14 Biomolecules

Classification of Carbohydrates & Glucose - Preparation and Structure

* Carbohydrates are called saccharides.

Classification

Carbohydrates

- Monosaccharides
  - Cannot be hydrolysed further to give simpler units of polyhydroxy aldehydes or ketones. Example - Glucose, fructose, ribose
- Oligosaccharides
  - Yield two to ten monosaccharides on hydrolysis. Example - Sucrose, maltose
- Polysaccharides
  - Yield a large number of monosaccharides on hydrolysis. Example - Starch, cellulose, glycogen

Carbohydrates

- Reducing sugars
  - Reduce Fehling's solution and Tollen's reagent
  - All monosaccharides are reducing sugars
  - Have free functional groups
- Non-reducing sugars
  - Do not reduce Fehling's solution and Tollen's reagent
  - Have bonded aldehydic or ketonic groups

Classification of Monosaccharides

* Monosaccharides are classified based on the number of carbon atoms and the functional group present in them.

* Different types of monosaccharides arelisted in the given table.

Carbon atoms	General term	Aldehyde	Ketone
3	Triose	Aldotriose	Ketotriose
4	Tetrose	Aldotetrose	Ketotetrose
5	Pentose	Aldopentose	Ketopentose
6	Hexose	Aldohexose	Ketohexose
7	Heptose	Aldoheptose	Ketoheptose

Glucose

Preparation of glucose

* By boiling sucrose with dilute HCl or H_2SO_4 in alcoholic solution

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

* By boiling starch with dilute H_2SO_4, at 393 K, under pressure

$$\underset{\text{Starch or cellulose}}{(C_6H_{10}O_5)_n} + nH_2O \xrightarrow[393K,\,2-3\text{atoms}]{H^+} \underset{\text{Glucose}}{nC_6H_{12}O_6}$$

Structure

$$\begin{array}{c} CHO \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array}$$

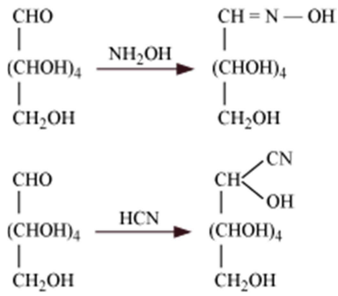
* Glucose has been assigned the above structure based on the following evidences.

(i) Molecular formula − $C_6H_{12}O_6$

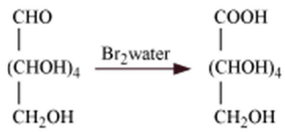
(ii) Suggestion of straight chain

$$\begin{array}{c} CHO \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array} \xrightarrow{HI,\,\Delta} \underset{n\text{-Hexane}}{CH_3-CH_2-CH_2-CH_2-CH_2-CH_3}$$

(iii) Confirmation of carbonyl (> C = O) group

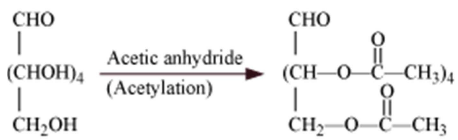


(iv) Confirmation of the presence of carbonyl group as aldehydic group



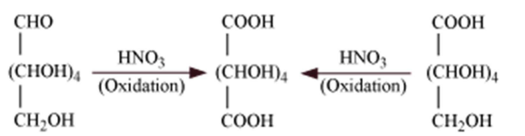
Gluconic acid

(v) Confirmation of the presence of five − OH groups



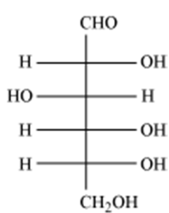
Glucose penta-acetate

(vi) Indication of the presence of a primary alcohol



Saccharic acid　　Gluconic acid

* The correct configuration of glucose is given by

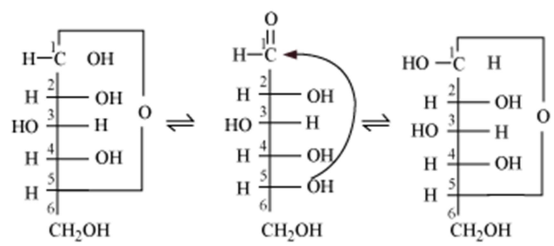


* Glucose is correctly named as D (+) − Glucose
* To understand **<u>the concept</u>** of configuration further, let us go through the following puzzle.

Cyclic Structure of Glucose

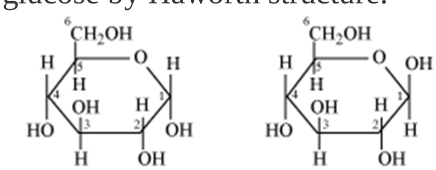
* The following reactions of glucose cannot be explained by its open-chain structure.
* Aldehydes give 2, 4-DNP test, Schiff's test, and react with $NaHSO_4$ to form the hydrogen sulphite addition product. However, glucose does not undergo these reactions.
* The penta-acetate of glucose does not react with hydroxylamine. This indicates that a free − CHO group is absent from glucose.
* Glucose exists in two crystalline forms, α and β.

  The α-form (m.p = 419 K) crystallises from a concentrated solution of glucose at 303 K and the β-form (m.p = 423 K) crystallises from a hot and saturated aqueous solution at 371 K. This behaviour cannot be explained by the open-chain structure of glucose.
* Glucose exists in two cyclic forms, which exist in equilibrium with the open- chain structure.



$\alpha - D - (+) -$ Glucose　　$\beta - D - (+) -$ Glucose

* Representation of the cyclic structure of glucose by Haworth structure:



$\alpha - D - (+) -$ Glucopyranose　　$\beta - D - (+) -$ Glucopyranose

Solved Examples

Ex.1 List the reactions of glucose which cannot be explained by its open-chain structure.

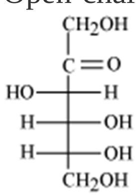
Sol. Limitations of the open-chain structure: Although the open-chain structure of D(+)-glucose explains most of its reactions, it fails to explain the following facts.

(i) D(+)-glucose does not undergo certain reactions of aldehydes. For example, glucose does not from 2, 4-DNP derivative, and does not respond to Schiff's reagent test.
(ii) Glucose reacts with NH_2OH to form an oxime, but glucose penta-acetate does not.
(iii) Glucose does not form the hydrogensulphite addition product with $NaHSO_3$.
(iv) The process of mutarotation in glucose

Structure of Fructose, Disaccharides & Polysaccharides

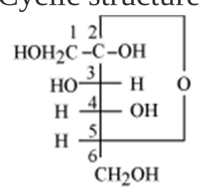
Structure of Fructose

* Open-chain structure:

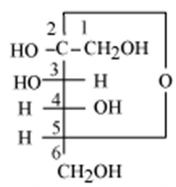


D – (–) – Fructose

* Cyclic structure:

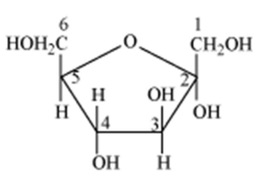


α – D – (–) – Fructofuranose

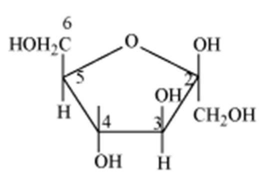


β – D – (–) – Fructofuranose

* Representation of the structure of fructose by Haworth structures



α – D – (–) – Fructofuranose



β – D – (–) – Fructofuranose

Disaccharides

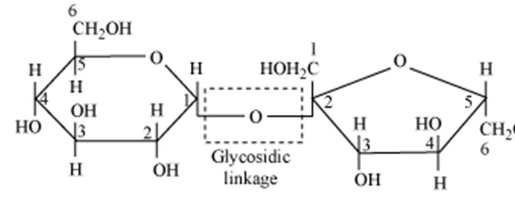
Glycosidic linkage – Linkage between two monosaccharide units through oxygen atom

Sucrose

* Hydrolysis of sucrose:

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\text{D}-(+)-\text{glucose}}{C_6H_{12}O_6} + \underset{\text{D}-(-)-\text{fructose}}{C_6H_{12}O_6}$$

* Structure:

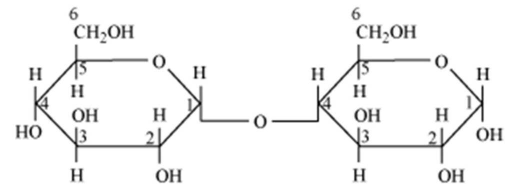


α – D – Glucose β – D – Fructose

* The product formed on the hydrolysis of sucrose is called invert sugar as the sign of rotation changes from dextro (+) of sucrose to laevo (–) of the product.
* Non-reducing sugar

Maltose

* Structure:

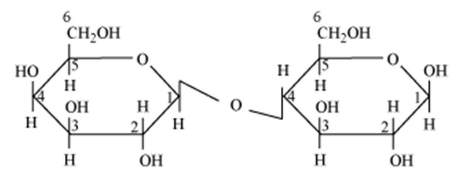


α – D – Glucose α – D – Glucose

* Reducing sugar

Lactose

* Commonly known as milk sugar
* Structure:



β – D – Galactose β – D – Glucose

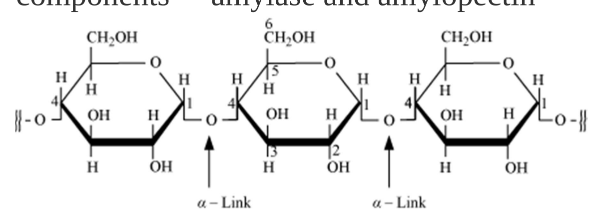
* Reducing sugar

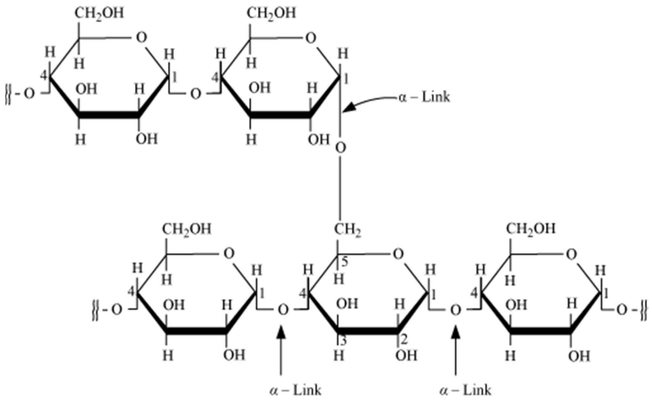
Polysaccharides

They mainly act as food storage or structural materials.

Starch

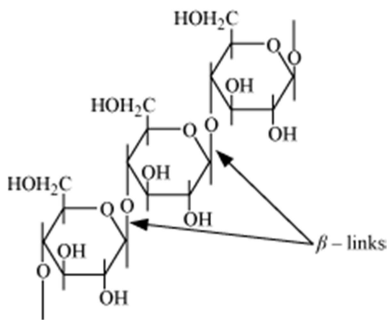
* Main storage-polysaccharide of plants
* Polymer of □-glucose; consists of two components – amylase and amylopectin





Cellulose

* Predominant constituent of the cell wall of plant cells.
* Straight-chain polysaccharide, composed of only □-D-Glucose



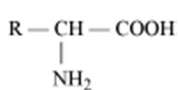
Glycogen

* Storage-polysaccharide in animal body
* Also known as *animal starch* because its structure is similar to amylopectin.

Proteins

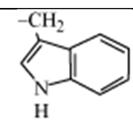
* Proteins are polymers of □ − amino acids.

Amino Acids



α-Amino acid
(R= side chain)

* Some amino acids with their symbols are listed in the given table.

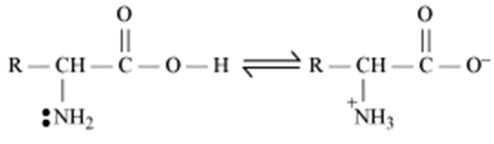
Name	Side chain, R	Three-letter symbol	One-letter code
1. Glycine	H	Gly	G
2. Alanine	− CH_3	Ala	A
3. Valine	$(H_3C)_2CH$−	Val	V
4. Leucine	$(H_3C)_2CH$− CH_2−	Leu	L
5. Isolecucine	$H_3C–CH_2–CH–$ (with CH_3 on CH)	Ile	I
6. Lysine	H_2N− $(CH_2)_4$ −	Lys	K
7. Glutamic acid	HOOC – CH_2 − H_2−	Glu	E
8. Aspartic acid	HOOC – CH_2 −	Asp	D
9. Cysteine	HS − CH_2 −	Cys	C
10. Methionine	H_3C− CH_2 – CH_2−	Met	M
11. Phenylalanine	C_6H_5− CH_2 −	Phe	F
12. Tryptophan		Trp	W

Classification of Amino Acids

* Based on the relative number of amino and carboxyl groups, they are classified as acidic, basic and neutral.
* Non-essential amino acids:
* Amino acids that can be synthesised in the body
* Example − Glycine, alanine, glutamic acid
* Essential amino acids:
* Amino acids that cannot be synthesised in the body, and must be obtained through diet
* Example − Valine, leucine, isolecuine

Properties of Amino Acids

* Colourless and crystalline solids
* Exist as dipolar ions, known as zwitter ions, in aqueous solution

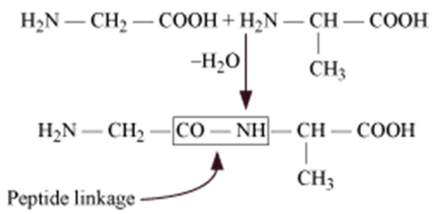


(Zwitter ion)

* In zwitter form, amino acids show amphoteric behaviour.
* All naturally occurring □-amino acids are optically active.

Structure of Proteins

* Proteins are polymers of □-amino acids, joined to each other by peptide linkage or peptide bond.
* Peptide linkage: Amide formed between −COOH group and −NH_2 group of two amino acid molecules.



Glycylalanine (Gly-Ala)

* Dipeptide − Contains two amino acid molecules

  Tripeptide − Contains three amino acid molecules

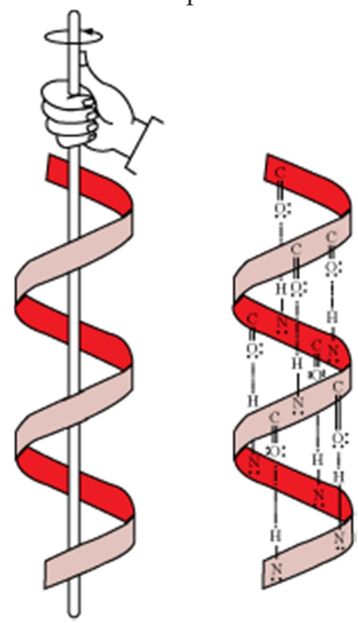
  Polypeptide − Contains more than ten amino acid molecules
* Based on the molecular shape, proteins are classified into two types −
* Fibrous proteins
* Globular proteins

Fibrous Proteins

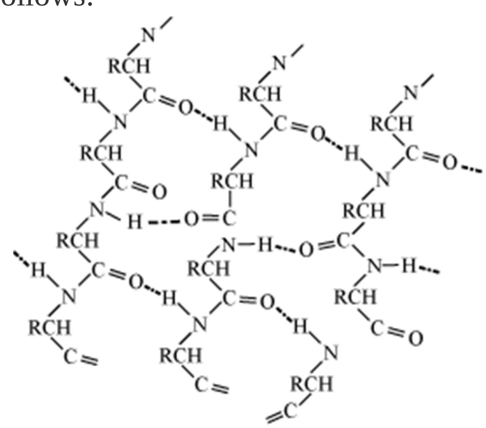
* In fibrous proteins, polypeptide chains run parallel and are held together by hydrogen and disulphide bonds.

Globular Proteins

* Polypeptide chains coil around, giving a spherical shape. Structures and shapes of proteins are studied at four different levels: primary, secondary, tertiary and quaternary.
* Primary structure of proteins: Contains one or more polypeptide chains, and each chain has amino acids linked with each other in a specific sequence. This sequence of amino acids represents the primary structure of proteins.
* Secondary structure of proteins: Shape in which a long polypeptide chain can exist; two types of secondary structures: □-helix, □-pleated sheet
* □-helix structure of protein is as follows:

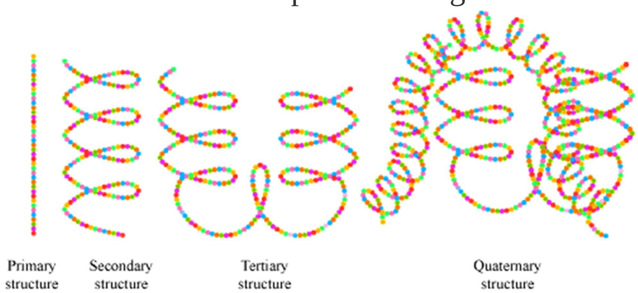


* □-pleated sheet structure of proteins is as follows:



* Tertiary structure of proteins: Overall folding of the polypeptide chains; results in fibrous and globular proteins; secondary and tertiary structures of proteins are stabilised by hydrogen bonds, disulphide linkages, van der Waals forces and electrostatic forces.

* Quaternary structure of proteins: Spatial arrangement of subunits, each containing two or more polypeptide chains
* The diagrammatic representations of the four structures of proteins are given below.



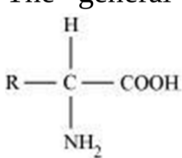
Denaturation of Proteins

* Loss of biological activity of proteins due to the unfolding of globules and uncoiling of helix.
* Example − Coagulation of egg white on boiling, curdling of milk

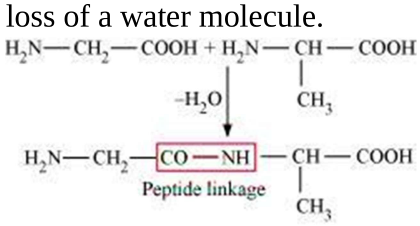
Solved Examples

Ex.1 Define the following terms in relation to proteins:
(i) Peptide linkage (ii) Denaturation

Sol. (i) ***Peptide linkage*:**
The general formula of amino acids is



. Proteins are formed by the bonding of large number of amino acids in a specific sequence. The bond with which amino acids are joined during the formation of proteins is known as the peptide bond or peptide linkage. Peptide linkage is an amide (− CO− NH−) bond formed between− COOH and − NH_2 groups by the loss of a water molecule.



(ii) ***Denaturation*:** The structure of a protein is essential to its activity. When a protein is subjected to physical change (such as change in temperature) or chemical change (such as change in pH), it loses its biological activity. This is known as denaturation of protein.

Ex. 2 Explain what is meant by
(i) A peptide linkage
(ii) A glycosidic linkage

Sol. (i) A peptide linkage : (Refer from above question)
(ii) The linkage formed by the reaction of the − OH group of anomeric carbon of a monosaccharide with the − OH group of other monosaccharide is called **glycosidic linkage**.

Ex.3 Explain the following terms:
(i) Invert sugar **(ii)** Polypeptides

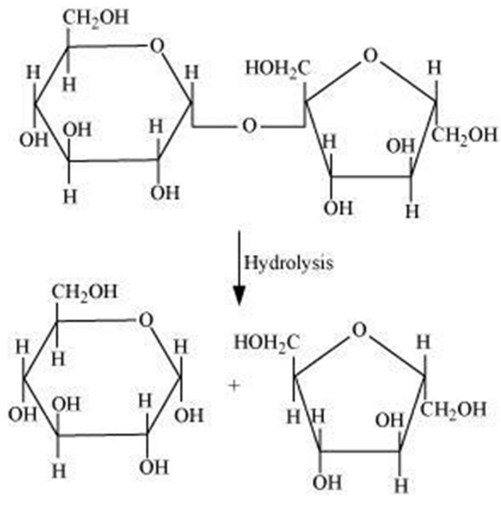
OR

Name the products of hydrolysis of sucrose. Why is sucrose not a reducing sugar?

Sol. (i) The product formed on the hydrolysis of sucrose with dilute acids or enzyme invertase is called **invert sugar**. These are known so because the sign of rotation changes from dextro (+) to laevo (−).
(ii) Two amino acids combine to form a peptide bond. When the number of combining amino acids is more than ten, the product obtained is known as **polypeptide**.

OR

On hydrolysis, sucrose gives one molecule of ∝-D glucose and one molecule of □- D-fructose.



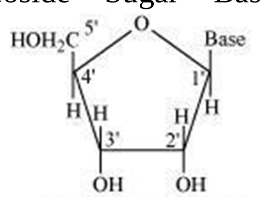
α – D – glucose β – D – fructose

The two hexoses in sucrose are joined through a glycosidic linkage involving C-1 of glucose and C-2 of fructose. Thus, sucrose is non-reducing sugar.

Ex.4 State clearly what are known as nucleosides and nucleotides.

Sol. A nucleoside is formed by the attachment of a base to $1'$ position of sugar.

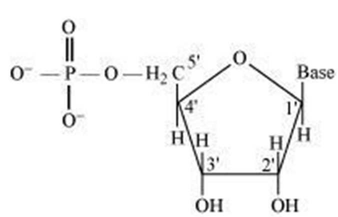
Nucleoside = Sugar + Base



Structure of a nucleoside

On the other hand, all the three basic components of nucleic acids (i.e., pentose sugar, phosphoric acid, and base) are present in a nucleotide.

Nucleotide = Sugar + Base + Phosphoric acid



Structure of a nucleotide

Enzymes, Vitamins & Nucleic Acids

Enzymes

* Enzymes are biocatalysts.
* Specific for a particular reaction and for a particular substrate
* For example, maltase catalyses hydrolysis of maltose

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} \xrightarrow{\text{Maltase}} \underset{\text{Glucose}}{2C_6H_{12}O_6}$$

* The name of an enzyme ends with '− ase'.
* Reduce the magnitude of activation energy

Vitamins

* Organic compounds required in the diet in small amounts to maintain normal health, growth and nutrition
* Classified into groups −
  Water-soluble vitamins: Vitamin C, B-group vitamins (B_1, B_2, B_6, B_{12})
  Fat-soluble vitamins: Vitamins A, D, E and K
* Some vitamins with their sources and the diseases caused by their deficiency are given in the following table.

Solved Examples

Ex.5 Name two water soluble vitamins, their sources and the diseases caused due to their deficiency in diet.

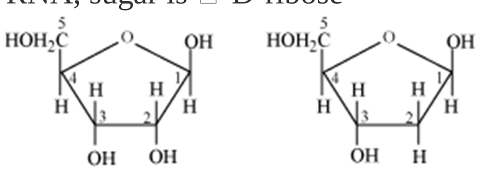
Sol. Thiamine (vitamin B_1) & riboflavin (vitamin B_2) are soluble in water.

Thiamine is found in unpolished rice, whole cereals, yeast, egg yolk, milk, green vegetables, etc. The deficiency of thiamine causes beriberi and loss of appetite.

Riboflavin is found in egg yolk, liver, milk and green leafy vegetables. The deficiency of riboflavin causes cracked lips, sore tongue and skin disorders.

Nucleic Acids

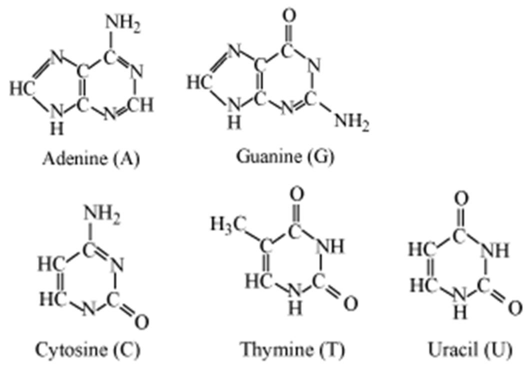
* Two types:
* Deoxyribonucleic acid (DNA)
* Ribonucleic acid (RNA)
* Chemical composition of nucleic acids:
* Nucleic acid contains a pentose sugar, phosphoric acid and a base (heterocyclic compound containing nitrogen).
* In DNA, sugar is □-D-2-deoxyribose; in RNA, sugar is □-D-ribose



β – D – ribose β – D – 2 – deoxyribose

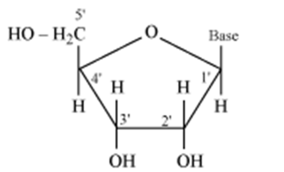
* Bases in DNA: Adenine (A), guanine (G), cytosine (C) and thymine (T)
* Bases in RNA: Adenine (A), guanine (G), cytosine (C) and uracil (U)

Name of vitamins	Sources	Deficiency diseases
Vitamin A	Fish liver oil, carrots, butter and milk	Xerophthalmia, night blindness
Vitamin B_1	Yeast, milk, green vegetables and cereals	Beri beri
Vitamin B_2	Milk, egg-white, liver, Kidney	Cheilosis, digestive disorders and burning sensation of the skin
Vitamin B_6	Yeast, milk, egg yolk, cereals and grams	Convulsions
Vitamin B_{12}	Meat, fish, egg and curd	Pernicious anaemia
Vitamin C	Citrus fruits, *amla* and green leafy vegetables	Scurvy
Vitamin D	Exposure to sunlight, fish and egg yolk	Rickets and osteomalacia
Vitamin E	Vegetable oils like wheat germ oil, sunflower oil	Increased fragility of RBCs and muscular weakness
Vitamin K	Green leafy vegetables	Delay of blood clotting

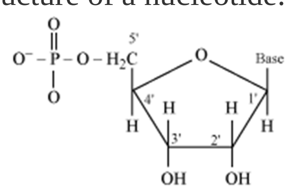


Structure of nucleic acids

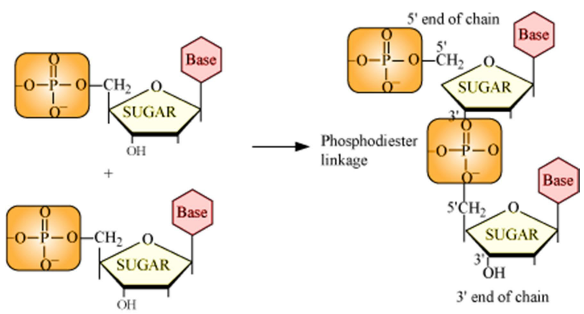
* Structure of a nucleoside:



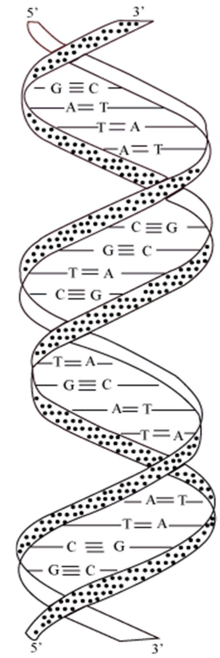
* Structure of a nucleotide:



* Formation of a di-nucleotide:



* In secondary structure, the helices of DNA are double-stranded while those of RNA are single-stranded.
* The two strands of DNA are complementary to each other.
* Reason: H-bonds are formed between specific pairs of bases.
* Double-strand helix structure of DNA:



* Types of RNA:
* Messenger RNA (m-RNA)
* Ribosomal RNA (r-RNA)
* Transfer RNA (t-RNA)
* Functional differences between RNA and DNA:

	RNA	DNA
1	DNA is not responsible for heredity.	DNA is the chemical basis of heredity.
2	Proteins are synthesised by RNA molecules in the cells.	DNA molecules do not synthesise proteins, but transfer coded messages for the synthesis of proteins in the cells.