MIND MAP

Biomolecules

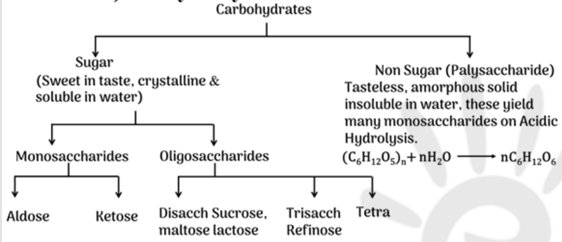
CARBOHYDRATES

Ex.

Glucose	$C_6H_{12}O_6$	$C_6(H_2O)_6$
Fructose	$C_6H_{12}O_6$	$C_6(H_2O)_6$
Cellulose and Starch	$(C_6H_{10}O_5)_n$	$(C_6(H_2O)_5)_n$

Carbohydrates are Polyhydroxy Aldehyde or Ketone. or

Substances which yield these (Polyhydroxy Aldehyde or Ketone) on Hydrolysis.



Monosaccharides (simple sugars)

These are the sugars which cannot be hydrolysed into smaller molecules.

Ex. - Glucose, Fructose, Ribose, Deoxynbose

If Aldehyde group is present in monosaccharide, then it is known as Aldose.

If Ketone group is present in Monosaccharide, then it is known as Ketose.

Oligosaccharides

These are the Sugars which yeild 2–10 Monosaccharides units on Hydrolysis.

Ex. - Sucrose, Maltose, Lactose

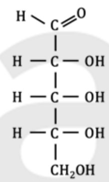
Polysaccharides

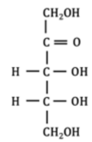
These are the non sugars which yeild a large no of Monosaccharide units on hydrolysis

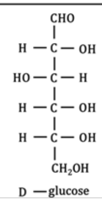
General formula - $(C_6H_{10}O_5)n$.

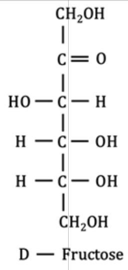
Ex.- Starch, Cellulose, Glycogen

On the basis of C-atom Monosaccharides can be further classified as, Trioses, Tetrases, Pentoses, Hexoses.

		Aldoses	Ketoses
3C	Tropose or Triose	Aldotriose	Ketotriose
4C	Tetrose	Aldotetrose	Ketotetrose
5C	Pentose	Aldopentose	Ketopentose
5C	Including —CHO	Aldopentose (Ribose)	

			Ketoses
5C	Including $-\underset{\underset{O}{\|}}{C}-$	Ketopentose	(Ributose) 
6C	Hexose	Aldohexose	Ketohexose

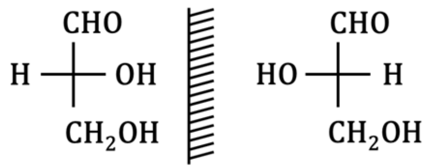
		Aldoses	
6C	Including —CHO	Aldohexose (Glucose)	

			Ketoses
6C	Including $-\underset{\underset{O}{\|}}{C}-$	Ketohexose (Fructose)	

Stereochemistry of Carbohydrates D & L-Sugars

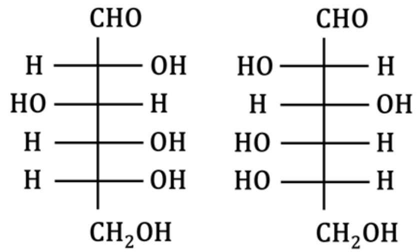
The series of Aldoses or Ketoses in which the configuration of the Penultimate C-atom (C-next to CH2–OH group) is described as D-sugars if –OH is towards RHS & L-sugars if it is towards LHS.

Fischer projection



D-Glyceraldehyde(+) L-Glyceraldehyde(-)

Aldohexose



D - Glucose L - Glucose

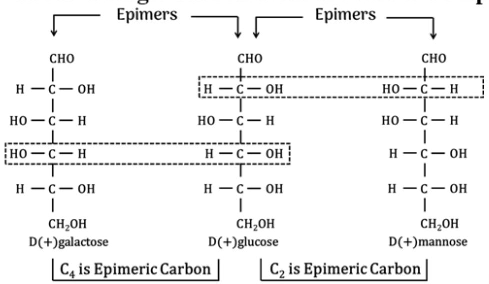
No. of C* = 4
No. of stereoisomers = $2^4 = 16$
No. of D-sugars = 8
No. of L-sugars = 8

MIND MAP

Biomolecules

Epimers

A pair of Diastereomers that differ only in the configuration about a single Carbon atom are said to be Epimers.



Preparation of Glucose

$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+}$ Dextro $C_6H_{12}O$ D-Glucose + Laevo $C_6H_{12}O$ D-Fructose

$(C_6H_{10}O_5)n$ Starch $\xrightarrow{nH^+/H_2O}$ $C_6H_{12}O_6$ D-Glucose

Structure of Glucose

It's molecular formula was found to be $C_6H_{12}O_6$

Reduction by HI / Red P/Δ

$CHO-(CHOH)_4-CH_2OH \xrightarrow{\text{Red P/HI}}$ n-Hexane

$H-C{=}O-(CHOH)_4-CH_2OH + NH_2-OH \longrightarrow H-C{=}N-OH-(CHOH)_4-CH_2OH$

Glucose Oxime

Ring Structure of Glucose

(i) Glucose does not give pink colour with Schiff' reagent.

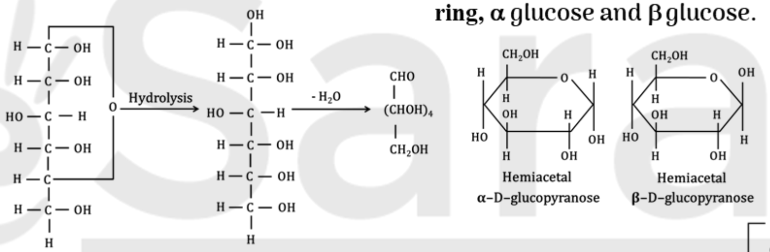
(ii) Does not form adduct with $NaHSO_3$, NH_3.

(iii) Glucose exists in two isomeric form.

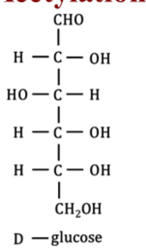
(iv) It shows mutarotation

(NH_3, $NaHSO_3$) but strong reagent (HCN, NH_2OH, $C_6H_5NH-NH_2$) break up ring.

Glucose exists in two forms as a ring, α glucose and β glucose.



Acetylation



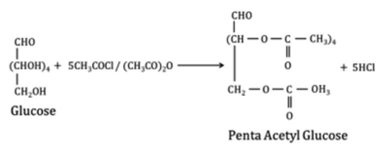
Reaction with HCN

$H-C{=}O-(CHOH)_4-CH_2OH + HCN \longrightarrow CN-H-C-OH-(CHOH)_4-CH_2OH$

Glucose Cyanohydrin

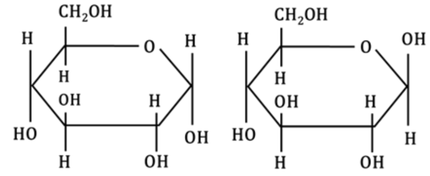
$C_6H_{12}O_6 \xrightarrow{HNO_3} COOH-(CH_2OH)_4-COOH$

(Saccharic acid)



Anomers

The two sugars that differs in configuration only on the Carbon that was the Carbonyl Carbon in the open chain form are called as Anomers.

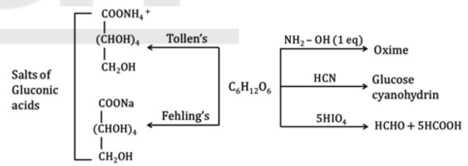


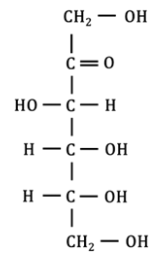
This change of Optical rotation with time is called Mutarotation.

It is caused by the conversion of α and β Glucopyranose Anomers into an equilibrium mixture of both.

Mutarotation is catalyzed by both Acid and Base, but also occurs even in pure water.

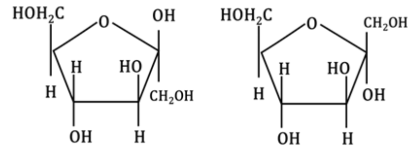
Mutarotation is a characteristic property of the cyclic hemiacetal form of glucose.





Fructose

Furanose structure (5 membered ring)



All Monosaccharides are reducing sugars and they show Mutarotation.

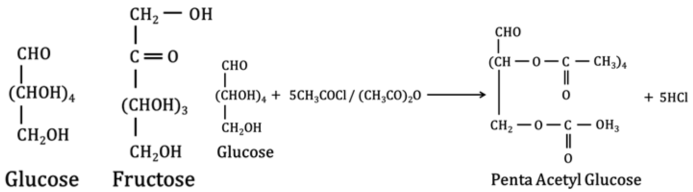
They will give positive Tollen's and Fehling Test

MIND MAP

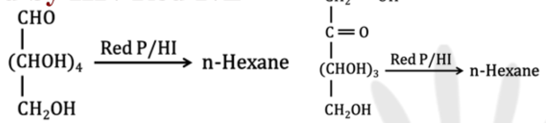
Biomolecules

General Reactions of Monosaccharies

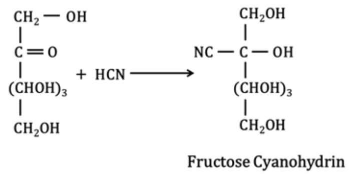
Acetylation



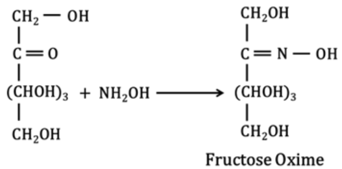
Red by HI / Red P/Δ



Reaction with HCN



Reaction with NH_2–OH (hydroxyl Amine)



Oxidation of Fructose

Fructose $\xrightarrow[\text{Fehling solution}]{\text{Tollen's Reagent}}$ Gluconic acid

Fructose $\xrightarrow{Br_2\text{ water}}$ No reaction

Disaccharides

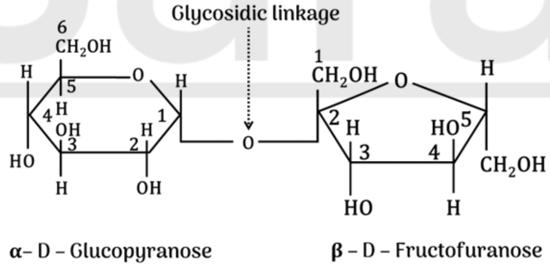
Lactose and Sucrose are disaccharides.

Sucrose is a non reducing sugar, gives negative test for Benedict and Tollen's reagent, they do not form Osazone and do not show Mutarotation.

Sucrose ($C_{12}H_{22}O_{11}$)

A dimer of α-D-Glucose & β-D-Fructose.
It is white, crystalline & sweet substance soluble in water obtained from the sugar cane.

Structure of Sucrose



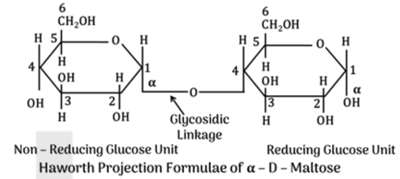
$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+}$ Dextro $C_6H_{12}O$ D-Glucose $\alpha[D] = -52.7°$ Dextro Isomer + Laevo $C_6H_{12}O$ D-Fructose $\beta[D] = -92.7°$ Laevo Rotatary

Mixture is laevorotatory (-)

Maltose

It is dimer of α-D-Glucose
It is obtained by partial hydrolysis of Starch by the enzyme diastase present in malt i.e., sprouted barley seeds.

$2\,(C_6H_{10}O_5)_n + nH_2O \xrightarrow{\text{Diastase}} nC_{12}H_{22}O_{11}$
Starch → Maltose

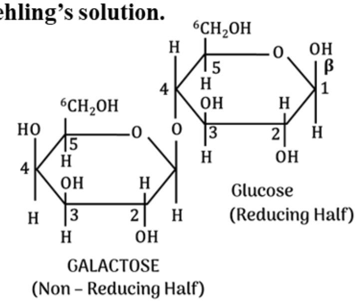


Haworth Projection Formulae of α – D – Maltose

Hydrolysis of one mole of maltose yields two moles of D-glucose.
Maltose is a reducing sugar since it reduces Tollen's reagents and Fehling's solutions.
(i) Both glucose units are present in the Pyranose form.
(ii) C_1 of one glucose unit is linked to C_4 of the other.

Lactose (Milk Sugar) $C_{12}H_{22}O_{11}$

Lactose occurs in milk and that is why it is called milk sugar.
Lactose on hydrolysis with dilute acid or by enzyme lactase, yields an equimolar mixture of D-glucose and D-galactose.
It is a reducing sugar, undergoes mutarotation and also reduces Tollen's or Fehling's solution.



MIND MAP

Biomolecules

Starch Amylum, $(C_6H_{10}O_5)_n$

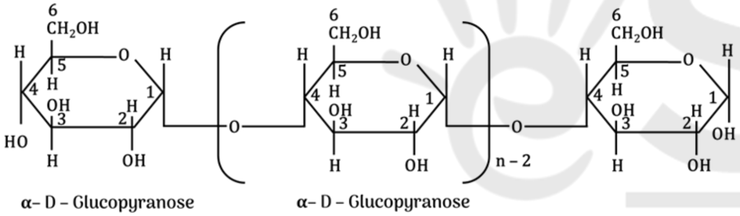
It is the chief food reserve material or storage polysaccharide of plants and is found mainly in seeds, roots wheat, maize, rice, potatoes, barley, bananas and sorghum.

Starch consists of two fractions, one being known as (amylose), which gives blue colour with Iodine.

This blue colour is believed to be due to the formation of an inclusion complex.

Amylopectin is insoluble in water and is stable towards both hydrolysis to maltose by the enzyme diastase and to D(+)-glucose by dilute acids (amylopectin gives about 50 percent of maltose).

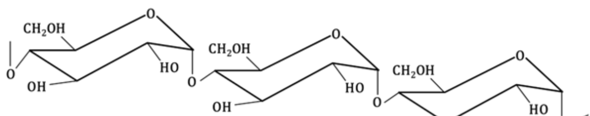
α–amylose consists of an unbranched chain, with a molecular weight varying between 10,000(n≈60) and 10,00,000(n≈6,000), The value of n depends on the source and treatment of α–amylose.



$$\underset{\text{Starch}}{(C_6H_{10}O_5)n} \xrightarrow{H^+/H_2O} (C_6H_{10}O_5)_{n'} \xrightarrow{H^+/H_2O} \underset{\text{Maltose}}{C_{12}H_{22}O_{11}}$$

$$\downarrow \text{Maltase}, H^+/H_2O$$

$$\underset{\text{D-Glucose}}{C_6H_{12}O_6}$$



(Amylose)

Glycogen $(C_6H_{10}O_5)_n$

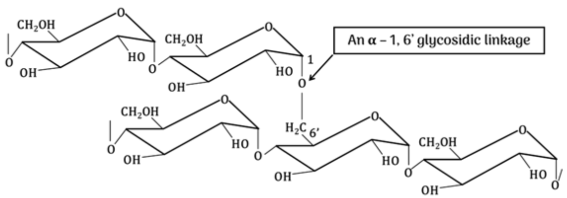
Glycogen is found in nearly all animals cells, occurring mainly in liver.

It is the reserve carbohydrate of animals so it is often known as 'animal starch'.

Glycogen is a white powder, soluble in water, the solution giving a purplish-red colour with Iodine.

On hydrolysis with dilute acid, glycogen gives D(+)-glucose.

Glycogen has a structure similar to Amylopectin, except that it has more cross-linking.



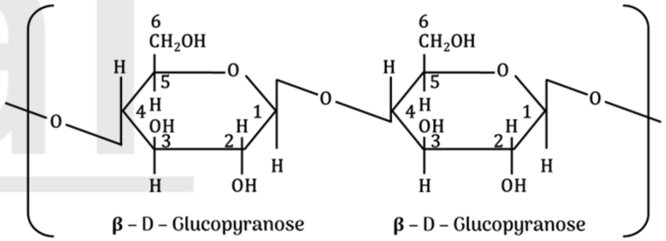
(Amylopectin)

Cellulose

Cellulose is colourless, solid which is insoluble in water & organic solvents.

But it is soluble in Ammonical Cupric Hydroxide (Schweizer's reagent) or in conc HCl cellulose is a regular polymer of d-glucopyranose residues connected by β–1,4 glycosidic linkages.

It is straight chain polymer.



Tests For Carbohydrates

(i) When heated in a dry test tube, it melts, turns brown and finally black, giving a characteristic smell of burning sugar.

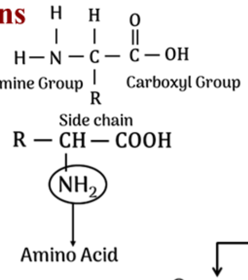
(ii) When warmed with a little concentrated H_2SO_4, it leaves a charred residue of carbon.

MIND MAP

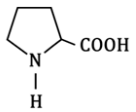
Biomolecules

Amino Acids And Proteins

Bifunctional compounds having an acidic carboxylic group(-COOH) & a basic amino(-NH_2) group are known as Amino acid. There are 20 amino acids commonly found in proteins and are standard amino acids. All are α amino acids.



Most of them have 1° amino group (– NH_2). However proline is a 2° amino.



Proline [P] (α- imino acid)

$CH_2 - COOH$ with NH_2 — (Gly) Glycine [G]

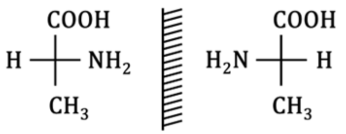
$Me - CH(NH_2) - COOH$ — Alanine [A]

$Ph - CH_2 - CH(NH_2) - COOH$ — Phenylalanine [F]

$HSCH_2 - CH(NH_2)CO_2H$ — Cysteine

All amino acids are chiral molecules with at least one chiral carbon (except glycine, H_2NCH_2COOH.

$CH_2(NH_2) - COOH$ — (Gly) Glycine [G]



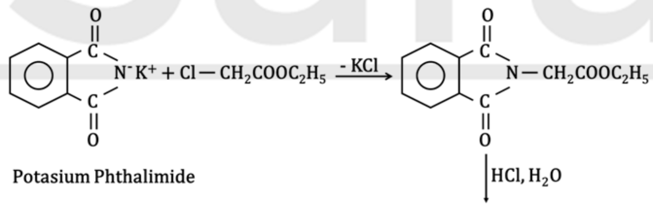
D-Alanine L-Alanine

Classification of Amino acids

- Occurence
  - Natural
  - Synthetic
- Requirement
  - Essential
  - Non Essential
  - Semi Essential
- Chemical Nature
  - Neutral
  - Acidic
  - Basic

Preparation of Amino Acids

Gabriel Phthalimide Synthesis



$Cl^- + H_3N - CH_2COOH$ + Phthalic acid

Amination of α-Halo acids

$$CH_3CH_2COOH \xrightarrow[\text{HVZ reaction}]{Br_2, P} CH_3CH(Br)COOH \xrightarrow{NH_3(excess)} CH_3CH(NH_2)COOH$$

α-Bromopropionic acid Alanine

Properties of Amino Acids

Although the amino acids are commonly shown as containing an amino group and a carboxyl group, $H_2NCHRCOOH$, certain properties, (both physical and chemical) are not consistent with this structure.

Physical Properties

In contrast to amines and carboxylic acids, the amino acids are nonvolatile crystalline solids, which melt with decomposition at fairly high temperatures.

They are insoluble in non-polar solvents like petroleum, ether, benzene and are appreciably soluble in water.

Their aqueous solutions behave like solutions of substances of high dipole moment.

Acidity and basicity constant are ridiculously low for –COOH and –NH_2 groups.

Glycine for example has $K_a = 1.6 \times 10^{-10}$ and $K_b = 2.5 \times 10^{-12}$, whereas most carboxylic acids have K_a values of about 10^{-5} and most aliphatic amines have K_b values of about 10^{-4}.

All these properties are quite consistent with a dipolar ion structure for the amino acids. $\overset{\oplus}{H_3N} - CH(R) - COO^-$ (Zwitter ion)

Physical properties - melting point, solubility, high dipole moment - are just what would be expected of such a salt.

$$\underset{\text{(II) Anion}}{H_2NCH(R)COO^-} \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} \underset{\text{(I) Neutral}}{\overset{\oplus}{H_3N}CH(R)COO^-} \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} \underset{\text{(III) Cation}}{\overset{\oplus}{H_3N}CH(R)COOH}$$

Isoelectric Point of Amino Acids

What happens when a solution of an amino acid is placed in an electric field depends upon the pH of the solution.

In quite alkaline solution, anions exceed cations, and there is a net migration of amino acid toward the anode.

In quite acidic solution, cations are in excess, and there is a net migration of amino acid toward the cathode.

If cation and anion are exactly balanced, there is no net migration ; under such conditions any one molecule exists as a positive ion and as a negative ion for exactly the same amount of time.

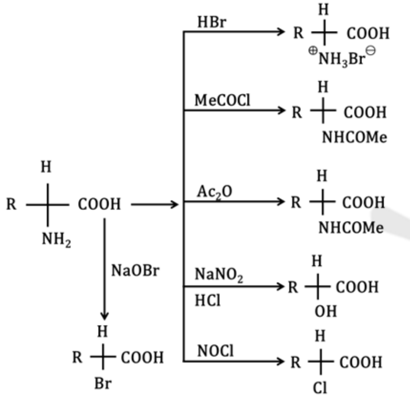
The hydrogen ion concentration of the solution in which a particular amino acid does not migrate under the influence of an electric field is called the isoelectric point (pH) of that amino acid.

MIND MAP

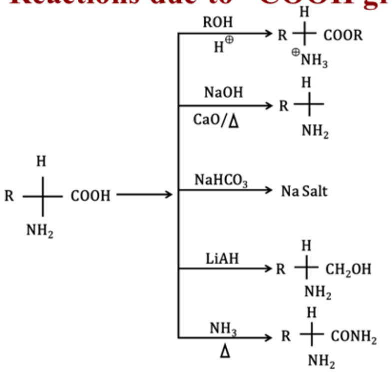
Biomolecules

An amino acid having –COOH group more than NH_2 group will have pI less than 7.
An amino acid having more – NH_2 more than COOH group such amino acid have pI more than 7.
Amino acid is positively charged (moves towards cathode) if pH of the solution < pI.
Amino acid is negatively charged (moves towards anode) if pH of the solution > pI.

Reactions due to –NH_2 group

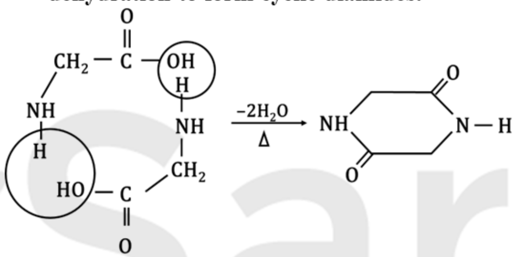


Reactions due to –COOH group

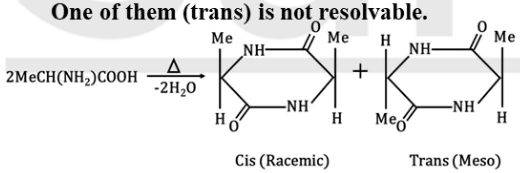


Heating Effect

(i) Heating of amino acids leads to intermolecular dehydration to form cyclic diamides.



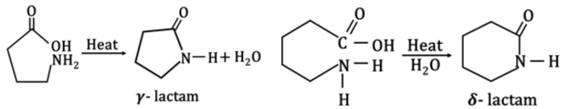
(ii) When alanine is heated, then two diastereomers are obtained.
One of them (trans) is not resolvable.

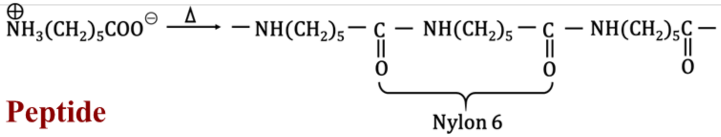


(iii) When β - amino acids are heated α, β - unsaturated salt are formed.

$$\underset{\displaystyle NH_2}{RCHCH_2COOH} \xrightarrow{\Delta} RCH = CH - COONH_4$$

(iv) γ, δ, ε - amino acids when heated alone gives γ, δ - lactam and polymer respectively.





Peptide

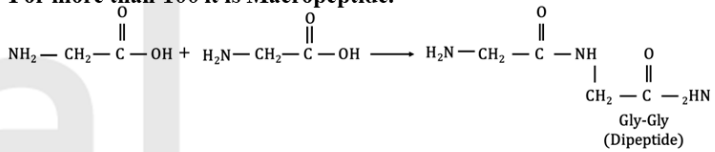
A peptide is a kind of amide formed by intermolecular reaction of the amino group of one amino acid and the carboxyl group of a second amino acid.

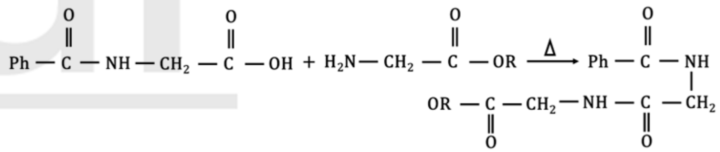
Dipeptides are made from two amino acids, tripeptides from three amino acids, etc. which may be the same or different.

If there are three to ten amino acid residues, the peptide is also called an Oligopeptide.

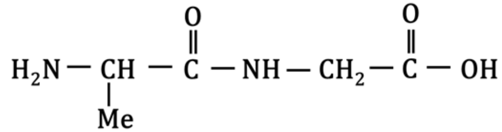
If they give 11 to 100 amino acid, they are Polypeptide.

For more than 100 it is Macropeptide.





By convention, the amino acid with the free amino group (N-terminal) is written at the left end and the one with the unreacted carboxyl group (C-terminal) at the right end.



Ala - Gly [Alanine-Glycine] (Dipeptide)

Total number of polypeptide possible = X^n.

[X = type of amino acid interacting,
n = number of amino acid molecule are interacting.]

Proteins

The name protein is taken from the Greek word "proteins", which means "first".

Of all chemical compounds, proteins must almost certainly be ranked first, for they are the substance of life.

Proteins make up a large part of the animal body, they hold it together and they run it.

They are found in all living cells.

Chemically, proteins are high polymers.

They are polyamides and the monomers from which they are derived are the a-amino carboxylic acids.

A single protein molecule contains hundreds or even thousands of amino acid units.

These units can be of twenty-odd different kinds.

A polypeptide with more than hundred amino acid residues, having molecular mass higher than 10,000 is called a Protein.

Proteins can be classified into two types on the basis of their molecular shape.

MIND MAP

Biomolecules

Fibrous Proteins

Globular Proteins

Structure of Proteins

Structure and shape of proteins can be studied at four different levels, i.e., primary, secondary, tertiary and quaternary, each level being more complex than the previous one.

Protein found in living system with definite configuration and biological activity is termed as native protein.

If a native protein is subjected to physical or chemical treatment, the hydrogen bonds are disturbed, then the protein is said to be denatured.

Thus denaturation leads to increase in entropy and loss of biological activity of the protein.

The denaturation may be reversible or irreversible.

During denaturation 2° and 3° structures are destroyed but 1° structure remains intact.

Thus, the coagulation of egg white on boiling of egg protein is an example of irreversible protein denaturation.

Tests of Proteins

Biuret Test

Addition of a very dilute solution of $CuSO_4$ to an alkaline solution of a protein is done.

A positive test is indicated by the formation of a pink violet to purple violet color.

Ninhydrin Test

The Ninhydrin test is a test for Amino acids and Proteins with a free $–NH_2$ group.

Amino acids are detected by Ninhydrin test.

All Amino acids give violet - coloured product with Ninhydrin (triketo hydroindene hydrate) except Proline and 4 - hydroxy Proline, which gives yellow colour with it.