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ZO 353: Biological chemistry
Semester V

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Chapter 3: Carbohydrates

Biochemistry--An Overview

Biochemistry is the study of the chemical substances found in living organisms and the chemical interactions of these substances with each other. It deals with the structure and function of cellular components, such as proteins, carbohydrates, lipids, nucleic acids, and other biomolecules.

There are two types of biochemical substances: bioinorganic substances and

Inorganic substances: water and inorganic salts.

Bioorganic substances: Carbohydrates, Lipids, Proteins, and Nucleic Acids.**Complex bioorganic/inorganic Molecules**: Enzymes, Vitamins, DNA, RNA, and Hemoglobin etc.

As isolated compounds, bioinorganic/bioorganic/complex substances have no life in and of themselves. Yet when these substances are gathered together in a cell, their chemical interactions are able to sustain life.

Plant Materials

It is estimated that more than half of all organic carbon atoms are found in the **carbohydrate materials** of plants. Human uses for carbohydrates of the plant kingdom extend beyond food. Carbohydrates in the form of cottonand linen are used as clothing. Carbohydrates in the form of wood are usedfor shelter and heating and in making paper.

Occurrence and Functions of Carbohydrates

Almost 75% of dry plant material is produced by photosynthesis. Most of the matter in plants, except water, are carbohydrate material. Examples of carbohydrates are cellulose which are structural component of the plants, starch the energy reservoir in plants and glycogen (animal starch) found in animal tissues and human body in smaller quantities. Plant products are themajor source of carbohydrates and average human diet contains 2/3 of carbohydrates. Recommended percents in the daily diet:

Recommended carbohydrates ~ 60 %

Recommended sucrose less than 10%

Usefulness of carbohydrates is their ability to **produce energy** whenthey under go oxydation during respiration.

Storage carbohydrate, in theform of glycogen, provides a short-term energy reserve for bodily functions. Carbohydrates supply carbon atoms for the synthesis of other biochemicalsubstances (proteins, lipids, and nucleic acids). Carbohydrates also form apart of the

structural carbohydrate ,framework of DNA and RNAmolecules. Carbohydrates linked to lipids as discussed in are structural components of **cell membranes**..

18.1 Classification of Carbohydrates

Organic compounds containing many -OH groups (polyhydroxy), and aldehydes or ketones functional groups. By convention, the ending "-ose" is reserved for sugars (e.g. sucrose and glucose) in the class of carbohydrates.

Carbohydrates are produced by the process of photosynthesis in which six carbon sugars or hexoses are produced using energy of sunlight, green pigment chlorophyll, CO_2 and H_2O by green plants. The hexoses producedare the raw material for the biosynthesis of glycogen, fats, proteins and nucleic acid in living systems.

Simpler Formula for Cabohydrates:

- $\mathbf{C_nH_{2n}O_n}$ or $C_n(H_2O)_n$ (hydrates of C)
- n= number of atoms

Monosaccharides

They consist of one sugar containing 3,4,5,6 and 7 carbon atoms and are usually colorless, water-soluble, crystalline solids. Some monosaccharides have a sweet taste. Examples of monosaccharides include glucose (dextrose), fructose (levulose), galactose, xylose and ribose.

Disaccharides

a sugar (a carbohydrate) composed of two monosaccharides.Oligosaccharide
An oligosaccharide is a saccharide polymer containing a small number (typically 3-10 monosaccharides

Polysacharides

Are relatively complex carbohydrates. They are polymers made up of many monosaccharides joined together by glycosidic bonds. They are insoluble in water, and have no sweet taste.

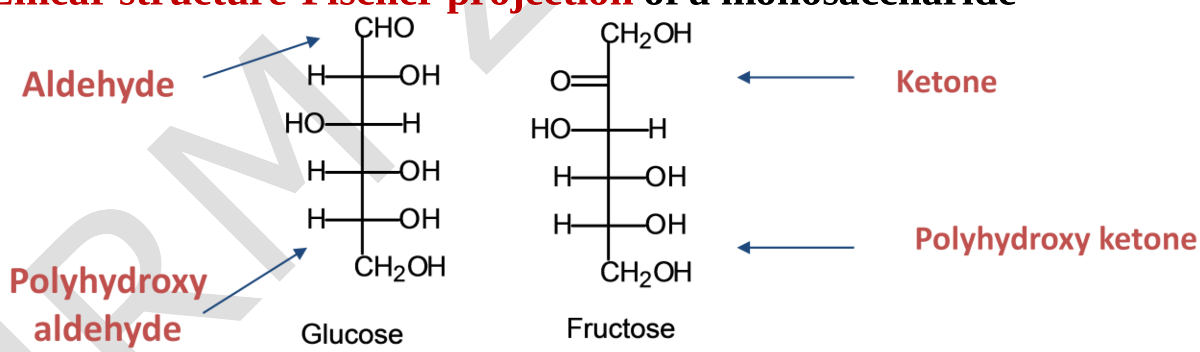
Monosaccharide structures and types

Aldoses :Aldehyde sugars are called aldoses.

Ketoses: Ketone sugars are called ketoses.

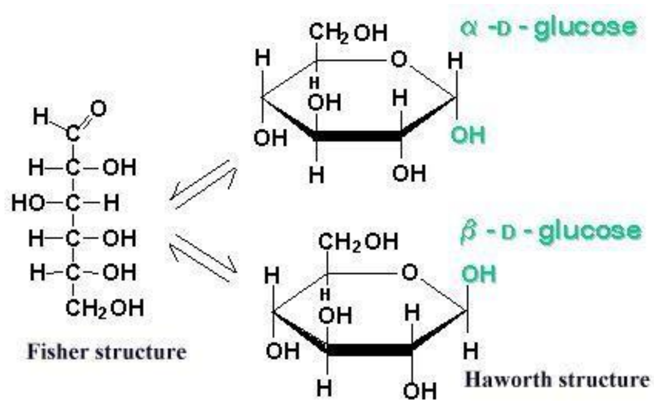
Drawing Sugar Molecules

□ **Linear structure-Fischer projection of a monosaccharide**



Aldose **Ketose**

□ **Haworth projection** showing cyclic forms: □- and □- forms.
The normal form of most sugars is in a **cyclic hemiacetal form** shown as aHaworth projection. In solution, less than 1% of a sugar will be in the linearform as shown in **Fischer structure** below on the right. In solution, over 99% of the sugar will be in a cyclic ring structure which is represented by **Haworth structures** on the left. The preferred form varies from sugar to sugar: some prefer to be a 6-member ring "pyranose", like glucose.



ALDEHYDE sugar or aldoses + alcohol --- hemiacetal (cyclic ring)

KETONE sugar or ketoses + alcohol --- hemiketal (cyclic ring

They are polyhydroxy aldehydes (sucah as glucose)or ketones (such as fructose) or compounds that produce such substances upon hydrolysis.

Sugars are classified according to their structures: according to number of carbon atoms in the sugar and number of sugar units/molecule in a polymer formed by the glycosidic bonds.

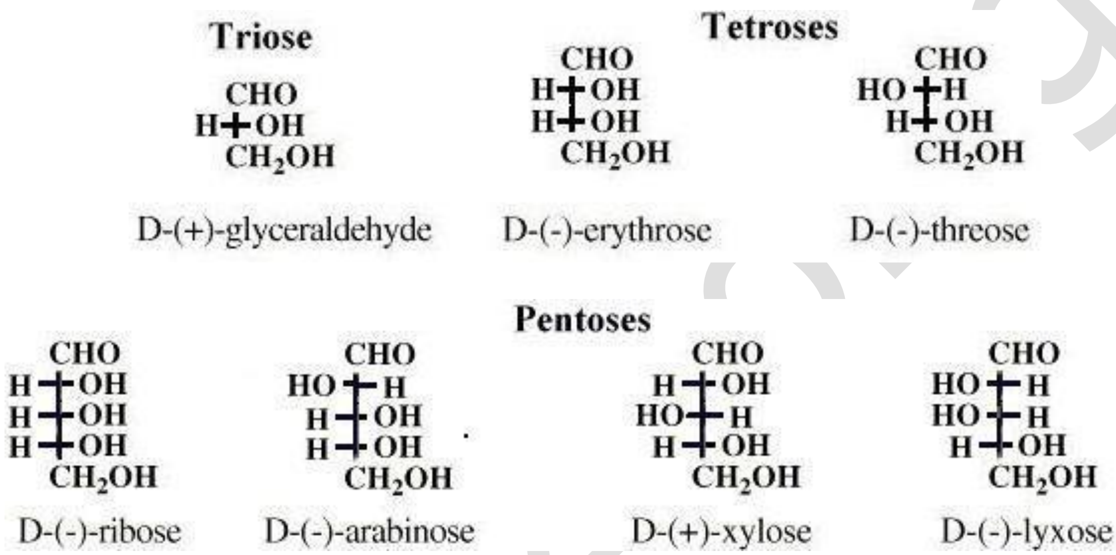
Number fo carbon atoms

- Triose sugar units containing three carbon atoms
- Tetroses sugar units containing four carbon tomsa
- Pentoses sugar units containing five carbon atoms
- Hexoses sugar units containing six carbon atoms

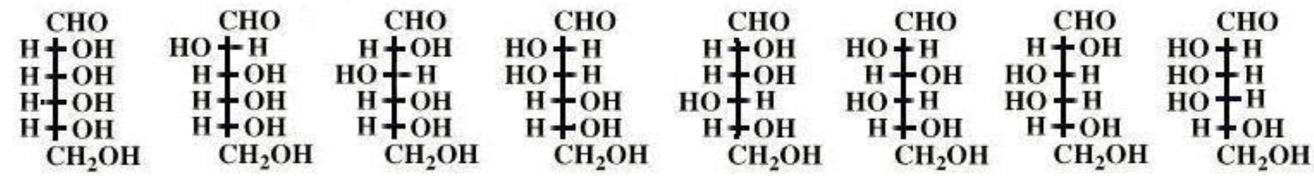
Steps for drawing Fischer structures of sugars:
A monosaccharides can be "sorted" according to the length of the carbon chain in the sugar unit.
1. write the carbon chain vertically with the aldehyde or ketone group toward the top of the chain.
2. number the carbons.

3. place the aldehyde or ketone group.
4. place H and OH groups.
5. identify the chiral centers.
6. note the highest numbered chiral center to distinguish D and L sugars.
7. write the correct common name for the sugar.

ldose-Trioses



hexoses



D-(+)-allose D-(+)-altrose D-(+)-glucose D-(+)-mannose D-(-)-gulose D-(-)-idose D-(+)-galactose D-(+)-talose

Mnemonics for remembering sugar names

All(allose) altruist (altrose) gladly (glucose) make (mannose) gum (gulose) in (idose) gallon (galactose) tanks (tallose)

Number fo units

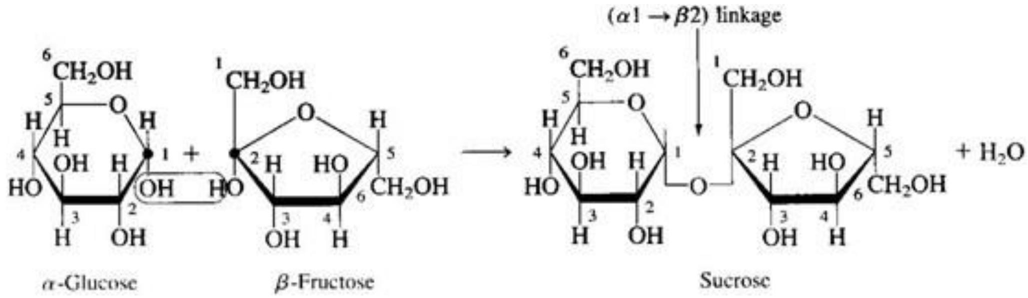
- **Saccharide**- (derived from Latin for sugar) is the chemical name for asugar unit:
- **Monosaccharide** (one sugar unit);
- **Disaccharide** (two sugar units);
- **Oligosaccharide** (2 to 10 sugar units);
- **Polysaccharide** (over 10 sugar units).

Monosaccharides also can be named based on their functional groups. **Aldoses**: Monosaccarides with aldehyde functional group. E.g. D-glucose

Ketoses: Monosaccarides with keto functional group. E.g. D-fructose**Simple carbohydrates: Monosaccharide** and **Disaccharide** of simple sugars such as glucose or fructose. **Disaccharide** are two monsaccharidesconnected by a bridging O atom called a glycosidic bond as in sucrose.

Glycosidic bond- covalent bond between a hemiacetal or hemiketal and an alcohol.

Glycoside- compound formed when a sugar in the cyclic form is bonded toan alcohol through a glycosidic bond to another sugar molecule as shown below.


(α1 → β2) linkage
α-Glucose
β-Fructose
Sucrose
+ H₂O

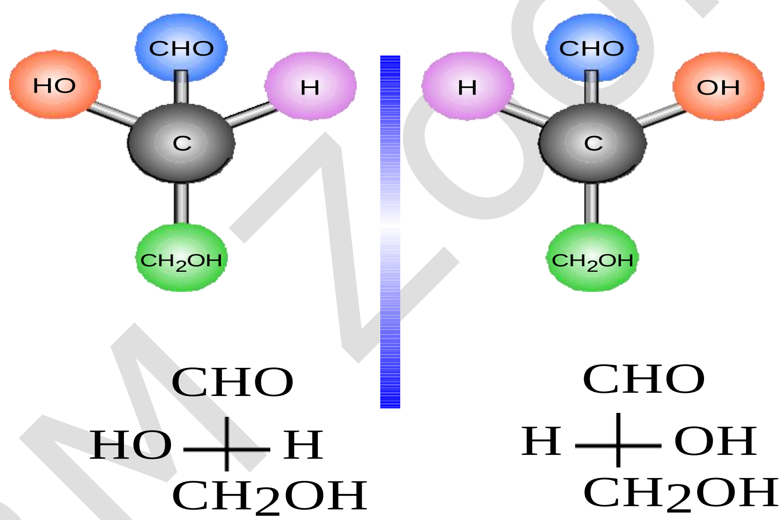
18.2 Chirality: Handedness in Molecules

Most monosaccharides exist in two forms: a "**left handed**" and "**right handed**" form - same as two hands

Two types of objects:

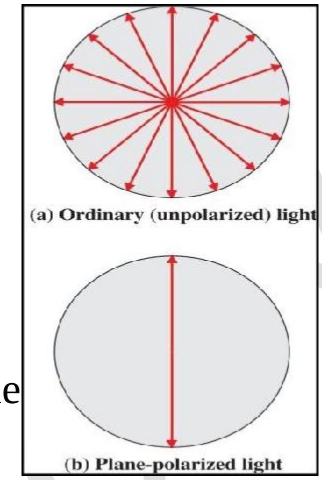
- **Superimposible on their mirror images**: -- images that coincide at all points when the imagesare laid upon each other -- a dinner plate with no design features -- Achiral

- **Non-superimposible on their mirror images**: Chiral (handedness)



Properties of light

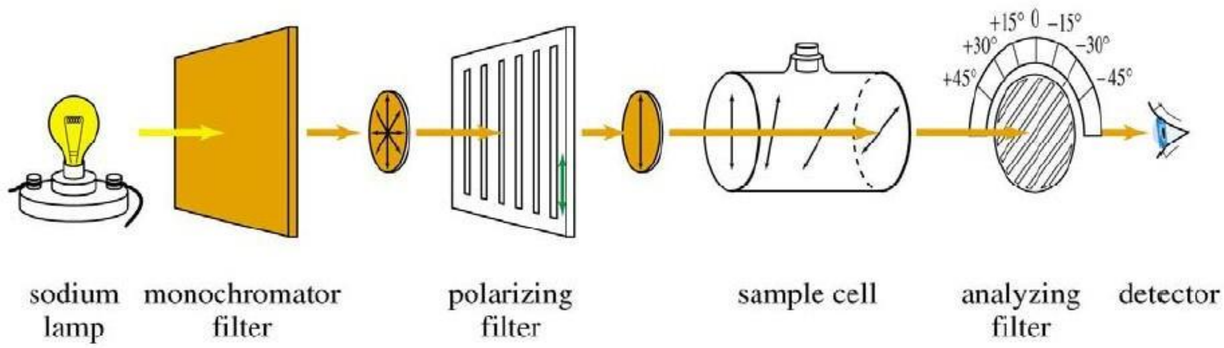
- Ordinary Light: Move in all directions
- Plane polarized light move only in one
- direction (see Figure on right below)



Plane polarized light is rotated clockwise (to right) or counterclockwise (to left) when passedthrough enantiomers

Direction and extent of rotation will depend upon the enantiomer

Same concentration of two enantiomers rotate light tosame extent but in opposite direction

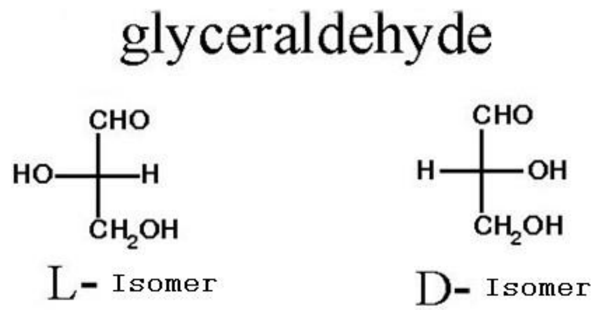


Light is passed through a polarized filter. A solution of an optical isomer willrotate the light one direction.

Classification of the molecule based on the rotation of plane-polarized light.

Dextrorotatory - rotate clockwise shown using **(+)** symbol or
- usually **D** isomers

Levorotatory - rotate anti-clockwise shown using **(-)** symbol or
- usually **L** isomers



18.3 Stereoisomerism: Enantiomers and Diastereomers

Stereoisomers are isomers that have the same molecular and structuralformulas but differ in the orientation of atoms in space.

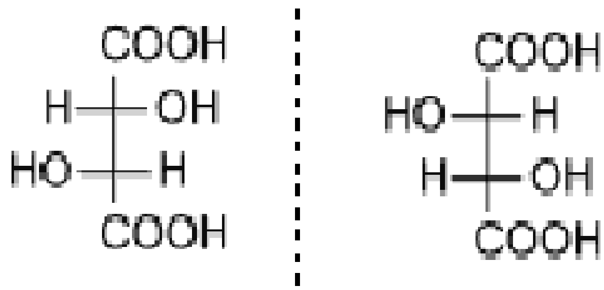
Two types:

Enantiomers are **stereoisomers** whose molecules are nonsuperimposable mirror images of each other. Molecules with chiral center.

Diastereomers are stereoisomers whose molecules are not mirror imagesof each other. They have more than one chiral centers. Diastereomers (or diastereoisomers) are stereoisomers that are not enantiomers (non-superposable mirror images of each other). Diastereomerscan have different physical properties and different reactivity. In another definition diastereomers are pairs of isomers that have opposite configurations at one or more of the chiral centers but are not mirror imagesof each other.

Example

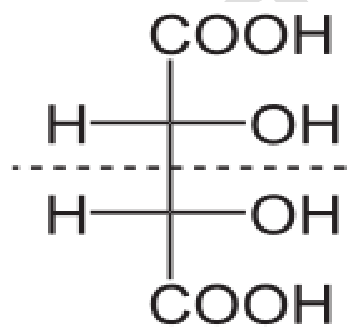
Tartaric acid contains two asymmetric centers, but two of the "isomers" areequivalent and together are called a meso compound. This configuration is not optically active, while the remaining two isomers are D- and L- mirror images, *i.e.*, enantiomers. The meso form is a diastereomer of the other forms.



natural) tartaric acid
L-(+)-tartaric acid
dextrotartaric acid

D-(-)-tartaric acid
levotartaric acid

(1:1)
DL-tartaric acid
"racemic acid"



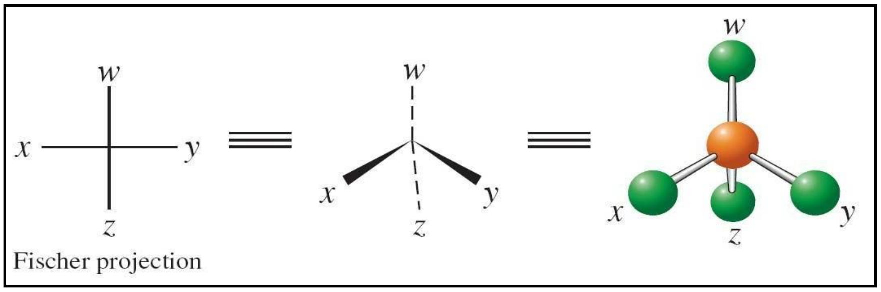
mesotartaric acid

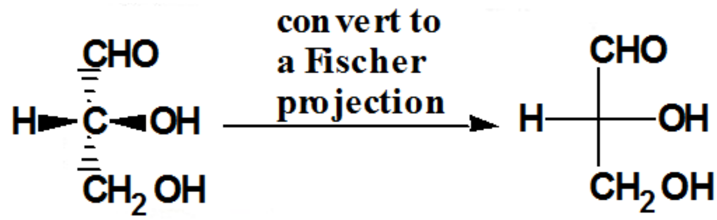
18.4 Designating Handedness Using Fischer Projections

Fischer projection formulas - a method for giving molecular chirality specifications in two dimensions. *A Fischer projection formula* is a two-dimensional structural notation for showing the spatial arrangement of groups about **chiral centers** in molecules.

The four groups attached to the atom at the chiral center assume a tetrahedral geometry and it is governed by the following conventions

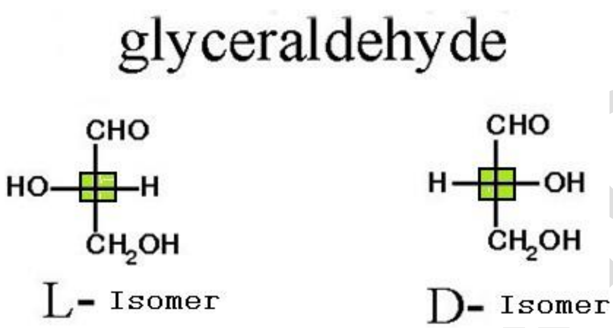
Vertical lines from the chiral center represent bonds to groups directed into the printed page. Horizontal lines from the chiral center represent bonds to groups directed out of the printed page.

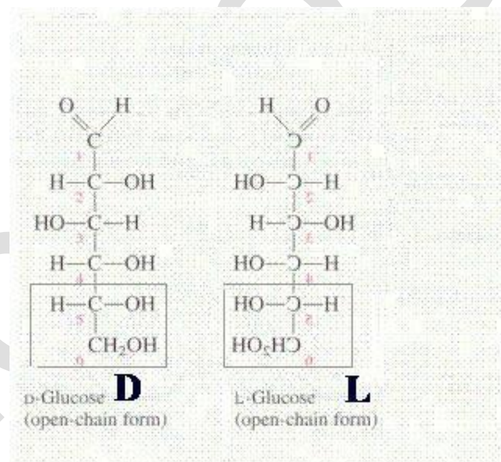

w
x
y
z
Fischer projection



(D)-Glyceraldehyde (D)-Glyceraldehyde

In a Fischer projection formula a chiral center (Carbon) is represented as theintersection of vertical and horizontal lines Functional groups of high priority will be written at top D and L system used to designate the handedness of glyceraldehyde enantiomers.





18.5 Properties of Enantiomers

As the right and left handed baseball players can't use same glove (chiral)but can use same hat (achiral) molecules behaves similarly.

- Two members of enantiomer pair (chiral) react differently with otherchiral molecules thus only one will fit into a enzyme.

Enantiomeric pairs have same solubility in achiral solvents like ethanol andhave different solubility in chiral solvent like D-2-butanol.

- Enantiomers have same boiling points, melting points and densities -all these are dependent upon intermolecular forces and chirality
  doesn't depend on themEnantiomers are optically active: Compoundsthat rotate plane polarized light.

Our body responds differently to different enantiomers:

One may give higher rate or one may be inactive
Example: Body response to D form of hormone epinephrine is 20 times greater than its L isomer.

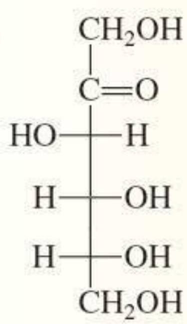
18.6 Classification of Monosaccharides

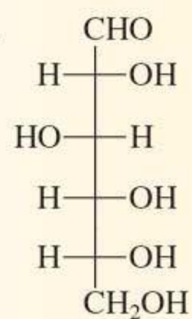
Triose --- 3 carbon atoms
Tetrose -- 4 carbon atoms
Pentoses – 5 carbon atoms
Hexoses -- 6 carbon atoms
Aldoses: Monosaccharides with one aldehydegroup
Ketoses: Monosaccharides with one ketone group
Combined # of C atoms and functional group:
Example: Aldohexose: Monosaccharide with aldehydegroup and 6 C atoms
Aldohexose: Monosaccharide with aldehydegroup and 6 C atoms – D-glucose

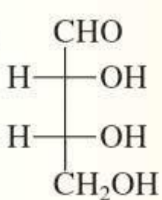
CHO
|

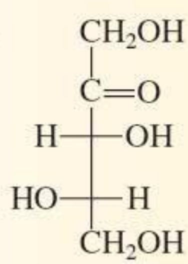
Ketohexose: Monosaccharide with aldehyde group and 6 C atoms – D-fructose

Classify each of the following monosaccharides according to both the number of carbon atoms and the type of carbonyl group present.

a.


b.


c.


d.


Answers: a. Ketohexose; **b.** Aldohexose; **c.** Aldotetrose; **d.** Ketopentose

Glucose

Glucose is the most common monosaccharide consumed and is the circulating sugar of the bloodstream. Insulin and glucagon regulateblood levels of glucose

1. Most abundant in nature
2. Nutritionally most important
3. Grape fruit good source of glucose (20 - 30% by mass) -- alsonamed grape sugar, dextrose and blood sugar (70 - 100 mg/100 mL of blood)
4. Six membered cyclic form

Fructose

Fructose is slightly sweeter than glucose. It is an intermediary in metabolism and is found in many fruits.

1. Ketohexose
2. Sweetest tasting of all sugars
3. Found in many fruits and in honey
4. Good dietary sugar-- due to higher sweetness
5. Five membered cyclic form

Galactose

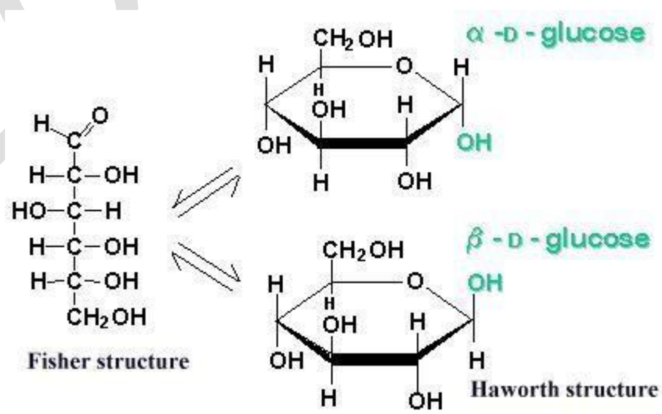
Galactose, a component of lactose (milk sugar) is also found in some plant gums and pectins. Galactosemia results from inabilityto metabolize galactose. If treated, galactosemia can be managed medically. Untreated galactosemia may result in mentalretardation, liver damage, or death.

1. Milk sugar
2. Synthesize in human
3. Also called brain sugar-- part of brain and nerve tissue
4. Used to differentiate between blood types
5. Six membered cyclic form

18.7 Cyclic Forms of Monosaccharides

2 forms of D-glucose:

- **Alpha**-form: -OH of C1 and CH_2OH of C5 are on opposite sides
- **Beta**-form: -OH of C1 and CH_2OH of C5 are on same sides



18.8 Haworth Projection Formulas

As useful as the Fischer projection is (it is an excellent way to keep track ofrelative stereochemistry), it gives a poor sense of the real structure of carbohydrates. (See Hemiacetal Formation in chapter 15.) The Haworth projection is a way around this limitation that does not require you to try toconvey the complete 3D image of the molecule. Sugars in Haworth projection can be classified according to the "ring size"(**five- furanoses** or **six-pyranoses**) which they assume in solution. A

Reactions of Monosaccharides

Five important reactions of monosaccharides:

- Oxidation to acidic sugars
- Reduction to sugar alcohols
- Glycoside formation
- Phosphate ester formation
- Amino sugar formation

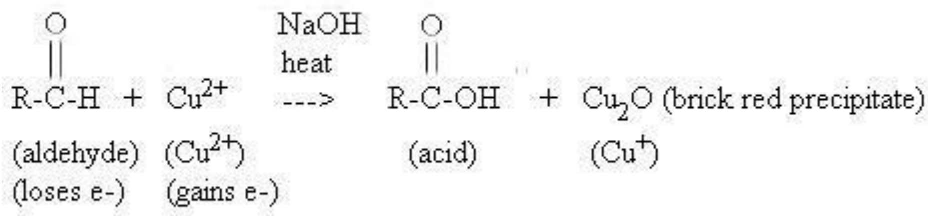
These reactions will be considered with respect to glucose. Other aldoses, aswell as ketoses, undergo similar reactions.

a) Oxidation to acidic sugars

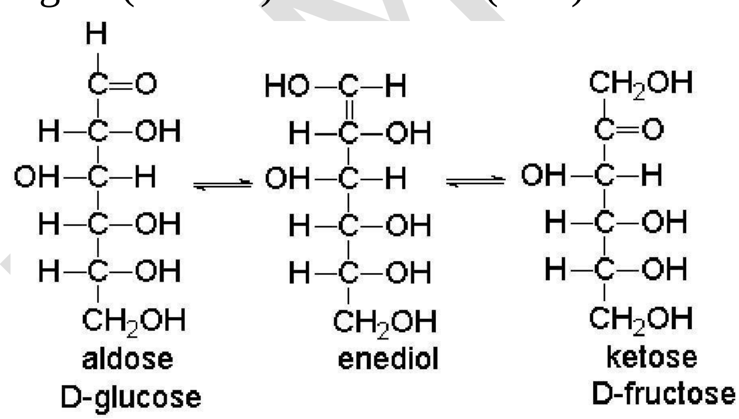
Reducing sugars- a sugar aldehyde or ketone which can be oxided to anacid and drive the reduction of a metal ion. Oxidation can yield three different types of acidic sugars depending on the type of oxidizing agent used:

A reducing sugar is a carbohydrate that gives a positive test with Tollens and Benedict’s solutions.
Aldehyde sugars should show positive test for the Benedict's test because ofthe aldehyde functional group in the molecule.

Benedict's Test for aldehydes:



Oxidation can yield three different types of acidic sugars depending on thetype of oxidizing agent used:
Weak oxidizing agents such as **Tollens** and **Benedict’s** solutions oxidize thealdehyde end to give an **aldonic acid**.
A reducing sugar is a carbohydrate that gives a positive test with Tollens and Benedict’s solutions.
However, keto sugars also gives a positive test for Benedict's test because keto sugars could be converted to aldehyde sugars through the enediol intermediate under the reaction conditions. Therefore, all **monosaccarides**both **aldoses and ketoses** show a positive behavior in the Benedict's test. and considered as **reducing sugars.** In biological systems keto form of aldehyde sugars (aldoses) are converted to ketone sugars (ketoses) via enediol (enol) froms as shown below. Therefore D-

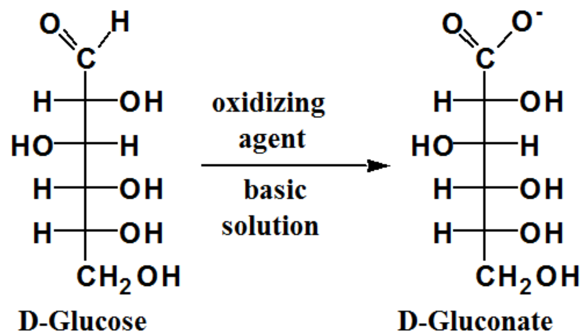


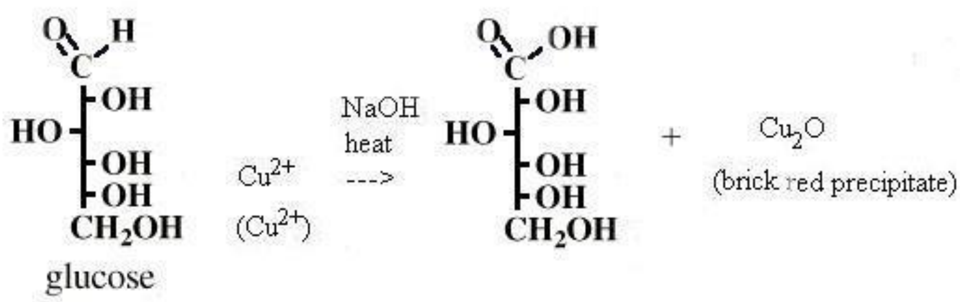
fructose which is a ketoneor keto sugar (ketose) will give a positive test for Benedict's test because of the ability of ketoses to get converted to aldoses (aldehydes).

Use of the Benedict's reagent to measure the level of glucose in

urine.

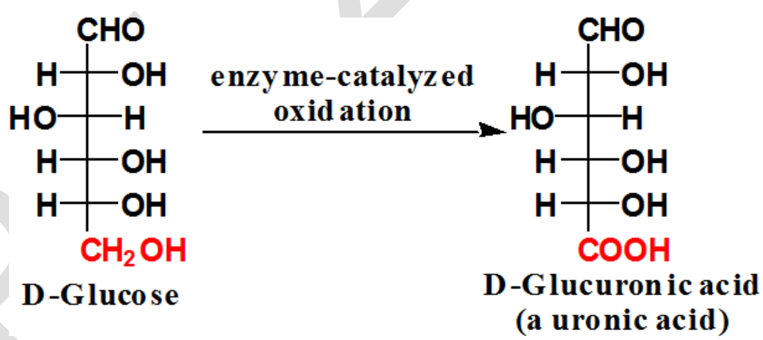
This test have been used in old days to detect excess boold sugar in diabeticpatients. This test shows positive behavior for all reducing.





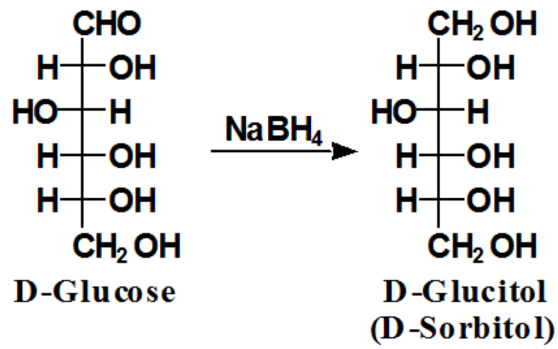
Enzyme oxidation

In biochemical systems enzymes can oxidize the primary alcohol end of an aldose such as glucose, without oxidation of the aldehyde group, to producean ***alduronic acid***.



b) Reduction to sugar alcohols: The carbonyl group in a monosaccharide (either an aldose or a ketose) is reduced to a hydroxyl group using hydrogenas the reducing agent.

The product is the corresponding polyhydroxy alcohol - **sugar alcohol**. **Sorbitol** - used as moisturizing agents in foods and cosmetics and as asweetening agent in chewing gum

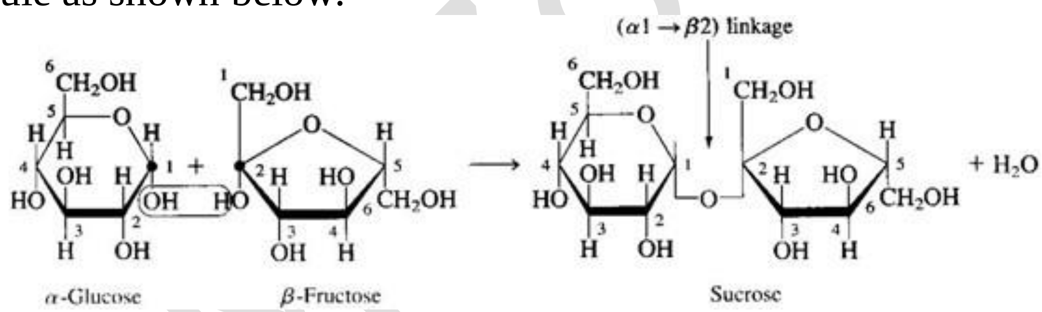


c) Glycoside formation

Simple carbohydrates: **Monosaccharide** and **Disaccharide** of simple sugars such as glucose or fructose. **Disaccharide** are two monsaccharidesconnected by a bridging O atom called a glycosidic bond as in sucrose.

Glycosidic bond- covalent bond between a hemiacetal or hemiketal and an alcohol.

Glycoside- compound formed when a sugar in the cyclic form is bonded toan alcohol through a glycosidic bond to another sugar molecule as shown below.



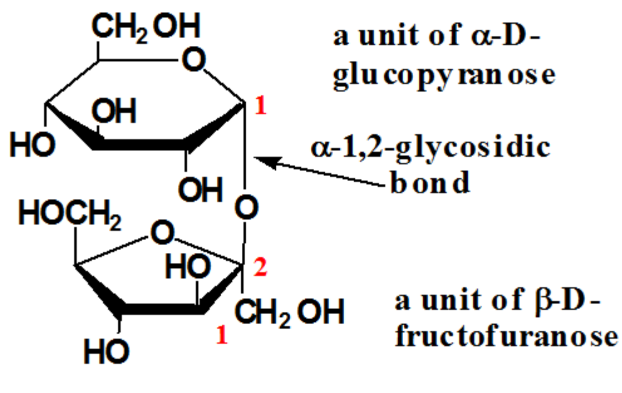
Phosphate ester formation

18.9 Disaccharides

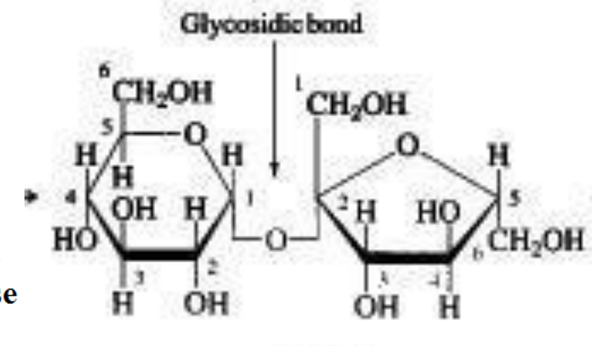
A disaccharide forms by reaction of the -OH group on the anomeric carbon ofone monosaccharide with an –OH group of a second monosaccharide.

The linkage between monosaccharides in a disaccharide is referred to as aglycosidic linkage and is named according to the number of the carbon at which the linkage begins and the carbon on the second monosaccharide atwhich the linkage ends.

-The glycosidic linkage is also designated a or β, depending upon whetherthe conformation at the anomeric carbon is up or down.



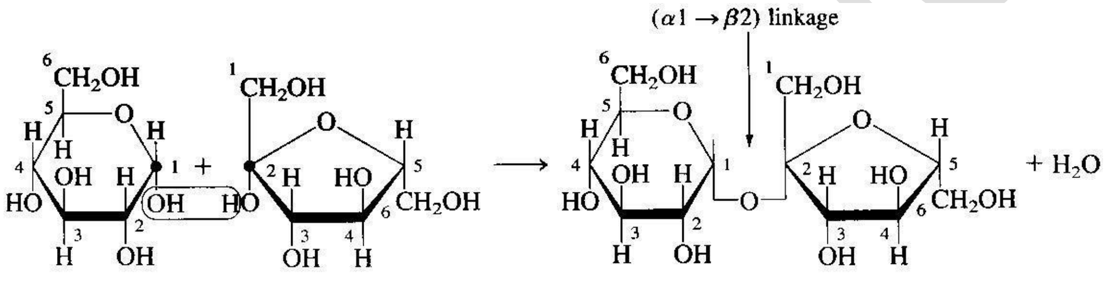
Sucrose



Sucrose

Sucrose

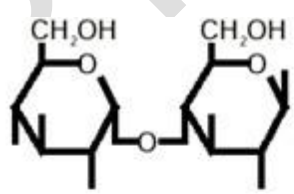
glucose + fructose --- glu □,□ (1---2) fructose sucrose, a non



α-Glucose β-Fructose Sucrose

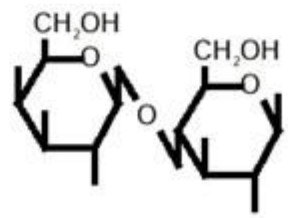
reducingsugar

Consider the three disaccharide structures maltose, lactose and sucrose andexplain why sucrose is NOT a reducing sugar.



MALTOSE

α-D-Glucopyranosyl-(1→ 4) β-D-Glucopyranose



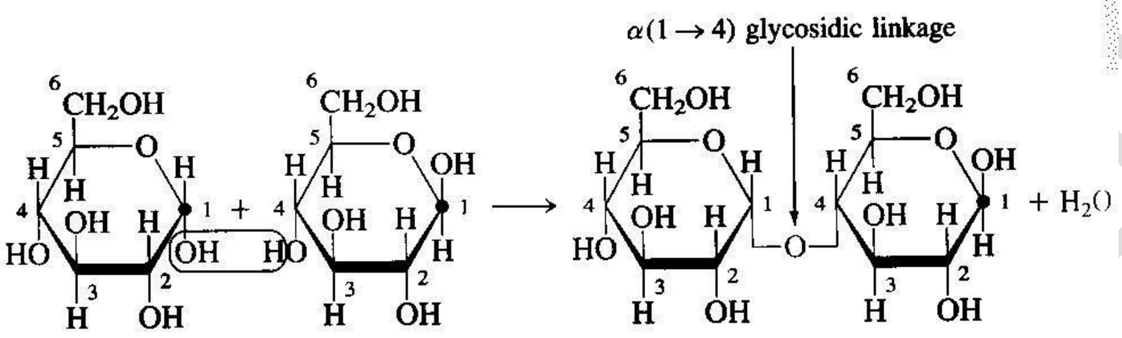
LACTOSE

β-D-Galactopyranosyl-(1→ 4) β-D-Glucopyranose

Disaccharides with □(1---4), □(1---4) and (1□---2□) glycosidic bonds thatyield disaccharide, maltose, lactose and sucrose, respectively. Both □(1--- 4) and □(1---4) glycosidic bonds leave one hemiacetal or hemiketal free andthese ends will show a postive behavior for the acetal and ketal groups which are unable to undergo enediol conversion or reaction with Benedict's reagent. Therefore **fructose** is considered as a **nonreducing sugar**.

Maltose

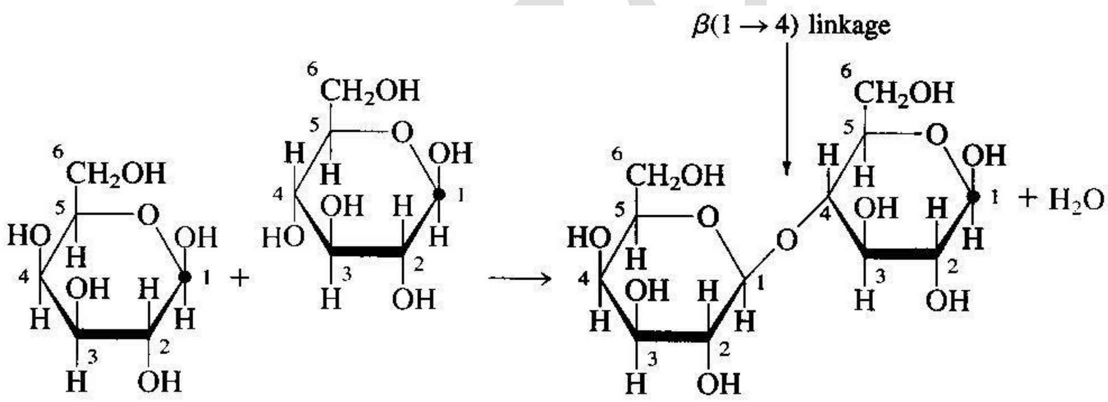
glucose + glucose --- glu □(1---4) glu maltose, a reducing sugar



α-D-Glucose β-D-Glucose β-Maltose

Lactose

galactose + glucose --- gal □(1---4) glu lactose, a reducing sugar



β-D-Galactose β-D-Glucose β-Lactose

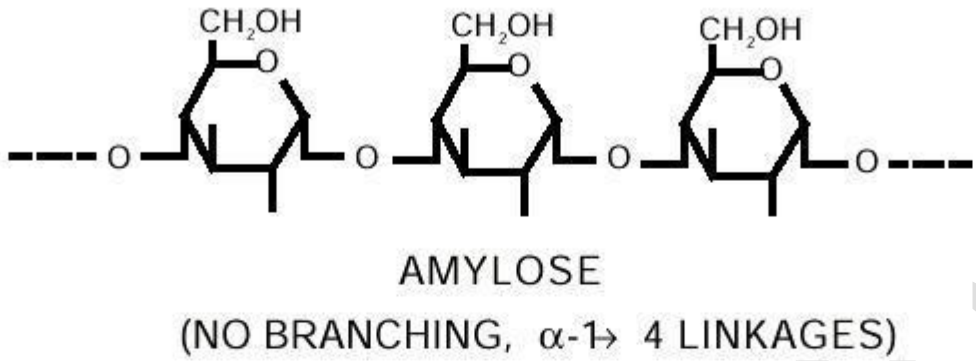
18.10 General Characteristics of Polysaccharides

- Storage polysaccharides
- Energy storage - starch and glycogen
- Structural polysaccharides
- Used to provide protective walls or lubricative coating to cells -cellulose and mucopolysaccharides.

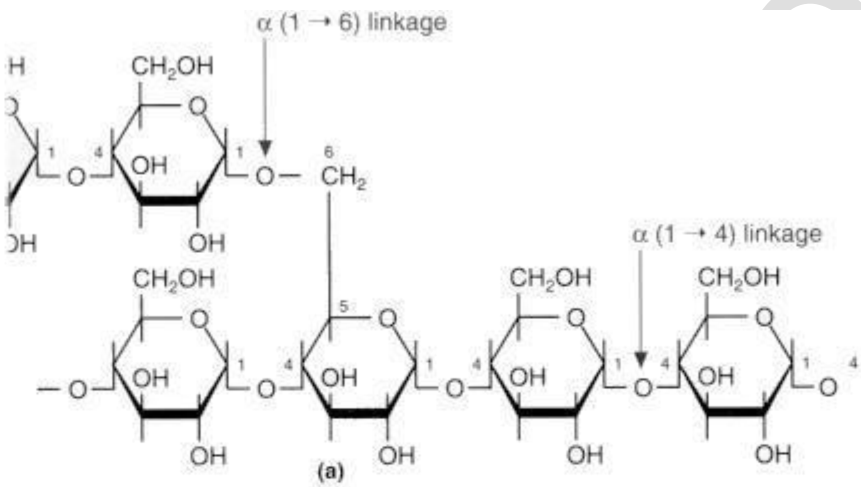
- Structural peptidoglycans
- Bacterial cell walls

18.11 Storage Polysaccharides

Amylose



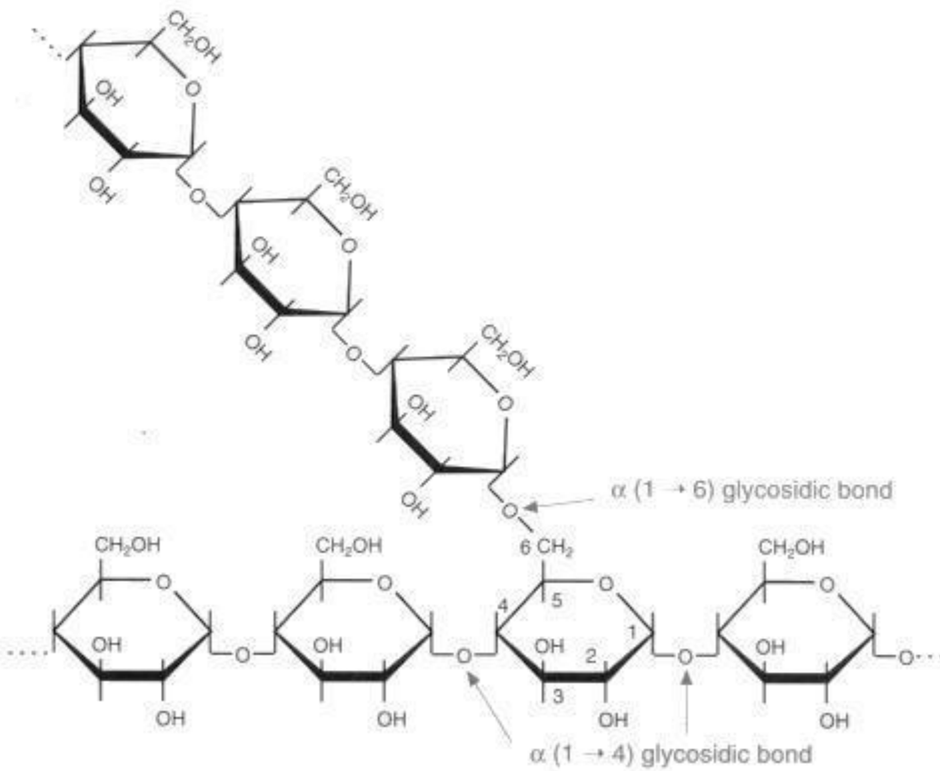
Amylopectin



Plant Starch

amylose	**amylopectin**
□(1---4) glucose	□(1---4) and □(1---6) glucose
linear molecule	branched molecule
coils up	open spiral molecule
less water soluble	more water soluble
non reducing sugar	non reducing sugar

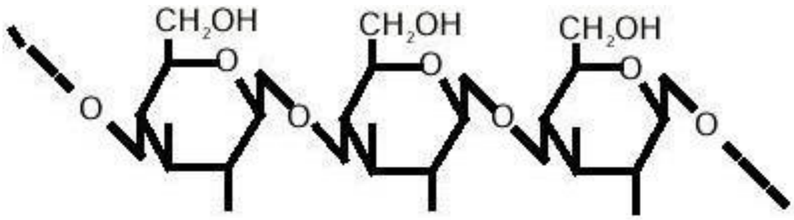
Glycogen



Animal Starch

glycogen
□(1---4) and □(1---6) glucose
branched molecule
open spiral
moleculemore
water soluble non
reducing sugar

Cellulose



CELLULOSE
(NO BRANCHING, β-1→ 4 LINKAGES)

Structural Polysaccharides:

Cellulose

□(1---4) glucose
ribbon molecule
ribbons stack
water insoluble
non reducing
sugar

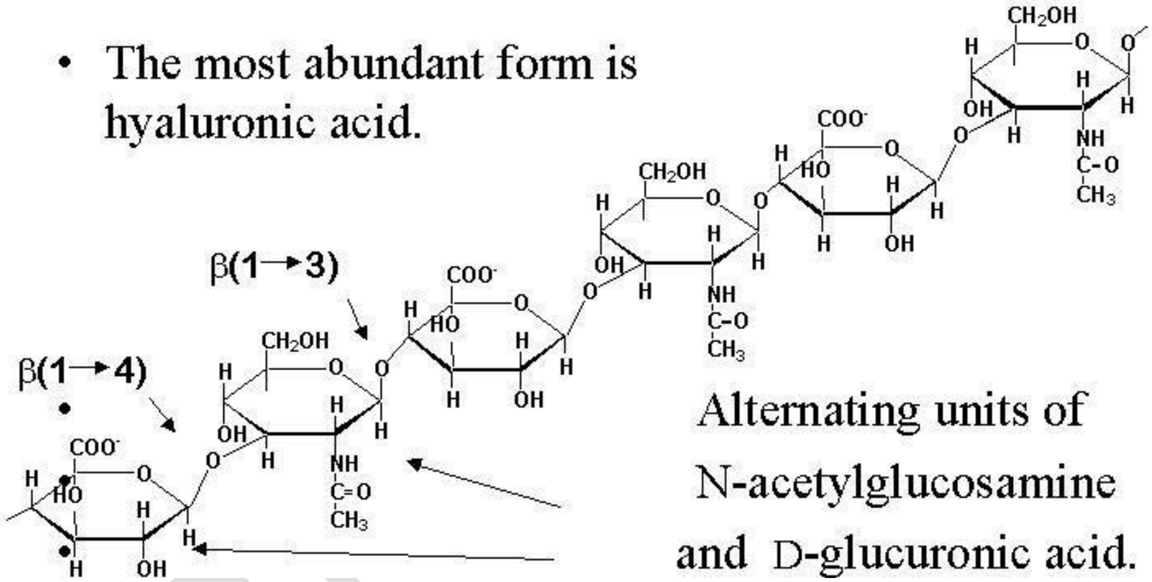
Chitin

□(1---4) N-
acetylglucosamineribbons
stack
water insoluble
non reducing sugar chitin
See bacterial cell wall, text book page 160, forstructure of N-acetylglucosamine

18.12 Structural Polysaccharides

Mucopolysaccharides

AMINOSUGAR or N-acetyl-D-glucosamine: glucose-derivative with an acetylated amino group on C-2 as found in N-acetylglucosamine.



Deoxysugar or D-deoxyribose: ribose-derivative with an oxygen missing on C-2.