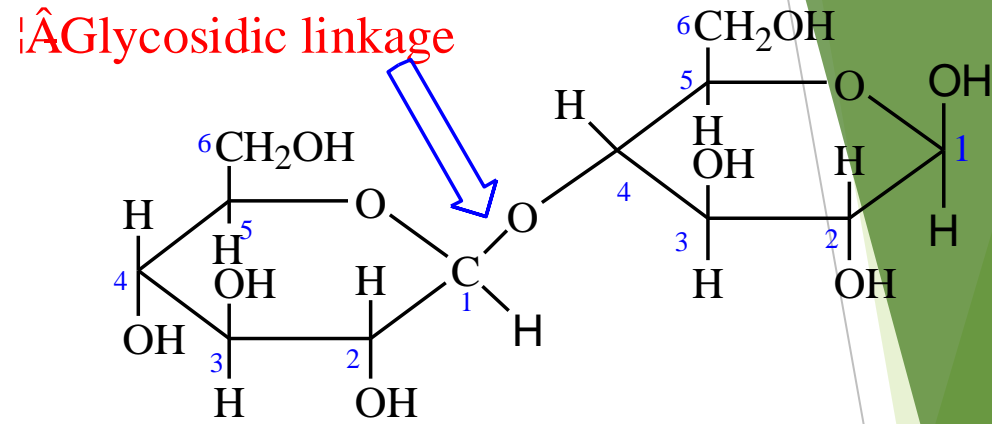
or





# CELLOBIOSE

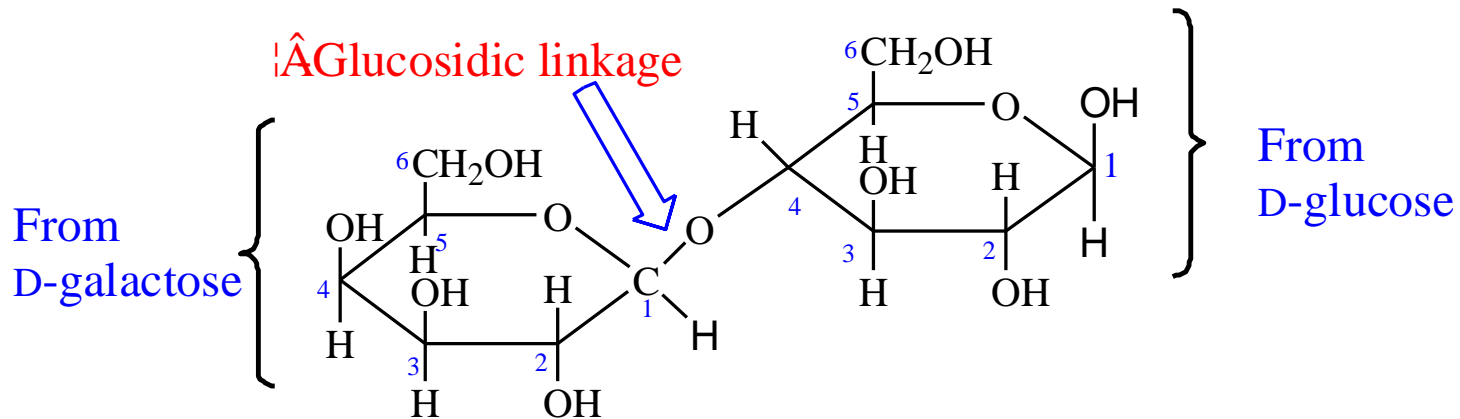
Structure:



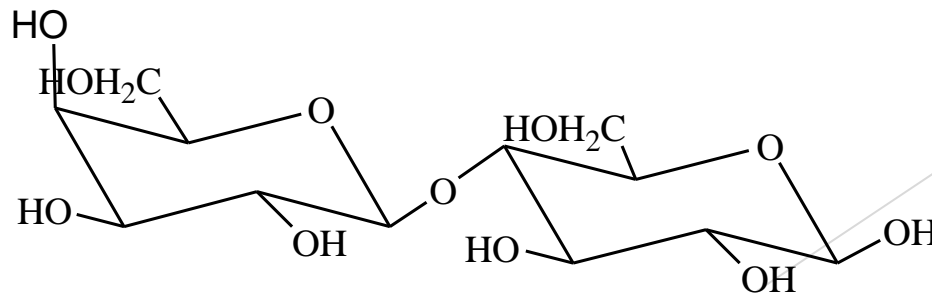
# LACTOSE

Lactose is a reducing sugar that hydrolyzes to yield D-glucose and D-galactose; the glycosidic linkage is  $\beta$ .

Structure:



or



# Oligosaccharides....

It occurs in glycoproteins, which are proteins to which oligosaccharides are covalently attached.

Trisaccharide	Raffinose	Fructose+ Galactose+ Glucose
Tetrasaccharide	Stachyose	2 Galactose+ Glucose+ Fructose
Pentasaccharide	Verbascose	3 Galactose+ Glucose+ Fructose

# Polysaccharide

Homopolysaccharides: polysaccharides that are polymers of a single monosaccharide.

Heteropolysaccharides: those made up of more than one type of monosaccharide.

Glucan: a homopolysaccharide consisting of glucose monomeric units.

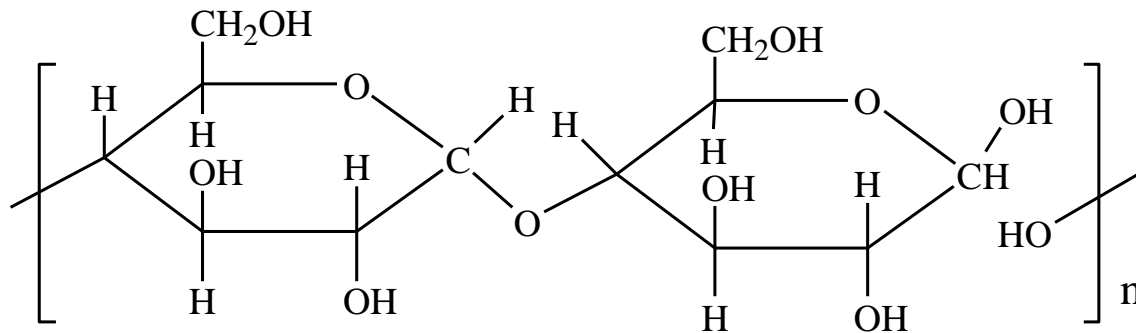
Galactan: a homopolysaccharide consisting of galactose units

Three important polysaccharides, all of which are glucans, glycogen, starch and cellulose.

# STARCH

Heating starch with water produce amylose (10-20%)and amylopectin(80-90%).

Structure of amylose:

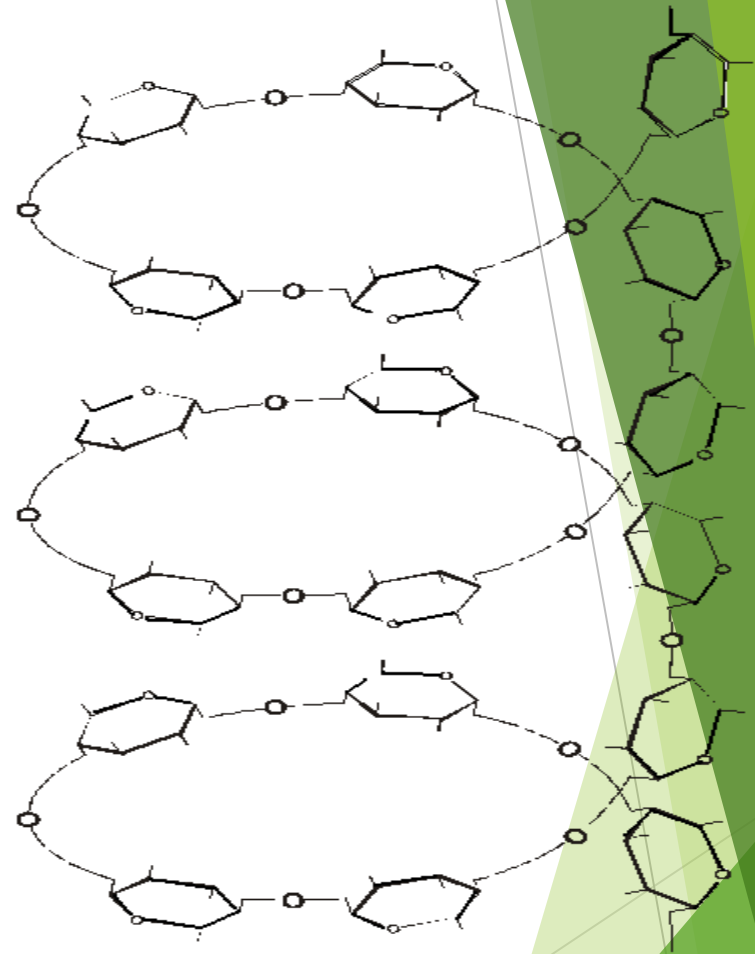


$n > 1000$  1:4-glycosidic linkages

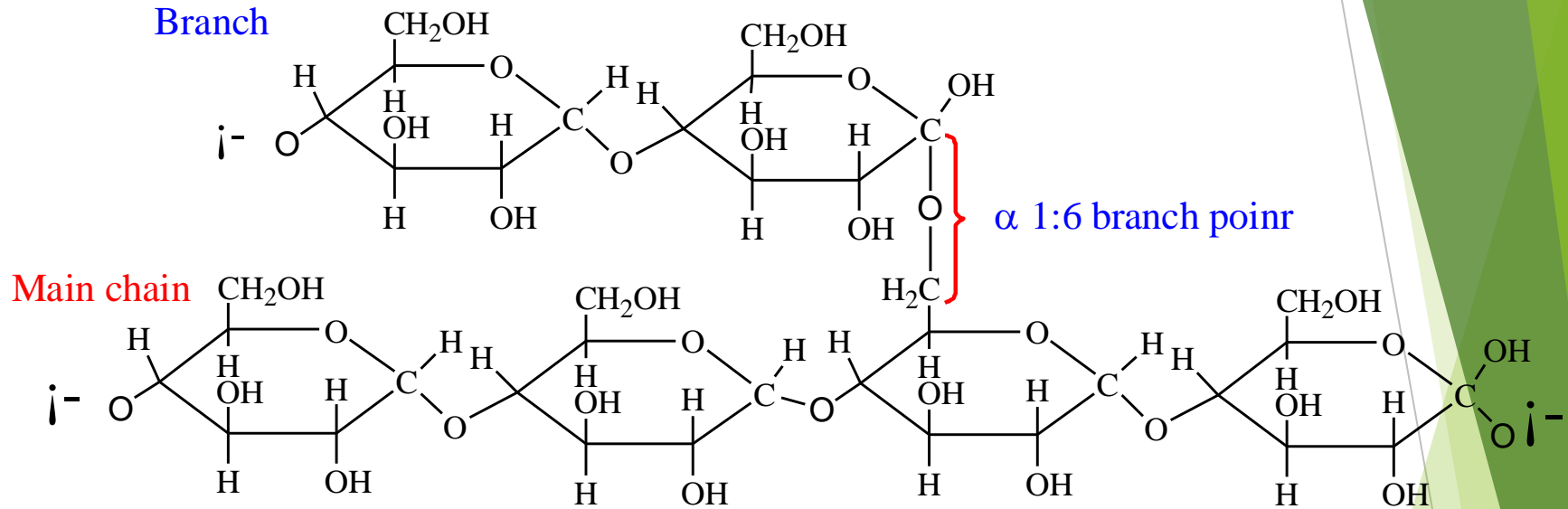
In amylopectin the chains are branched. Branching takes place between C-6 and C-1at intervals of 20-25 glucose units.

# Amylose

- The amylose chain forms a helix.
- This causes the blue colour change on reaction with iodine.
- Amylose is poorly soluble in water, but forms micellar suspensions



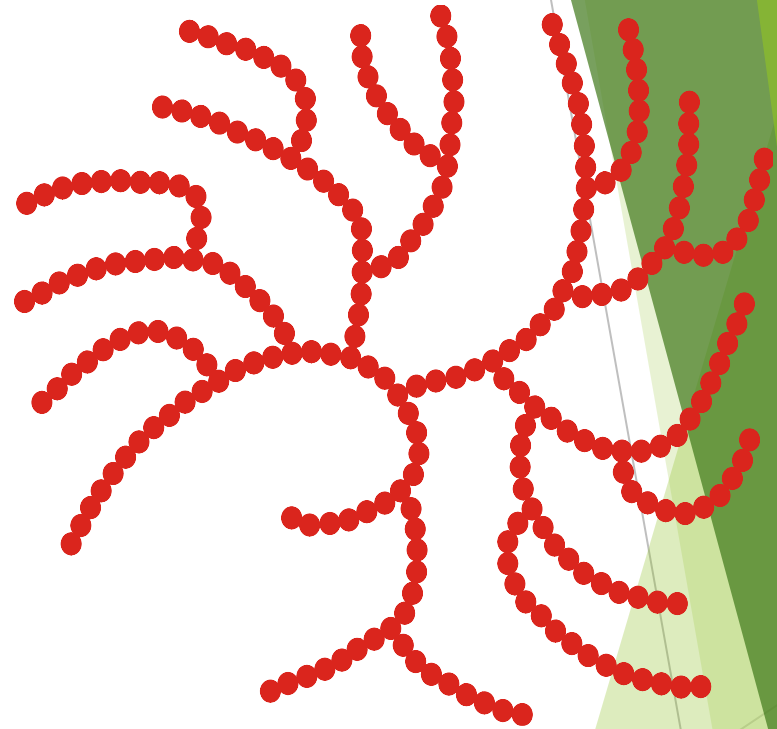
Partical structure of amylopectin:



The molecular weight is about 1-6 million, include hundreds of interconnecting chains of 20-25 glucose units.

## Amylopectin

- Amylopectin causes a red-violet colour change on reaction with iodine.
- This change is usually masked by the much darker reaction of amylose to iodine.



Amylopectin



# GLYCOGEN

In glycogen the chains are much more highly branched and the molecular weight is very high.

Polymer of  $\alpha$ -1 $\rightarrow$ 4 linked subunit and branching at  $\alpha$ -1 $\rightarrow$ 6 (similar to amylopectin)

Highly branched

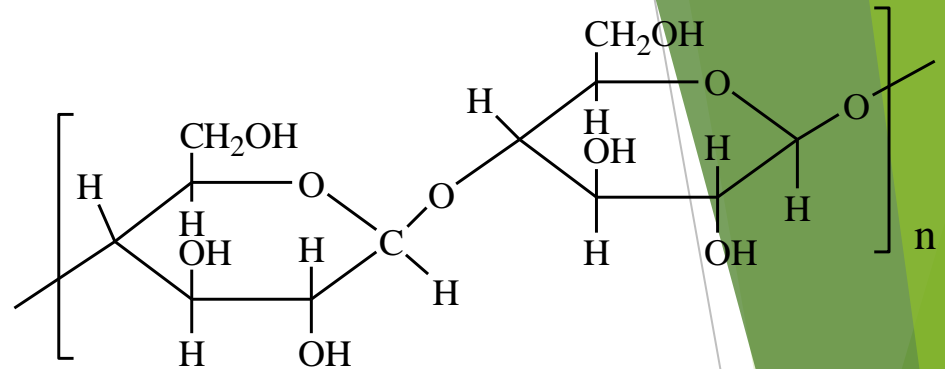
The size and structure of glycogen suits its function:

- (1) Its size makes it too large to cross cell membranes.
- (2) The structure of glycogen solves the enormous osmotic pressure within the cell.
- (3) The high branch structure of glycogen simplifies the cell's logistical problems.

Glucose (from glycogen) is highly water soluble and as an ideal source of "ready energy".

# CELLULOSE

A portion of cellulose structure:

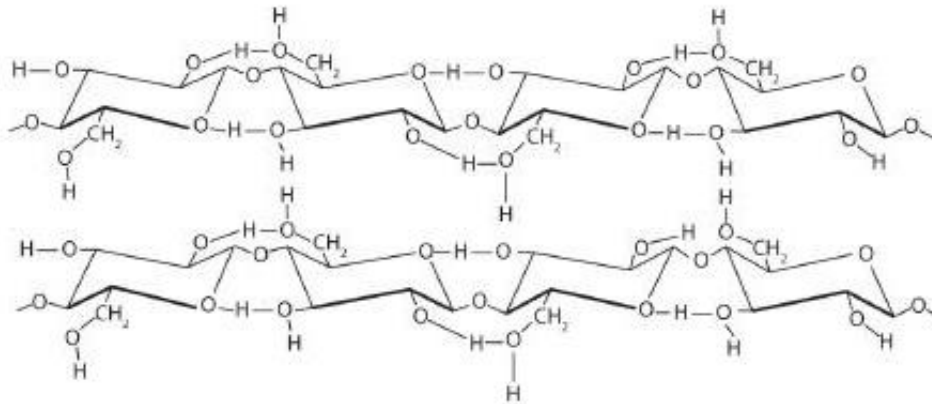


The glycosidic linkages are  $\beta$ , 1:4

## Special property:

The outside -OH groups are ideally situated to "zip" the chains make together by forming hydrogen bonds.

Zippering many cellulose chains together in this way gives a highly insoluble.



- ▶ cellulose is found in its purest form from the seed hairs of cotton
- ▶ wood cellulose, on the other hand forms a composite with lignin and other polysaccharides

- ▶ Bacterial cellulose: *Gluconacetobacter* are involved in the production of a very peculiar form of cellulose
- ▶ Cellulose acetate: ester of cellulose
- ▶ Ethylcellulose: microencapsulated drug delivery systems
- ▶ Hydroxypropyl cellulose: soluble both in water and organic solvent, used as a lubricant, corneal erosions neuroparalytic keratitis

Dextran

In bacteria and yeast

Made of  $\alpha$ - 1 $\rightarrow$ 6 linked polyglucose and have  $\alpha$ - 1 $\rightarrow$ 3 branches

Synthetic dextran are used in several commercial products e.g.  
Sephadex

Chitin

Linear homopolysaccharide of N acetyl glucosamine residue in  
 $\beta$ - 1 $\rightarrow$ 4 linkage

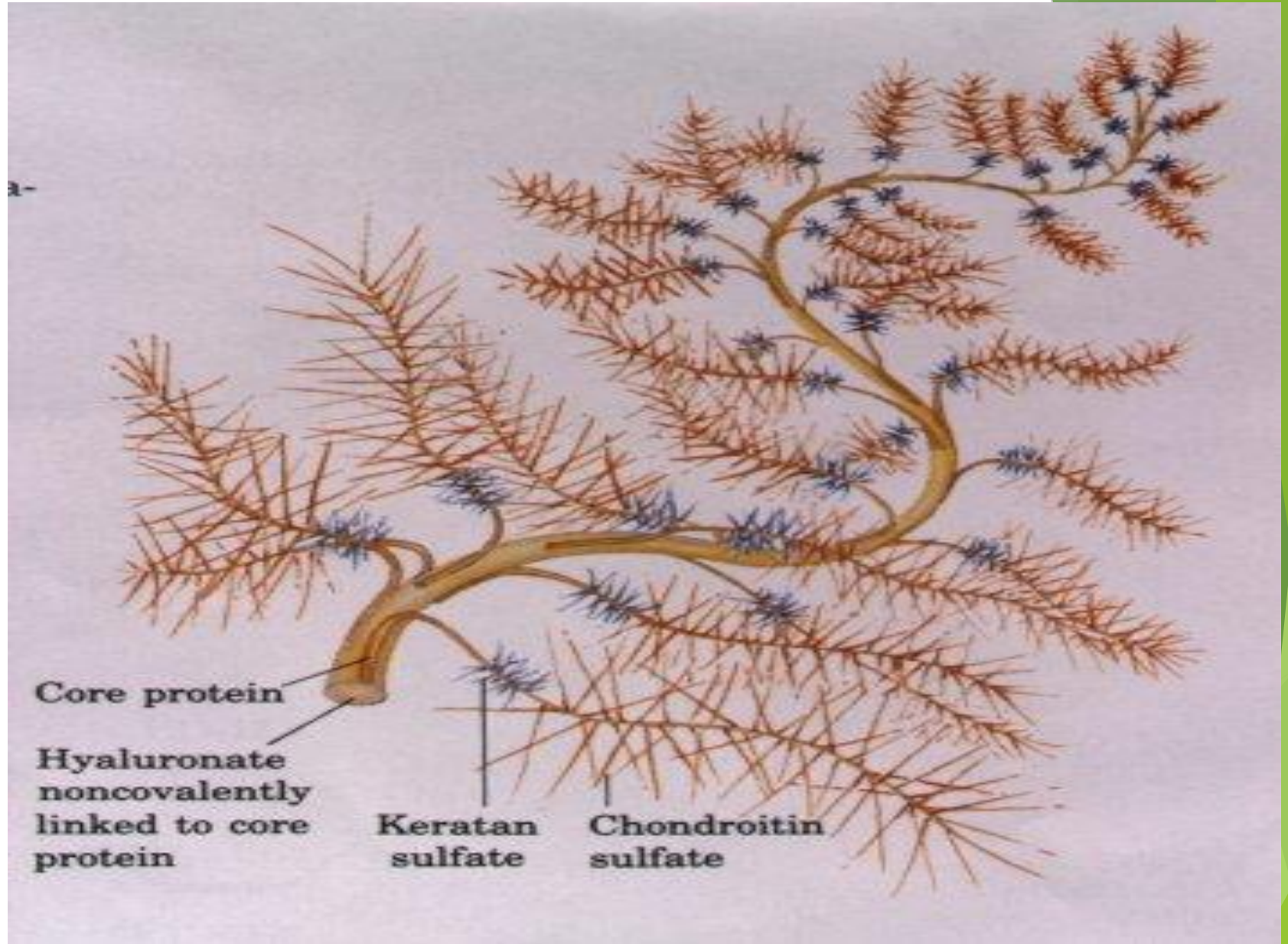
Heteropolysaccharides in the body are the glycosaminoglycans (GAGs). These molecules are long unbranched polysaccharides containing a repeating disaccharide unit.

- ▶ GAGs are highly **negatively charged** molecules, with extended conformation that imparts high viscosity to the solution.
- ▶ GAGs are located primarily on the **surface of cells or in the extracellular matrix (ECM)**.
- ▶ Along with the high viscosity of GAGs comes **low compressibility**, which makes these molecules ideal for a **lubricating fluid in the joints**.
- ▶ At the same time, their **rigidity** provides **structural integrity** to cells and provides passageways between cells, allowing for cell migration.

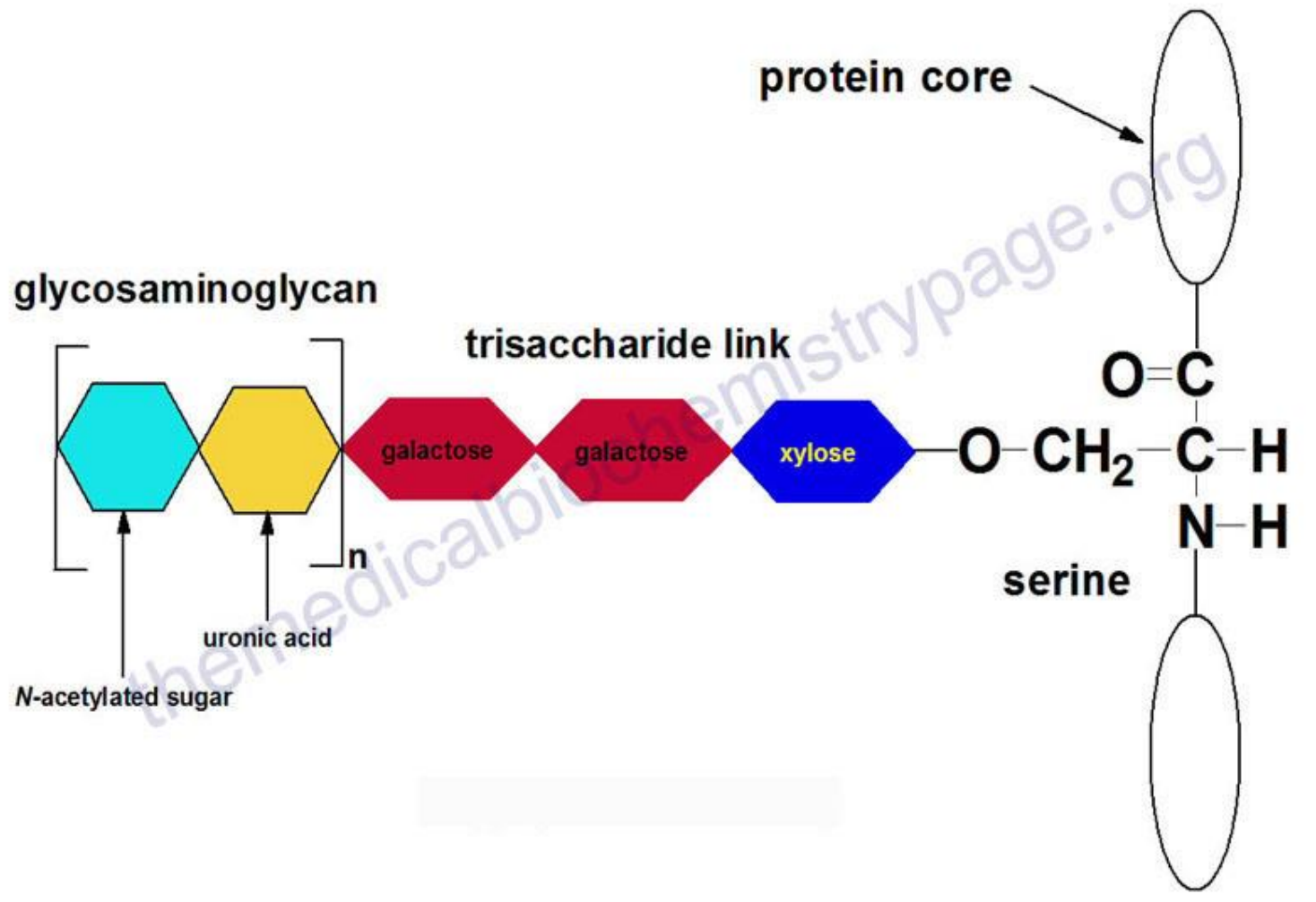
- ▶ The disaccharide units contain either of two modified sugars, called amino sugars *N*-acetylgalactosamine (GalNAc) or *N*-acetylglucosamine (GlcNAc),
- ▶ and an acidic sugar uronic acid such as glucuronic acid or iduronic acid.
- ▶ The amino group is usually acetylated.
- ▶ This eliminates the positive charge.
- ▶ In some glycosaminoglycans, one or more of the hydroxyls of the amino sugar is **esterified with sulfate**.
- ▶ The combination of these sulfate groups and the **carboxylate groups** of the uronic acid residues gives the glycosaminoglycans a very high density of **negative charge**.

- ▶ **Keratan sulfate** is an exception in which **galactose** is present, instead of an acidic sugar.
- ▶ **Hyaluronic acid** does not contain **sulfate**.





# Linkage



# Classification of Glycosaminoglycans

The classification is based on:

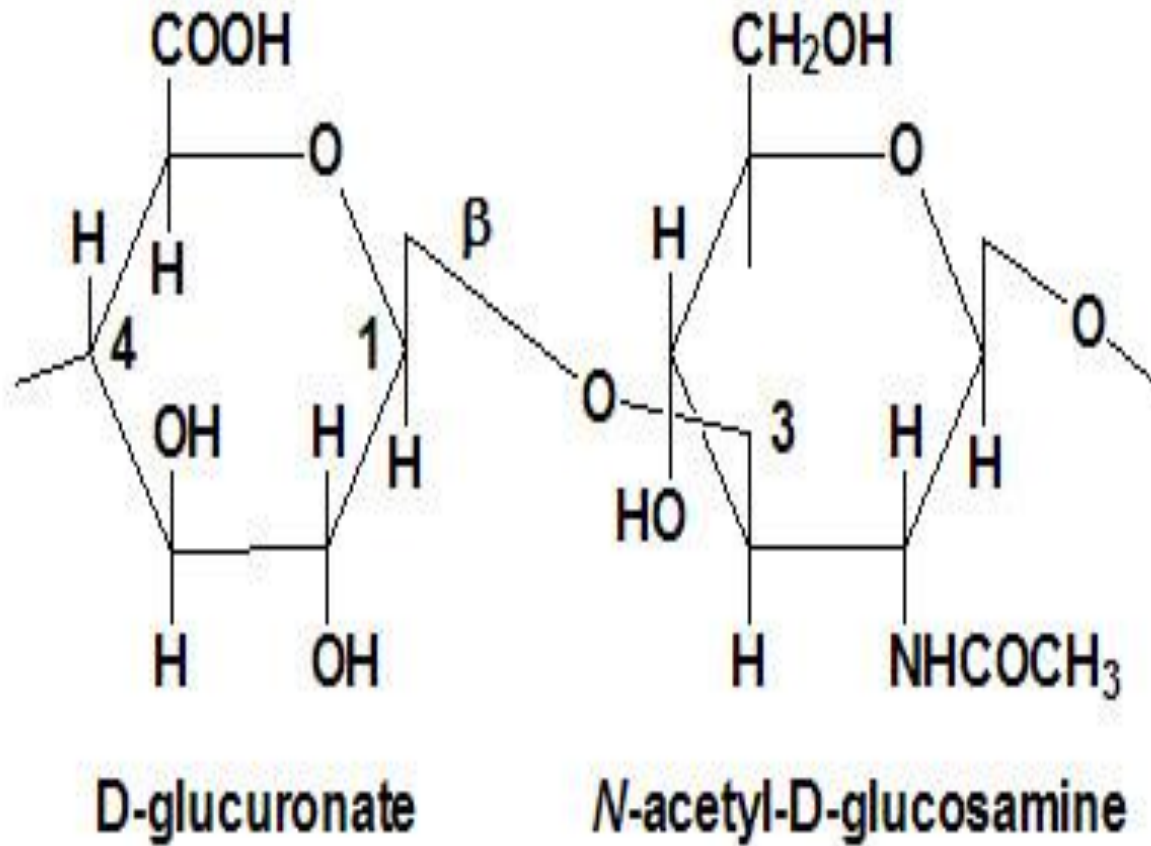
OR the GAGs differ from each other:

- Monomeric (acidic & amino sugar) composition
- Degree & location of sulfation
- Type of glycosidic linkages
- Chain length of the disaccharides
- Nature of the core protein
- Their tissue distribution
- Their biologic functions

The specific GAGs of physiological significance are:

- ✓ Hyaluronic Acid
- ✓ Dermatan Sulfate
- ✓ Chondroitin Sulfate
- ✓ Heparin
- ✓ Heparan Sulfate
- ✓ Keratan Sulfate

# Hyaluronic acid



# Hyaluronic acid

- ❖ Hyaluronic acid is unique among the GAGs in that it does not contain any sulfate and is not found covalently attached to proteins as a proteoglycan.
- ❖ It is, however, a component of non-covalently formed complexes with proteoglycans in the ECM.
- ❖ Only GAG present both in animals and bacteria.
- ❖ **Found** in synovial fluid, vitreous humor, ECM of loose connective tissue, Umbilical cord, Cartilage

## Specific function:

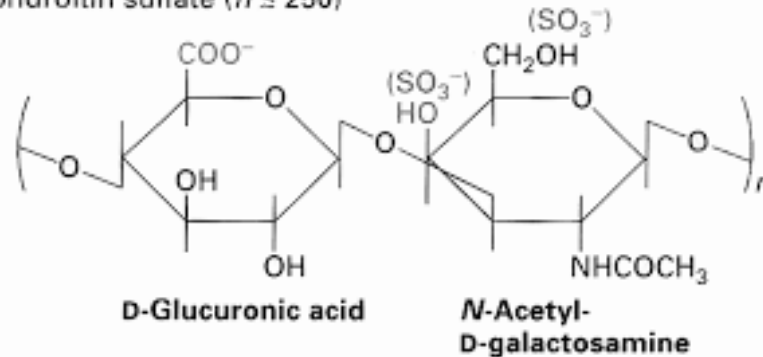
- ❖ **Hyaluronic acid is especially high in concentration in embryonic tissues and is thought to play an important role in permitting cell migration during morphogenesis and wound repair.**
- ❖ **Act as lubricators and shock absorbers.**

# Chondroitin sulfate

Made up of glucuronic acid and N- acetyl galactosamine sulphate

- ▶ most abundant GAG
- ▶ Cartilage (bind collagen and hold the fibers strongly)
- ▶ Tendons
- ▶ ligaments
- ▶ Heart valves

Chondroitin sulfate ( $n \leq 250$ )

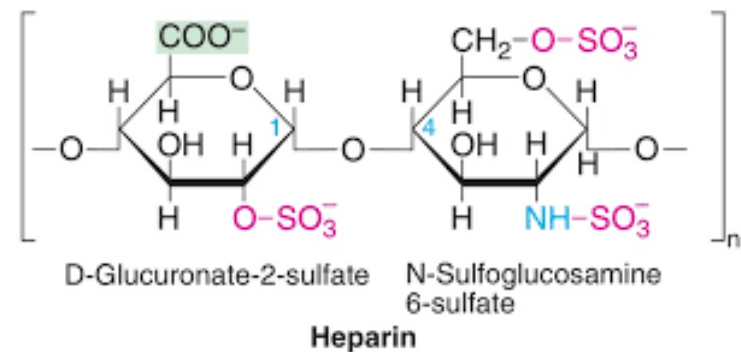




# Heparin

## (Natural anticoagulant)

- ❖ Composed of alternating unit of N-sulfo, D-glucosamine 6-sulphate and glucronate 2- sulphate
- ❖ It is an intracellular GAG.
- ❖ Component of intracellular granules of mast cells lining the arteries of the lungs, liver and skin
- ❖ more sulfated than heparan sulfate
- ❖ Having highest negative charge density of any known biological macromolecule

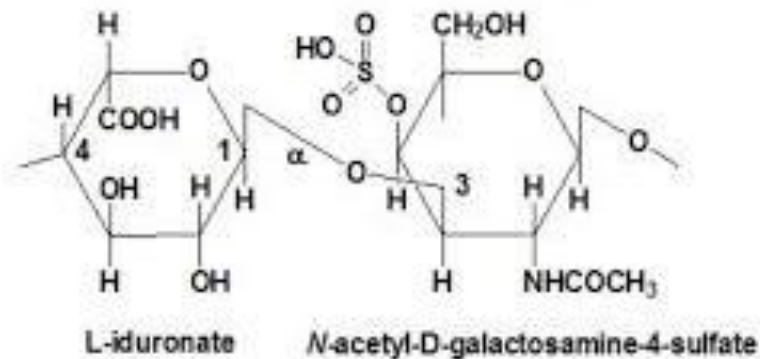


## Specific function:

- ▶ Heparin and warfarin are widely used in the treatment of thrombotic and thromboembolic conditions, such as deep vein thrombosis and pulmonary embolus.
- ▶ Heparin is administered first, because of its prompt onset of action, whereas warfarin takes several days to reach full effect.

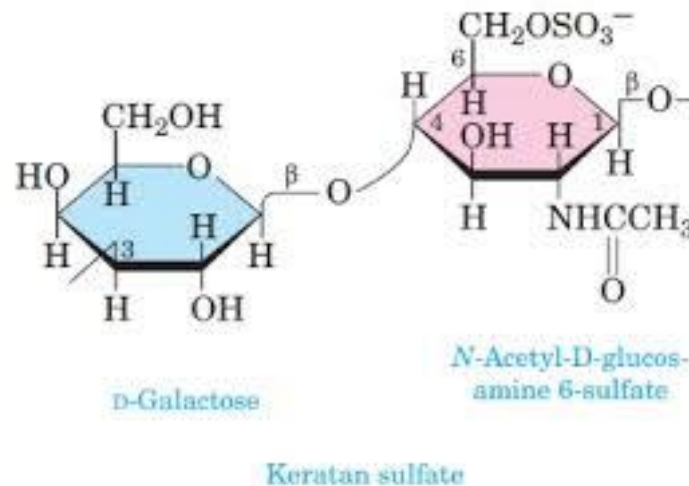
# Dermatan sulfate

- ▶ Made up of L-iduronic acid and N acetyl galactosamine sulphate
- ▶ Sclera- gives shape to the eye.
- ▶ Binds LDL -plays a role in the development of atherosclerosis.
- ▶ Contribute to the elasticity of skin, blood vessels, heart valve



# Keratan sulfate

- ▶ Contains D- galactosamine and N-acetyl glucaosamine 6-sulphate
- ▶ cornea,
- ▶ bone,
- ▶ cartilage aggregated with chondroitin sulfates
- ▶ Both keratan sulfate I and dermatan sulfate are present in the cornea. They and play a critical role in cor



- ▶ In various types of arthritis, proteoglycans may act as autoantigens, thus contributing to the pathologic features of these conditions.
- ▶ The amount of chondroitin sulfate in cartilage diminishes with age.

# Other polysaccharides

- ▶ **Chitin** (poly glucose amine), found in fungal cell walls and the exoskeletons of insects.
- ▶ **Dextran** (poly 1-2, 1-3 and 1-4 glucose), the storage polysaccharide in fungi and bacteria.
- ▶ **Inulin** (poly fructose), a plant food store.  $\beta$ - 1→2 linkage
- ▶ **Agar** (poly galactose sulphate), found in algae and used to make agar plates.
- ▶ **Murein** (a sugar-peptide polymer), found in bacterial cell walls.
- ▶ **Lignin** (a complex polymer), found in the walls of xylem cells, is the main component of wood.

# Structure analysis of polysaccharides

## Information on polysaccharide structures

- Monosaccharide component
- Sugar linkage type
- Sugar sequence
- Monosaccharide configuration ( $\alpha$  or  $\beta$  and D or L)
- Molecular weight
- Amount and position of substitute units
- Degree of branching

► **Monosaccharide component**

**The polysaccharide samples are hydrolyzed by HCl/MeOH and TFA, then analyzed by HPLC or GC**



**HPLC:**

**High pressure/performance  
liquid chromatography**



► **Sugar linkage type**

**Chemical methods:**

**Periodate Oxidation and Smith degradation**

**Methylation analysis**



**GC-MS:**

**Gas chromatography-  
Mass spectrometer**

## Physical methods:

### NMR(Nuclear Magnetic Resonance)



- Sugar linkage type
- Monosaccharide configuration
- Substitute units
- Degree of branching

## Physical methods:

### FT-IR (Fourier transform infrared spectroscopy)



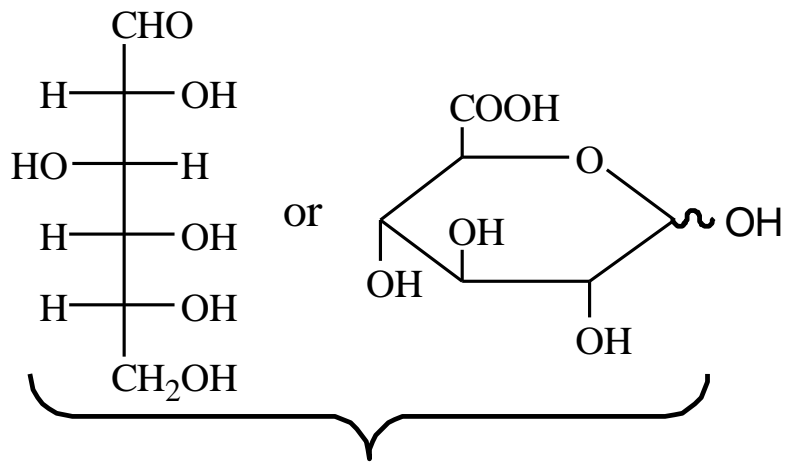
- Monosaccharide configuration
- Substitute units

## Physical methods:

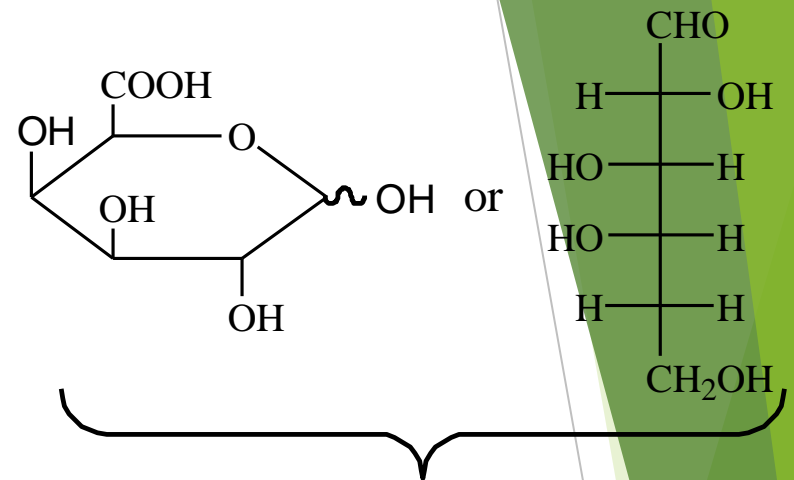
### MS (Mass spectrometer)



- Sugar linkage type
- Monosaccharide configuration
- Substitute units
- Degree of branching
- Molecular weight



**D-Glucuronic acid**  
(ÀÏ(ÎÑ)ÏÇÈÇËá)



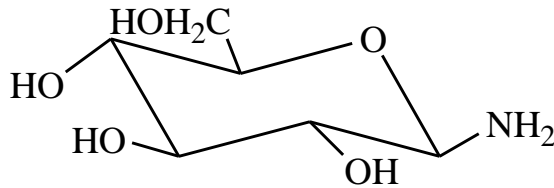
**D-Galacturonic acid**  
(°ëÈèÏÇÈÇËá)

## Sugar Acid

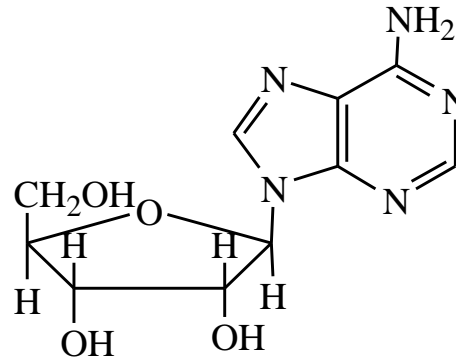
**DEOXY SUGARS:** monosaccharides in which an –OH group has been replaced by –H.

# GLYCOSYLAMINES

Glycosylamine: sugars in which an amino group replaces the anomeric –OH. For example:



**β-D-Glucopyranosyl amine**

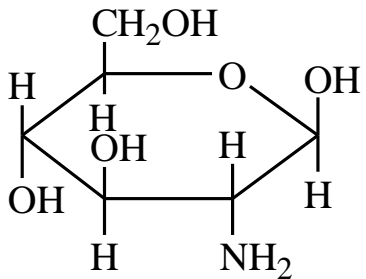


**Adenosine**  
(ribose)

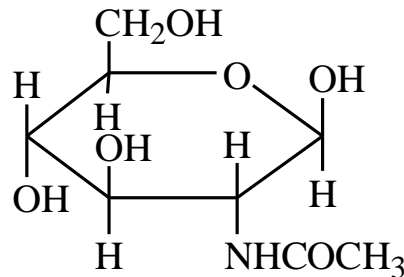
Nucleoside: glycosylamines in which the amino component is a pyrimidine or a purine and in which the sugar component is either D-ribose or 2-deoxy-D-ribose.

# AMINO SUGARS

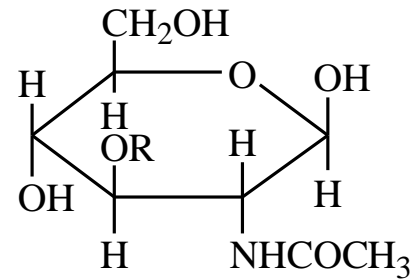
Amino sugar: a sugar in which an amino group replaces a nonanomeric –OH group.



**D-Glucosamine**  
(D-GlcNAc)



**N-Acetyl-D-Glucosamine**  
(NAM)



**N-Acetylmuramic acid**  
(NAG)



D-glucosamine can be obtained by hydrolysis of chitin. The repeating units in chitin is N-acetylglucosamine and the glycosidic linkages are  $\beta$ , 1:4. The structure of chitin is smaller than that of cellulose.

D-glucosamine can also be isolated from heparin.

# Fibers

- ▶ Found in food derived from plants
- ▶ Includes polysaccharides such as cellulose, hemicellulose, pectins, gums and mucilages
- ▶ Also includes non-polysaccharides such as lignin, cutins and tannins
- ▶ Fibers are not a source of energy in non ruminants because digestive enzymes cannot break down fibers but ruminants can do
- ▶ The bacteria in nonruminants GI tract can breakdown some fibers.



# classification of fibers based on their solubilities in water

(1) Soluble fibers: includes gum, pectin, some hemicellulose and mucilages found in fruits, oats, barley and legumes .

Actions on body:

- (i) Delay GI transit (benefits digestive disorders)
- (ii) Delay glucose absorption (benefits diabetes)
- (iii) Lowers blood cholesterol (benefits heart disease)

# classification of fibers based on their solubilities in water

(2) Insoluble fibers: includes cellulose, many hemicellulose, lignin found in wheat bran , corn bran, whole grain bread, cereals and vegetables (carrot, cabbage)

Actions in body:

- (i) Accelerates GI transit and increases fecal weight (promotes bowel movement)
- (ii) Slows starch hydrolysis and delays glucose absorption (Benefits diabetes)

# Requirements for carbohydrate

- ▶ Carbohydrates are not essential nutrients, because the carbon skeletons of amino acids can be converted into glucose .
- ▶ However, the absence of dietary carbohydrate leads to ketone body production ,and degradation of body protein whose constituent amino acids provide carbon skeletons for gluconeogenesis .

# Glucose and the nervous system

- ▶ Glucose is the only fuel normally used by brain cells. Because neurons cannot store glucose, they depend on the bloodstream to deliver a constant supply of this precious fuel.

## Glycemic Index

The ability of the body to digest different carbohydrates can be described by the glycaemic index (GI)

Low GI foods release glucose more slowly and steadily; high GI foods cause a more rapid rise in blood glucose levels.