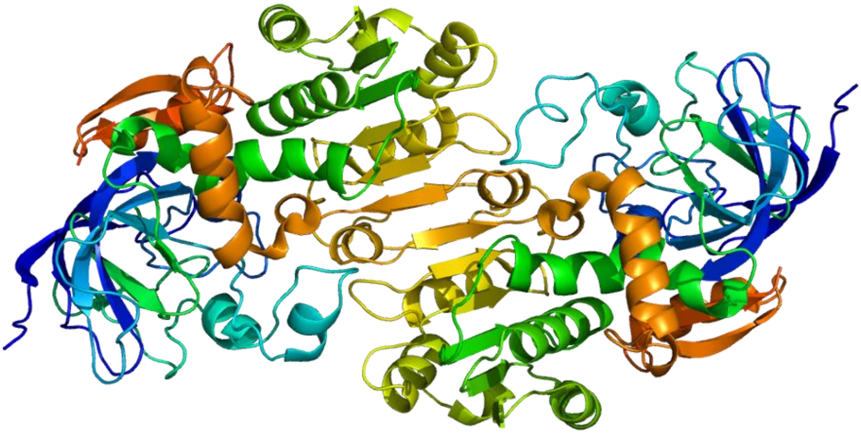
SOUTH VALLEY UNIVERSITY

جامعة جنوب الوادى

Biochemistry



By

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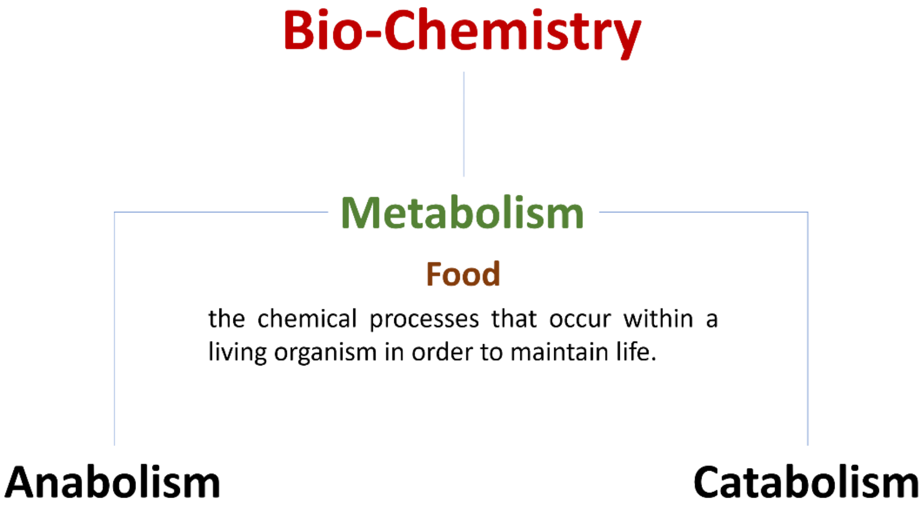
Chemistry department --- Faculty of Science

Biochemistry

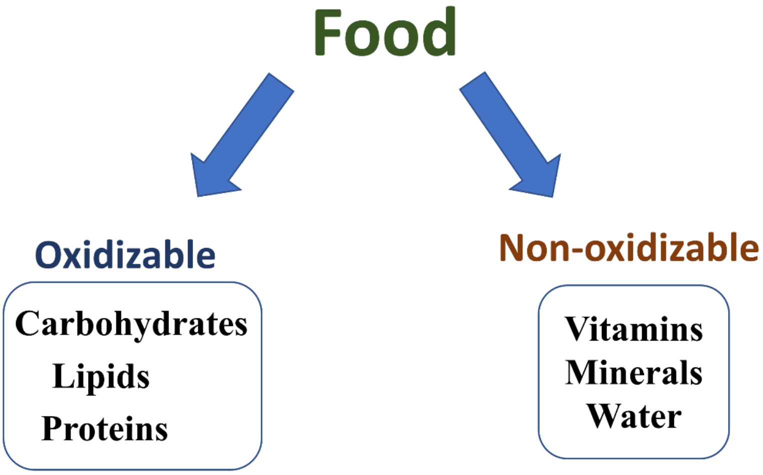
Introduction:

Biochemistry is concerned with the chemical composition of cell parts and knowledge how the biochemical reactions occur, as well as the chemical and physical nature of different types of nutrients, the biological function of these substances from cells and their intermediate metabolism.

Our course is focused on studying the chemical compounds that are components of living cells and the materials that can be used in their biosynthesis, including **carbohydrates, lipids,** and **proteins**.



the chemical processes that occur within a living organism in order to maintain life.



UNIT 1: CARBOHYDRATES

Introduction. Classification, Properties and Biological importance. Isomers, epimers, enantiomers, mutarotation, open chain, and closed chain structures of glucose. Chemical reactions.

UNIT 2: LIPIDS

Introduction, Classification, Properties and Biological importance. Fatty acid nomenclature and structure, Triglycerides formation and its applications.

UNIT 3: AMINOACIDS AND PROTEINS

Amino acids: classification- essential and non-essential amino acids, Zwitter ions, Concept of isoelectric point, protein structures, biological significance.

Chemistry of Carbohydrates

Introduction

Carbohydrates received their name from the fact that the general empirical formula for many members of the class can be written $C_n(H_2O)_n$, hydrated carbon. Sugars, starches, and cellulose-compounds which have important structural and energy functions in the living materials-are all carbohydrates. (Sugars are water soluble carbohydrates).

It would be difficult to overestimate the importance of human beings of carbohydrates.

Photosynthesis:

The production of carbohydrates in nature occurs in green palnts by a process called photosynthesis. Plants contain the green pigments chlorophyll which catalyzes the conversion of carbon dioxide and water into sugar. The reaction is thermodynamically unfavourable but proceed because the necessary energy is supplied by the sun in the form of sunlight.

$$6\,CO_2 + 6\,H_2O \underset{\text{- energy, animal metabolism}}{\overset{\text{+ Light, Chlorophyll}}{\rightleftharpoons}} C_6(H_2O)_6 + 6\,O_2$$

While plants build up carbohydrates from carbon dioxide and water, animals degrade carbohydrates to carbon dioxide and water. The animal obtains carbohydrates by eating plants and combine the carbohydrates with oxygen from the air to carry out the reverse of the photosynthesis reaction. The oxidation of carbohydrates supplies the animal with the energy (according to the above equation) necessary to sustain life, and it also regenerates carbon dioxide for use by the plants in photosynthesis.

All carbohydrates are polyhydroxy aldehydes, polyhydroxy ketones, or molecules which yield polyhydroxy aldehydes or ketones on hydrolysis. Monosaccharides are the smallest carbohydrate molecules and include the four-, five-, and six-carbon sugars. Sucrose, table sugar, is one of the disaccharides; disaccharides can hydrolyse to two monosaccharides. Polysaccharides, which include starch and cellulose, yield many monosaccharides molecules upon hydrolysis.

Definition and Classification

Carbohydrates are polyhydroxy aldehydes, polyhydroxy ketones or compounds that can be hydrolyzed to them. There are three major classes of carbohydrates:

1. Monosaccharides

Monosaccharides, or simple sugars, consist of a single polyhydroxy aldehyde or ketone unit. The most abundant monosaccharide in nature is the six-carbon sugar D-glucose, sometimes referred to as dextrose.

2. Disaccharides

Can be hydrolysed to two monosaccharides molecules. For Ex: sucrose, lactose, and maltose.

3. Polysaccharides

The polysaccharides are sugar polymers containing more than 20 or so monosaccharide units, and some have hundreds or thousands of units. Example: starch. Polysaccharides are of two types based on their function and composition. Based on function, polysaccharides of two types: storage and structural.

A. Storage polysaccharide - starch.

B. Structural polysaccharide - cellulose.

General properties of carbohydrates

- Carbohydrates act as energy reserves, also stores fuels, and metabolic intermediates.

- Ribose and deoxyribose sugars forms the structural frame of the genetic material, RNA and DNA.

- Polysaccharides like cellulose are the structural elements in the cell walls of bacteria and plants.

- Carbohydrates are linked to proteins and lipids that play important roles in cell interactions.

Monosaccharides

($C_6H_{12}O_6$)

Monosaccharides

- The word "Monosaccharides" derived from the Greek word "Mono" means Single and "saccharide" means sugar

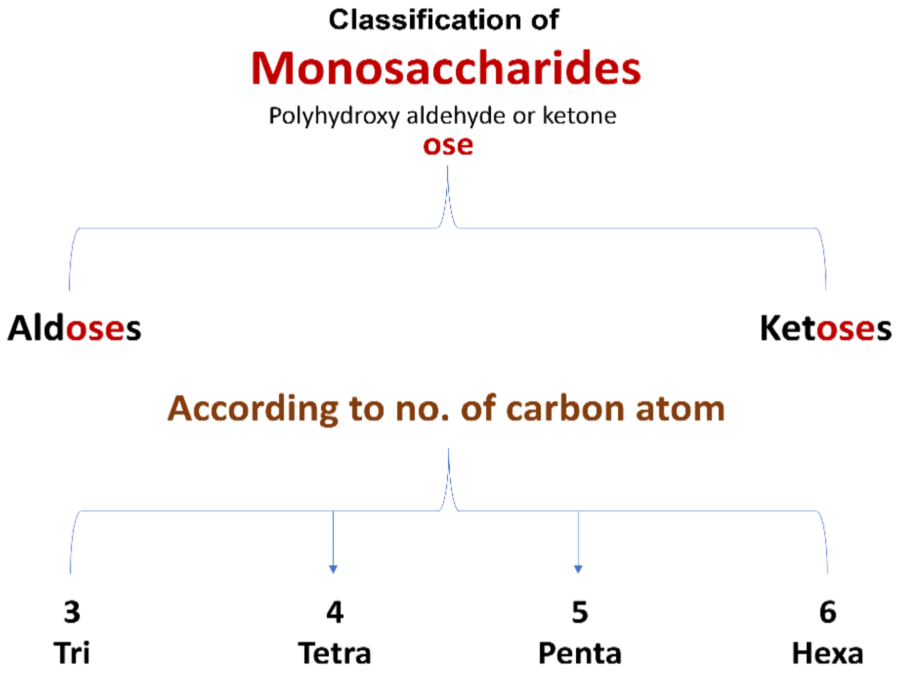
- Monosaccharides are polyhydroxy aldehydes or ketones which cannot be further hydrolysed to simple sugar.

- Monosaccharides are simple sugars. They are sweet in taste. They are soluble in water. They are crystalline in nature.

- They contain 3 to 10 carbon atoms, 2 or more hydroxyl (OH) groups and one aldehyde (CHO) or one ketone (CO) group.

Classification of Monosaccharides

Monosaccharides are classified in two ways. **(a)** First of all, based on the number of carbon atoms present in them and **(b)** secondly based on the presence of carbonyl group. The naturally occurring monosaccharides contain three to seven carbon atoms per molecule. Monosaccharides of specific sizes may be indicated by names composed of a stem denoting the number of carbon atoms and the suffix ***-ose***. For example, the terms *triose*, *tetrose*, *pentose*, and *hexose* signify monosaccharides with, respectively, three, four, five, and six carbon atoms. Monosaccharides are also classified as aldoses or ketoses. Those monosaccharides that contain an aldehyde functional group are called aldoses; those containing a ketone functional group on the second carbon atom are ketoses. Combining these classification systems gives general names that indicate both the type of carbonyl group and the number of carbon atoms in a molecule. Thus, monosaccharides are described as aldotetroses, aldopentoses, ketopentoses, ketoheptoses, and so forth. Glucose and fructose are specific examples of an aldohexose and a ketohexose, respectively.

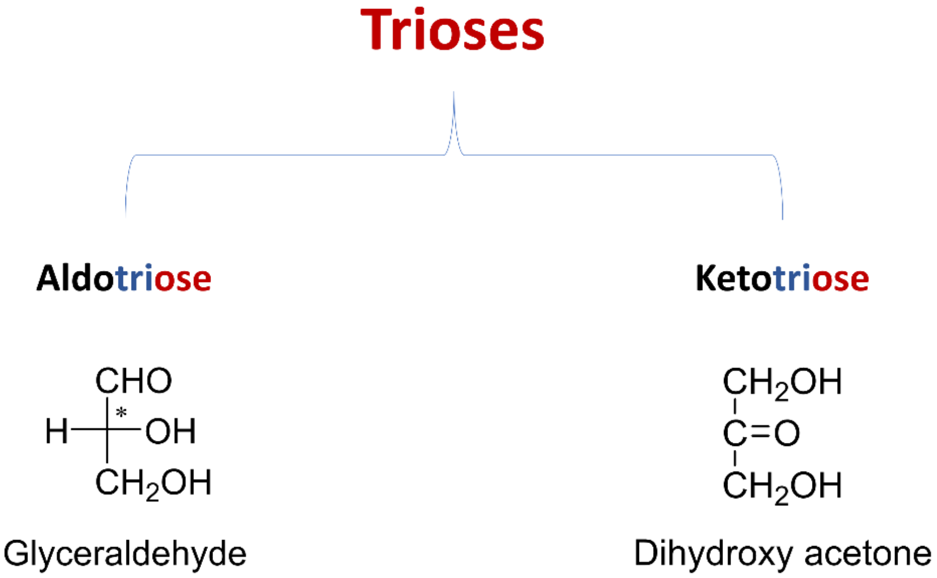


Trioses

Trioses are “Monosaccharides” containing 3 carbon atoms. The molecular formula of triose is $C_3H_6O_3$.

Characteristics

- Trioses are simple sugars
- They are soluble in water
- They are sweet in taste.
- The triose may contain an aldehyde group (aldotriose) or a ketone group (ketotriose). Example Glycerose and Dehydroxyacetone.

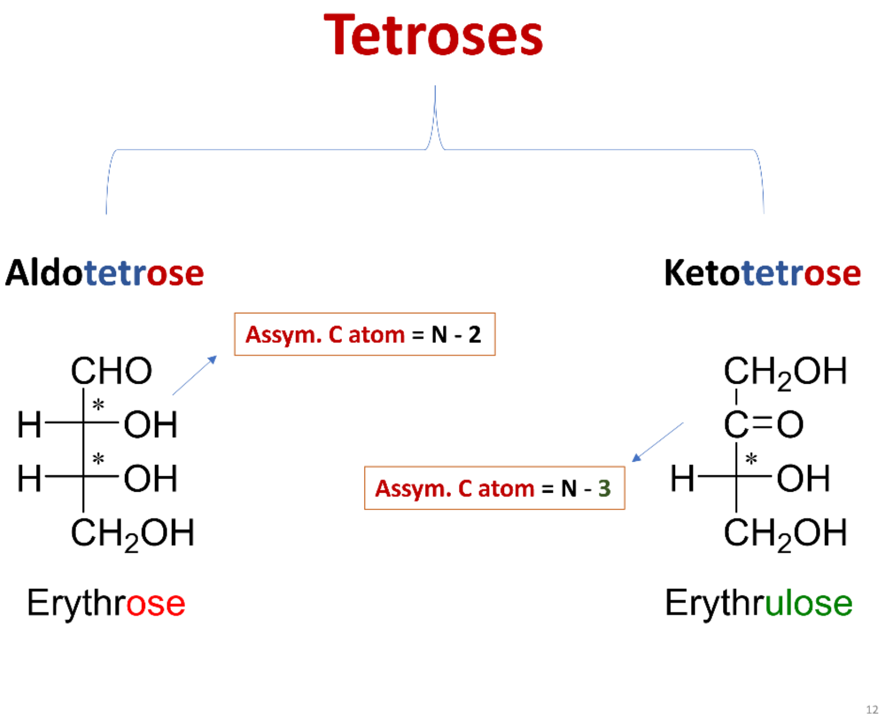


Tetroses

Tetroses are “Monosaccharides” containing 4 carbon atoms. The molecular formula of tetrose is **$C_4H_8O_4$**

Characteristics

- Tetroses are simple sugars
- Tetroses are soluble in water
- They are sweet in taste.
- They are crystalline forms.
- The tetroses may contain an aldehyde group (aldotetrose) or ketone group (ketotetrose).

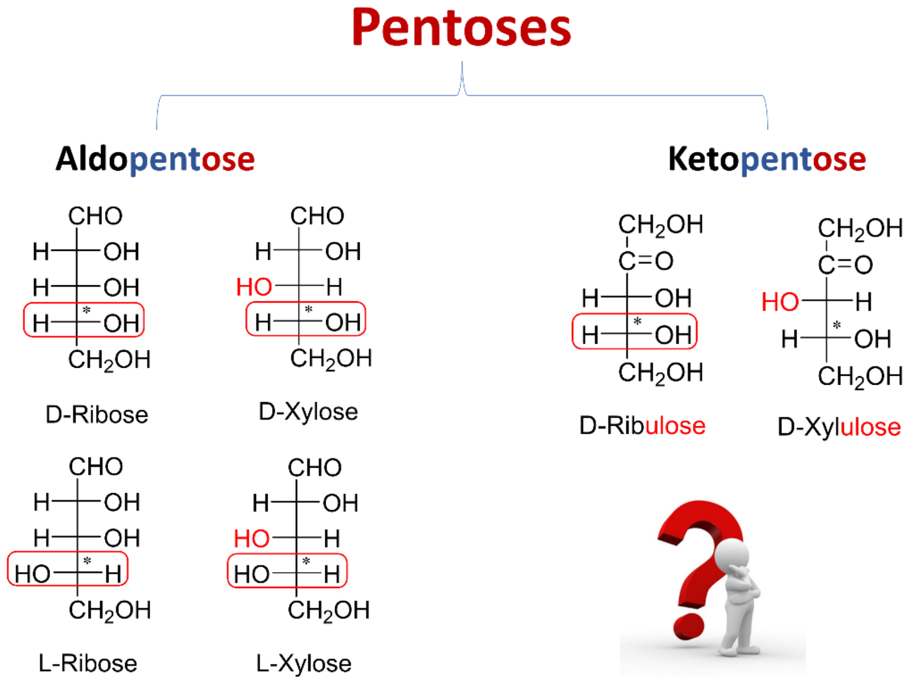


Pentoses

Pentoses are "Monosaccharides" containing 5 carbon atoms. It is an important component of "nucleic acid". The molecular formula of Pentose is **$C_5H_{10}O_5$**

Characteristics

- Pentoses are simple sugars
- Pentoses are soluble in water
- They are sweet in taste.
- They are crystalline forms.
- The pentoses may contain an aldehyde group (aldopentose) or a ketone group (ketopentose).

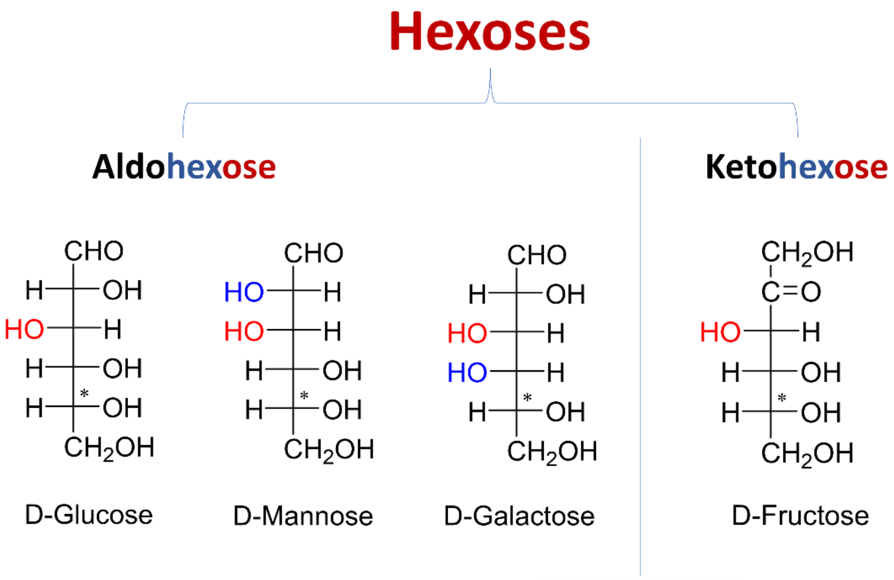


Hexoses

Hexoses are monosaccharides containing 6 carbon atoms. The molecular formula of Hexose is **$C_6H_{12}O_6$**

Characteristics

- Hexoses are simple sugars
- Hexoses are soluble in water
- They are sweet in taste.
- They are crystalline forms.
- The pentoses may contain an aldehyde group (aldohexose) or ketone group (ketohexose).



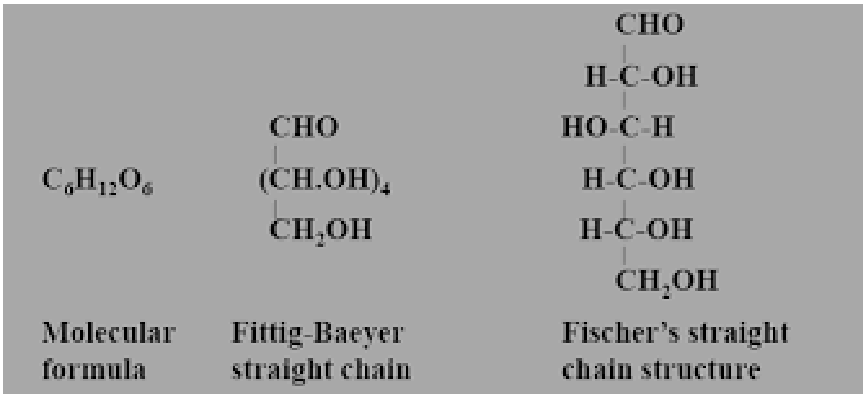
Structure of Monosaccharides

1. Straight or Open Chain Structure

arranged in a straight line. It is also called open chain structure because the two ends remain separate, and they are not linked. Open chain structure is of two types –

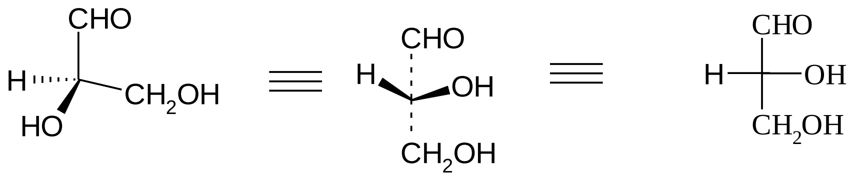
(a) Structure proposed by Fittig and Baeyer

(b) Structure proposed by Fischer known as Fischer's Projection Formula.



Fischer Projection for Depicting Carbohydrates:

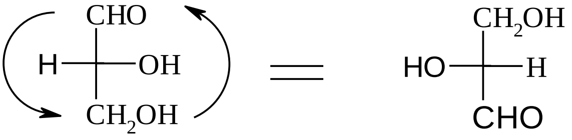
Teterahedral carbon atom is represented in a Fischer projection by two crossed lines as shown in the following.



(R)- glyceraldehyde

Fischer projection

Recall also that Fischer projection can be rotated on the page by 180 ºC without their meaning but not 90 ºC or 270 ºC.

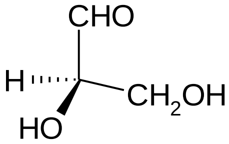


(R) - glyceraldehyde

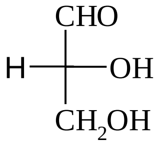
D, L-Sugars:

Three Dimensional

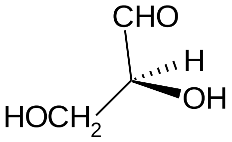
Fischer projection



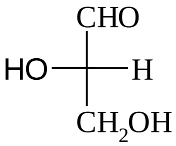
R(+)- glyceraldehyde



D- glyceraldehyde



S(-)- glyceraldehyde



L- glyceraldehyde

In Fischer Projection:

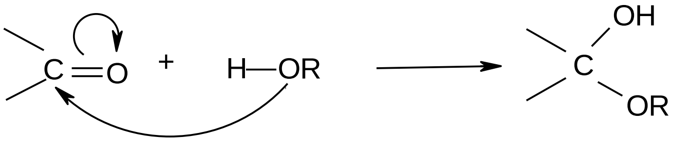
- All D-sugars have the hydroxyl group at the lowest chiral carbon atom on the right.
- All L-sugars have the hydroxyl group at the lowest chiral carbon atom on the left.

- None that the D-and L-natations have no relation to the direction in which a given sugar rotates plane polarized light, a D sugar may be either dextrorotatory or levorotatory.
- The D, L-system of carbohydrate nomenclature is of limited use, since it describes the configuration at only one stereogenic center and says nothing about other stereogenic centers that may by present. The advantage of the system, though, is that it allows a person to relate one sugar to another rapidly.
- Asymmetric carbon atom in aldoses **= N-2** and in Ketoses = **N-3** (**N** is the no. of all carbon atoms in the sugar).
- Number of isomers depends on the number of stereogenic centers (Asymmetric carbon atoms). number of isomers **$= 2^n$**, where **n** is the number of stereogenic center.
- Glyceraldehyde have only one stereogenic center (chiral carbon atom) so it is of two isomers D and L.

Cyclic Structures of monosaccharides:

Hemiacetal Formation:

- Alcohols undergo a rapid and reversible nucleophilic addition reaction with ketones and aldehydes to form hemiacetals.

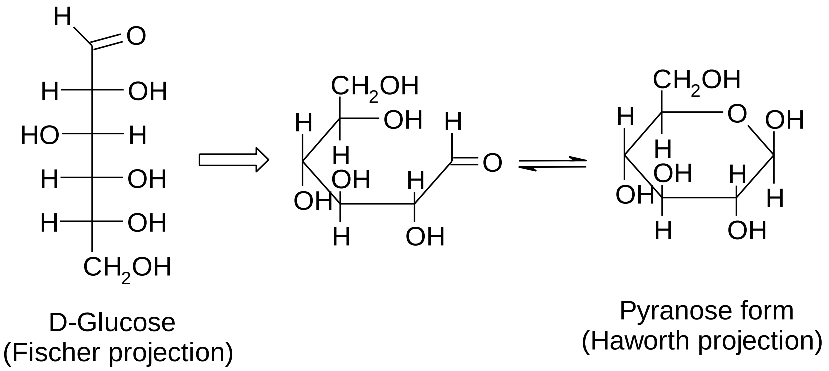


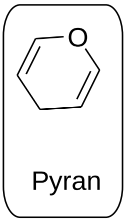
Aldehyde or Ketone

Hemiacetal

- If the hydroxyl group and the carbonyl group in the same molecule: an intramolecular nucleophilic addition can take place, leading to the formation of a cyclic hemiacetal.
- Five and six-membered cyclic hemiacetals are formed.
- Many carbohydrates therefore exist in an equilibrium between open-chain and cyclic forms.
- Glucose exists in aqueous solution primarily as the Six-membered
- Pyranose ring formed by intramolecular nucleophilic addition of the hydroxyl group at C_5 to the C_1 aldehyde group.

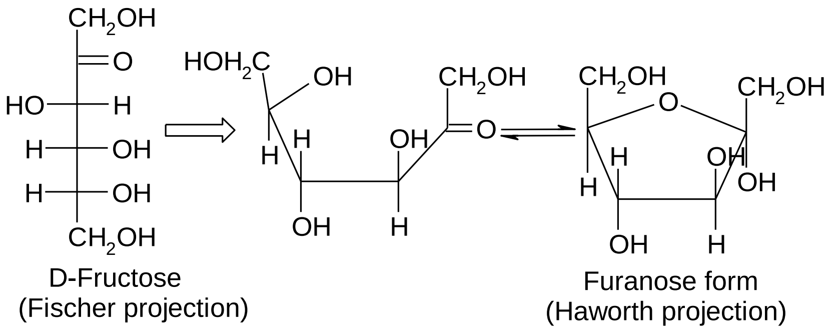
So that the pyranose form of glucose can be formed by the nucleophilic attack of the hydroxyl group on carbon number five on the aldehydic group as shown below.

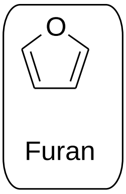




Fructose exists to the extent of about 20% as the five membered furanose ring formed by addition of the hydroxyl group at C_5 to the C_2 ketone group.

So that the furanose form of fructose can be formed by the nucleophilic attack of the hydroxyl group of carbon number five on the ketonic group as shown below.





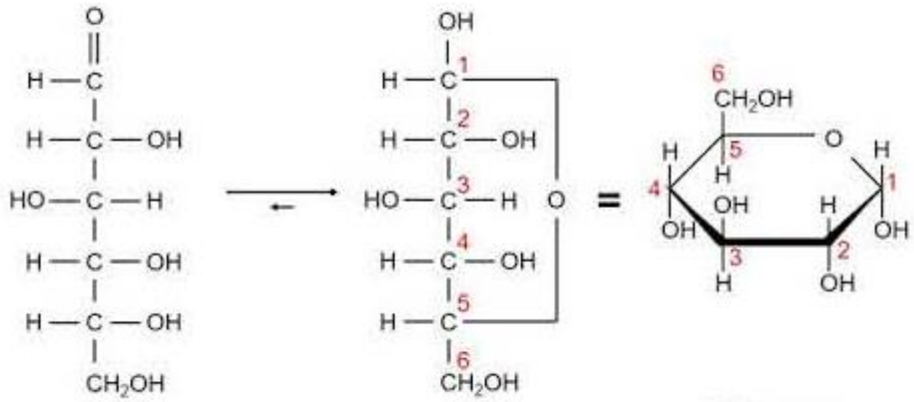
The interconversion of Fischer and Haworth Projections

in a Haworth Projection:

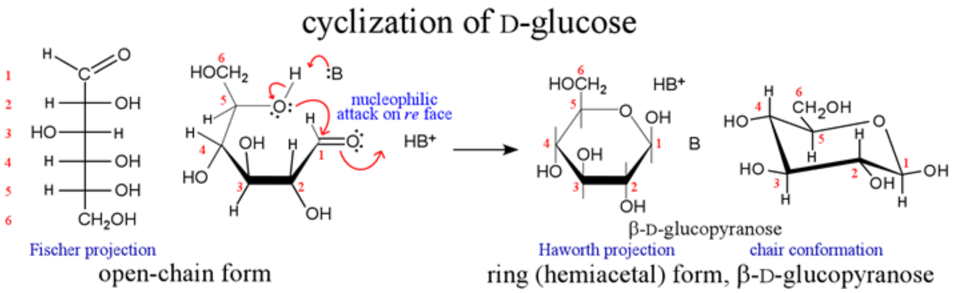
- The hemiacetal ring is drawn as if it were flat and is viewed edge on with oxygen atom at the upper right.
- Hydroxyl group on the right in a Fischer projection is down in a Haworth projection.
- Hydroxyl group on the left in a Fischer projection is up in Haworth projection.
- For D-sugars the terminal CH_2OH group is up in Haworth projection.
- For L-sugars the terminal CH_2OH group is down in Haworth projection.

Examples:

Cyclization of monosccharides



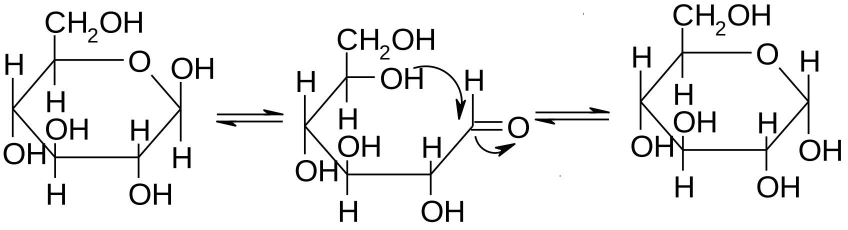
Glucose Glucose Glucose



MUTAROTATION:

D-Glucose exists in two crystalline forms; one melts at 150ºC, the other at 146ºC. The fact that neither form shows a carbonyl frequency in the infrared suggests that these two crystalline forms are the α- and β -hemiacetals. X-ray diffraction studies confirm that this is indeed the case. The crystals melting at 150ºC are β-D-glucose, and they show the anomeric hydroxyl group to be in the equatorial position. The crystals of α-D-glucose melt at 146ºC, and crystallography shows the same molecular structure except for the anomeric hydroxyl, which here is in the axial position. A solution freshly prepared by dissolving β-D-glucose crystals in water gives a specific rotation of + 18.7º. This value slowly rises with time to +52.5º. The α-D-glucose shows a rotation, determined immediately upon dissolution, of +112º, but this value also changes slowly with time to a final value of +52.5º.

The slow change of optical rotation in solution is called mutarotation, and it can be interpreted as involving the interconversion of hemiacetals through the aldehyde intermediate. The equilibrium mixture contains 64 % of the β-isomer, 36 % of the α-isomer, and only about 0.02 % of free aldehyde. Although the equilibrium percentages will differ in different solutions, enough aldehyde is generally present in reaction mixtures to allow the occurrence of ordinary aldehyde reactions such, as oxidation. reduction, and the formation of carbonyl derivatives. The fact that the carbonyl carbon is not asymmetric in the aldehyde form while it is in the hemiacetal, made the original structural and stereochemical determinations more difficult.



β-D-Glucopyranose

$[\alpha]_D$=+18.7º

Aldehyde form

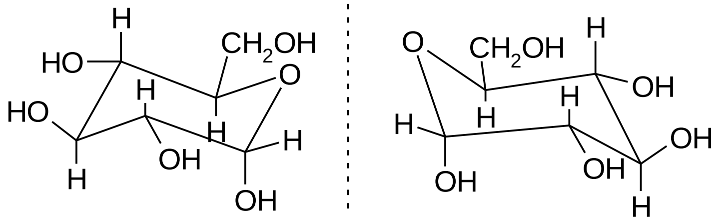
(Open-chain form)

α-D-Glucopyranose

$[\alpha]_D$=+112º

It should be understood that the mirror image of D is L, the mirror image of (+) is (-), but the mirror image of **α** is **α** and not **β**, as shown in the following example (i.e., α-implies an axial 1-hydroxyl group in both enantiomers).

Mirror images



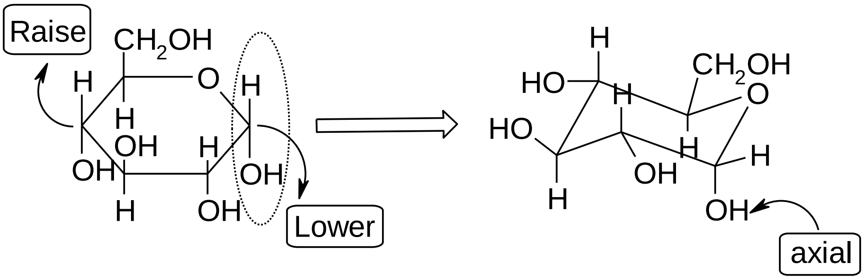
α-D-(+) Glucopyranose α-L-(-) Glucopyranose

Conformations of Monosaccharides:

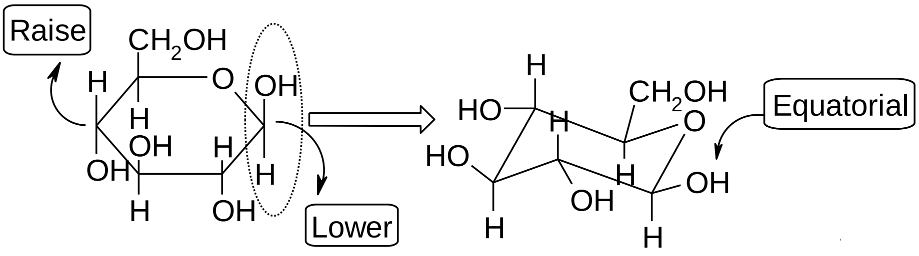
Pyranose rings like cyclohexane rings have a chair like geometry with axial and equatorial substituents.

Haworth projections can be converted into chair representations by the following three steps:

1- Draw the Haworth projection with the ring oxygen atom at the upper right.
2- Raise the left most carbon atom(C_4) above the ring plane.
3- Lower the anomeric carbon atom (C_1) below the ring plane.



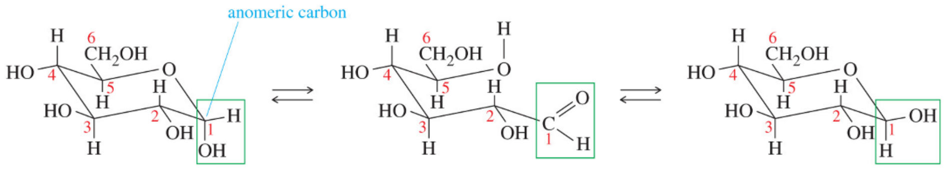
α-D-Glucopyranose



β-D-Glucopyranose

Note that in β-D-glucopyranose all the substituents on the ring are equatorial, thus β-D-glucopyranose is the least sterically and most stable of the eight D-aldohexoses.

Anomers of Glucose



α-D-glucopyranose open-chain form β-D-glucopyranose

- The hydroxyl group on the anomeric (hemiacetal) carbon is down (axial) in the α anomer and up (equatorial) in the β anomer.
- The β anomer of glucose has all its substituents in equatorial positions.
- The hemiacetal carbon is called the anomeric carbon, easily identified as the only carbon atom bonded to two oxygens.

Reactions and Interconversion of Monosaccharides

Reactions of Monosaccharides

Oxidation → Sugar acids

Reduction → Sugar alcohols
Or De-oxy sugar

Reaction with NH_3 → Sugar amine

Ruff Degradation → aldose with one less carbon atom

Kiliani–Fischer Synthesis → aldose with one more carbon atom

Reaction with phenylhydrazine → Osazone

Esterification and etherification

Formation of Glycosides

1- *Oxidation of Monosaccharides:*

Like other aldehydes. aldoses are easily oxidized to yield carboxylic acids. Aldoses reacts with oxidizing reagents to yield the oxidized sugar and a reduced metallic.

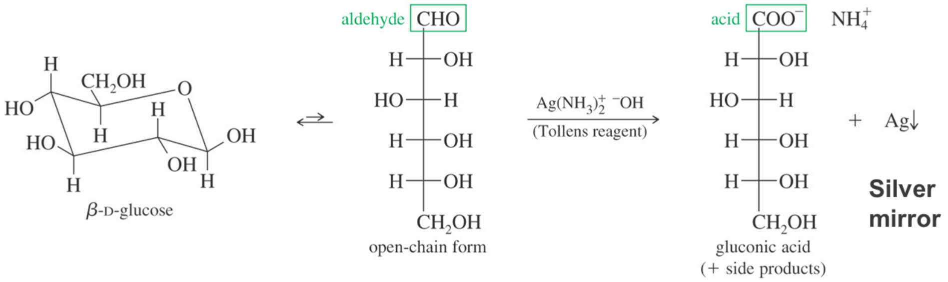
Oxidizing reagents like:

1- Tollen's reagent (Ag^+ in aqueous ammonia) produce silver metal as a mirror.

2- Fehling's reagent (Cu^{++} in aqueous sod. tartrate) produce reddish precipitate of cuprous oxide.

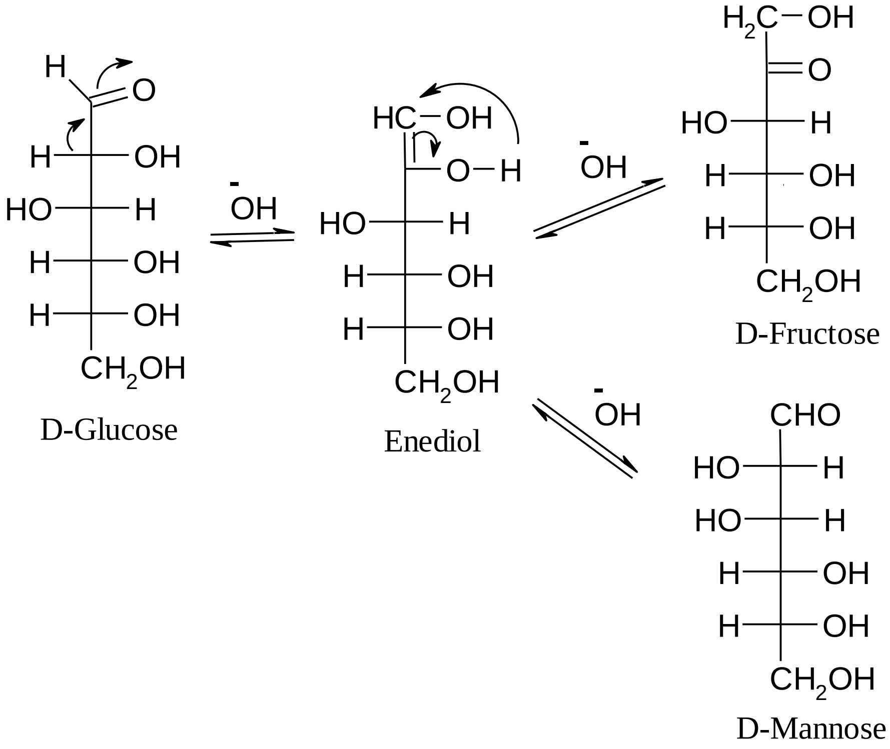
3- Benedict's reagent (Cu^{++} in aqueous sod. citrate) produce reddish precipitate of cuprous oxide.

All aldoses are reducing sugars because they contain a free aldehyde group (or hemiacetal), but some ketoses (α-hydroxy ketones or hemiketal) are reducing sugars as well. Therefore, a free aldehyde (or hemiacetal), an α-hydroxy ketones or (hemiketal) is necessary for a positive test. For example, fructose reduces Tollen's, Fehling's and Benedict's reagents even though it contains no aldehyde group. This occurs because fructose is readily isomerized to an aldose in the basic solution by a series of Keto-enol tautomeric shifts. Once formed the aldose is oxidized normally. These tests cannot be used to distinguish between aldoses and ketoses, since both react with the reagent.



ALKALINE ISOMERIZATION OF MONOSACCHARIDES:

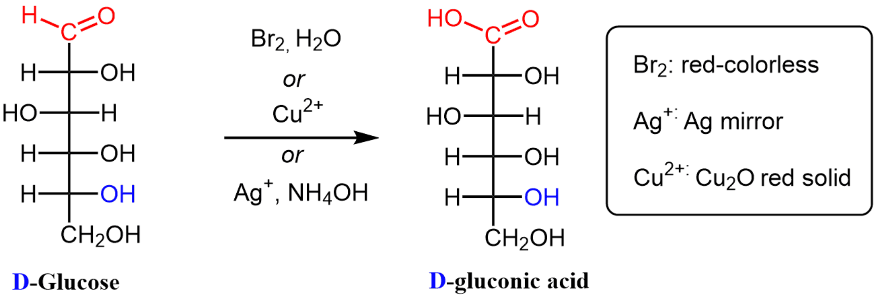
Chemical isomerization of glucose to fructose, an internal oxidation-reduction reaction, can be accomplished by treatment with alkali, but a variety of other isomeric and decomposition products are also produced. For example, when D-glucose is treated with base, the unstable enediol is formed. In this transient intermediate the stereochemistry of C-2 is lost. The enediol can then revert back to any of the three more stable hydroxy carbonyl compounds.

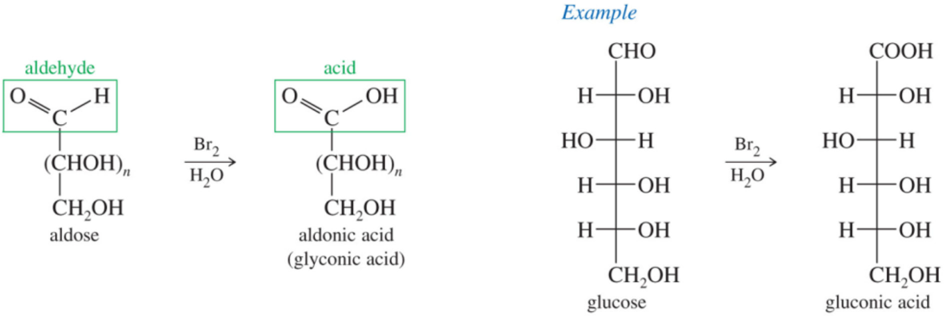


The enzyme catalyzed interconversion of glucose and fructose plays a key role in carbohydrate metabolism in living organisms.

Glycosides however are nonreducing. They don’t react with Tollen's reagent because the acetal group can’t open to a free aldehyde (open-chain form) under basic conditions. Although the Tollen and Fehling reagents serve as useful tests for reducing sugars. They don’t give good yields of carboxylic acid products because the alkaline conditions used cause decomposition of the carbohydrate skeleton. It has been found however that a buffered solution of aqueous bromine oxidizes aldoses to monocarboxydic acids called **aldonic acids**. The reaction is specific for aldoses. ketoses are not oxidized by bromine water.

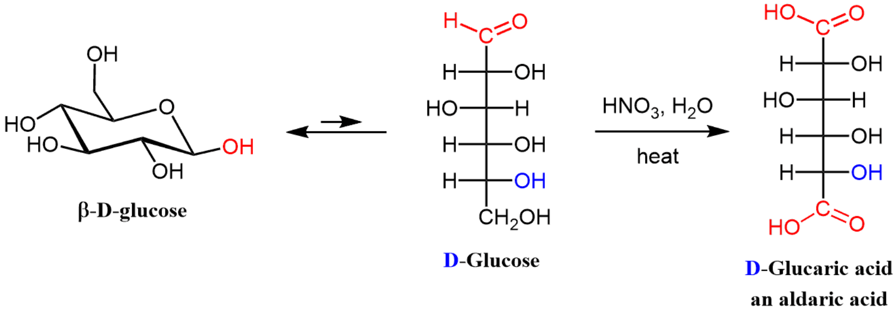
Carbohydrates can be oxidized to aldonic acids with Br_2, Tollens and Benedict's reagent





If more powerful oxidizing agent such as warm dilute nitric acid used, Aldoses oxidized to dicarboxylic acids called aldaric acids. Both CHO and CH_2OH are oxidized.

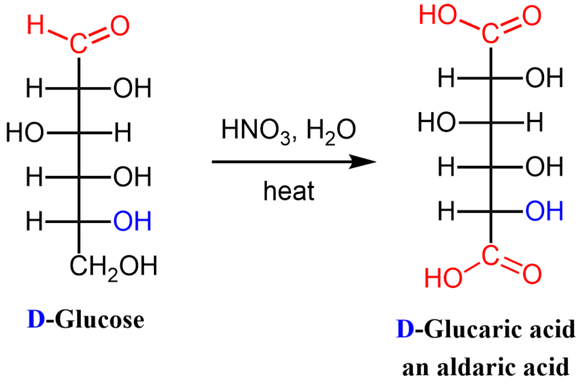
Cyclic hemiacetals are always in equilibrium with the open chain form and can also be oxidized



β-D-glucose

D-Glucose

D-Glucaric acid
an aldaric acid



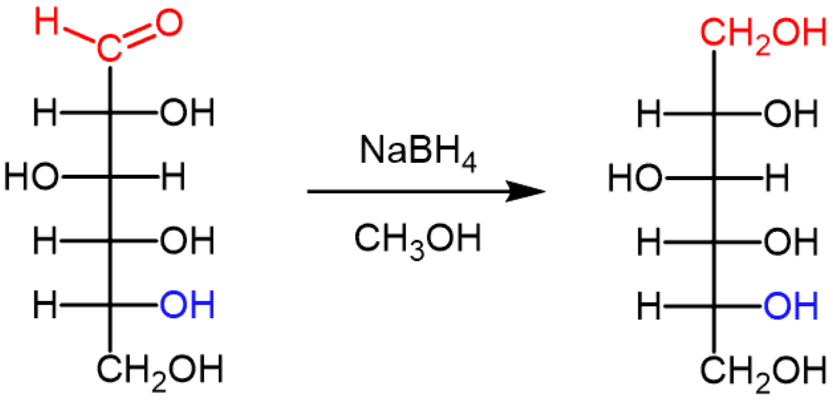
D-Glucose

D-Glucaric acid
an aldaric acid

2- ***Reduction of Monosaccharides:***

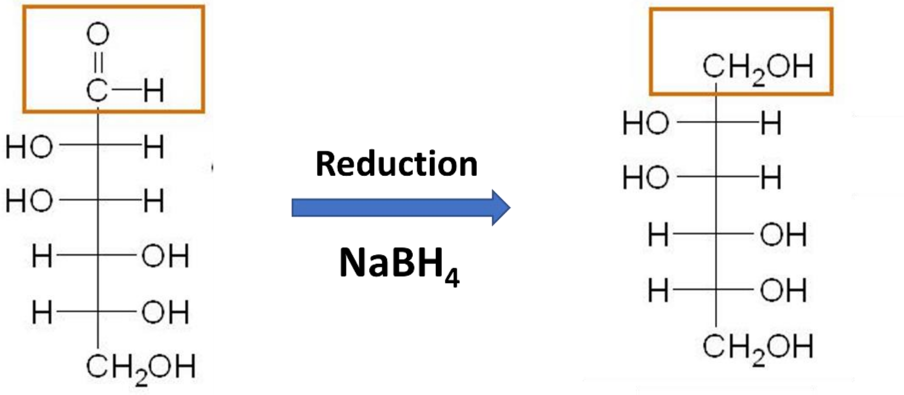
- C═O of aldoses or ketoses can be reduced to C—OH by $NaBH_4$ or H_2/Ni.
- Name the sugar alcohol by adding ***-itol*** to the root name of the sugar called **alditol**.
- Reduction of D-glucose produces **D-glucitol**, commonly called **D-sorbitol**.
- Reduction of D-mannose produces **D-mannitol**.

- Reduction of D-fructose produces a mixture **of D-glucitol** and **D-mannitol**.



D-Glucose

D-Glucitol
an alditol



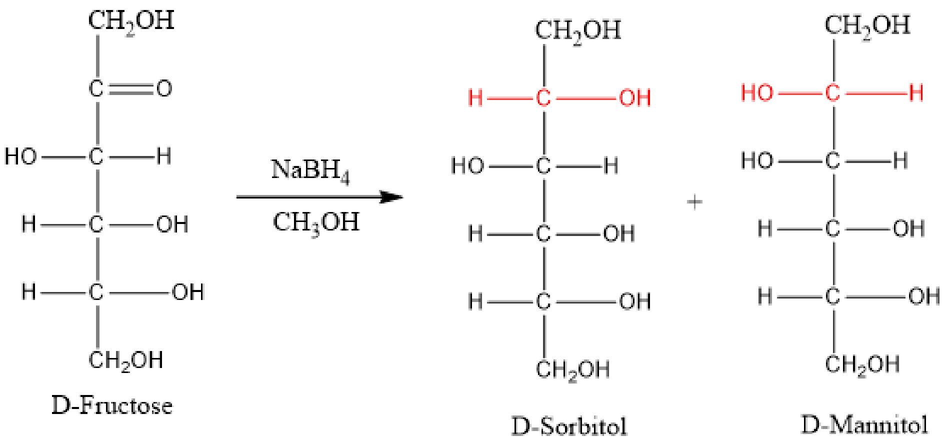
D-Mannose

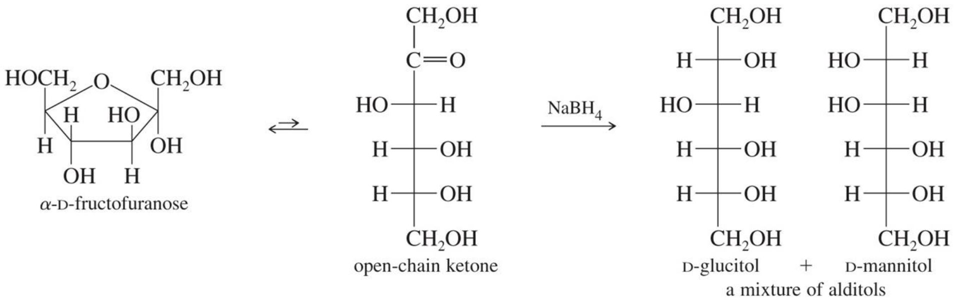
D-Mannitol

Reduction of Fructose

- Reduction of fructose creates a new asymmetric carbon atom, which can have either configuration.

- The products are **a mixture** of glucitol (sorbitol) and mannitol.



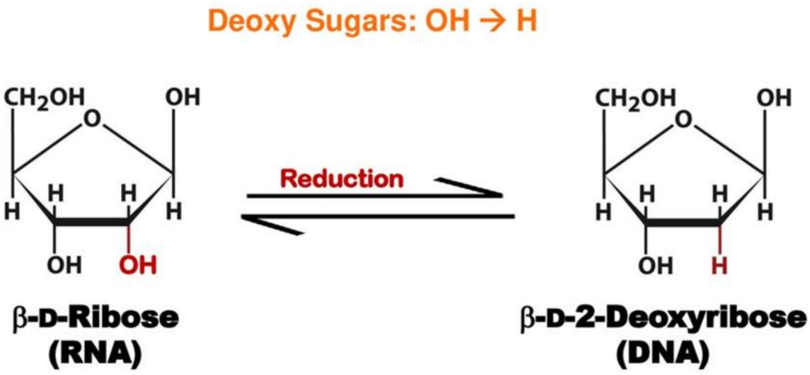


What are the products of the reductions of D-ribose and ribulose?

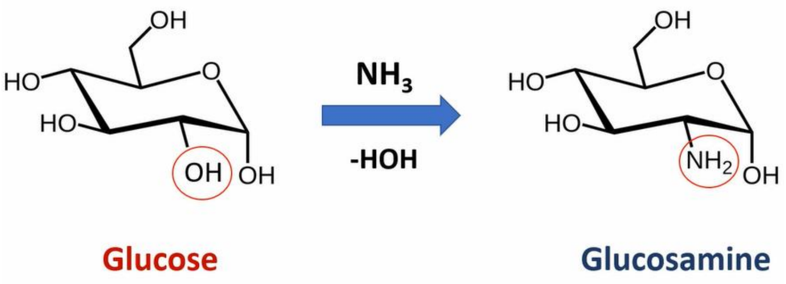
<u>Another reduction of monosaccharides to form deoxy sugars:</u>

- ➢ Reduction (*via* reductases) of an OH group to H generates the corresponding deoxy sugar.
- ➢ Nomenclature based on simply prefixing the sugar with n-deoxy-, where n is the position of OH reduced replaced.

- For example, reduction of the OH group at C2 of ribose generate **2-deoxyribose** --- a component of **DNA**

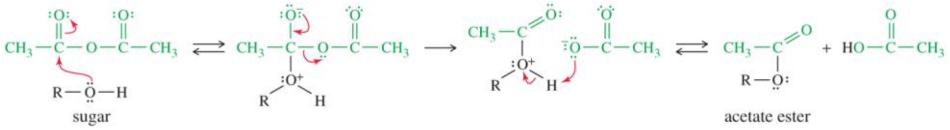


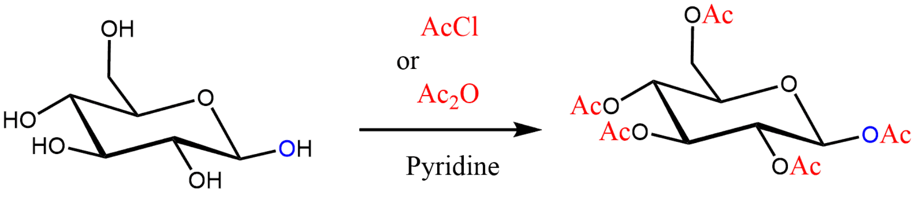
3- *Reaction with Ammonia NH_3 to give sugar amin.*



4- *Ester Formation:*

- Acetic anhydride or acid chloride with a base catalyst like pyridine converts all the oxygens to acetate esters, including the anomeric one to produce penta-*O*-acetyl derivative.
- Esters are readily crystallized and purified



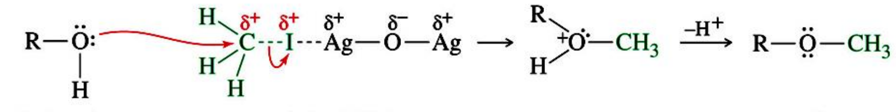


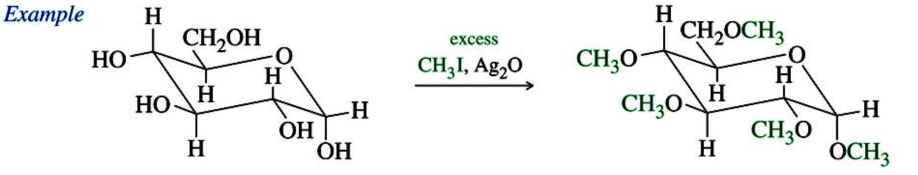
β-D-glucose

5- ***Ether Formation:***

- Reaction of the sugar with methyl iodide and silver oxide will convert the hydroxides to methyl ethers.
- The methylated sugar is stable in base.

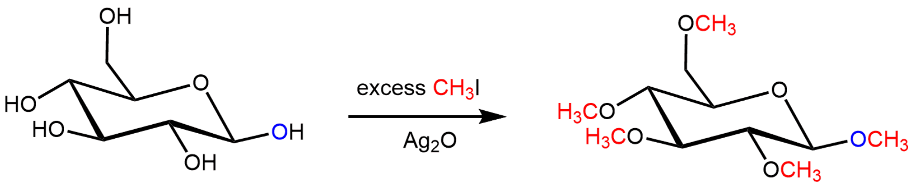
For example. α-D-glucopyranose is converted into its pentamethyl ether in 85% yield on reaction with iodomethane and silver oxide.





α-D-glucopyranose

methyl 2,3,4,6-tetra-*O*-methyl-α-D-glucopyranoside



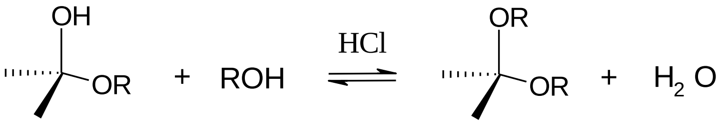
β-D-glucose

β-D-Glucopyranose

β-D-Glucopyranose pentamethyl ether

6- *Glycoside Formation:*

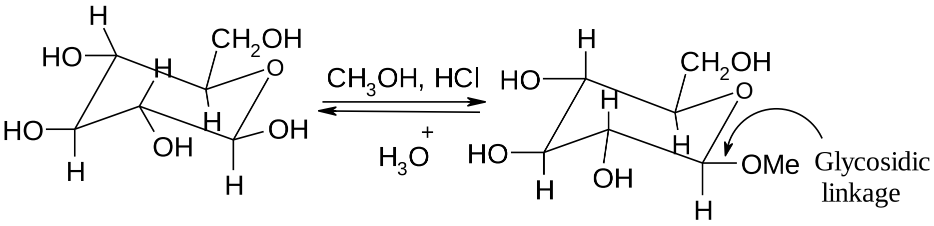
Treatment of hemiacetal with an alcohol and acid catalyst yields an acetal.



Hemiacetal

Acetal

In the same way, treatment of a monosaccharide hemiacetal with an alcohol and an acid catalyst yields an acetal in which the anomeric hydroxyl has been replaced by an alkoxy group.

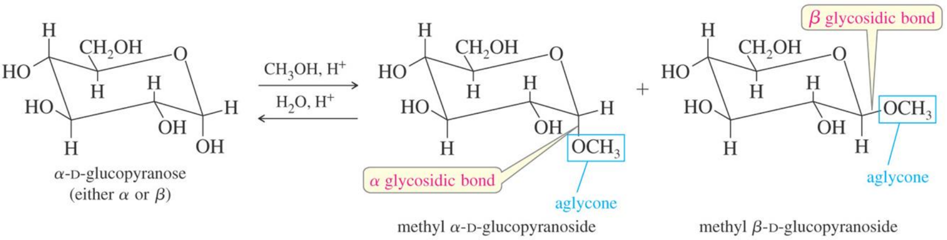


β-D-Glucopyranoside

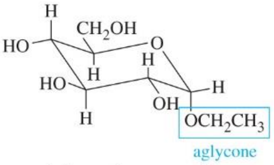
Methyl-β-D-Glucopyranoside

(an acetal)

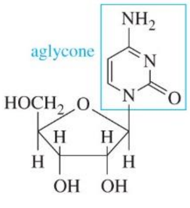
carbohydrate acetals are called glycosides. They are named by citing the alkyl group and adding the **-oside** suffix to the name of the specific sugar.



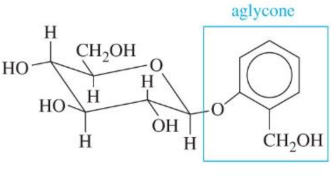
- React the sugar with alcohol in acidic catalyst.
- Since the open-chain sugar is in equilibrium with its α- and β-hemiacetal, both anomers of the acetal are formed.
- ***Aglycone*** is the term used for the group bonded to the anomeric carbon.
- Some aglycones are bonded through an oxygen atom (a true acetal), and others are bonded through other atoms such as nitrogen.



ethyl α-D-glucopyranoside

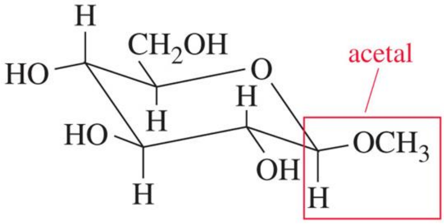


cytidine, a nucleoside (Section 23-21)

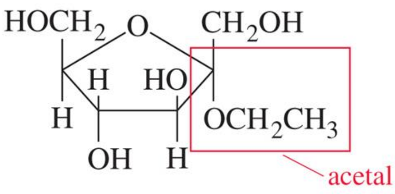


salicin, from willow bark

Glycosides are stable to water and can be converted back to the free monosaccharide by hydrolysis with aqueous acid.



methyl β-D-glucopyranoside
(or methyl β-D-glucoside)



ethyl α-D-fructofuranoside
(or ethyl α-D-fructoside)

- Glycosides are acetals, stable in base, so they do not react with Tollens reagent.

7- *Synthesis and interconversion of the monosaccarides:*

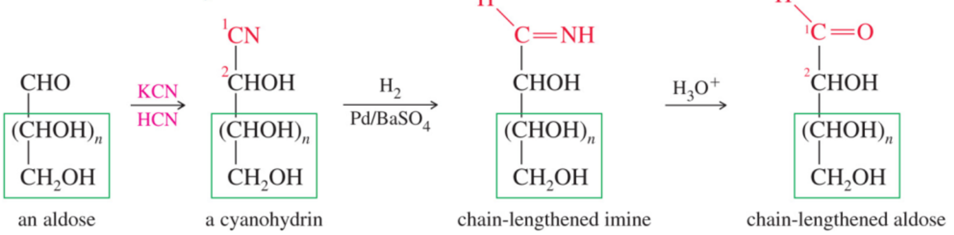
Conversion of an aldose into the next higher aldose (Chain Lengthening):

A) The Kiliani-Fischer synthesis: This method has been carried out as follows:

- Aldose reacts with HCN to form cyanohydrins.
- Conversion of the nitrile into an imine intermediate by catalytic hydrogenation over a palladium catalyst.
- Hydrolysis of the intermediate yield formyl group.

So, The **Kiliani–Fischer synthesis** lengthens an aldose carbon chain by adding one carbon atom to the aldehyde end of the aldose. This synthesis is useful both for determining the structure of existing sugars and for synthesizing new sugars.

The Kiliani–Fischer synthesis



Two cyanohydrins

Two imines

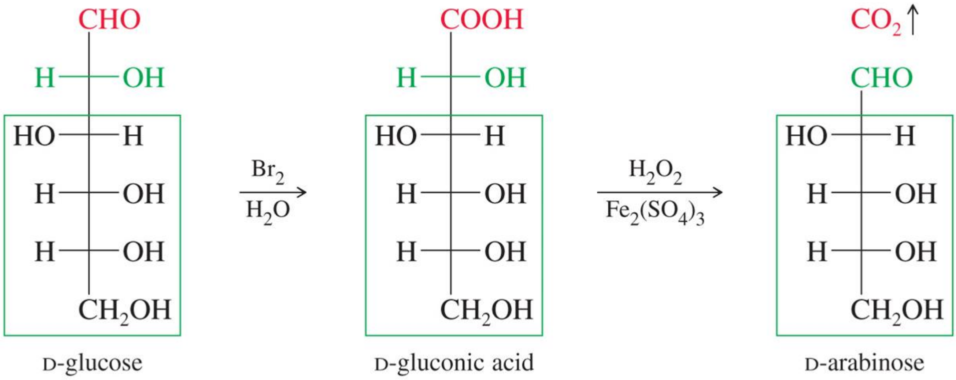
Two aldoses

8- Conversion of an aldose into the next lower aldose (Chain Shortening):

A) Ruff's Degradation:

In this method

- The Ruff degradation is a two-step process that begins with the bromine water oxidation of the aldose to its aldonic acid.
- Treatment of the aldonic acid with hydrogen peroxide and ferric sulfate oxidizes the carboxyl group, so that CO_2 and H_2O are eliminated to give the lower aldose.

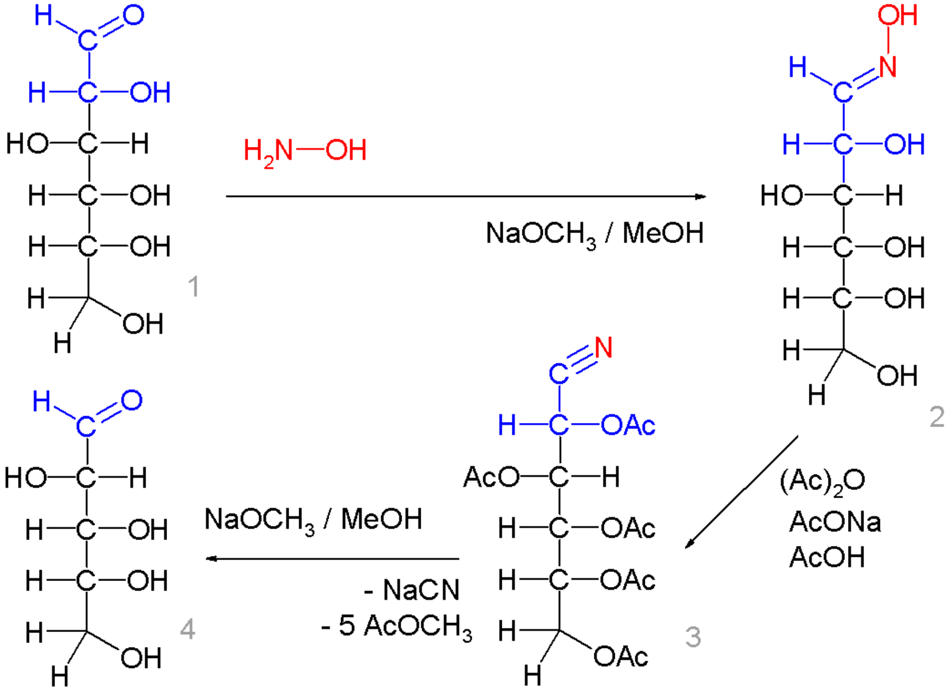


B) The Wohl Degradation:

This degradation can be carried out by the following:

a- The aldose aldehyde carbonyl group is first converted into oxime by treatment with hydroxylamine.

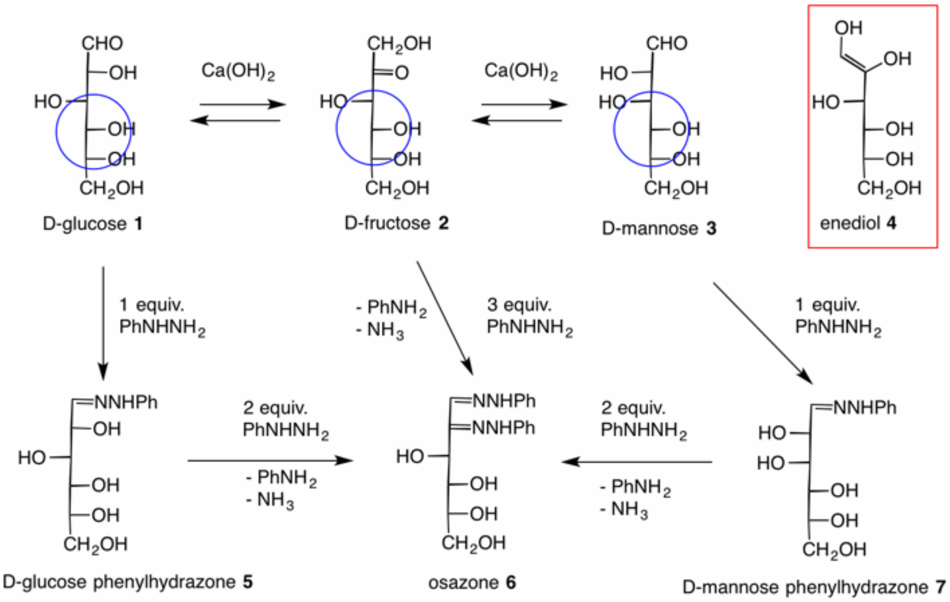
b- The resulting cyanohydrin loss HCN under basic conditions (a retro nucleophilic addition reaction).



So that Wohl degradation shortens an aldose chain by one carbon atom

9- *Osazone Formation:*

- The aldose reacted with excess of phenyl hydrazine to give the corresponding osazone.



Conversion of an aldose into the corresponding ketose:

Hydrolysis of the previous osazone with HCl then reduced with zinc and acetic acid glacial to give the corresponding ketose.

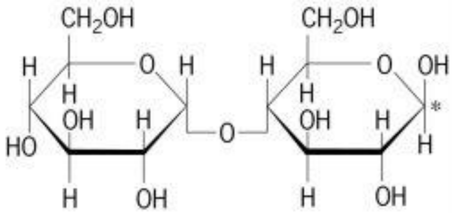
Disaccharides

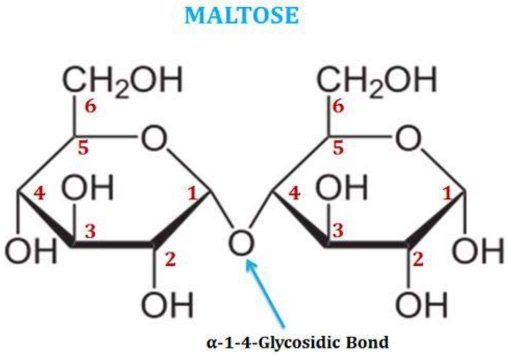
Disaccharides are formed when two monosaccharides are joined together **by an O-glycosidic linkage** and a molecule of water is removed.

Among the most common disaccharides are:

- **Maltose (Malt sugar)**
- **Lactose (Milk sugar)**
- **Sucrose (Cane or beet sugar)**

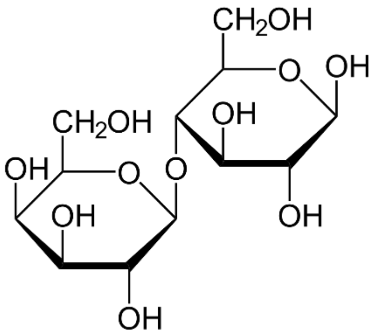
Maltose ($C_{12}H_{22}O_{11}$):



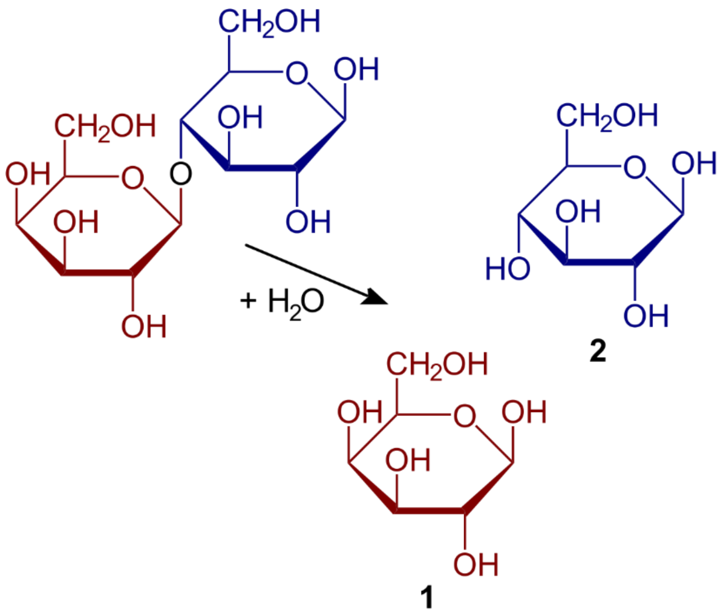


- **Maltose** or malt sugar is a disaccharide formed from two units of glucose.
- Maltose is the disaccharide produced when amylase breaks down starch.
- Maltose can be broken down into two glucose molecules by hydrolysis. In living organisms.
- It has reducing properties as it has one hemiacetal free.
- Maltose reacts with phenyl hydrazine to form osazone, also it can form ester by its reaction with acetic anhydride.
- An aqueous solution of maltose is fermented by yeast to give ethyl alcohol and carbon dioxide.

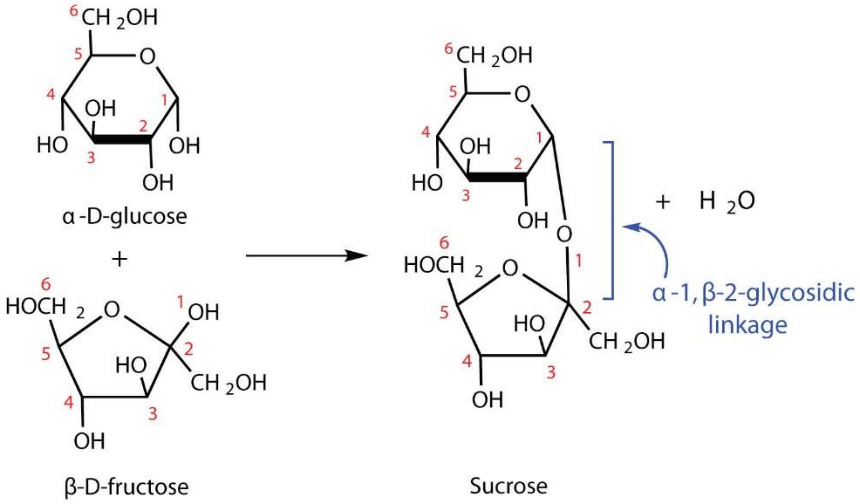
Lactose



- Lactose (milk sugar) is a disaccharide derived from the condensation of galactose and glucose
- It found in appreciable quantities in milk to the extent of about 2-8%.
- Like maltose, it also has reducing properties. Its reactivity is mainly due to presence of a free hemiacetal-aldehyde group in the glucose unit of molecule.
- Lactose can be broken down into glucose and galactose molecules by hydrolysis.



Sucrose



- ❖ Sucrose is commonly known as table sugar (Cane sugar).
- ❖ It is a white, odourless, crystalline powder with a sweet taste.
- ❖ The molecule is a disaccharide derived from glucose and fructose.
- ❖ It is very soluble and very sweet.
- ❖ As both aldehyde & ketone groups are linked together it does not have reducing properties.

Polysaccharides

Polysaccharides contain hundreds or thousands of carbohydrate units. Polysaccharides are *not* reducing sugars, since the anomeric carbons are connected through glycosidic linkages.

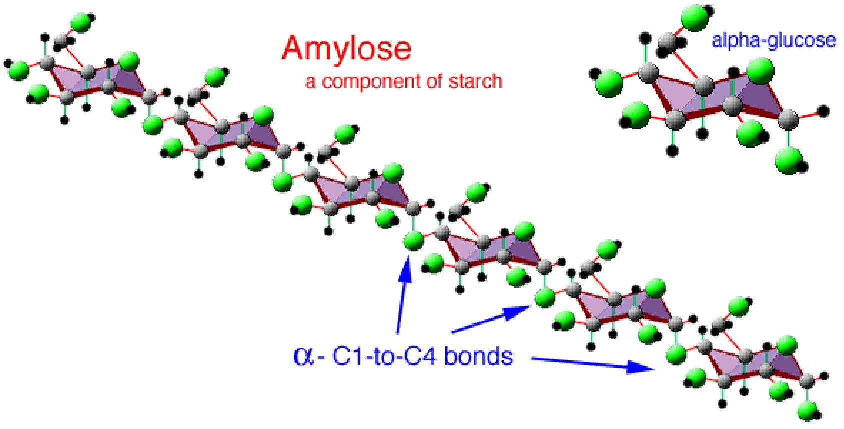
Nomenclature:

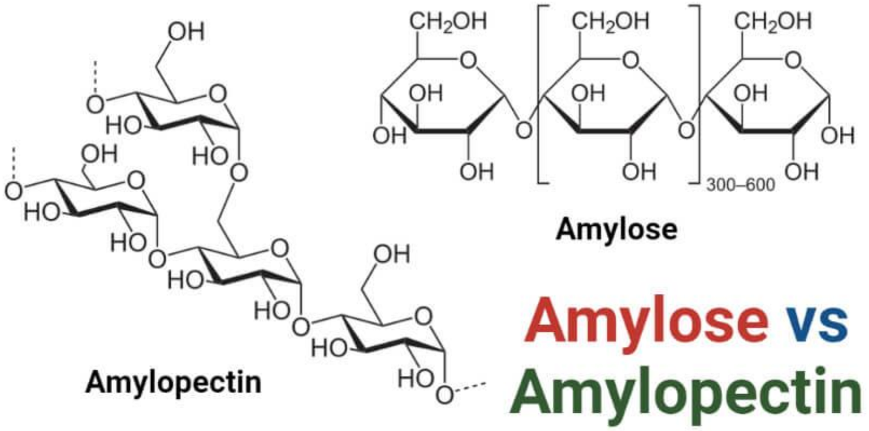
Homopolysaccharide- a polysaccharide is made up of **one type** of monosaccharide unit

Heteropolysaccharide- a polysaccharide is made up of more than **one type** of monosaccharide unit.

Starch

- Starch is a polymer consisting of D-glucose units.
- Starches (and other glucose polymers) are usually insoluble in water because of the high molecular weight, but they can form thick colloidal suspensions with water.
- Starch is a **storage** compound in plants, and made of glucose units
- It is a homopolysaccharide made up of two components: **amylose** and **amylopectin**.
- Most starch is 10-30% amylose and 70-90% amylopectin.
- **Amylose** – a straight chain structure formed by **1,4 glycosidic bonds** between **α-D-glucose** molecules.

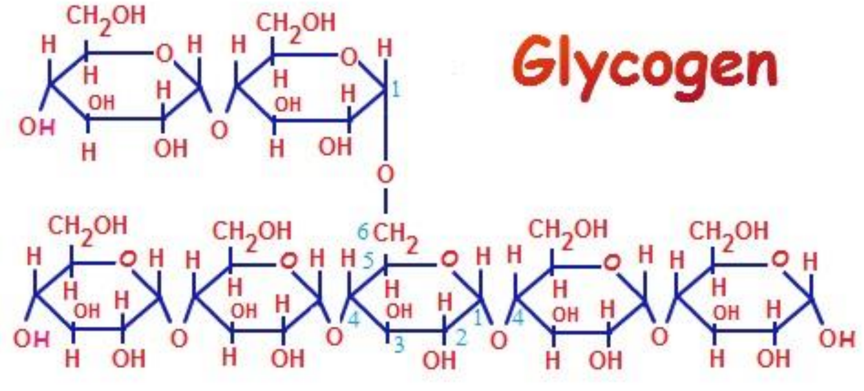




- The amylose chain forms a helix.
- This causes the blue colour change on reaction with iodine.
- Amylose is poorly soluble in water, but forms micellar suspensions
- Amylopectin-a glucose polymer with mainly **α**-(1→4) linkages, but it also has branches formed by **α**-(1→6) linkages. Branches are generally longer than shown above.
- Amylopectin causes a red-violet colour change on reaction with iodine.

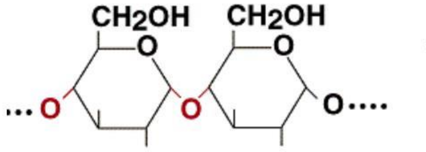
- This change is usually masked by the much darker reaction of amylose to iodine.

Glycogen



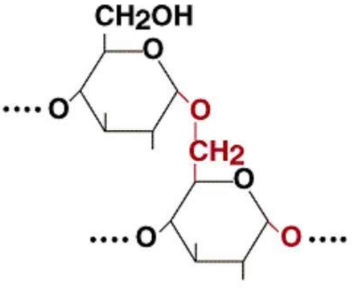
Structure of glycogen

* Glycogen: branched-chain homopolysaccharide made of α-D-glucose linked by α-1,4 linkage.



α-1,4-Glycosidic linkage

(a)



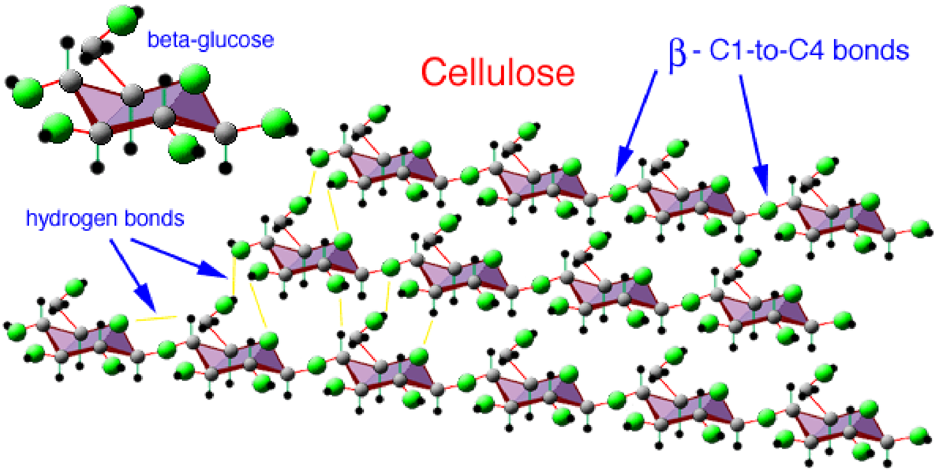
α-1,6-Glycosidic linkage

(b)

After every 8-10 glucose residues there is a branch containing α-1,6 linkage.

- Storage polysaccharide in animals
- Glycogen constitutes up to 10% of liver mass and 1-2% of muscle mass
- Glycogen is stored energy for the organism
- Similar in structure to amylopectin, only difference from starch: number of branches
- Alpha (1,6) branches every 8-12 residues
- Like amylopectin, glycogen gives a red-violet color with iodine

Cellulose



- The β-glucose molecules are joined by condensation, i.e. the removal of water, forming β-(1,4) glycosidic linkages.

- The glucose units are linked into straight chains each 100-1000 units long.
- Weak hydrogen bonds form between parallel chains binding them into cellulose microfibrils.
- Cellulose microfibrils arrange themselves into thicker bundles called microfibrils. (These are usually referred to as fibres.)
- The cellulose fibres are often “glued” together by other compounds such as hemicelluloses and calcium pectate to form complex structures such as plant cell walls.
- Because of the β-linkages, cellulose has a different overall shape from amylose, forming extended straight chains which hydrogen bond to each other, resulting in a very rigid structure.
- Cellulose is an important structural polysaccharide and is the single most abundant organic compound on earth. It is the material in plant cell walls that provides strength and rigidity; wood is 50% cellulose.
- Most animals lack the enzymes needed to digest cellulose, although it does provide needed roughage (dietary fiber) to stimulate contraction of the intestines and thus help pass food along through the digestive system

- Some animals, such as cows, sheep, and horses, can process cellulose through the use of colonies of bacteria in the digestive system which are capable of breaking cellulose down to glucose; ruminants use a series of stomachs to allow cellulose a longer time to digest. Some other animals such as rabbits reprocess digested food to allow more time for the breakdown of cellulose to occur.
- Cellulose is also important industrially, from its presence in wood, paper, cotton, cellophane, rayon, linen, nitrocellulose (guncotton), photographic films (cellulose acetate), etc.

UNIT 2: LIPIDS

Introduction, Classification, Properties and Biological importance. Fatty acid nomenclature and structure, Triglycerides formation and its applications.

Introduction

There is a lot of interest these days on healthy diets as well as concerns about heart problems. There is also a strong market for the sales of omega-3 fatty acids, which are said to help lower fat levels in blood. But too many people rely on the supplements to help their hearts and don't understand the chemistry behind it all. Yes, taking omega-3 fatty acids will give you some of the fatty acids your body requires. No, this is not a substitute for eating a healthy diet and exercising. You can't sit in front of the TV set, eating your large pizza, and expect these pills to keep your health. You've got to do things the hard way - eat your vegetables and get some exercise.

Fatty Acids

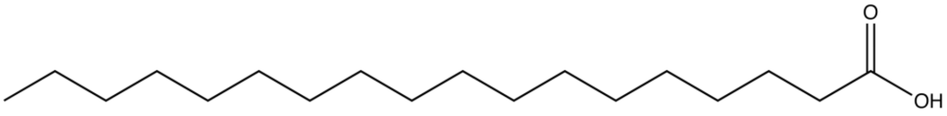
A lipid is an organic compound such as fat or oil. Organisms use lipids to store energy, but lipids have other important roles as well. Lipids consist of repeating units called fatty acids. Fatty acids are organic compounds that have the general formula

$CH_3(CH_2)_nCOOH$, where n usually ranges from 2 to 28 and is always an even number.

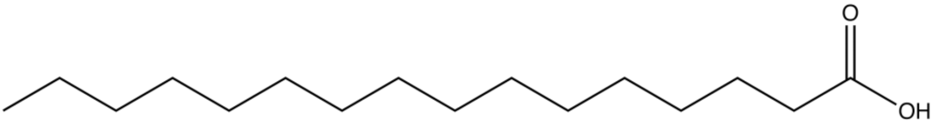
- **There are two types of fatty acids: saturated fatty acids and unsaturated fatty acids.**

Saturated Fatty Acids

In saturated fatty acids, carbon atoms are bonded to as many hydrogen atoms as possible. This causes the molecules to form straight chains, as shown in the figure below. The straight chains can be packed together very tightly, allowing them to store energy in a compact form. This explains why saturated fatty acids are solids at room temperature. Animals use saturated fatty acids to store energy. For example: Stearic and palmitic



stearic acid

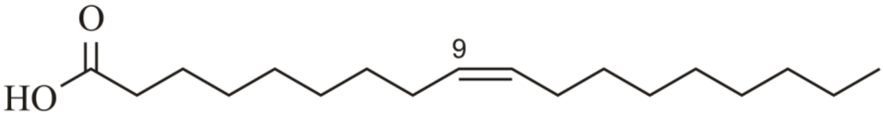


palmitic acid

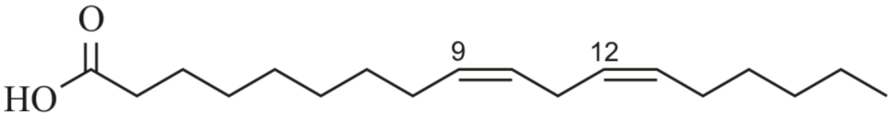
Unsaturated Fatty Acids

In unsaturated fatty acids, some carbon atoms are not bonded to as many hydrogen atoms as possible due to the presence of one or more double bonds in the carbon chain. Instead, they are bonded to other groups of atoms. Wherever carbon binds with these other groups of atoms, it causes chains to bend (see figure above). The bent chains cannot be packed together very tightly, so unsaturated fatty acids are liquids at room temperature. Plants use unsaturated fatty acids to store energy.

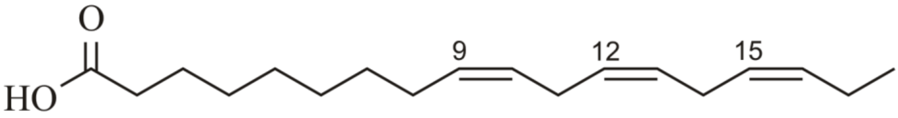
Unsaturated fatty acids



oleic acid (9-octadecenoic)



linoleic acid (9,12-octadecadienoic)



linolenic acid (9,12,15-octadecatrienoic)

Lipids and Diet

Unsaturated fat is generally considered to be healthier because it contains fewer calories than an equivalent amount of saturated fat. Additionally, high consumption of saturated fats is linked to an increased risk of cardiovascular disease. Some examples of foods with high concentrations of saturated fats include butter, cheese, lard, and some fatty meats. Foods with higher concentrations of unsaturated fats include nuts, avocado, and vegetable oils such as canola oil and olive oil.

Humans need lipids for many vital functions, such as storing energy and forming cell membranes. Lipids can also supply cells with energy. In fact, a gram of lipids supplies more than twice as much energy as a gram of carbohydrates or proteins. Lipids are necessary in the diet for most of these functions. Although the human body can manufacture most of the lipids it needs, there are others, called essential fatty acids, that must be consumed in food. Essential fatty acids include omega-3 and omega-6 fatty acids. Both of these fatty acids are needed for important biological processes, not just for energy.

Although some lipids in the diet are essential, excess dietary lipids can be harmful. Because lipids are very high in energy, eating too many may lead to unhealthy weight gain. A high-fat diet may also increase lipid levels in the blood. This, in turn, can increase the risk for health problems such as cardiovascular disease. The dietary lipids of most concern are saturated fatty acids, trans fats, and cholesterol. For example, cholesterol is the lipid mainly responsible for narrowing arteries and causing the disease atherosclerosis.

Types of Lipids

Lipids may consist of fatty acids alone, or they may contain other molecules as well. For example, some lipids contain alcohol or phosphate groups. They include:

1- **triglycerides (simple lipids)**: the main form of stored energy in animals.

2- **phospholipids**: the major components of cell membranes.

3- **steroids**: serve as chemical messengers and have other roles.

Triglycerides

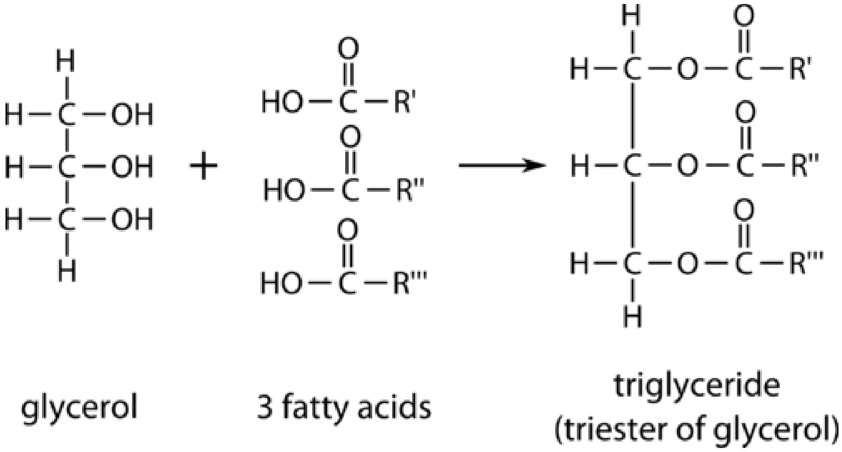
animal fats and vegetable oils

Triglycerides

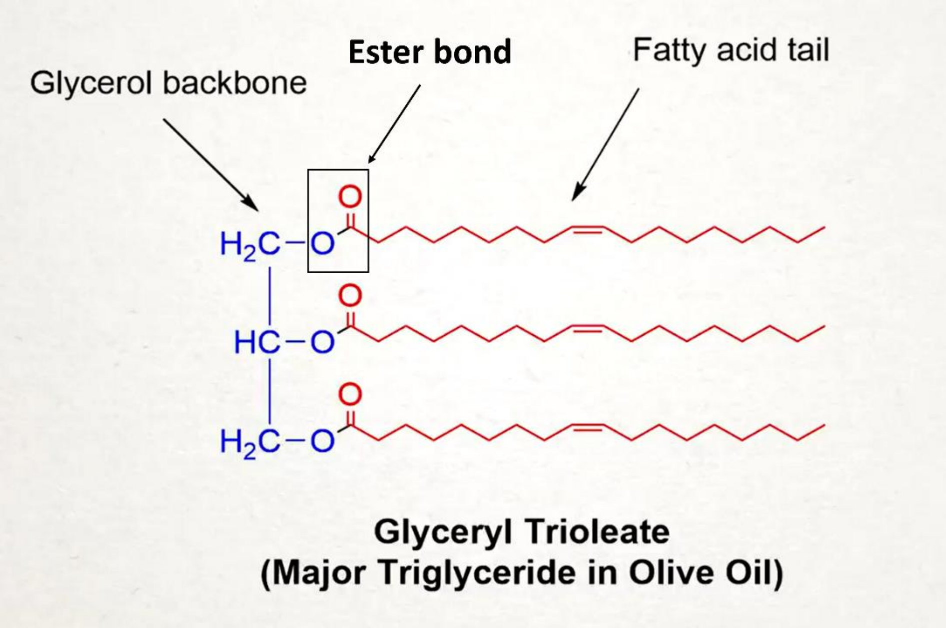
Are esters of the glycerol with fatty acids (R-COOH),

R contain 7-21 carbon atoms

One type of lipid is called a triglyceride, an ester derived from glycerol combined with three fatty acid molecules.



Glycerol is a triol, an alcohol which contains three hydroxyl functional groups. A fatty acid is a long carbon chain, generally from 12 to 24 carbons in length, with an attached carboxyl group. Each of the three fatty acid molecules undergoes an esterification with one of the hydroxyl groups of the glycerol molecule. The result is a large triester molecule referred to as a triglyceride.

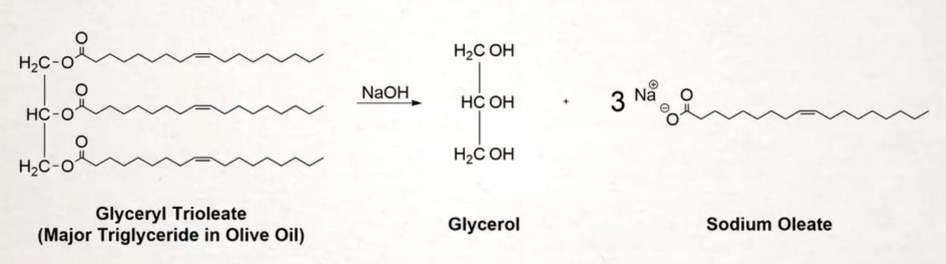


Triglycerides function as a long-term storage form of energy in the human body. Because of the long carbon chains, triglycerides are nearly nonpolar molecules and thus do not dissolve readily in polar solvents such as water. Instead, oils and fats are soluble in nonpolar organic solvents such as hexane and ethers.

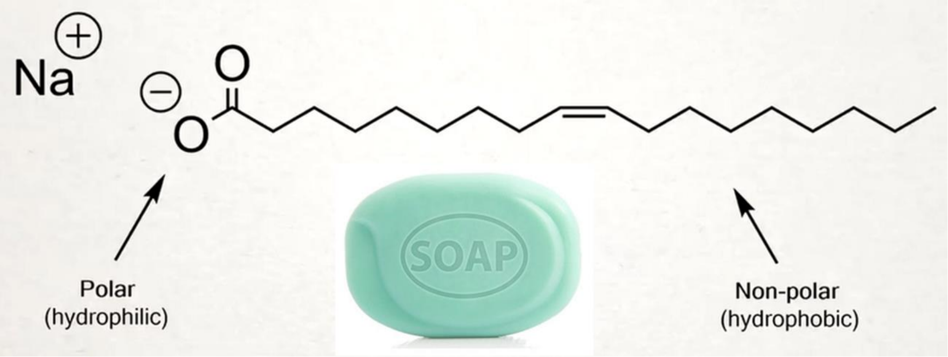
Applications of Fats and oils

Saponification reaction

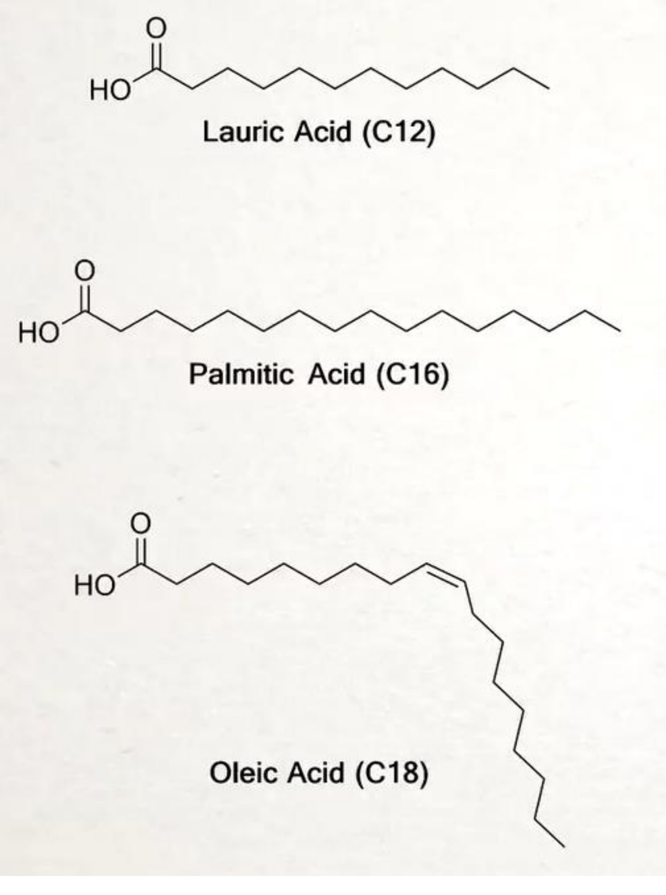
Saponification of an ester with NaOH yields the sodium salt of a carboxylic acid. Saponification of a triglyceride yields a salt of a long-chain fatty acid, which is a soap.



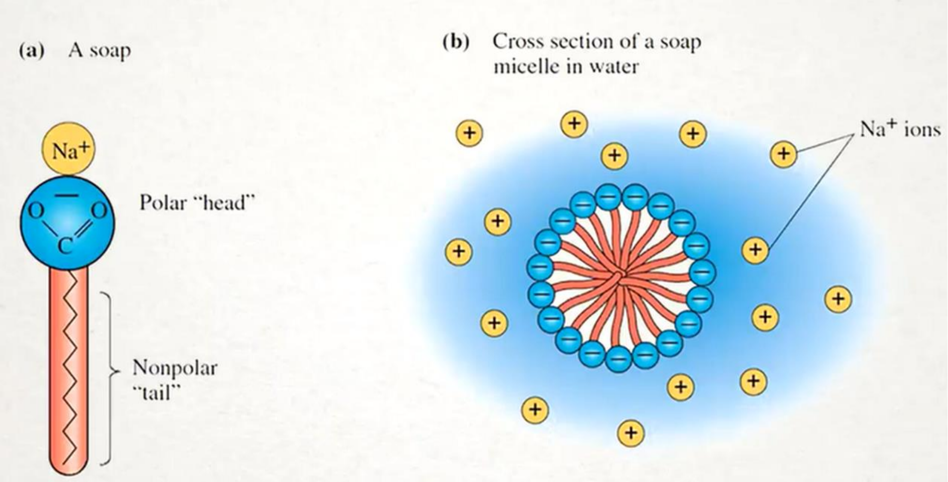
A molecule of a soap contains a long hydrocarbon chain plus an ionic end. The hydrocarbon portion of the molecule is hydrophobic and soluble in nonpolar substances, while the ionic end is hydrophilic and water-soluble. Because of the hydrocarbon chain, a soap molecule as a whole is not truly soluble in water. However, soap is readily suspended in water because it forms micelles, clusters of hydrocarbon chains with their ionic ends facing the water.



Depending on the base that is used and the source of triglycerides, the final soap can have very different Properties.



The value of a soap is that it can emulsify oily dirt so that it can be rinsed away. This ability to act as an emulsifying agent arises from two properties of the soap. First, the hydrocarbon chain of a soap molecule dissolves in nonpolar substances, such as droplets of oil. Second, the anionic end of the soap molecule, which is attracted to water, is repelled by the anionic ends of soap molecules protruding from other drops of oil. Because of these repulsions between the soap-oil droplets, the oil cannot coalesce, but remains suspended.



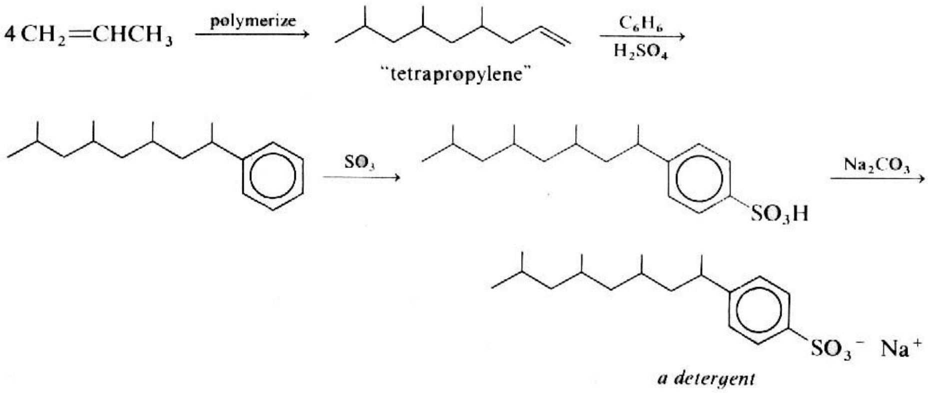
A micelle of the alkyl carboxylate ions of a soap

A disadvantage of soaps is that they form insoluble salts (bathtub ring) with Ca^{2+}, Mg^{2+} and other ions found in hard water. ("Softening" water involves exchanging these ions for Na^{+})

$$\underset{\text{sodium stearate}}{2\ CH_3(CH_2)_{16}CO_2Na} + Ca^{2+} \longrightarrow \underset{\substack{\text{calcium stearate}\\ \text{insoluble}}}{[CH_3(CH_2)_{16}CO_2]_2Ca} + 2\ Na^{+}$$

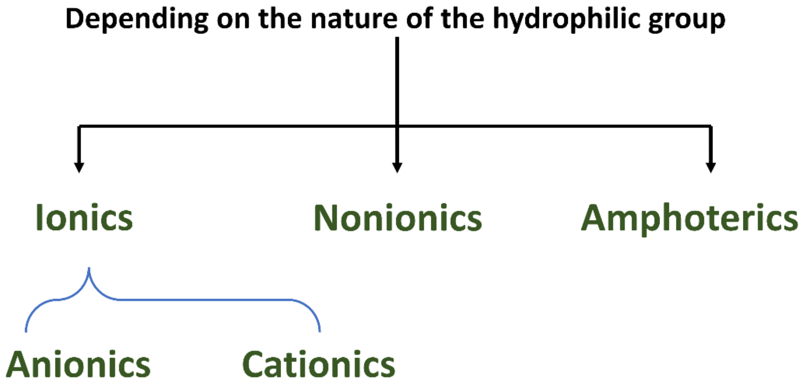
Most laundry products and many toilet “soaps” and shampoos are not soaps, but detergents. A detergent is a compound with a hydrophobic hydrocarbon end plus a sulfonate or sulfate ionic end. Because of this structure, a detergent has the same emulsifying properties as a soap. The advantage of a detergent is that most metal alkyl sulfonates and sulfates are water-soluble; detergents do not precipitate with the metal ions found in hard water.

One of the first detergents in common use was a highly branched alkyl benzenesulfonate. The alkyl portion of this compound is synthesized by the polymerization of propylene and is attached to the benzene ring by a Friedel-Crafts alkylation reaction. Sulfonation, followed by treatment with base, yields the detergent.



Although the microorganisms in septic tanks or sewage-treatment plants can break down continuous-chain alkyl groups into smaller organic molecules, they cannot degrade branched chains. The reason for this difference in biodegradability is that long-chain hydrocarbons are degraded two carbons at a time by way of a keto ester. Branching interferes with the formation of the ketone group, and thus blocks the entire sequence. To prevent the build-up of detergents in rivers and lakes, present-day detergents are designed with biodegradability in mind. One type of biodegradable detergent is an alkyl benzenesulfonate with a continuous-chain, rather than a branched-chain, alkyl group. Other type of biodegradable detergent is a continuous-chain alkyl sulfate and alkyl ether sulfate (Texapon).

Classification of surfactants



We will focus on this part of detergents next year.

Biodiesel formation:

Biodiesel

Biodiesel is an oxygenated, non- toxic, sulfur-free, biodegradable, and eco-friendly. It is a renewable resource, and it is produced from vegetable oils or animal fats and an alcohol, used for cooking and transportation fuel because its fuel has mono-alkyl esters of long chain fatty acids meeting a standard requirement (ASTM OR European standards). One main process for producing biodiesel is **transesterification**. Biodiesel has high viscosities, and this can be derived from the injection and atomization characteristics of vegetable oil, viscosity of vegetable oil can be reduced to improve the efficiency of diesel engines and this can be obtained by converting vegetable oil into biodiesel. The four main methods to solve problem occurrence of high fuel viscosity are dilution, micro emulsification, pyrolysis, and transesterification.

Biodiesel production process:

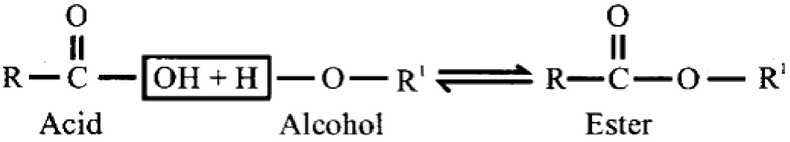
- In order to understand the chemical process, we must know the chemistry of esterification and transesterification.

Chemistry of Esterification

It is the general name for a chemical reaction in which two reactants (typically an alcohol and an carboxylic acid) form an ester as the reaction product.

Esters are common in organic chemistry and biological materials, and often have a pleasant characteristic, fruity odour.

The reaction:



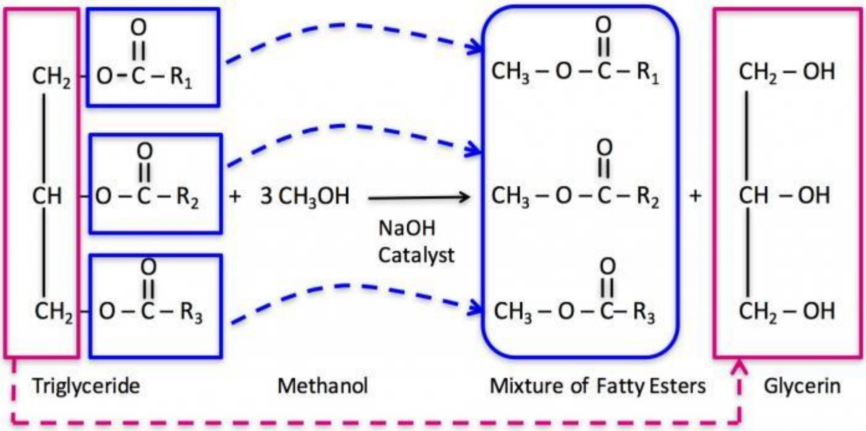
$$R-\overset{O}{\overset{\|}{C}}-\boxed{OH + H}-O-R^1 \rightleftharpoons R-\overset{O}{\overset{\|}{C}}-O-R^1$$

Chemistry of Transesterification

- In organic chemistry, transesterification is the process of exchanging the organic alkyl group of an ester with the organic alkyl group of an alcohol.
- These reactions are often catalysed by the addition of an acid or base catalyst.

- The reaction can also be accomplished with the help of enzymes (biocatalysts) particularly lipases.

A generic transesterification reaction has been reflected by this reaction



$$\begin{matrix} CH_2-O-\overset{O}{\overset{\|}{C}}-R_1 \\ | \\ CH-O-\overset{O}{\overset{\|}{C}}-R_2 \\ | \\ CH_2-O-\overset{O}{\overset{\|}{C}}-R_3 \end{matrix} + 3\,CH_3OH \xrightarrow[\text{Catalyst}]{\text{NaOH}} \begin{matrix} CH_3-O-\overset{O}{\overset{\|}{C}}-R_1 \\ CH_3-O-\overset{O}{\overset{\|}{C}}-R_2 \\ CH_3-O-\overset{O}{\overset{\|}{C}}-R_3 \end{matrix} + \begin{matrix} CH_2-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{matrix}$$

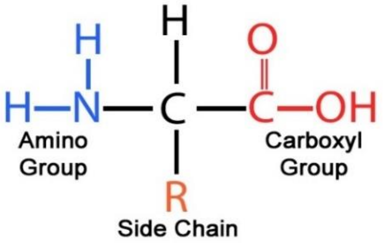
Amino acids and proteines

Amino acids

Amino acids are the building blocks of proteins. It has both an amino group (-NH_2) and an acid group (-COOH). There are more than 300 amino acids that occur in nature and many more yet to be characterized. Only 20 of the amino acids are found in the protein structure. The genetic code exists for only the 20 amino acids.

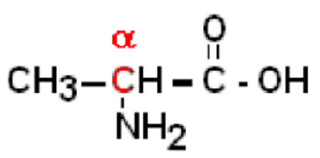
Structure of amino acids

Each amino acid has 4 different groups attached to α-carbon (which is carbon atom next to carboxylic group – COOH).



The properties of each amino acid are determined by its specific side chain (R-groups). R-groups vary in structure, size, electric charge, and solubility in water from one amino acid to other.

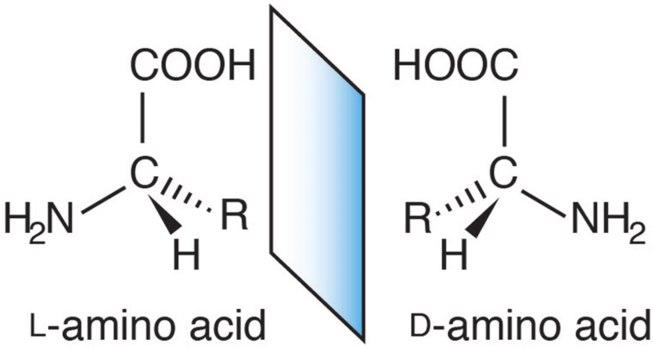
Amino acids found in proteins are α-amino acids. The amino group is always found on the carbon adjacent to the carboxyl group.



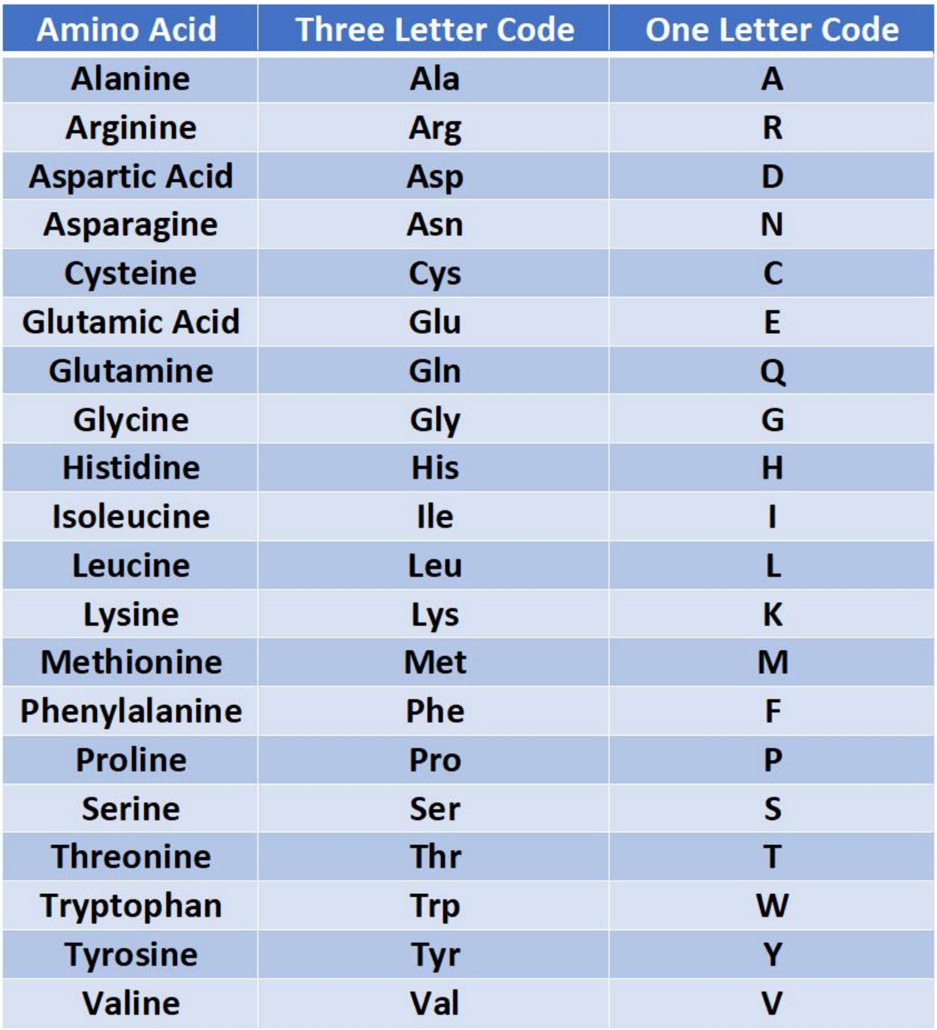
$$CH_3-\overset{\alpha}{C}H(NH_2)-\overset{O}{\overset{\|}{C}}-OH$$

Chirality – amino acids (except glycine) have a tetrahedral C_α bonded to four different chemical groups. As a result of this, amino acids are optically active or chiral. Common amino acids are all L stereoisomers. “CO-R-N” mnemonic is used for distinguishing L and D stereoisomers.

Looking down the H-C bond, CO-R-N spelled clockwise indicates the L stereoisomer.

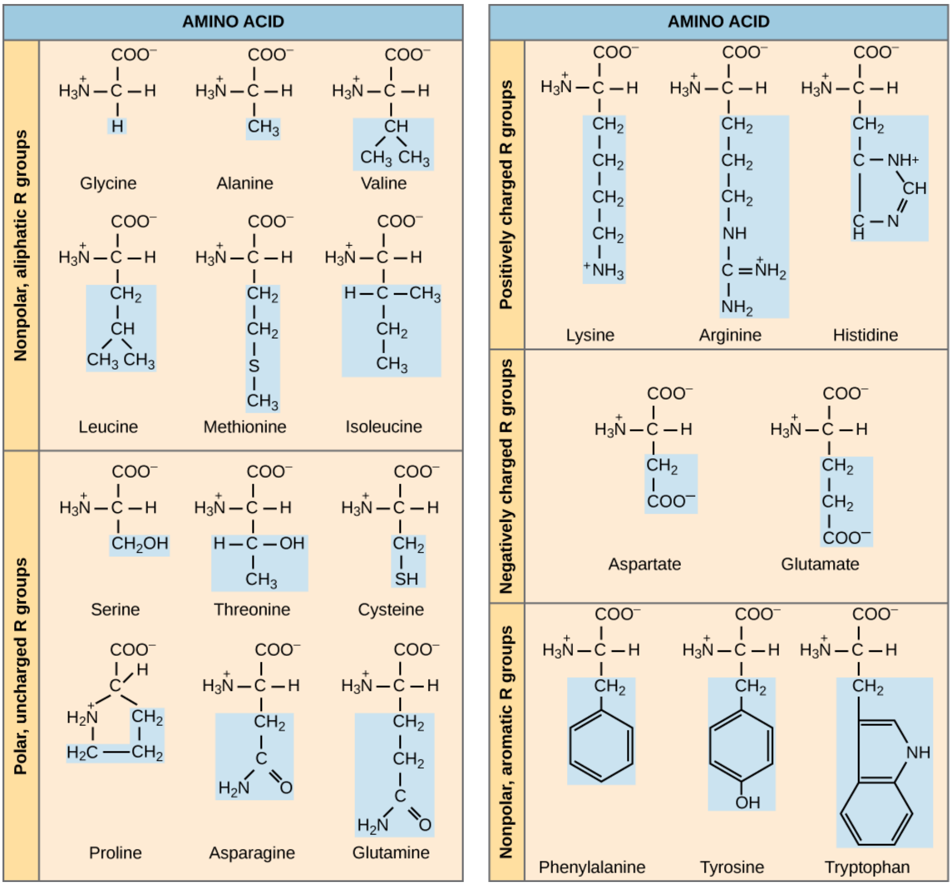


There is no definitive answer on why the L isomer is found in proteins. Both D and L isomers have identical energies. Repetitive substructure in proteins (helices, sheets, turns) require all amino acids to have the same configuration. Apparently, living systems evolved from L amino acids based upon an initial random choice. Amino acid names are often abbreviated as either **3** letters or single letter as shown in the next table:



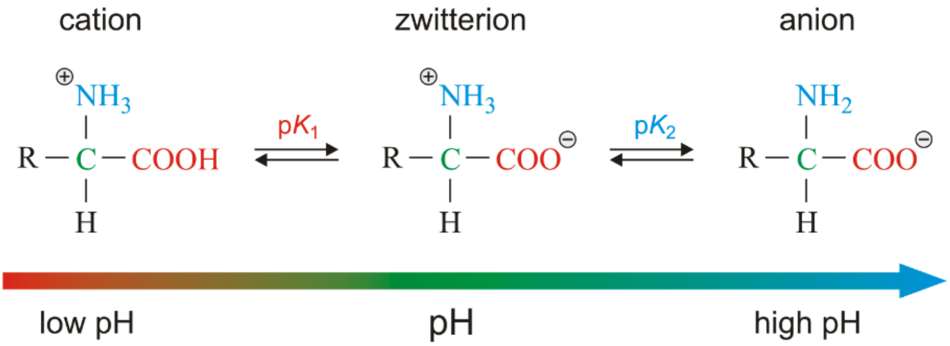
Amino Acid	Three Letter Code	One Letter Code
Alanine	Ala	A
Arginine	Arg	R
Aspartic Acid	Asp	D
Asparagine	Asn	N
Cysteine	Cys	C
Glutamic Acid	Glu	E
Glutamine	Gln	Q
Glycine	Gly	G
Histidine	His	H
Isoleucine	Ile	I
Leucine	Leu	L
Lysine	Lys	K
Methionine	Met	M
Phenylalanine	Phe	F
Proline	Pro	P
Serine	Ser	S
Threonine	Thr	T
Tryptophan	Trp	W
Tyrosine	Tyr	Y
Valine	Val	V

The twenty common amino acids:

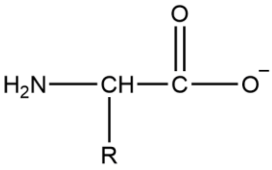


Zwitter Ions

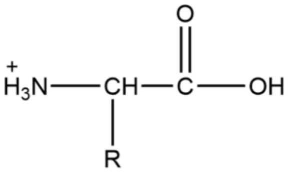
At physiological pH of 7, the carboxyl group of an amino acid is in its conjugate base form ($-COO^-$) and the amino group is in its conjugate acid form ($-NH^{3+}$). Thus, each amino acid can behave as either an acid or a base. Such molecules which can behave both like an acid and a base are termed amphoteric molecules. Also, molecules that bear both positive and negative charges are called zwitter ions.



Amino acids contain ionizable groups. The predominant ionic form of these molecules in solution therefore depends on the pH. At acidic pH (pH <7) the carboxyl group (-COOH) is uncharged and the ammonium group $(-NH^{3+})$ is protonated. Therefore, the net charge on the amino acid is positive (+1). At basic pH (pH >7) the carboxyl group (-COO-) loses its proton and becomes charged and the amino group $(-NH_2)$ becomes uncharged by losing the proton. Therefore, the net charge on the amino acid is negative (-1). The pH at which the amino acid has no net charge and is electrically neutral is called as the isoelectric point (pI).



$H_2N-CH(R)-C(=O)-O^-$



$H_3N^+-CH(R)-C(=O)-OH$

Classification of amino acids

I) **Nutritional classification** – Based on the ability of the body to synthesize amino acids, they can be classified as essential and non-essential amino acids.

1. *Essential amino acids* – These amino acids cannot be formed (synthesized) in the body and so,
it is essential to be included in the diet. Their deficiency in the body affects growth, health and protein synthesis. The following amino acids are essential:

1. Valine
2. Isoleucine
3. Lysine
4. Leucine
5. Methionine.
6. Tryptophan
7. Threonine
8. Phenyl alanine

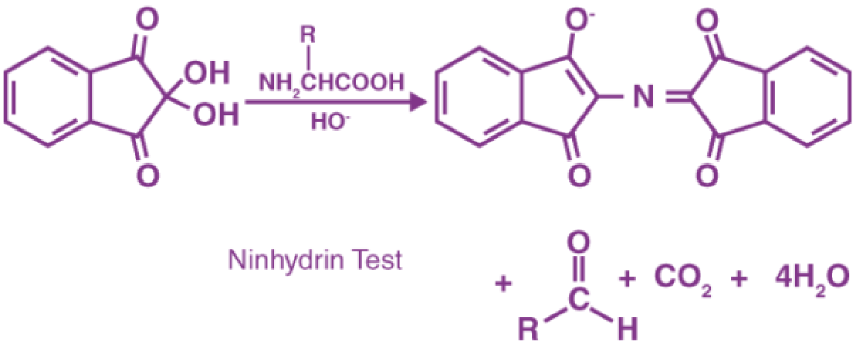
2. *Semi-essential amino acids* – These amino acids are formed in the body but not in sufficient amount for body requirements especially in children. The semi-essential amino acids are:

1. Arginine
2. Histidine

3. *Non-essential amino acids* – The amino acids that can be synthesized in the body by regular metabolism in enough amounts are called as non-essential amino acids. They need not be included in the diet. They are;

1. Glycine
2. Alanine
3. Cysteine
4. Tyrosine
5. Proline
6. Serine
7. Asparagine
8. Glutamine
9. Aspartic acid
10. Glutamic acid.

Identification of amino acids by ninhydrin test as follow:



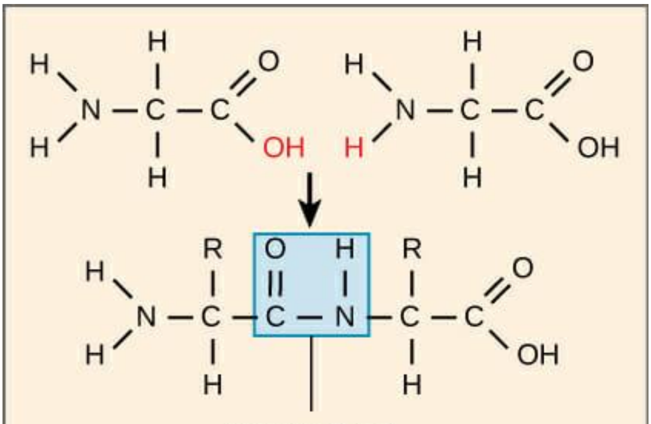
Proteins – Introduction

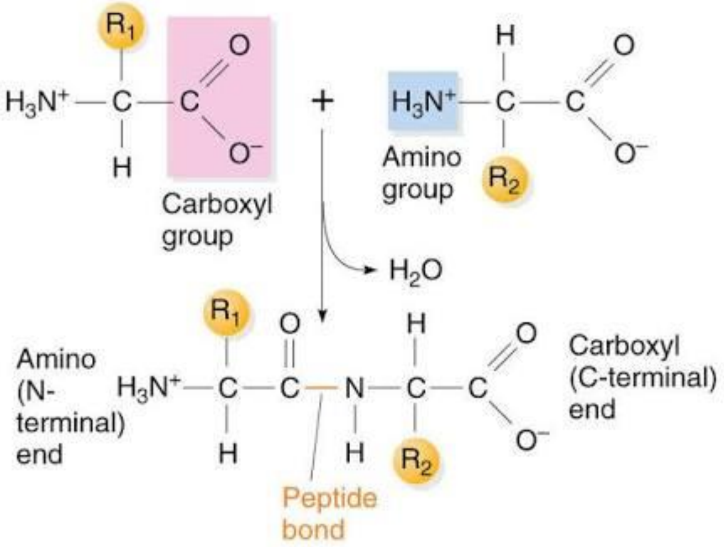
Proteins are polypeptides, which are made up of many α-amino acids linked together through amide linkages called peptide bonds. The structure of an amino acid contains amino group, carboxyl group, and R group which is usually carbon based and gives the amino acid it's specific properties. These properties determine the interactions between atoms and molecules, which are: van der Waals force between temporary dipoles, ionic interactions between charged groups, and attractions between polar groups.

Proteins form the very basis of life. They regulate a variety of activities in all known organisms, from replication of the genetic code to transporting oxygen, and are generally responsible for regulating the cellular machinery and determining the phenotype of an organism. Proteins accomplish their tasks in the body by three-dimensional tertiary and quaternary interactions between various substrates. The functional properties depend upon the proteins three-dimensional structure. The (3D) structures arise because particular sequences of amino acids in a polypeptide chain fold to generate, from linear chains, compact domains with specific structures. The folded domains either serve as modules for larger assemblies or they provide specific catalytic or binding sites.

Peptide Bonds

To make a protein, amino acids are connected together by a type of amide bond called a “peptide bond”. This bond is formed between the alpha amino group of one amino acid and the carboxyl group of another in a condensation reaction. When two amino acids join, the result is called a dipeptide, three gives a tripeptide, etc. Multiple amino acids result in a polypeptide (often shortened to “peptide”). Because water is lost in the course of creating the peptide bond, individual amino acids are referred to as “amino acid residues” once they are incorporated. Another property of peptides is polarity: the two ends are different. One end has a free amino group (called the “N-terminal”) and the other has a free carboxyl group (“C-terminal”).

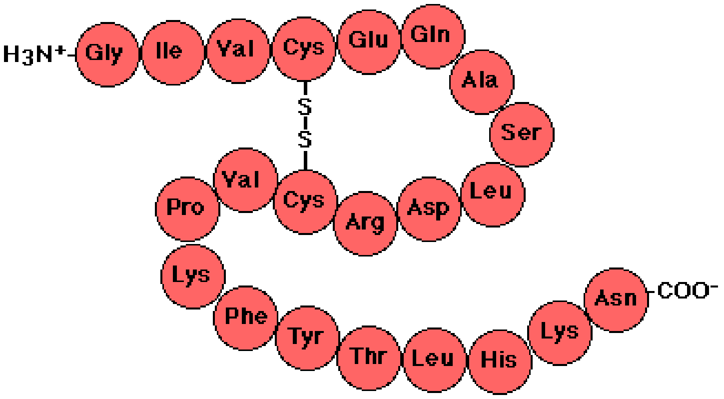




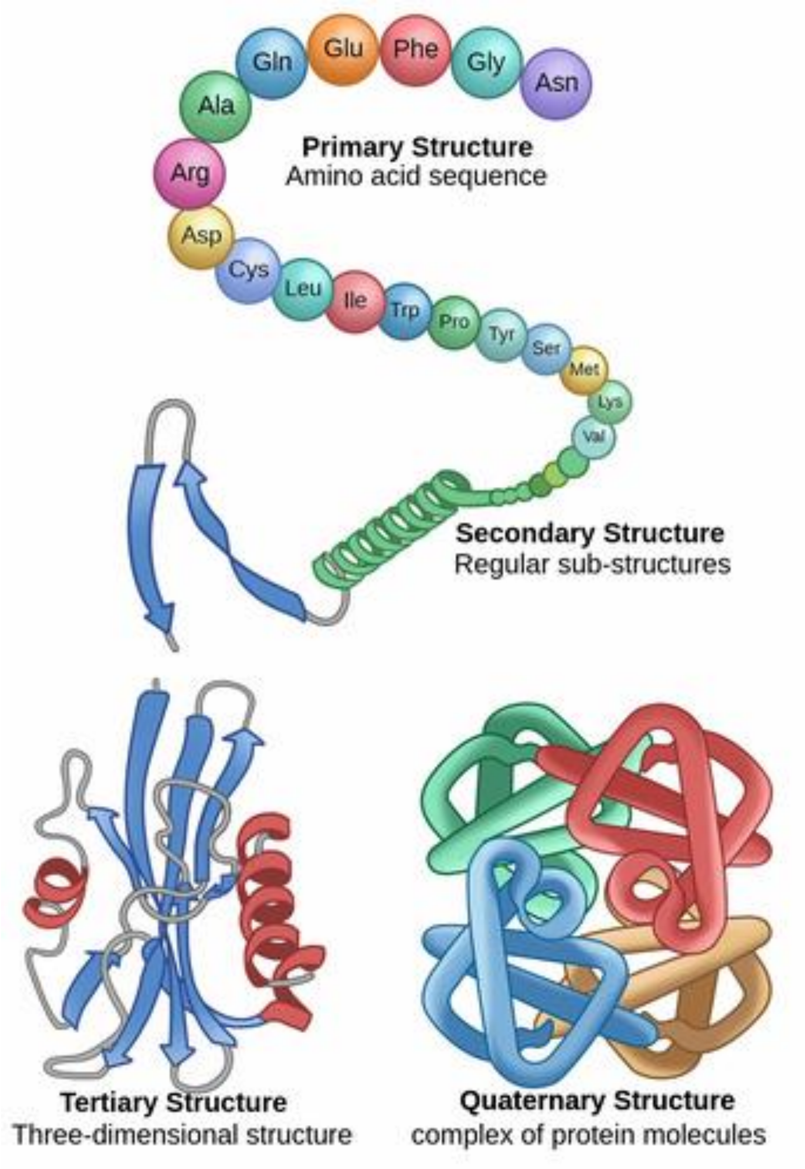
Protein Structure

It is convenient to discuss protein structure in terms of four levels (**Primary, secondary, tertiary, and quaternary**) of increasing complexity.

In primary structure _ Primary structure is simply the sequence of residues making up the protein. Thus, primary structure involves only the covalent bonds linking residues together.



All of these structures are shown in this figure.



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