# Shree H.N.Shukla College of Science
## S.Y.B.Sc. Sem-3
### BC-301: BIOMOLECULES
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## Unit-1 CARBOHYDRATE

Carbohydrates are the single most abundant class of organic molecules found in nature. The name carbohydrate arises from the basic molecular formula (CH2O)n, which can be rewritten (C _ H2O)n Carbohydrates may be defined as polyhydroxy aldehydes or ketones or compounds which produce them on hydrolysis. The term 'sugar ' is applied to carbohydrates soluble in water and sweet to taste.

## Function of carbohydrate

Carbohydrates participate in a wide range of functions

1. They are the most abundant dietary source of energy (a Cal/S) for all organisms.
2. Carbohydrates are precursors for many organic compounds (fats, amino acids).
3. Carbohydrate (as a glycoproteins and glycolipids) participate in the structure of cell membrane and cellular functions such as cell growth, adhesion and fertilization.
4. They are structural components of many organisms These include the fiber (cellulose) of plants, exoskeleton of some insects and the cell wall of microorganisms.
5. Carbohydrates also serve as the storage form of energy( glycogent)o meett he immediate energy demands of the body.

## CLASSIFICATION OF CARBOHYDRATES

Carbohydrates are often referred to as saccharides (Greek: sakcharon-sugar). They are broadly classified into three major groups monosaccharide's, oligosaccharides and polysaccharides This categorization is based on the number of sugar units. Mono- and oligosaccharides are sweet to taste, crystalline in character and soluble in water, hence they are commonly known as sugars.
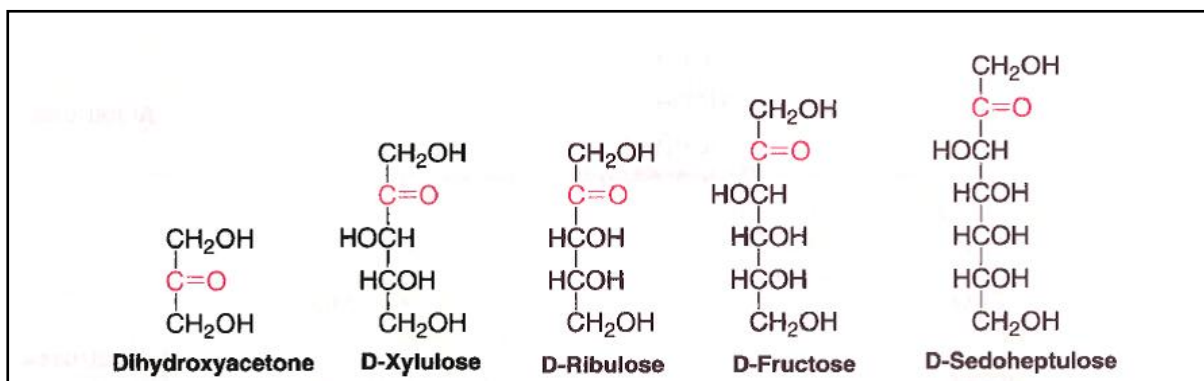
## Monosaccharides

Monosaccharide(sG reek: mono-one)are the simplest group of carbohydrates and are often referred to as simple sugars. They have the general formula $Cn(H2O)n$, and they cannot be further hydrolysed. The monosaccharides are divided into different categories, based on the functional group and the number of carbon atoms
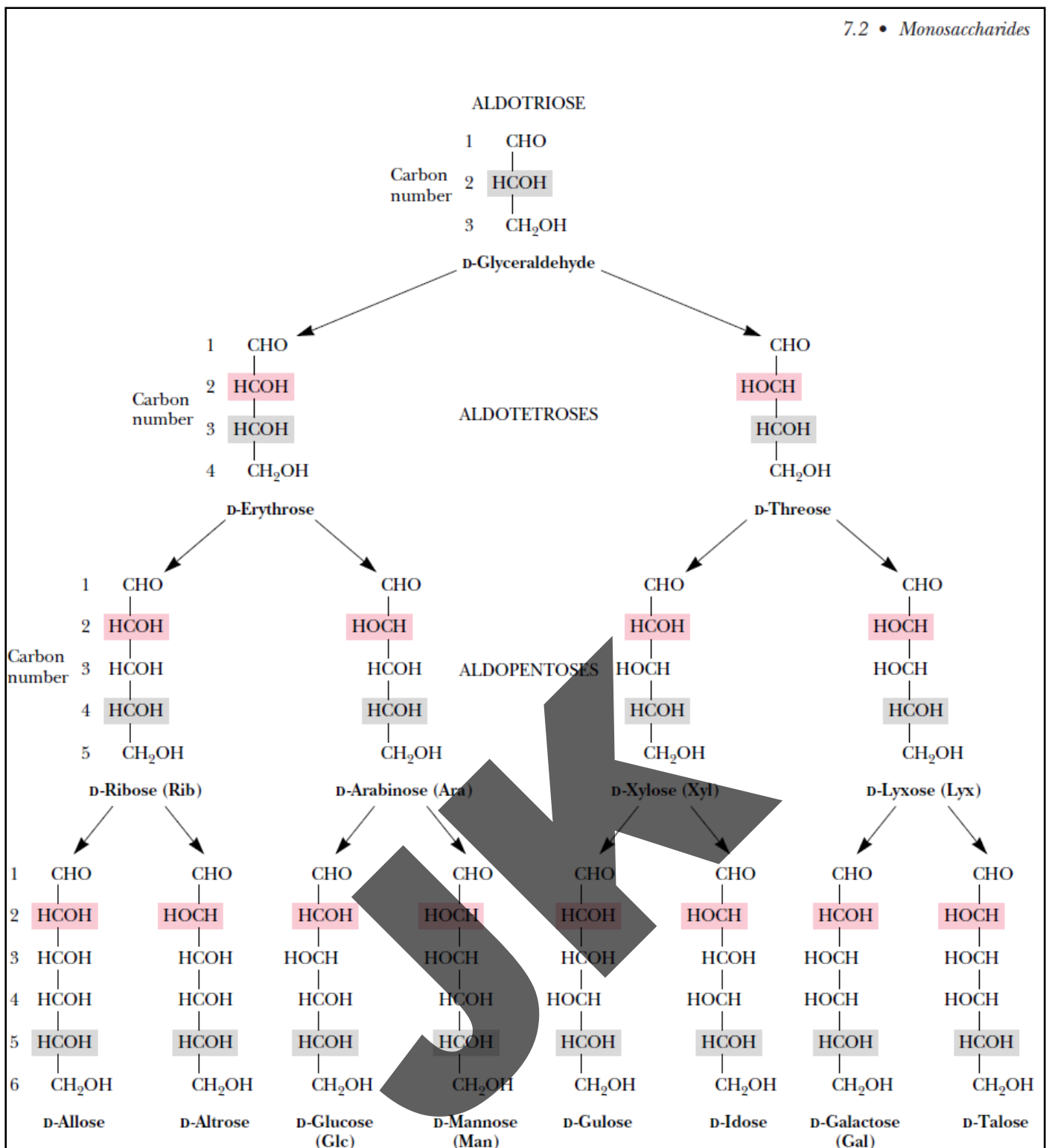
**Aldoses**: When the functional group in monosaccharidesis an aldehyd $\left(-\overset{H}{\underset{}{C}}=O\right)$ They are known as aldoses e.g. glyceraldehyde, glucose.

**Ketoses:** When the functional group is a keto $\left(-\overset{|}{\underset{|}{C}}=O\right)$ group, they are referred to as ketoses e.g. dihydroxyacetone fructose.

Based on the number of carbon atoms, themonosaccharides are regarded as trioses (3C),tetroses (4C), pentoses (5C), hexoses (6C) andheptoses( 7C).Theset ermsa long with functionalgroups are used while naming monosaccharides.For instance, glucose is an aldohexose whilefructose is a ketohexose.

| Monosaccharides (empirical formula) | Aldose | Ketose |
|---|---|---|
| Trioses ($C_3H_6O_3$) | Glyceraldehyde | Dihydroxyacetone |
| Tetroses ($C_4H_8O_4$) | Erythrose | Erythrulose |
| Pentoses ($C_5H_{10}O_5$) | Ribose | Ribulose |
| Hexoses ($C_6H_{12}O_6$) | Glucose | Fructose |
| Heptoses ($C_7H_{14}O_7$) | Glucoheptose | Sedoheptulose |

**ALDOTRIOSE**

Carbon number

1 CHO
2 HCOH
3 CH$_2$OH

**D-Glyceraldehyde**

**ALDOTETROSES**

Carbon number

1 CHO
2 HCOH
3 HCOH
4 CH$_2$OH

**D-Erythrose**

1 CHO
2 HOCH
3 HCOH
4 CH$_2$OH

**D-Threose**

**ALDOPENTOSES**

Carbon number

1 CHO
2 HCOH
3 HCOH
4 HCOH
5 CH$_2$OH

**D-Ribose (Rib)**

1 CHO
2 HOCH
3 HCOH
4 HCOH
5 CH$_2$OH

**D-Arabinose (Ara)**

1 CHO
2 HCOH
3 HOCH
4 HCOH
5 CH$_2$OH

**D-Xylose (Xyl)**

1 CHO
2 HOCH
3 HOCH
4 HCOH
5 CH$_2$OH

**D-Lyxose (Lyx)**

1 CHO
2 HCOH
3 HCOH
4 HCOH
5 HCOH
6 CH$_2$OH

**D-Allose**

1 CHO
2 HOCH
3 HCOH
4 HCOH
5 HCOH
6 CH$_2$OH

**D-Altrose**

1 CHO
2 HCOH
3 HOCH
4 HCOH
5 HCOH
6 CH$_2$OH

**D-Glucose (Glc)**

1 CHO
2 HOCH
3 HOCH
4 HCOH
5 HCOH
6 CH$_2$OH

**D-Mannose (Man)**

1 CHO
2 HCOH
3 HCOH
4 HOCH
5 HCOH
6 CH$_2$OH

**D-Gulose**

1 CHO
2 HOCH
3 HCOH
4 HOCH
5 HCOH
6 CH$_2$OH

**D-Idose**

1 CHO
2 HCOH
3 HOCH
4 HOCH
5 HCOH
6 CH$_2$OH

**D-Galactose (Gal)**

1 CHO
2 HOCH
3 HOCH
4 HOCH
5 HCOH
6 CH$_2$OH

**D-Talose**

## Olilgosaccharides

Oligosaccharides (Creek: oligo-few) contain2-1O monosaccharide molecules which areliberated on hydrolysis. Based on the number of monosaccharide units present, the oligosaccharides are further subdivided to disaccharides, trisaccharides etc.
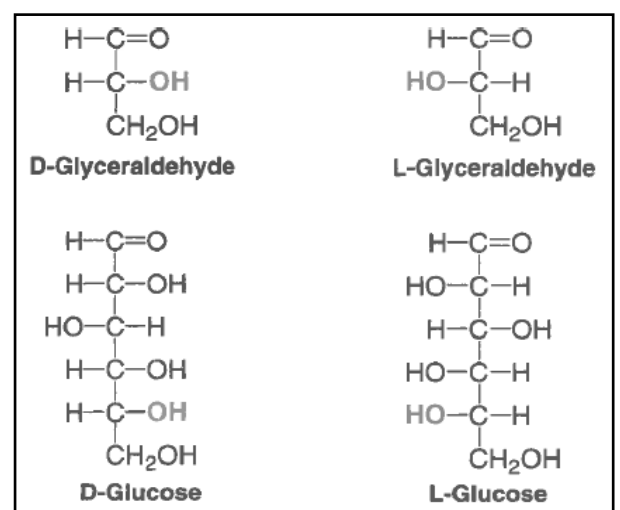
## Polysace harides

Polysaccharides are polymers of monosaccharide units with high molecular weight (up to a million). They are usually tasteless( non-sugars) and form colloids with water. The polysaccharides are of two types homopolysaccharides and heteropolysaccharides.

## Stereoisomerismis

Stereoisomerisms an important character ofmonosaccharides. Stereoisomers are thecompounds that have the same structuralformulae but differ in their spatial configuration.

A carbon is said to be asymmetric when it isattached to four different atoms or groups. Ihe

Number of asymmetric carbon atoms (n)determines the possible isomers of a given compound which is equal to 2n. Glucosecontains 4 asymmetric carbons, and thus has 16 isomers.

H—C=O
H—C—OH
CH$_2$OH
**D-Glyceraldehyde**

H—C=O
HO—C—H
CH$_2$OH
**L-Glyceraldehyde**

H—C=O
H—C—OH
HO—C—H
H—C—OH
H—C—OH
CH$_2$OH
**D-Glucose**

H—C=O
HO—C—H
H—C—OH
HO—C—H
HO—C—H
CH$_2$OH
**L-Glucose**

## D and L-isomers

The D and L isomers are mirror images of each other. The spatial orientation of -H and -OH groups on the carbon atom (Cs for glucose) that is adjacent to the terminal primary alcohol carbon determines whether the sugar is D- or L-isomer. lf the -OH group is on the right side, the sugar is of D-series,a nd if on the left side, it belongs to L-series. The structures of D- and L-glucose based on the reference monosaccharide, D- and L-glyceraldehyde.

It may be noted that the naturally occurring monosaccharideisn the mammalian tissues aremostly of D-configuration.The enzyme machinery of cells is specific to metabolise D-series ofmonosaccharides.

## Optical activity of sugars

Optical activity is a characteristic feature of compounds with asymmetric carbon atom. When a beam of polarized light is passed through a solution of an optical isomer, it will be rotated either to the right or left. The term dextrorotatory (+) and levorotatory (-) are used to compounds that respectively rotate the plane of polarized light to the right or to the left.

An optical isomer may be designated as D(+), D(-), L(+) and L(-) based on its structural relation with glyceraldehyde.l t may be noted that the D- and L-configurations of sugars are primarily based on the structure of glyceraldehyde, the optical activities however, may be different.

**Racemic mixture** : lf D- and L-isomers are present in equal concentration, it is known as racemic mixture or DL mixture. Racemic mixture does not exhibit any optical activity, since the dextro- and levorotatorv activities cancel each other.

## Epimers

♣ if two monosaccharides differ from each other in their configuration around a single specific carbon (other than anomeric) atom. They are referred to as epimers to each orher .

♣ For instance, glucose and galactose are epimers with regard to carbon C4 they differ in the arrangement of -OH of C4.. Glucose and mannose are epimers regard to carbon 2 (C2-epimers).



D-Galactose    D-Glucose    D-Mannose
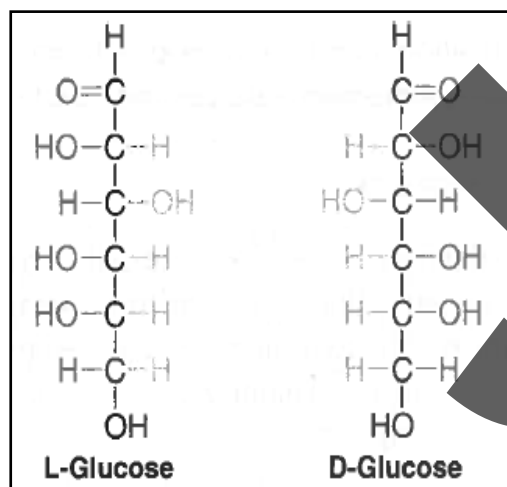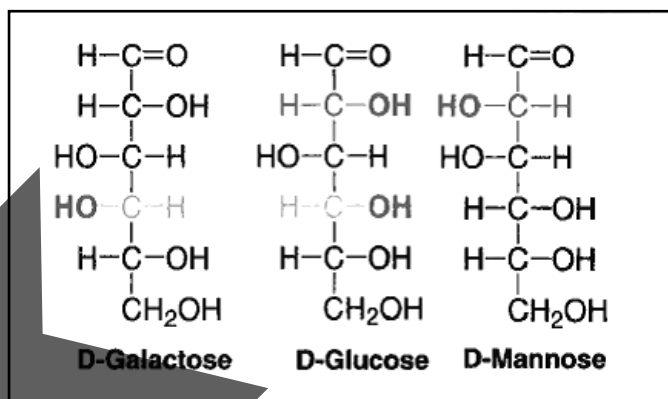


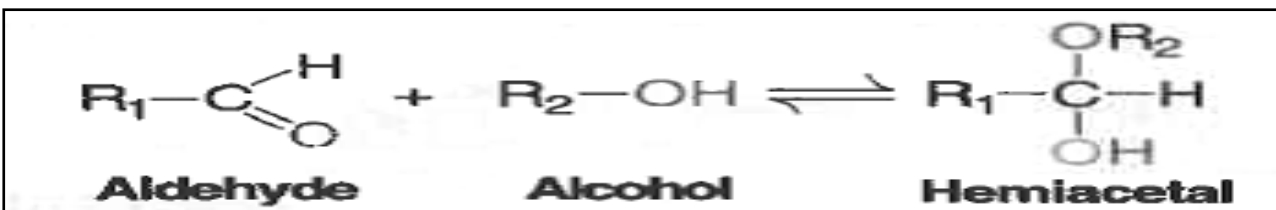L-Glucose    D-Glucose

### Enantiomers

Enantiomers are a special type of stereoisomers that are mirror images of each other. The two members are designated as D- and L-sugars. Enantiomers of glucose are depicted in (Fig).

Majority of the sugars in the higher animals (including man) are of D-type. The term diastereomers is used to represent the stereoisomer that are not mirror images of one another.

## STRUCTURE OF GLUCOSE

For a better understanding structure, let us consider the hemiacetals and hemiketals, produced when an aldehyde or a with alcohol.The hydroxyl group of monosaccharide react with its own aldehyde or keto functionalgroup to form hemiacetal and hemiketal.

Thus,the aldehyde group of glucose at C1 reacts withalcohol group at C5 to form two types of cyclichemiacetals namely a and B, as depicted inFig.2.6. The configuration of glucose isconveniently represented either by Fischerformulae or by Haworth projection formulae.



Aldehyde    Alcohol    Hemiacetal

## Pyranose and furanose structures

Haworth projection formulae are depicted by a six-membered ring pyranose (based on pyran) or a five-membered ring furanose (based on furan). The cyclic forms of glucose are known as a-D-glucopyranose and c-D-glucofuranose.

HAWORTH PROJECTION FORMULAS
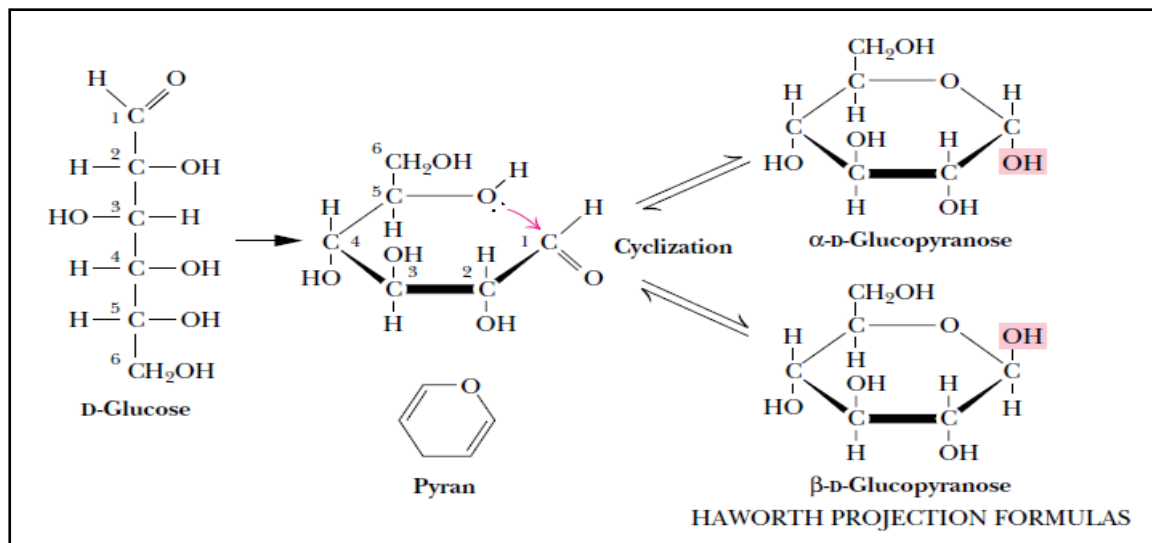
## Anomers-mutarotation

The α and β cyclic forms of D-glucose are known as anomers. They differ from each other in the configuration only around C1 known as anomeric carbon (hemiacetal carbon). In case of α- anomer, the -OH group held by anomeric carbon is on the opposite side of the group -CH2OH of sugar ring. The reverse is true for B-anomer.The anomers differ in certain physical and chemical properties
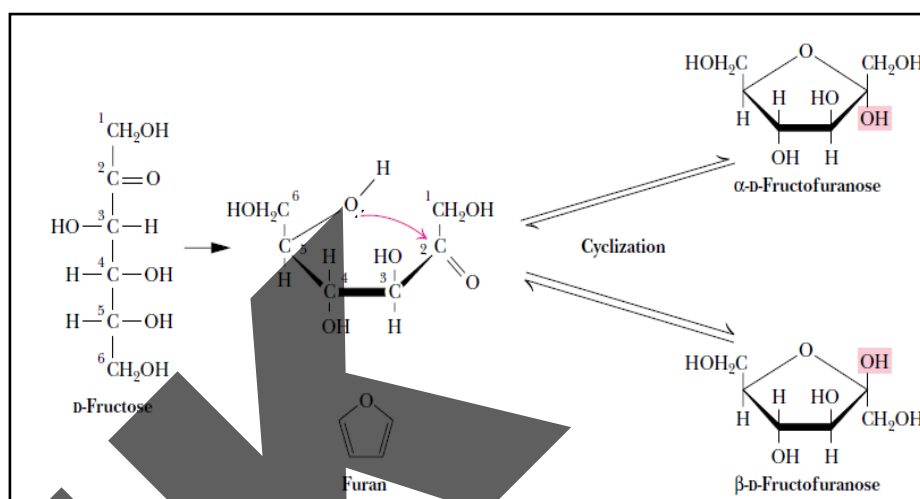
## Mutarotation:

The α and β anomers of glucose have different optical rotations. Thespecific optical rotation of a freshly preparedglucose (c anomer) solution in water is +112.2owhich gradually changes and attains anequilibrium with a constant value of +52.7)0. In the presence of alkali, the decrease in opticalrotation is rapid. The optical rotation of β-glucose is +18.7o. Mutarotation is defined asthe change in the specific optical rotationrepresenting the interconversion of α and β. forms of D-glucose to an equilihrium mixture' Mutarotation depicted It summaries below.

The equilibrium mixture contains 63% β-anomer and 36% α-anomer of glucose with 1% open chain form. ln aqueous solution' the β forn is more predominant due to its stable conformation. The α and β forms of glucose are interconvertible which occurs through a linear form.

$$\alpha\text{-D-Glucose} \rightleftharpoons \text{Equilibrium mixture} \rightleftharpoons \beta\text{-D-Glucose}$$
$$+112.2° \qquad +52.7° \qquad +18.7°$$
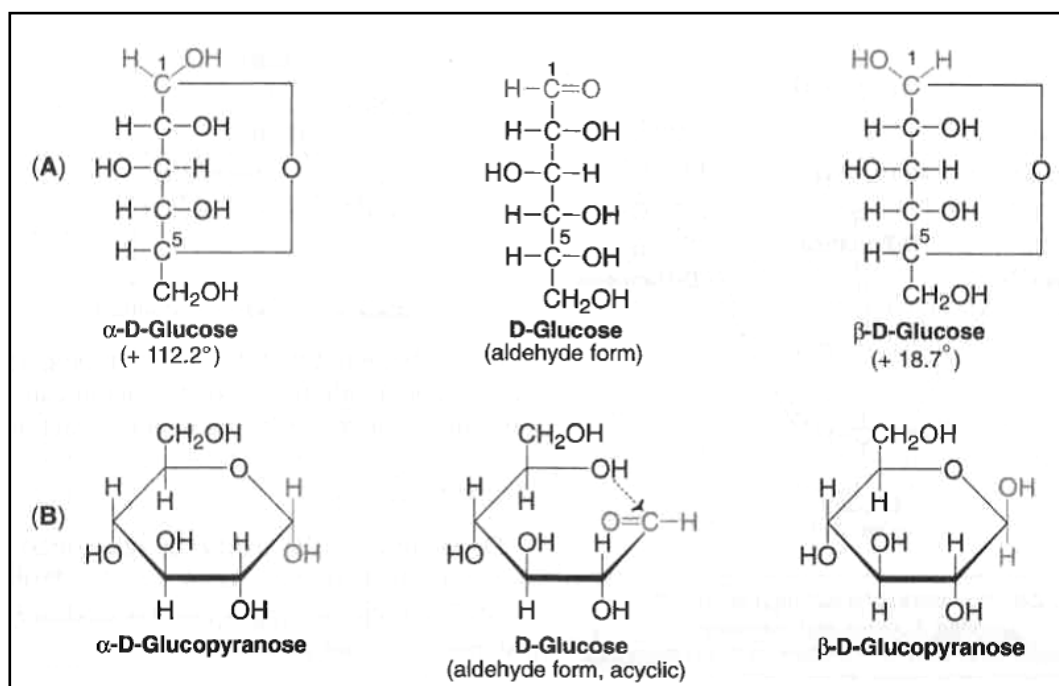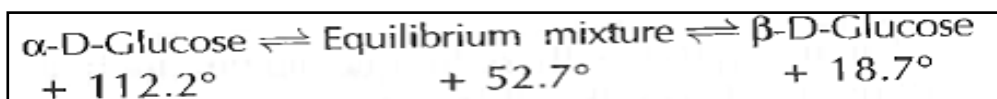
Reducing disaccharides lso give osazonesmaltose sunflower-shaped, and lactose powderpuff shaped.

## GLYCOSIDES

Glycosides are formed when the hemiacetal or hemiketal hydroxyl group (of anomeric carbon) of a carbohydrater eactsw ith a hydroxyl group of another carbohydrate or a noncarbohydrate (e.g. methyl alcohol, phenol, glycerol). The bond so formed is known as glycosidic bond and the non-carbohydrate moiety (when present) is referred to as a glycone.

The monosaccharidesa re held together by glycosidic bonds to result in di-, oligo- or polysaccharide.

**Naming of glycosidic bond** : The nomenclature of glycosidic bonds is based on the Iinkages between the carbon atoms and the status of the anomeric carbon (α orβ ). For instance, lactose-which is formed by a bond between C1 of β-galactose and C4 of glucose is named as β(.1-4) glycosidic bond. The other glycosidic bonds are described in the structure of di- and polysaccharides.

## DERIVATIVESO F MONOSACCHARID

There are several derivatives of monosaccharides, some of which are physiologically important

**1. Sugar acids :** Oxidation of aldehyde or primary alcohol group in monosaccharide results in sugar acids. Cluconic acid is produced from glucose by oxidation of aldehyde (C1 group) whereas glucuronic acid is formed when primary alcohol group (C6) is oxidized.

**2. Sugar alcohols (polyols)** : They are produced by reduction of aldoses or ketoses For instance, sorbitol is formed from glucose and mannitol from mannose.

**3. Alditols :** The monosaccharides, on reduction, yield polyhydroxy alcohols, known as alditols. Ribitol is a constituent of flavin coenzymes; glycerol and myo-inositol are componentso f lipids.X ylitol is a sweetener used in sugarless gums and candies.

**4. Amino sugars** : When one or more hydroxyl groups of the monosaccharides are replaced by amino groups, the products formed are amino sugars e.g. D-glucosamine, D-galactosamine. They are present as constituents of heteropolysaccharide.

The amino groups of amino sugars are sometimes acetylated e.g. N-acetyl D-glucosamrne. N-Acetylneuraminic acid (NANA) is a derivative of N-acetylmannose and pyruvic acid. It is an important constituent of glycoproteins and glycolipids. The term sialic acid is used to include NANA and its other derivatives. Certain antibiotics contain amino sugars which may be involved in the antibiotic activity e.g. erythromycin.

**5. Deoxysugars** : These are the sugars that contain one oxygen less than that present in the

parent molecule. The groups -CHOH and -CH2OH become -CH2 and -CH3 due to the absence of oxygen.D -2-Deoxyriboseis the most important deoxysugar since it is a structural constituent of DNA (in contrast to D-ribose in RNA).

**6. L-Ascorbic acid (vitamin C)**: This is a water-soluble vitamin, the structure of which closely resemblesth at of a monosaccharide.
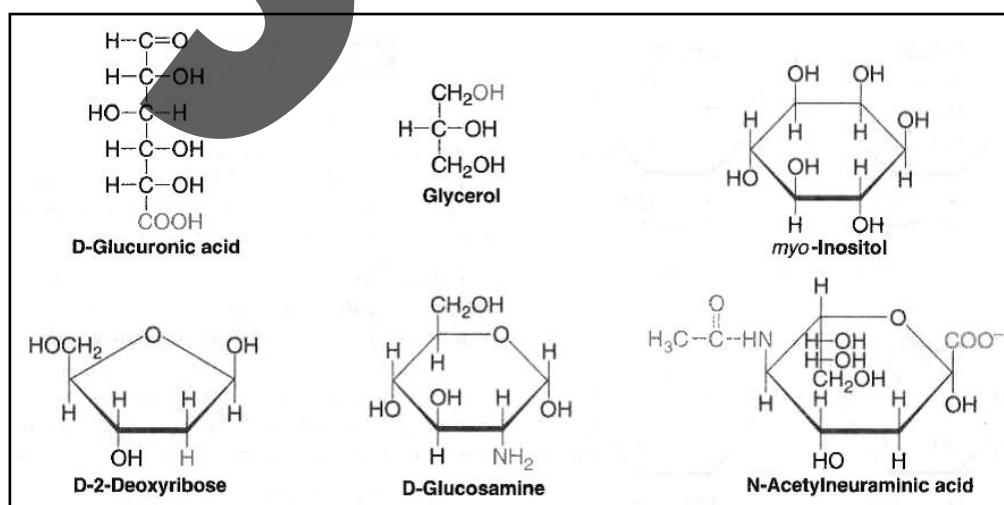


## Disaccharide

disaccharide consists of two monosaccharide units ( simillar or dissimilar) held together by a glycosidic hond.

They are crystalline, water-soluble and sweet to taste. The disaccharides are of two types

1. Reducing disaccharides with free aldehyde or keto group e.g. maltose, lactose.
2. Non-reducing disaccharides with no free aldehyde or keto group e.g. sucrose, trehalose.

## Maltose

Maltose is composed of two a-D-glucose units held together by cl (1-->4) glycosidic bond. The free aldehydeg roup present on C1 of second glucose answers the reducing reactions, besides the osazone formations (sunflower-shaped). Maltose can be hydrolysed by dilute acid or the enzyme maltase to liberate two molecules of cr-D-glucose.

ln isomaltose, the glucose units are held together by o (1 →6) glycosidic linkage.
Cellobiose is another disaccharide, identical in structure with maltose, except that the former has (1 ->4) glycosidic linkage. Cellobiose is formed during the hydrolysis of cellulose.

## Sucrose

Sucrose (cane sugar), mostly produced by sugar cane and sugar beets. Sucrose is made up of α-D-glucose and β- D-fructose. The two monosaccharide are held together by a glycosidic bond (α1--> β2), between C1 of α-glucose and C2 of β-fructose. The reducing groups of glucose and fructose are involved in glycosidic bond, hence sucrose is a non-reducing sugar, and it cannot form osazones.

Sucrose is the major carbohydrate produced in photosynthesis. lt is transported into the storage organs of plants (such as roots, tubers and seeds)Sucrose is the most abundant among the naturally occurring sugars. lt has distinct advantages over other sugars as a storage and transport form. This is due to the fact that in sucrose, both the functional groups (aldehyde and keto) are held together and protected from oxidative attacks.

Sucrose is an important source of dietary carbohydrate. lt is sweeter than most other common sugars( except fructose) namelyglucose, lactose and maltose. Sucrose is employed as asweetening agent in food industry. The intestinalenzyme-sucrase-hydrolyses sucroseto glucoseand fructose which are absorbed.

## Inversion of sucrose

Sucrose, as such is dextrorotatory (+66.5o). But when hydrolysed, sucrose becomes levorotatory (-28.20). The process of change in optical rotation from dextrorotatory (+) to levorotatory (-) is referred to as inversion. The hydrolysed mixture of sucrose, containing glucose and fructose, is known as invert sugar.

The process of inversion is explained below. Hydrolysis of sucrose by the enzyme sucrose (invertasd or dilute acid liberate some molecule each of glucose and fructose. ft is postulated that sucrose (dextro) is first split into α-D-glucopyranose (+52.50) and β-D-fructofuranose, both being



Maltose
(α-D-glucosyl (1 → 4) α-D-glucose)

Sucrose
(α-D-glucosyl (1 → 2) β-D-fructose)

Lactose
(β-D-galactosyl (1 → 4) β-D-glucose)

dextrorotatory. However, β-D-fructofuranose is less Stable and immediately gets converted to β-D-fructopyranose which is strongly levorotatory (-920). The overall effect is that dextro sucrose (+66.50) on inversion is converted to levo form (28.20).

## Lactose

Lactose is more commonlv known as milk sugar since it is the disaccharide found in milk.

Lactose is composed of β-D-galactose and B-Dglucose held together by β (1 →4) glycosidicbond. The anomeric carbon of C1 glucose is free,hence lactose exhibits reducing properties andforms osazones

Lactose of milk is the most importantcarbohydratein the nutrition of young mammals.

It is hydrolysed by the intestinal enzyme lactaseto glucose and galactose.

## Polysaccharide

Polysaccharide consist of repeat units of monosaccharides or their derivatives, held together by glycosidic bonds. They are primarily concerned with two important functions-structural, and storage of energy. Polysaccharides are linear as well as branched polymers. This is in contrast to structure of proteins and nucleic acids which areonly linear polymers. The occurrence ofbranches in polysaccharidesis due to the factthat glycosidic linkages can be formed at anyone of the hydroxyl groups of a monosaccharide.Polysaccharides are of two types

1. **Homopolysaccharide** which on hydrolysisyield only a single type of monosaccharide Theyare named based on the nature of themonosaccharide unit. Thus, glucans are polymersof glucose whereas fructosans are polymers offructose.
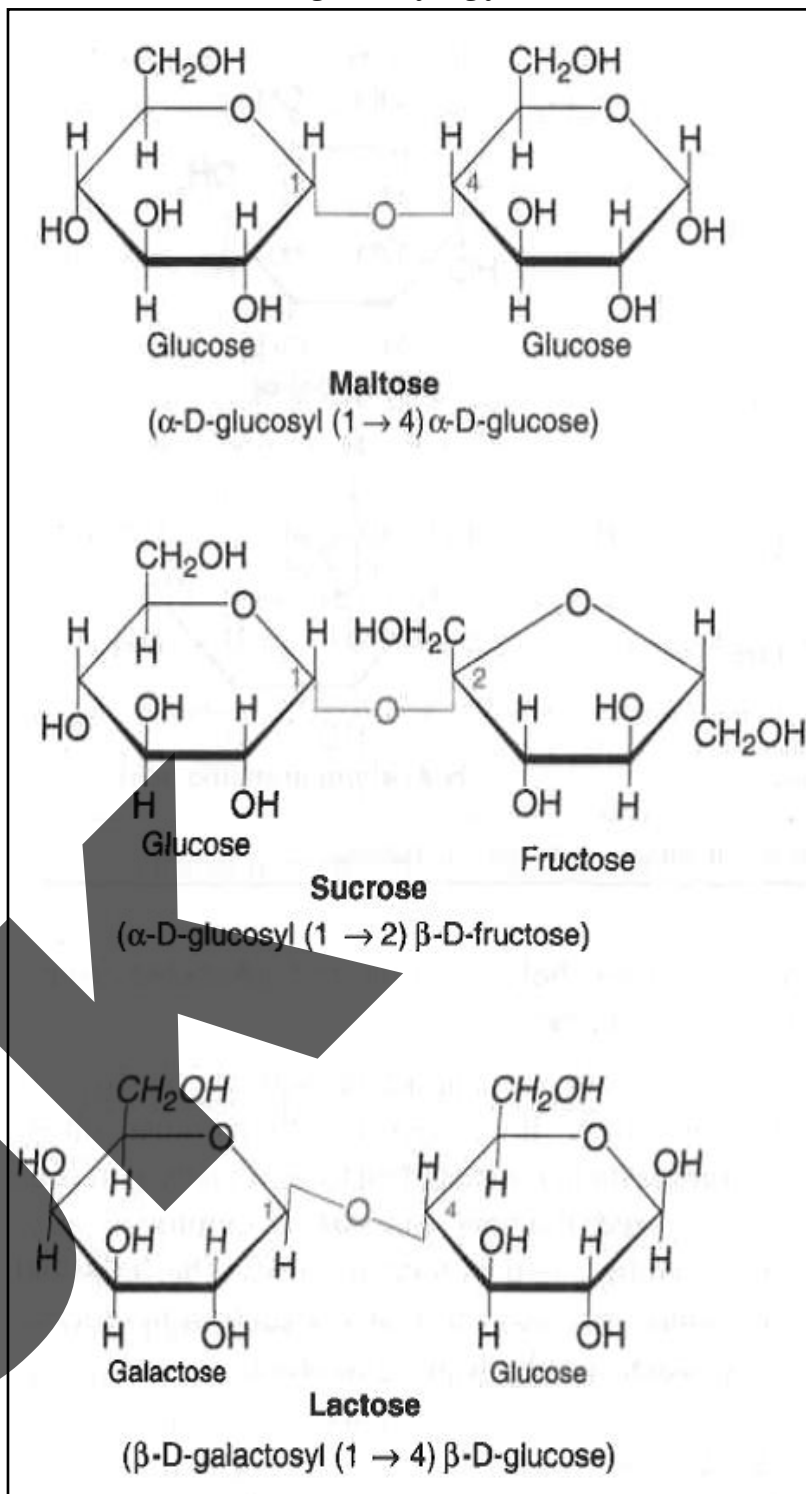
2. **Heteropolysaccharides** on hydrolysis yielda mixture of a few monosaccharides or theirderivatives

## Starch

Starch is the carbohydrate reserve of plants which is the most important dietary source for higher animals, including man. High content of starch is found in cereals, roots, tubers, vegetables etc. Starch is a homopolymer composed of D-glucose units held by D-glycosidic bonds. lt is known as glucosan or glucan.

Starch consists of two polysaccharide components-water soluble amylose (15-20%) and a water insoluble amylopectin (80-85%). Chemically, amylose is a long un branched chain with 200-1,00O D-glucose units held by α (1→4) glycosidic linkages. Amylopectin on the other hand, is a branched chain with a (1 → 6) glycosidic bonds at the branching points and α (1 → 4) linkages everywhere else (Fig).

Amylopectin molecule containing a few thousand glucose units looks like a branched tree (20-30 glucose units per branch). Starches are hydrolysed by amylase (pancreatic or salivary) to liberate dextrins, and finally maltose and glucose units. Amylase act specifically on a (1 -> 4) glycosidic bonds.
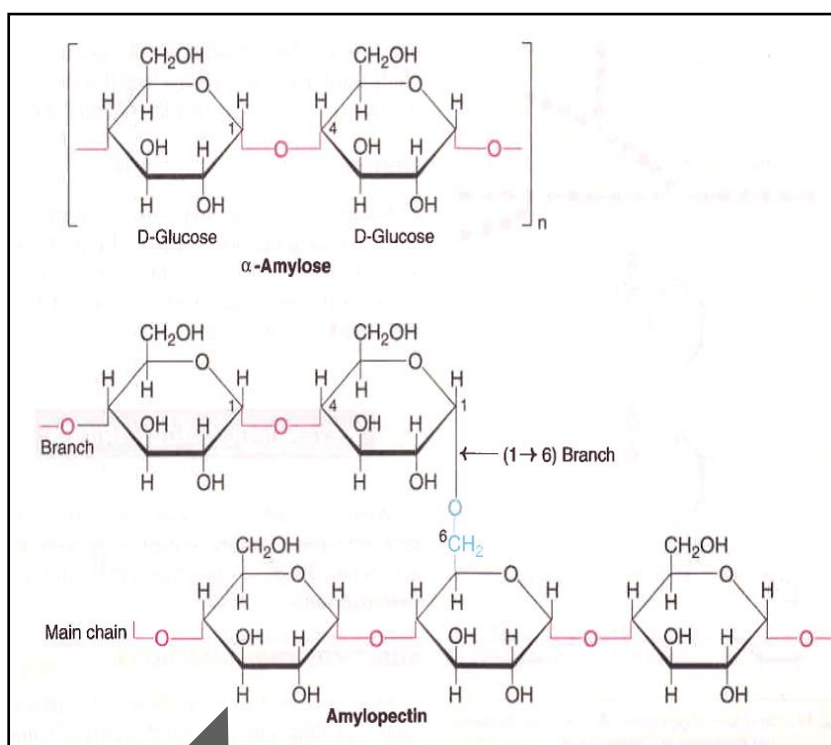
## Dextrins

Dextrins are the breakdown products of starch by the enzyme amylase or dilute acids. Starch is sequentially hydrolysed through different dextrins and, finally, to maltose and glucose. The various intermediates (identified by iodine colouration) are soluble starch (blue), amylodextrin (violet), erythrodextrin (red) an achrodextrin (no colour).

## Glycogen

Glycogen is the carbohydrate reserve in animals, hence often referred as a animal starch.It is present in high concentration in liver, followed by muscle, brain etc. Glycogen is also found in plants that do not possess chlorophyll (e.g. yeast, fungi).

The structure of glycogen is similar to that of amylopectin with more number of branches. Glucose is the repeating unit in glycogen joined together by α (1→4) glycosidic bonds, and a (1→ 6) glycosidic bonds at branching points The molecular weight (up to 1 x 108 and the number of glucose units (up to 25,000) vary in glycogen depending on the source from which glycogen is obtained.
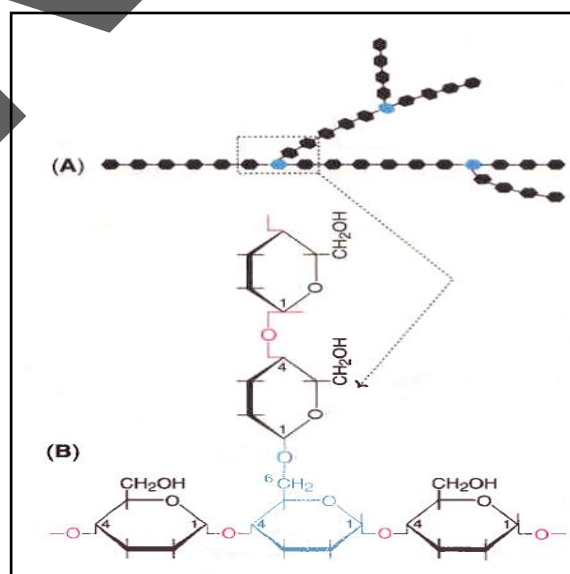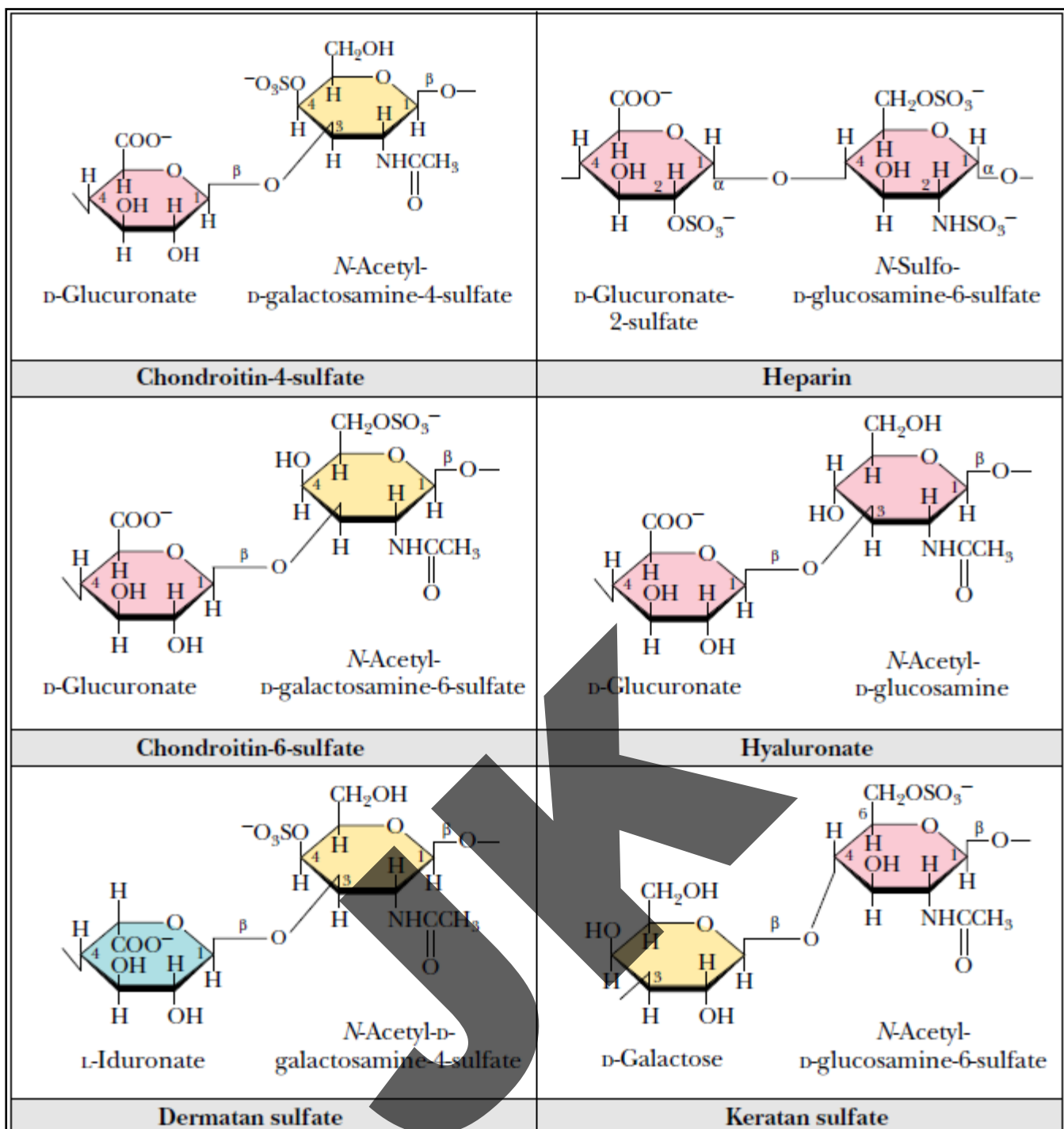
## Cellulose

The structural polysaccharides have properties that are dramatically different from those of the storage polysaccharides, even though the compositions of these two classes are similar. The structural polysaccharide cellulose is the most abundant natural polymer found in the world. Found in the cell walls of nearly all plants, cellulose is one of the principal components providing physical structure and strength. The wood and bark of trees are insoluble, highly organized structures formed from cellulose.

Cellulose is a linear homopolymer of D-glucose units, just as in _-amylose. The structural difference, which completely alters the properties of the poly- mer, is that in cellulose the glucose units are linked by β(1--->4)glycosidic bonds, whereas in _-amylose the linkage is α(1-→4). The conformational difference between these two structures is shown in (Fig) The α(1-→4) linkage sites of amylose are naturally bent, conferring a gradual turn to the polymer chain, which results in the helical conformation already described .
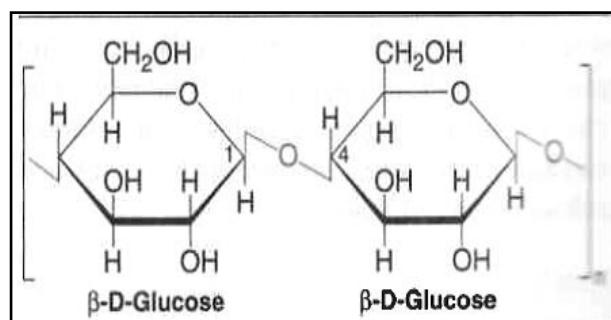
## chitin

A polysaccharide that is similar to cellulose, both in its biological function and its primary, secondary, and tertiary structure, is chitin. Chitin is present in the cell walls of fungi and is the fundamental material in the exoskeletons of insects, and spiders. The structure of chitin, repeating

| Chondroitin-4-sulfate | Heparin |
| D-Glucuronate / N-Acetyl-D-galactosamine-4-sulfate | D-Glucuronate-2-sulfate / N-Sulfo-D-glucosamine-6-sulfate |

| Chondroitin-6-sulfate | Hyaluronate |
| D-Glucuronate / N-Acetyl-D-galactosamine-6-sulfate | D-Glucuronate / N-Acetyl-D-glucosamine |

| Dermatan sulfate | Keratan sulfate |
| L-Iduronate / N-Acetyl-D-galactosamine-4-sulfate | D-Galactose / N-Acetyl-D-glucosamine-6-sulfate |

## Agarose

An important polysaccharide mixture isolated from marine red algae (Rhodophyceae) is agar, which consists of two components, agarose and agaropectin. Agarose (Fig.) is a chain of alternating D-galactose and 3,6- anhydro-L-galactose, with side chains of 6-methyl-D-galactose. Agaropectin is similar, but contains in addition sulfate ester side chains and D-glucuronic acid.

The three-dimensional structure of agarose is a double helix with a threefold screw axis, as shown in (Fig.) The central cavity is large enough to accom- modate water molecules. Agarose and agaropectin readily form gels containing large amounts (up to 99.5%) of water. Agarose can be processed to remove most of the charged groups, yielding a material (trade name Sepharose) useful for purification of macromolecules in gel exclusion chromatography.

Agarose is the principal neutral gelling component of agar extracted from algae. Agarose is a complex range of polysaccharide chains composed of alternating α-(1-3)-D-galactosyl-β-(1-4)-anhydro-L-galactosyl units.



Agarose

3,6-anhydro bridge



Agarase Specificity

β-(1-4)-(3,6)-anhydro-L-galactose    α-(1-3)-D-galactose