

CARBOHYDRATES

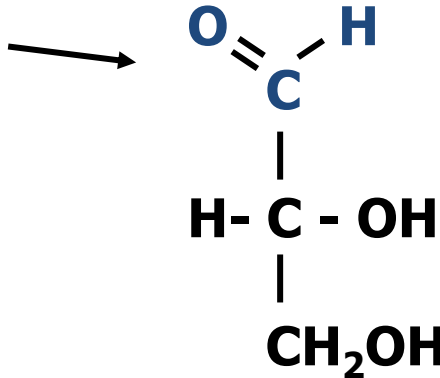
STRUCTURE AND CLASSIFICATION

- 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)

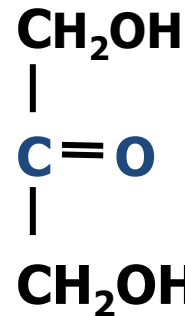
CARBOHYDRATES

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)	Glycerose
		4 (aldotetrose)	Erythrose
		5 (aldopentose)	Ribose
		6 (aldohexose)	Glucose
			Galactose
			Mannose
Ketone	Ketose	3 (ketotriose)	Dihydroxyacetone
		4 (ketotetrose)	Erythrulose
		5 ketopentose)	Xylulose
		6 (ketoheptose)	Fructose
		7 Ketoheptose	Sedoheptulose

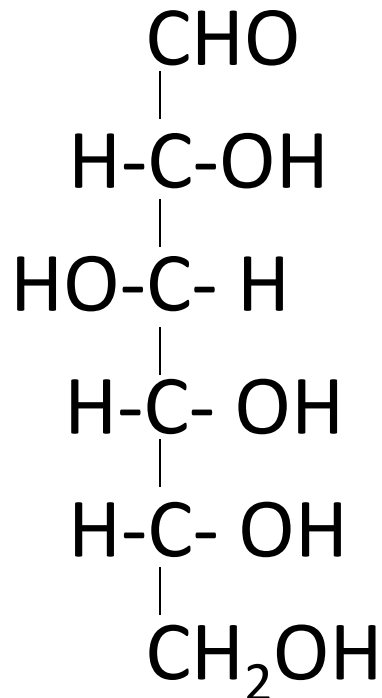
Examples For Monosaccharide

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.

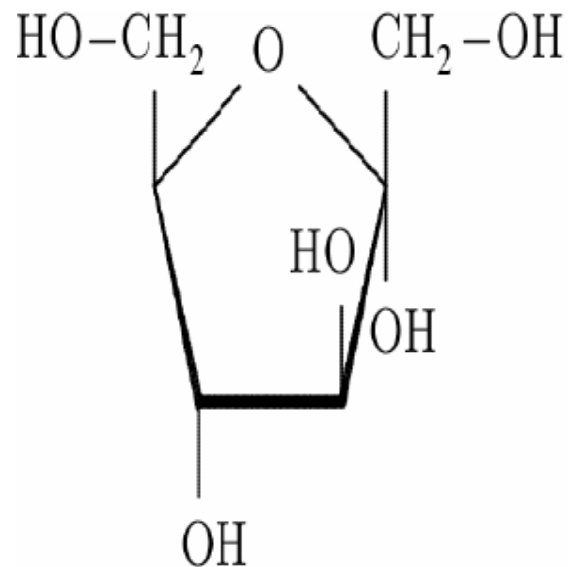
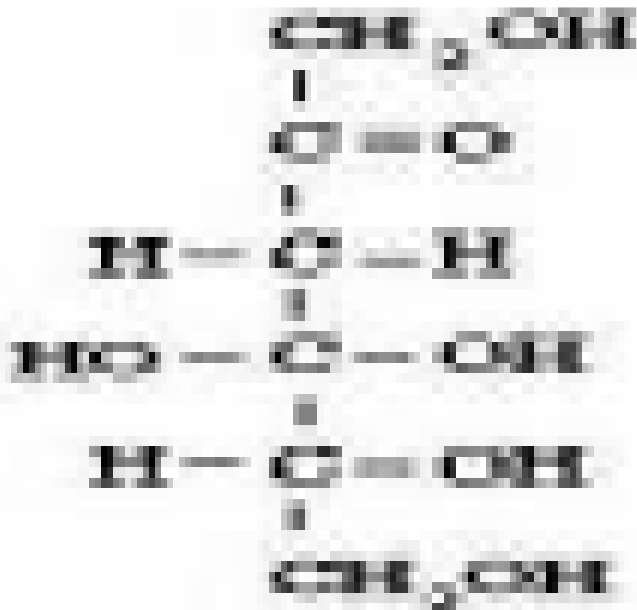


Fructose (Levulose); Fruit sugar

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

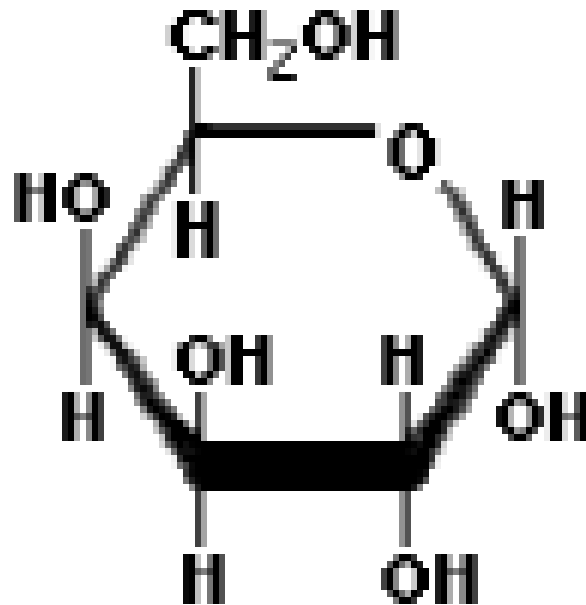
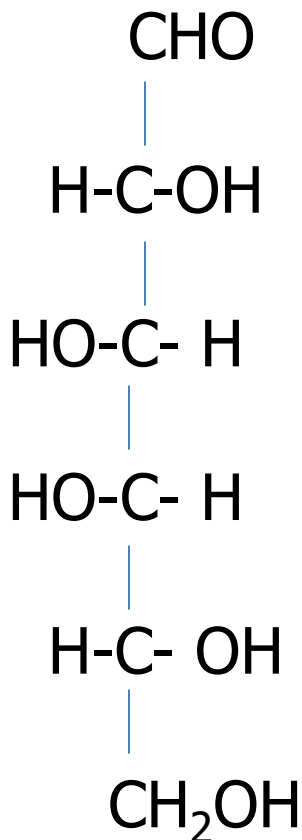


Galactose

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.

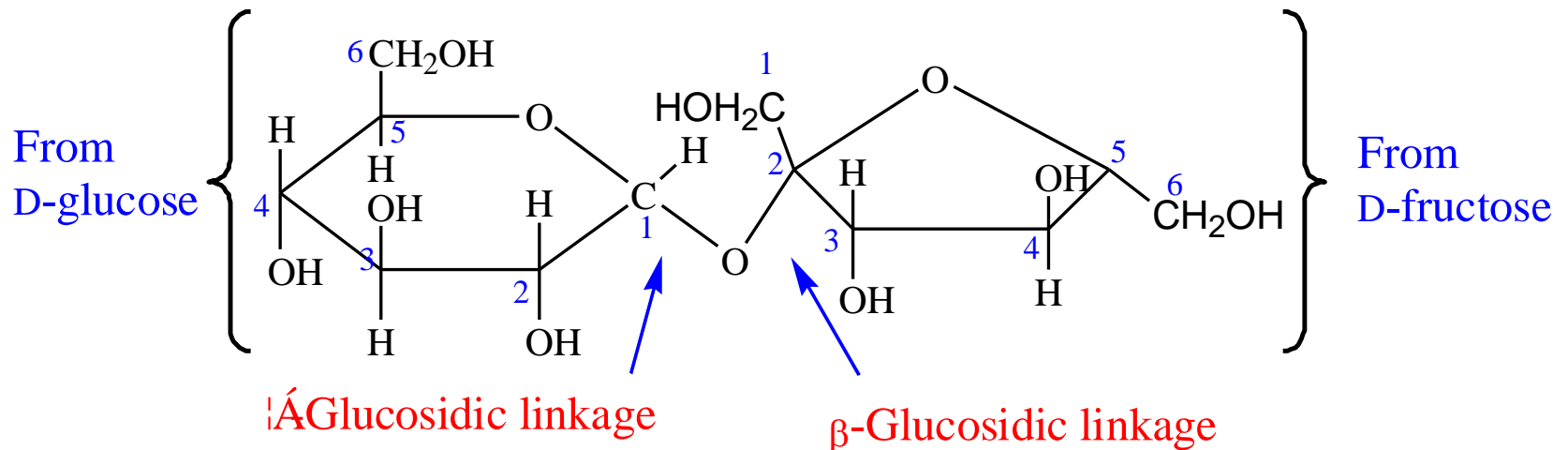
Sucrose (Table sugar, Cane sugar, Beet sugar) is composed of glucose and fructose

DISACCHARIDES

SUCROSE

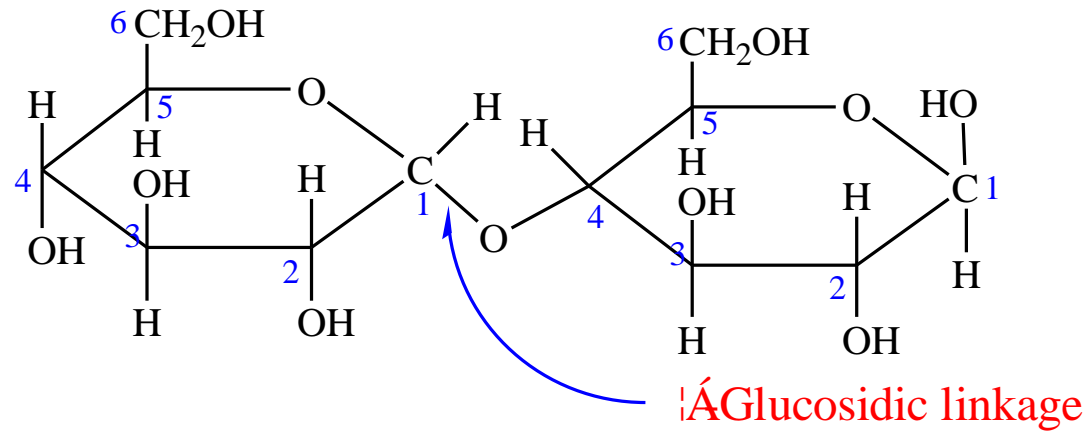
Sucrose: the most widely occurring disaccharide of ordinary table sugar.

Structure:

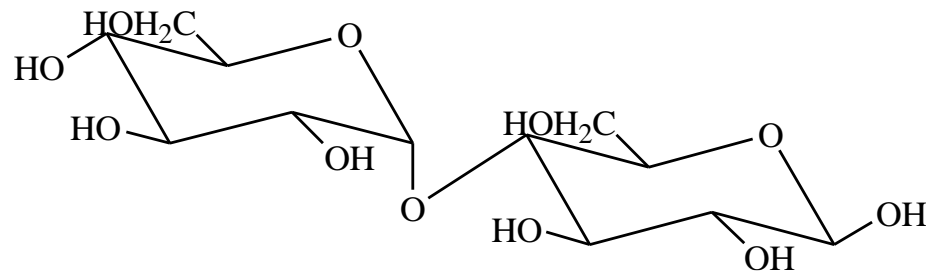


MALTOSE

Structure:

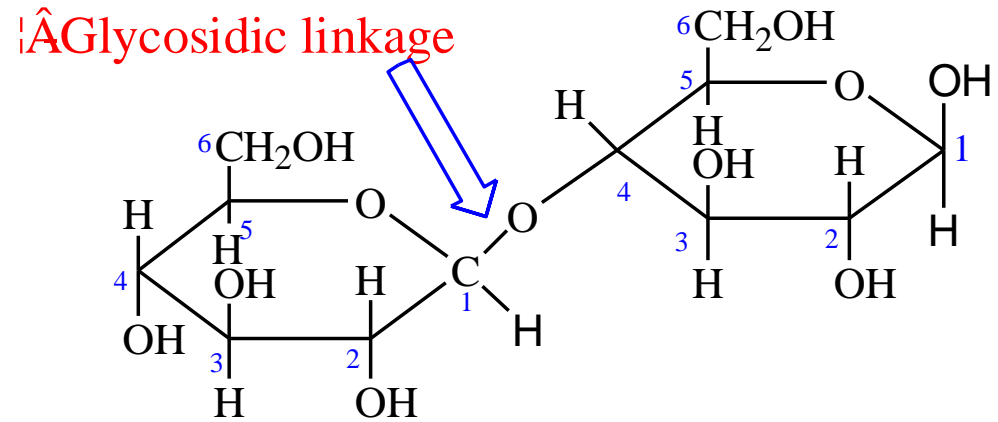


or



CELLOBIOSE

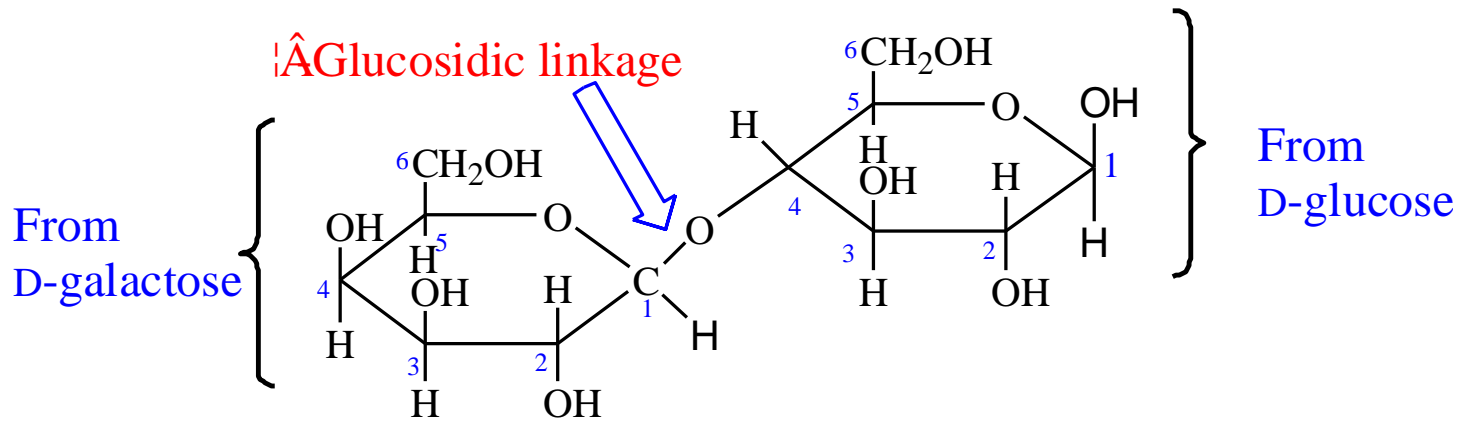
Structure:



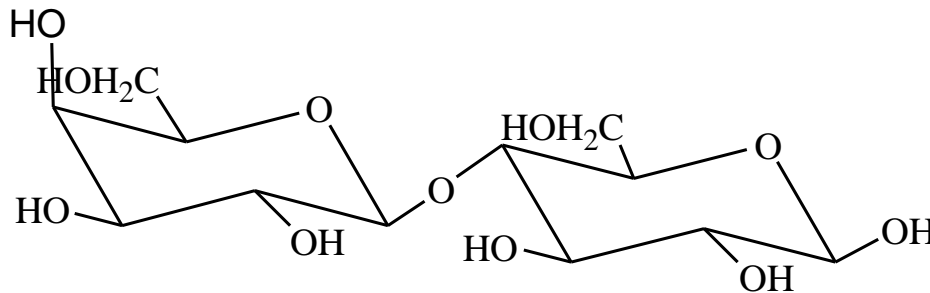
LACTOSE

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

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.

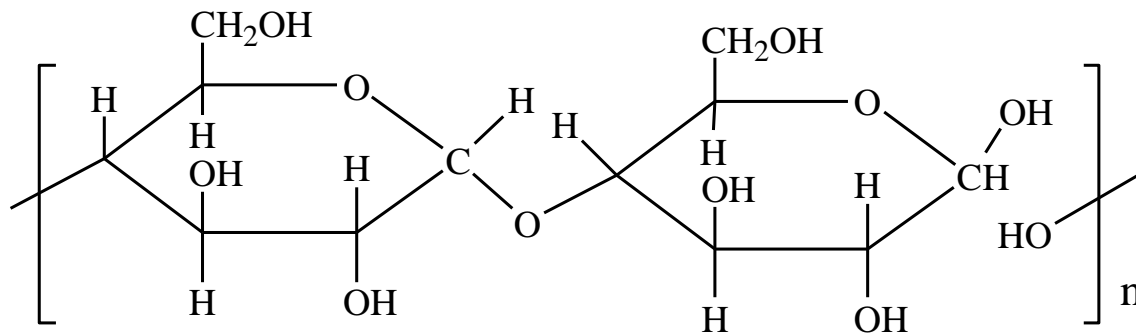
Galactan: a homopolysaccharide consisting of galactose units

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:

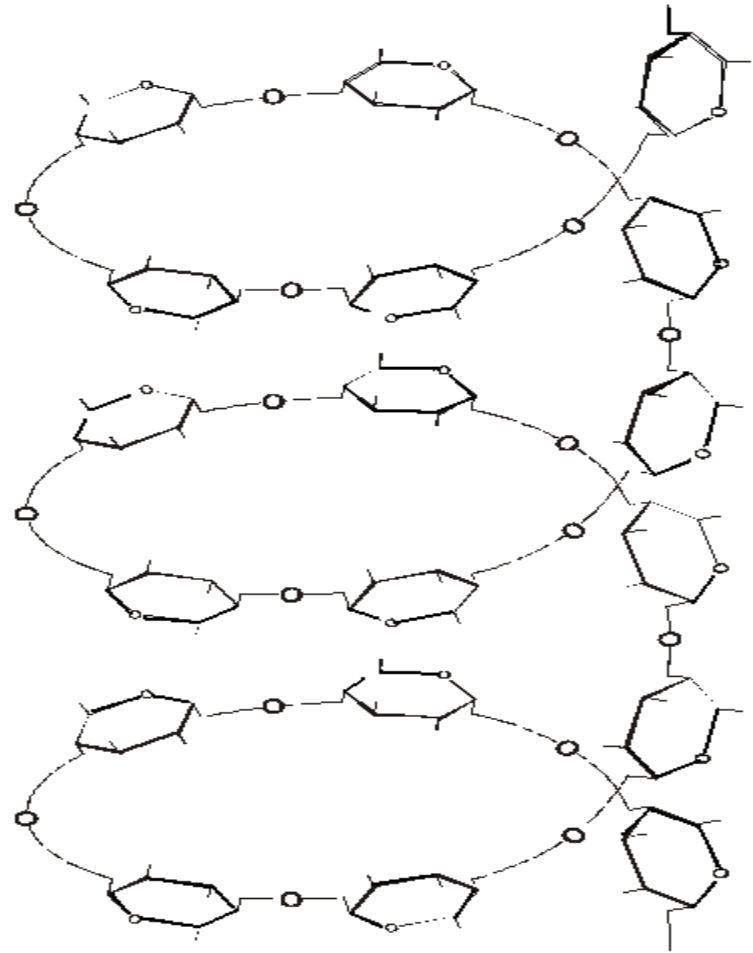


$n > 1000$ 1:4-glycosidic linkages

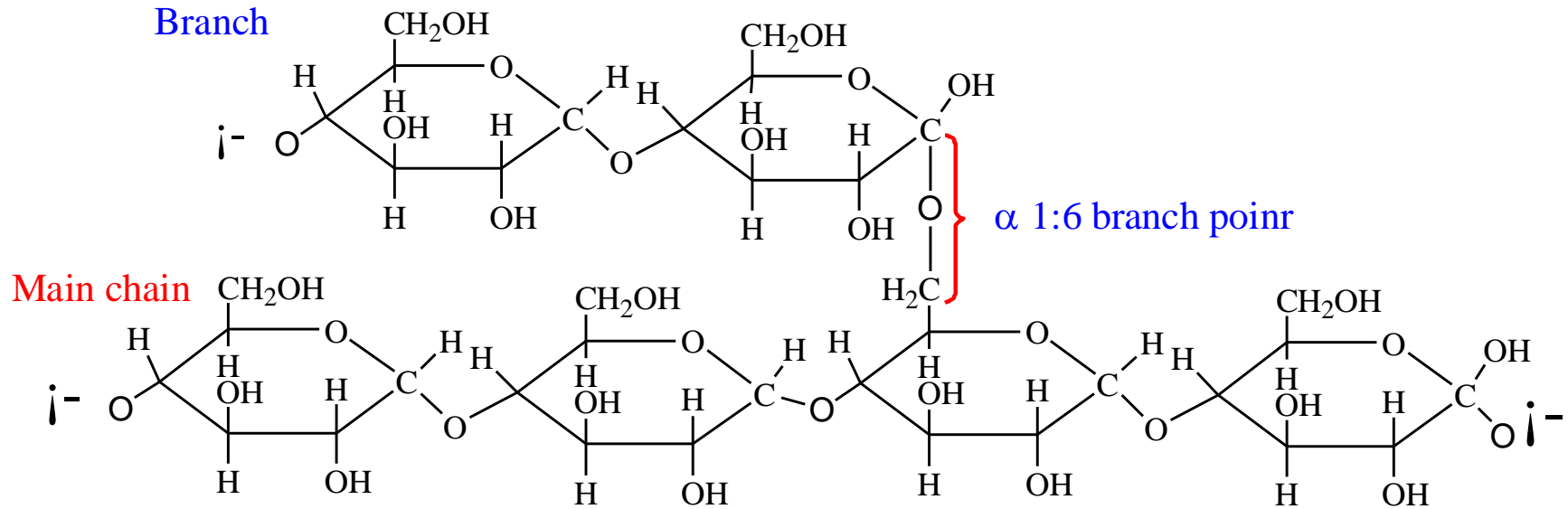
In amylopectin the chains are branched. Branching takes place between C-6 and C-1at intervals of 20-25 glucose units.

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



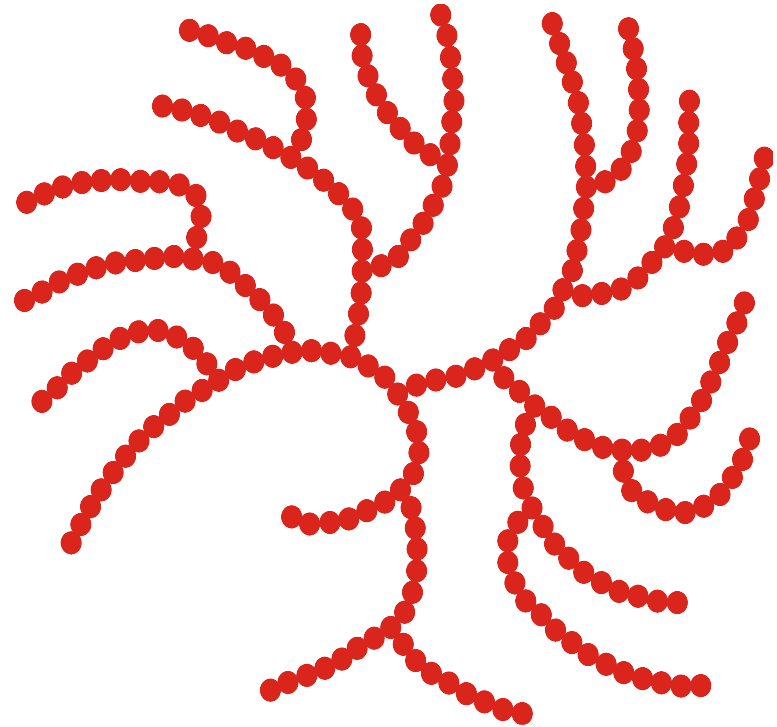
Partical structure of amylopectin:



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 α -1 \rightarrow 4 linked subunit and branching at α -1 \rightarrow 6 (similar to amylopectin)

Highly branched

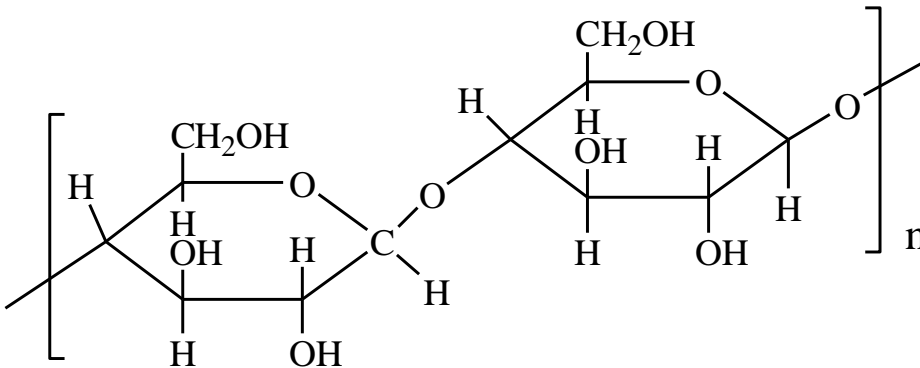
The size and structure of glycogen suits its function:

- (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 β , 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.

Dextran

In bacteria and yeast

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

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

Sephadex

Chitin

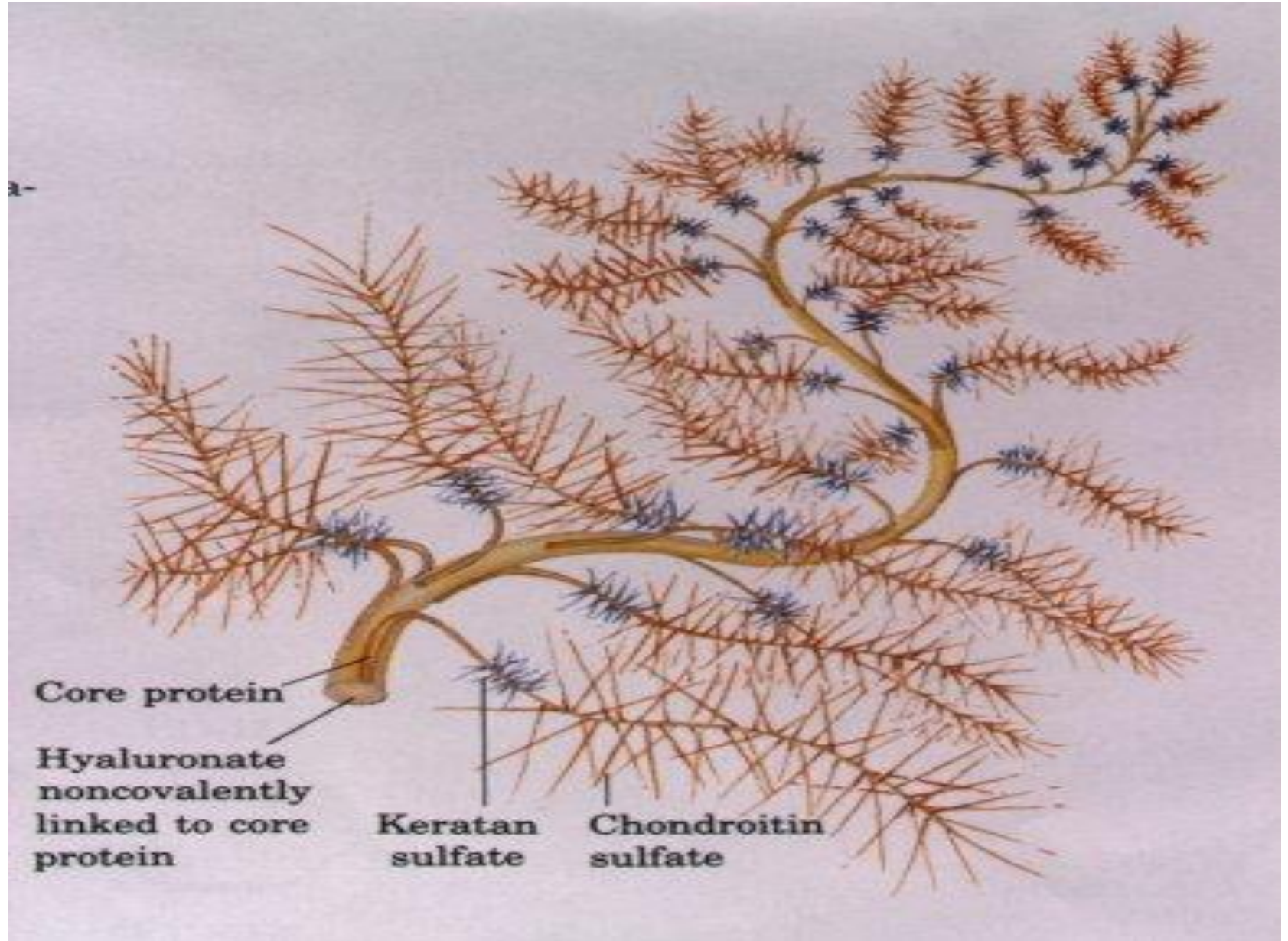
Linear homopolysaccharide of N acetyl glucosamine residue in β - 1 \rightarrow 4 linkage

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

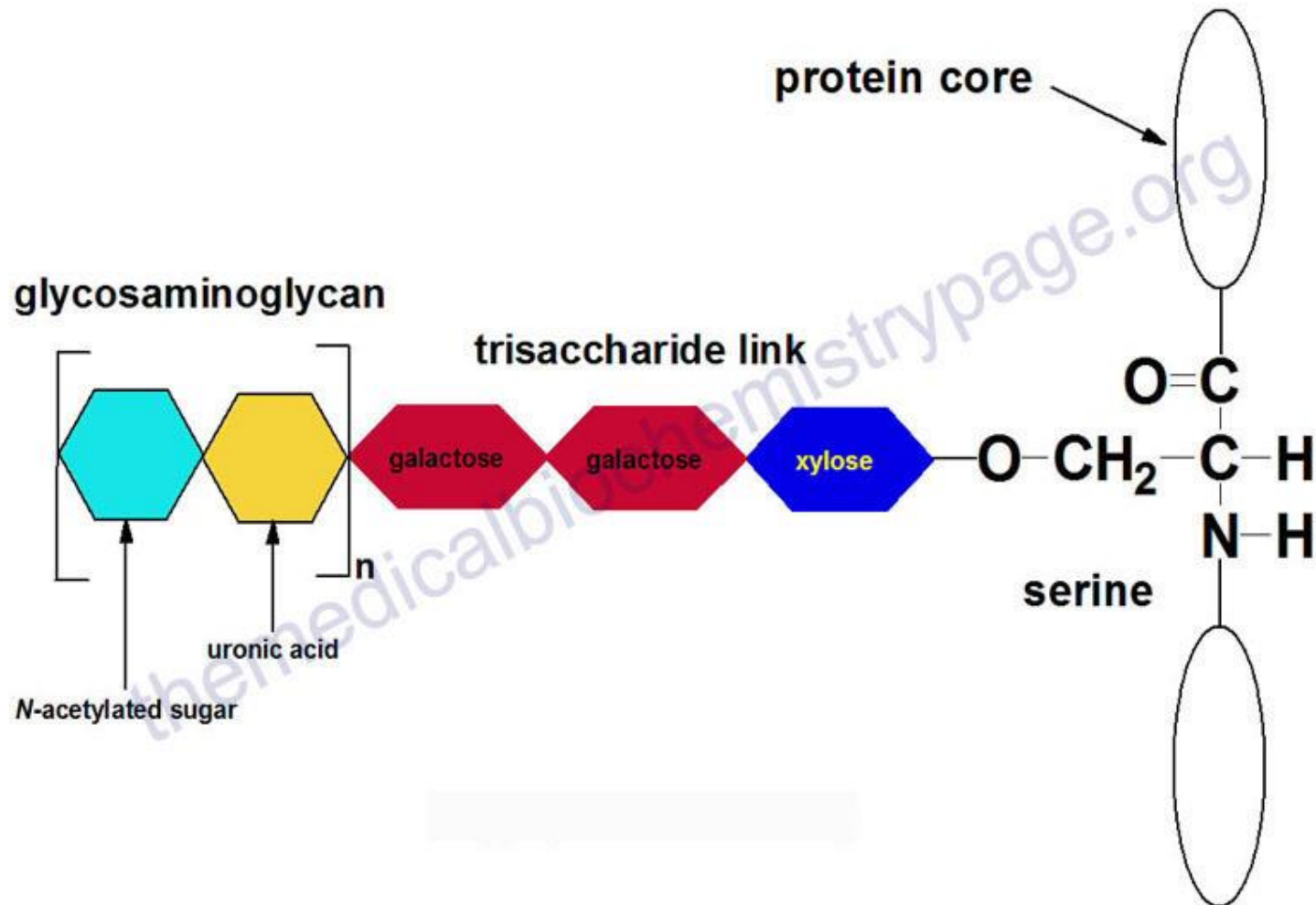
- GAGs are highly **negatively charged** molecules, with extended conformation that imparts high viscosity to the solution.
- GAGs are located primarily on the **surface of cells or in the extracellular matrix (ECM)**.
- Along with the high viscosity of GAGs comes **low compressibility**, which makes 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:

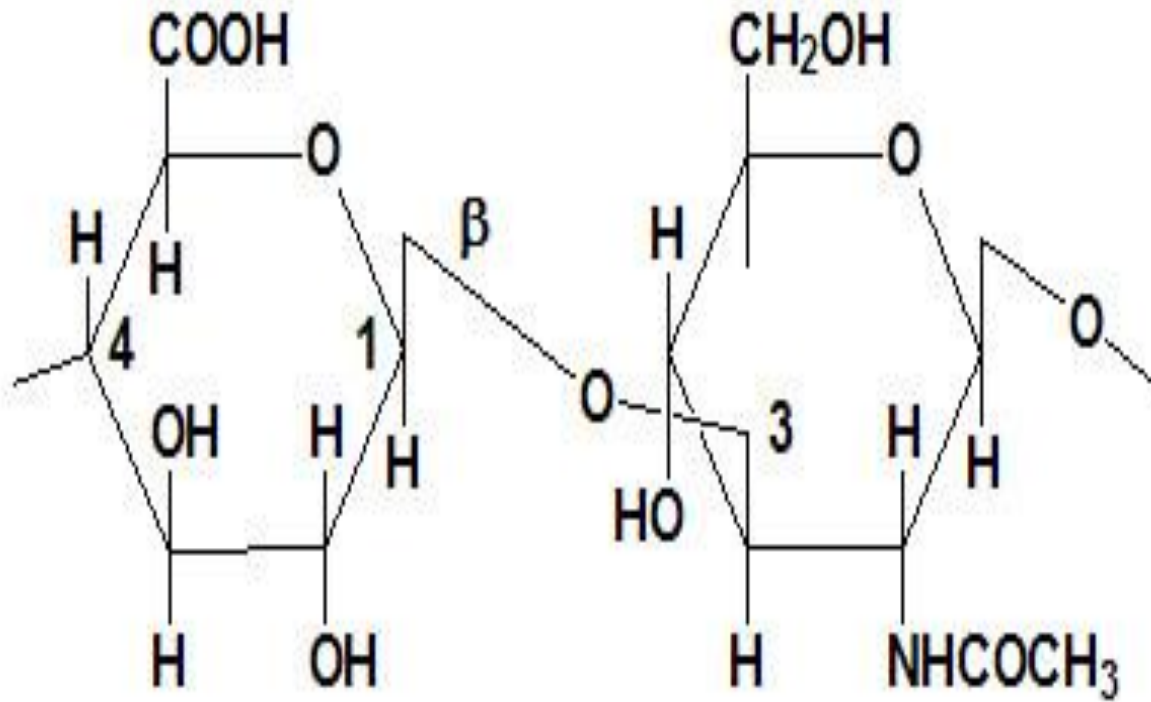
OR the GAGs differ from each other:

- 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



D-glucuronate

N-acetyl-D-glucosamine

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

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 valves

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 lie between collagen fibrils and play a critical role in corneal transparency.

- 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. β - 1 \rightarrow 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 (α or β 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)



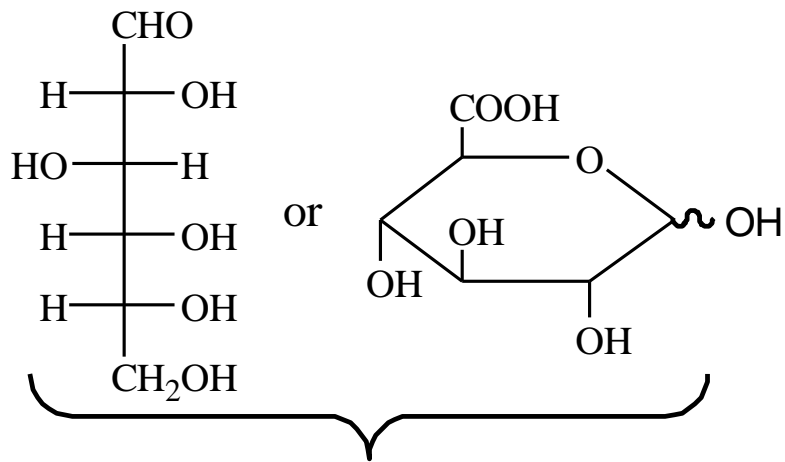
- Monosaccharide configuration
- Substitute units

Physical methods:

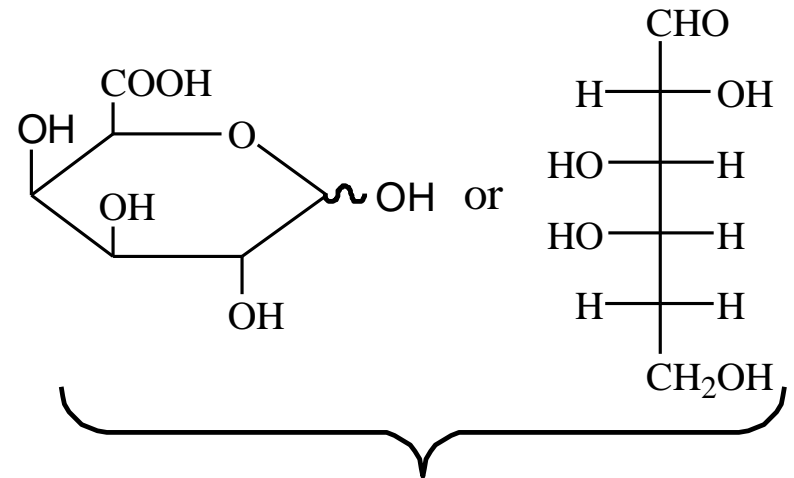
MS (Mass spectrometer)



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



D-Glucuronic acid
(ÀÏ(ÎÑ)ÏÇÈÇËá)



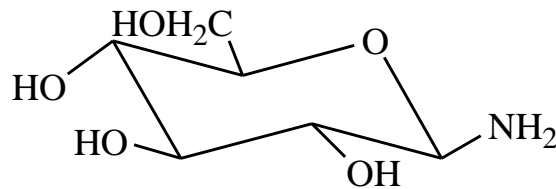
D-Galacturonic acid
(°ëÈéÏÇÈÇËá)

Sugar Acid

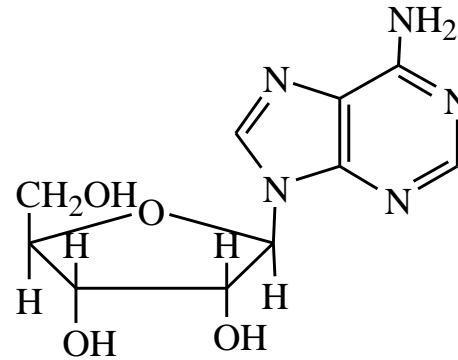
DEOXY SUGARS: monosaccharides in which an –OH group has been replaced by –H.

GLYCOSYLAMINES

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



β-D-Glucopyranosyl amine

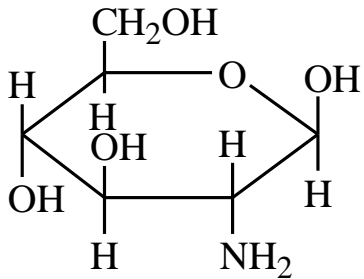


Adenosine
(ribose)

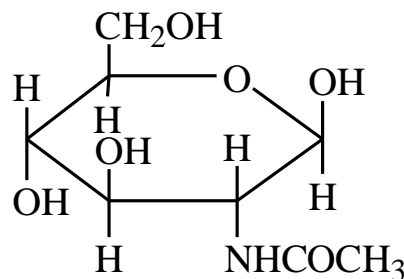
Nucleoside: glycosylamines in which the amino component is a pyrimidine or a purine and in which the sugar component is either D-ribose or 2-deoxy-D-ribose.

AMINO SUGARS

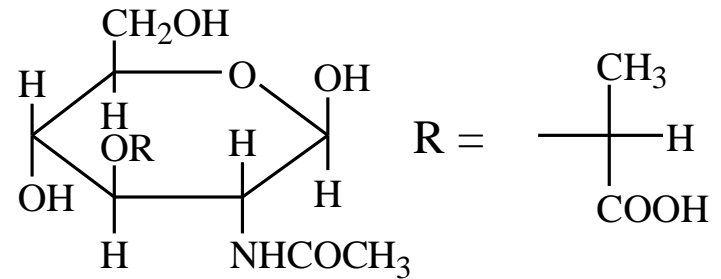
Amino sugar: a sugar in which an amino group replaces a nonanomeric –OH group.



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 β , 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.