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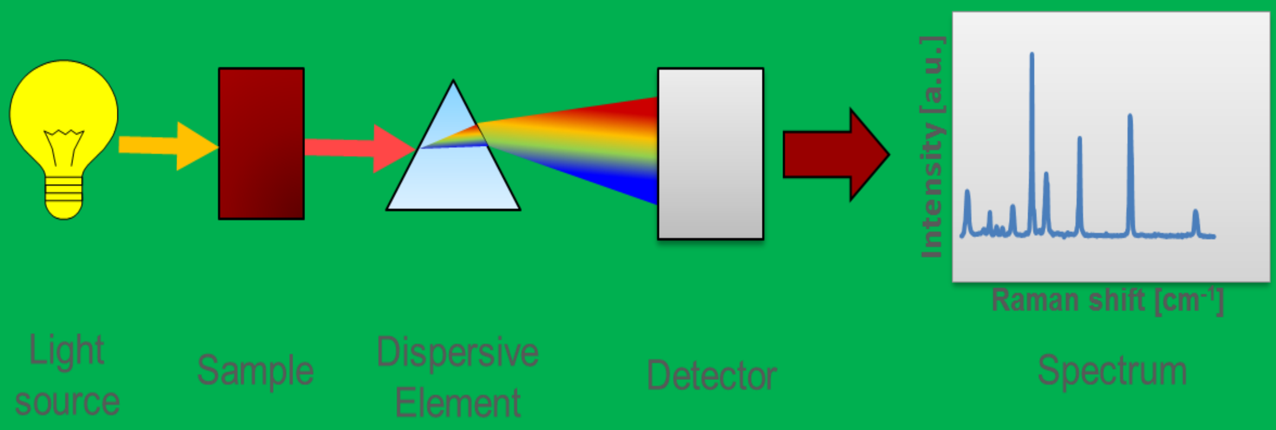
B.Sc VI SEMESTER

APPLIED CHEMISTRY



DEPARTMENT OF CHEMISTRY
SCHOOL OF SCIENCES
UTTARAKHAND OPEN UNIVERSITY
HALDWANI, (NAINITAL)
UTTARKHAND-263139

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SCHOOL OF SCIENCE

DEPARTMENT OF CHEMISTRY

UTTARAKHAND OPEN UNIVERSITY

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UNIT- 1 CARBOHYDRATES

CONTENTS

1.1 OBJECTIVES

After going through this unit you will be able to:

- Define carbohydrates,
- Differentiate and classify the three major groups of carbohydrates,
- Define anomers, mutarotatation, configuration and mechanism of osazone formation,
- Describe ether and ester formation,
- Differentiate between reducing and non reducing sugars,
- Define interconversion of glucose and fructose,
- Describe the chain lengthening and chain shortening of aldose
- Discuss about Erythreo and threo distereomers conversion of glucose
- Determination of ring size of monosaccharides,
- Know about configuration of monosaccharides
- Discuss about Erythreo and threo distereomers conversion of glucose
- Describe ether and ester formation,
- Determination of ring size of monosaccharides,
- Cyclic structure of D-glucose
- Mechanism of mutarotation
- Types of disaccharides and their properties
- Structure of ribose and deoxyribose

1.2 INTRODUCTION

Carbohydrates are a class of naturally occurring organic compounds of carbon, hydrogen andoxygen which are primarily produced by plants. They are extremely widespread in plants comprising upto 80% of dry weight. These are ultimate source of our food. In higher animals the simple sugar glucose is an essential constituent of blood and occurs in a polymeric form as glycogen in the liver and muscle.

In the green plants, carbohydrates are produced by a process called photosynthesis. This process involves the conversion of simple compounds CO_2 and H_2O into glucose ($C_6H_{12}O_6$) and is catalysed by green colouring pigment chlorophyll present in the leaves of plants. The energy required for this conversion is supplied by sun in the form of sunlight.Carbohydrates are very useful for human beings. They provide us all the three basic necessities of life i.e., foog (starch containing grain), clothes (cellulose in the form of cotton , linen and rayon) and shelter (cellulose in the form of wood used for making our houses and furniture etc.). Carbohydrates are also important to the economy of many nations. For example, sugar is one of the most important commercial commotidies. The term carbohydrates arose because the general formula for most of them could be written as $C_x (H_2O)_y$ and thus they may be regarded as hydrates of carbon. However, this definition was not found to be correct e.g., rhamnose, a carbohydrate, is having the formula $C_6H_{12}O_5$ while acetic acid having formula $C_2H_4O_2$ is not a carbohydrate. Simple carbohydrates are also known as sugars or saccharides (Latin: Saccharum; Greek : Sakcharon, Sugar) and the ending of the names of most sungars is –ose. Examples: glucose, fructose, sucrose, maltose, arabinose, etc.Chemically, carbohydrates contain mainly two functional groups, carbonyl group (aldehyde or or ketone) and a number of hydroxyl groups. Accordingly carbohydrates are now defined optically active polyhydroxy aldehydes or polyhydroxy ketones or the compound that can be hydrolysed to either of them.

The carbohydrates are an important class of naturally occurring organic compounds. They occur naturally in plants (where they are produced photosynthetically), when the word "carbohydrate" was coined, it originally referred to compounds of general formula C n(H2O) n . However, only the simple sugars or monosaccharaides fit this formula exactly. The other types of carbohydrates, oligosaccharides,and polysaccharides, are based on monosaccharaides units and have slightly different general formula. Carbohydrates also called “saccharides” which means sugar in Greek.Many commonly encountered carbohydrates are polysaccharides, including glycogen, which is found in animals, and starch and cellulose, which occur in plant.

1.3CLASSIFICATION AND NOMENCLATURE

1.3.1 Classification

Carbohydrates, in general, may be classified into two classes:

1.3.1.1 **Sugars.** These are crystalline substances which are sweet and water soluble. For examples, glucose, fructose and cane sugar.

1.3.1.2 **Non-sugars**. These are tasteless, insoluble in water and amorphous. For example. Starch, cellulose, etc.

However, these days Carbohydrates are systematically classified into three major group:

1.3.2 Monosaccharides. The simplest carbohydrates that cannot be hydrolysed into simpler carbohydrates, are called monosaccharides.depending upon whether they contain an aldehyde or keto groups, they may be called aldoses or ketoses. For example, a five carbon monosaccharide having aldehyde group is called aldopentose and six carbon monosaccharide containing a keto group is called keto-hexose. A few examples of monosaccharides are given below:

Aldotetroses. Erythrose and Threose; $CH_2OH(CHOH)_2$

CHO. Ketotetroses. Erythrulose, $CH_2OHCOCHOHCH_2OH$.

Aldopentoses. Ribose, arabinose, Xylose and Lyxose. $CH_2OH(CHOH)_2$ CHO.

All have a common molecular formula but different structures.

Ketopentoses. Ribulose and Xylulose;$CH_2OHCO(CHOH)_2$ CH_2OH.

Aldohexoses. Glucose, mannose, galactose; $CH_2OH(CHOH)_4$ CHO.

Ketohexoses. Fructose, Sorbose etc. $CH_2OHCO(CHOH)_2$ CH_2OH.

1.3.3.Oligosaccharides. These are the carbohydrates which can be hydrolysed into a definite number of monosaccharide molecules. Depending upon the number of monosaccharides that are obtained from them on hydrolysis, they may be called di-, tri- or tetra- saccharides: For example:Disaccharides: sucrose, lactose, maltose. All these have the same molecular formula $C_{12}H_{22}O_{11}$. Trisaccharides: raffinmose ($C_{18}H_{22}O_{16}$).Tetrasaccharides: stachyose ($C_{24}H_{42}O_{21}$).

1.3.4.Polysaccharides. Carbohydrates that yield a large number of molecules (more than ten molecules) of monosaccharides on hydrolysis are called polysaccharides. The common examples are starch, cellulose, glycogen, etc.

1.3.5.Nomenclature;

Carbohydrates contain hydroxy and aldehydic or ketonic groups. They are named according to IUPAC system of nomenclature

Compound	Common name	IUPAC name
$CH_2OHCHOHCHO$	Glyceraldehyde	2, 2-dihydroxy propanol
$CH_2OHCOCH_2OH$	Dihydroxyacetone	1,2-dihydroxy propanone
$CH_2OH(CHOH)_4$ CHO	Glucose	2,2,4,5,6-pentahydroxyhexanal
$CH_2OH(CHOH)_2COCH_2OH$	Fructose	1,2,4,5,6-pentahydroxyhexan-2-one

1.4MONOSACCHARIDES

The monosaccharides are again classified on the basis of two factors:

1.By the carbonyl function. Those containing the aldehydic function,-CHO, are called aldoses. Others containing the keto group, -CO-, are called ketoses.

2.By the number of Carbonyl atoms in the molecule. These monosaccharides containing 2,4,5,6 etc., carbon atoms are designated as trioses, tetroses, pentoses, hexoses, and so on.

Monosaccharides are polyhydric aldehydes and ketones which cannot be hydrolysed into simpler carbohydrates.

1.4.1Structures of monosaccharides

The common monosaccharides are given in table.

Table. Monosaccharides

No of carbn atoms	**Class**	**Molecular formula aldoses**	**Structural formula**	**Examples**

2	aldotrioses	$C_2H_6O_2$	$CH_2OHCHOHCHO$	Glyceraldehyde
4	aldotetroses	$C_4H_8O_4$	$CH_2OH(CHOH)_2CHO$	Erythrose, Threose
5	Aldopentose	$C_5H_{10}O_5$	$CH_2OH(CHOH)_2CHO$	Arabinose, Ribose, Xylose, Lyxose
6	aldohexoses	$C_6H_{12}O_6$	$CH_2OH(CHOH)_4CHO$	Glucose, galactose, mannose, allose, talose, gulose, iodose, etc.
2	ketotrioses	$C_2H_6O_2$	$CH_2OHCOCH_2OH$	dihydroxyacetone
4	ketotetroses	$C_4H_8O_4$	$CH_2OHCOCHOHCH_2OH$	erythrulose
5	ketopentoses	$C_5H_{10}O_5$	$CH_2OHCO(CHOH)_2CH_2OH$	Ribulose, Xylulose
6	ketohexoses	$C_6H_{12}O_6$	$CH_2OHCO(CHOH)_2CH_2OH$	Fructose, Sorbose, Tagatose, Psicose

1.4.2 Glucose

Glucose is most common monosaccharide. It is known as Dextrose because it occurs in nature principally as optically dextrorotatory isomer. Glucose is found in most sweet fruits, especially grapes (20-20%), and honey. It is an essential constituent of human blood. The blood normally conatains 65 to 110 mg (0.06 to 0.1%) of glucose per 100 ml. In diabetic persons the

level may be much higher. In combined form glucose occurs in abundance in cane sugar and polysaccharides such as starch and cellulose.

Preparation of Glucose

1. **From sucrose (Cane sugar)**

When sucrose in boiled with dilute HCl or H2SO4 in alcoholic solution, glucose and fructose are obtained in equal amounts.

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

2. **From Starch**

Glucose is produced commercially by the hydrolysis of starch by boiling it with dilute H2SO4 at high temperature under pressure.

$$\underset{\text{Starch}}{(C_6H_{10}O_5)_n} + nH_2O \xrightarrow{HCl} \underset{\text{Glucose}}{nC_6H_{12}O_6}$$

in this process, an aqueous solution of starch obtained from corn is acidified with dilute H2SO4. It is then heated with high pressure steam in an autoclave. When the hydrolysis is complete, the liquid is neutralized with sodium carbonate to pH of 4-5. The resulting solution is concentrated under reduced pressure to get the crystals of glucose.

Physical properties of glucose

Some important physical properties of glucose are mentioned as under:

1. It is colourless sweet crystalline compound having m.p.419 K.
2. It is readily soluble in water, sparingly soluble in alcohol and insoluble in ether.
3. It forms a monohydrate having m.p. 291 K.
4. It is optically active and its solution is dextrorotatory. The specific rotation of fresh solution is + 112^0 C.
5. It is about three fourth as sweet as sugarcane i.e., sucrose.

Chemical properties of glucose

Chemical properties of glucose can be studied under the following headings:

(A) Reactions of aldehydic group

1. **Oxidation**. (a) Glucose gets oxidized to gluconic acid with mild oxiding agents like bromine water

$$\underset{\text{Glucose}}{CH_2OH\ (CHOH)_4CHO} \xrightarrow[Br_2,\ H_2O]{[O]} \underset{\text{Gluconic acid}}{CH_2OH\ (CHOH)_4COOH}$$

Only-CHO group is affected.

(b) A strong oxidizing agent like nitric acid oxidizes both the terminal groups viz. –CH_2OH and CHO groups and saccharic acid or glucaric acid is obtained.

$$\underset{\text{Glucose}}{CH_2OH\ (CHOH)_4CHO} \xrightarrow[[O]]{HNO_3} \underset{\text{Glucaric acid}}{COOH\ (CHOH)_4COOH}$$

(c) Glucose gets oxidized to gluconic acid with ammonical silver nitrate (Tollen's reagent) and alkaline copper sulphate (Fehling solution). Tollen's reagent is reduced to metallic silver (silver mirror) and Fehling solution to cuprous oxide which is a red precipitate.

(i) With Tollen's reagent

$$AgNO_2 + NH_4OH \longrightarrow AgOH + NH_4NO_2$$

$$2AgOH \longrightarrow Ag_2O + H_2O$$

$$\underset{\text{Glucose}}{CH_2OH(CHOH)_4CHO} + Ag_2O \longrightarrow \underset{\text{Gluconic acid}}{CH_2OH(CHOH)_4COOH} + \underset{\text{Silver mirror}}{2Ag\downarrow}$$

(ii)With Fehling solution

$$CuSO_4 + 2NaOH \longrightarrow Cu(OH)_2 + Na_2SO_4$$

$$Cu(OH)_2 \longrightarrow CuO + H_2O$$

$$\underset{\text{Glucose}}{CH_2OH(CHOH)_4CHO} + 2CuO \longrightarrow \underset{\text{Gluconic acid}}{CH_2OH(CHOH)_4COOH} + \underset{\text{Red ppt.}}{Cu_2O}$$

2.**Reduction** (a) glucose is reduced to sorbitol or Glucitol on treatment with sodium amalgam and water.

$$\underset{\text{Glucose}}{CH_2OH(CHOH)_4CHO} + 2[H] \xrightarrow[H_2O]{Na/Hg} \underset{\text{Sorbitol}}{CH_2OH(CHOH)_4CH_2OH}$$

(b) On reduction with conc. HI and red P at 272 K glucose gives a mixture of n-hexane and 2- idohexane

$$\underset{\text{Glucose}}{CH_2OH(CHOH)_4CHO} \xrightarrow{HI/red\ P} \underset{\text{n-hexane}}{CH_3(CH_2)_4CH_3} + \underset{\text{2-Iodohexane}}{CH_3(CH_2)_3CHICH_3}$$

3.Reaction with HCN. Like aldehydes, glucose reacts with HCN forming cyanohydrins.

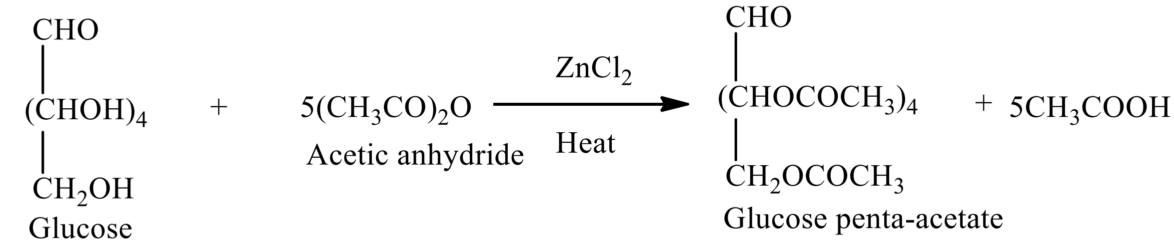
$$\underset{\text{Glucose}}{CH_2OH(CHOH)_4CHO} + HCN \longrightarrow \underset{\text{Glucose cyanohydrin}}{CH_2OH(CHOH)_4CH}\begin{matrix} \diagup OH \\ \diagdown CN \end{matrix}$$

4. Reaction with hydroxylamine. Glucose forms glucose oxime.

$$\underset{\text{Glucose}}{CH_2OH(CHOH)_4CHO} + NH_2OH \longrightarrow \underset{\text{Glucose oxime}}{CH_2OH(CHOH)_4CH{=}NOH} + H_2O$$

(A) Reactions of hydroxyl groups

1. **Reaction with acetic anhydride or acetyl chloride**. Glucose forms penta acetate with acetic anhydride of acetyl chloride.



2. **Reaction with methyl alcohol**. Glucose reacts with methy alcohol in the presence of dry HCl gas to form methyl glucoside.

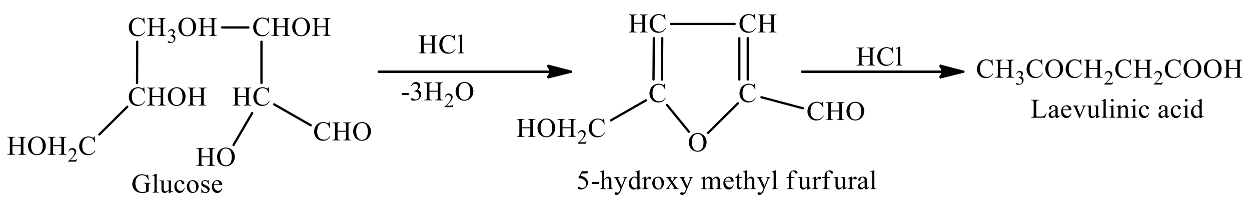
$$\underset{\text{Glucose}}{C_6H_{11}O_5\,OH} + H\,OCH_3 \xrightarrow{\text{Dry HCl}} \underset{\text{Methyl glycoside}}{C_6H_{11}O_5OCH_3} + H_2O$$

3. **Reaction with metallic hydroxides**. Glucose reacts with calcium hydroxide to form calcium glucosate which is water soluble.

$$\underset{\text{Glucose}}{C_6H_{11}O_5\,OH} + \underset{\text{calcium hydroxide}}{H\,OCaOH} \longrightarrow \underset{\text{calcium-glucosate}}{C_6H_{11}O_5OCaOH} + H_2O$$

(A) Miscellaneous reactions

1. Action of acids. On warming with conc.HCl, glucose forms 5-hydroxy methyl furfural, which on further reaction gives laevulinic acid.

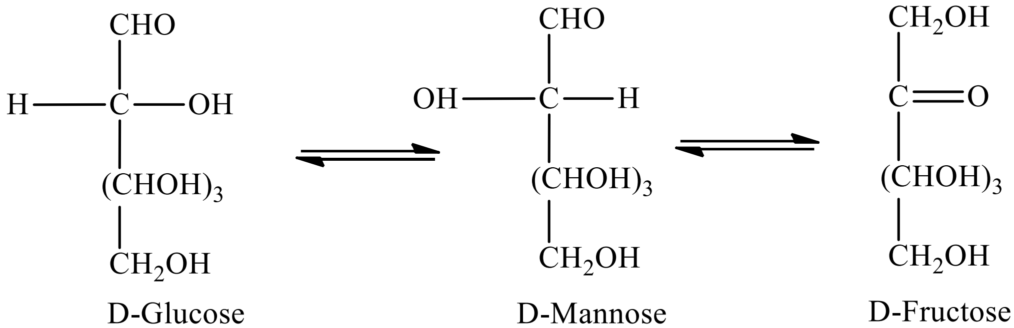


2. Fermentation. Glucose undergoes fermentation into ethyl alcohol in the presence of the enzyme zymase.

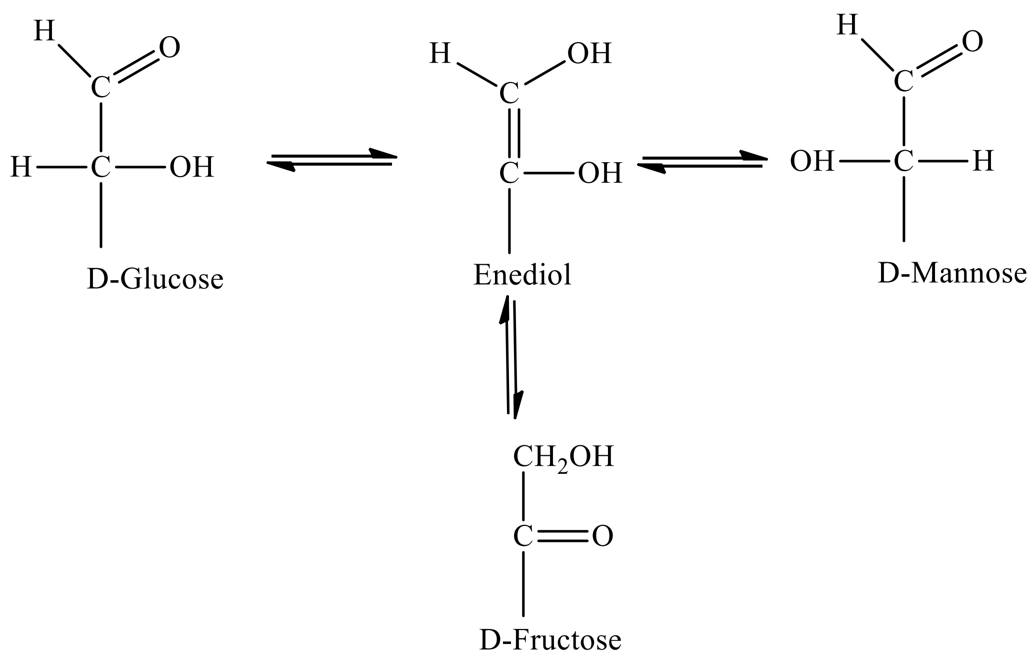
$$\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow{\text{Zymase}} \underset{\text{Ethyl alcohol}}{2C_2H_5OH} + 2CO_2$$

This reaction called alcoholic fermentation is the basis of manufacture of wines and alcohol.

3. Reaction with Alkalies. When warmed with strong sodium hydroxide solution, glucose forms a brown resinous product. In dilute alkali solution, D-glucose rearranges to give a mixture of D-glucose, D-mannose and d-fructose.



The above equilibrium is established via the enediol starting from any of these three hexoses.



That is why D-Fructose, although it has a ketonic C=O group, reduces Fehling's solution or Tollen's reagent. The rearrangement reaction of a monosaccharides in weakly alkaline solutions to give a mixture of isomeric sugars, is named as Lobry de Bruyn Van Ekestein rearrangement.

Structure of glucose

1. On the basis of elemental analysis and molecular weight determination the molecular formula of glucose is $C_6H_{12}O_6$.
2. The reduction of glucose with red phosphorus and HI gives n-hexane.

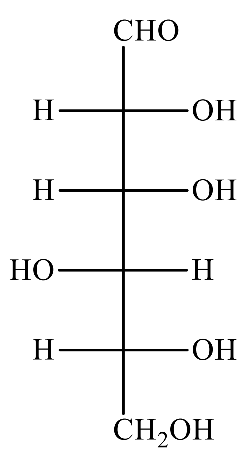
$$\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow{\text{HI/redP}} \underset{\text{n-hexane}}{CH_3CH_2CH_2CH_2CH_2CH_3}$$

Therefore, the six carbon atoms of glucose form a straight chain.

3. It forms penta acetate on treatment with acetic anhydride which indicates the presence of five hydroxyl groups in the molecule.
4. Glucose reacts with hydroxyl amine to form an oxime and with hydrogen cyanide to form cyanohydrins. It indicates the presence of a carbonyl group. It also forms phenylhydrazone on treatment with phenylhydrazine.
5. The mild oxidation of glucose with bromine water or sodium hypobromide yields a monocarboxylic acid (gluconic acid) containing same number of carbon atoms as in glucose, i.e., six. This indicates that the carbonyl group must be aldehyde group.
6. The catalytic reduction of glucose gives a hexahydric alcohol (sorbitol) which gives hexaacetate on treatment with acetic anhydride. The sixth hydroxyl group must be obtained by the reduction of aldehyde group, thus further confirming the presence of an aldehyde group and five hydroxyl groups in glucose.
7. Oxidation of gluconic acid with nitric acid yields a dicarboxylic acid (glucaric acid) with the same number of carbon atoms as in glucose. Thus besides aldehyde group, glucose must contain a primary alcoholic group also, which generates the second carboxylic group on oxidation.
8. Glucose is a stable compound and does not undergo dehydration easily, indiacating that not more than one hydroxyl group is bonded to a single carbon atom. Thus all the hydroxyl groups are attached to different carbon atoms.

Open –chain structure of glucose

On the basis of above reactions, Fisher assigned an open chain structure of glucose shown below as structure I



I

D-(+)-Glucose

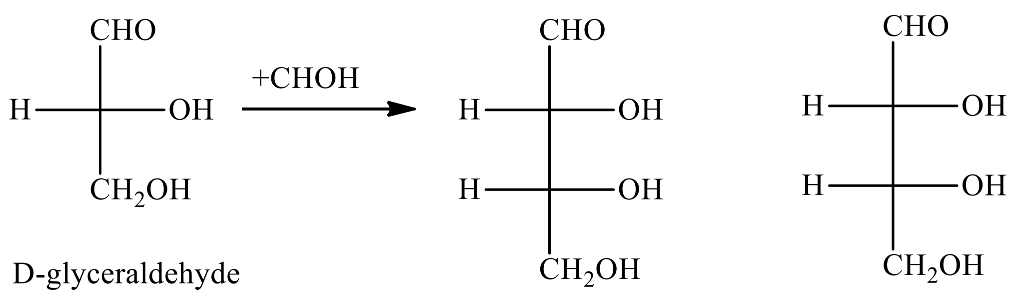
The above structure of glucose is also confirmed by the cleavage reaction of glucose with periodic acid.Five moles of periodic acid are consumed by one mole of glucose giving five moles of formic acid and one mole of formaldehyde.

$$\underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Periodic acid}}{5HIO_4} \longrightarrow HCHO + 5HCOOH + 5HIO_3$$

Configuration of D-Glucose

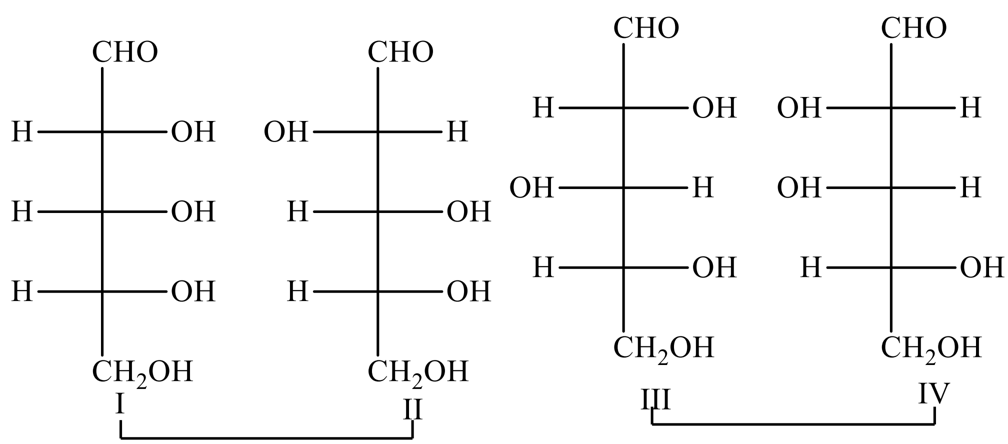
The configuration of D-glucose was proved by Emil Fisher by arguments similar to the ones stated below.

1. Construction of four possible D-pentoses. Taking the configuration of D-glyceraldehyde as the standard, two possible D-aldotetroses (A and B) may be constructed by adding a CHOH just below CHO, placing OH to the right and then to the left.



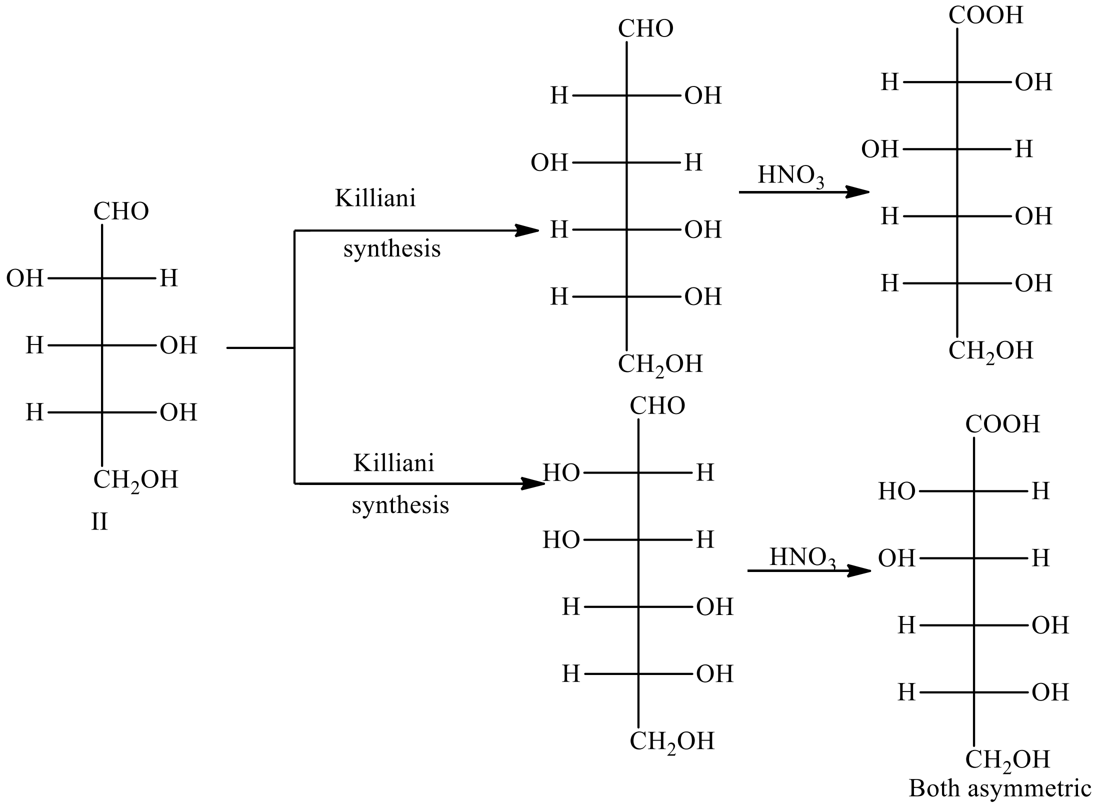
D-glyceraldehyde A B

Similarily, each of the two D-tetroses (A and B) gives two D-aldopentoses. Thus four possible D-aldopentoses are:



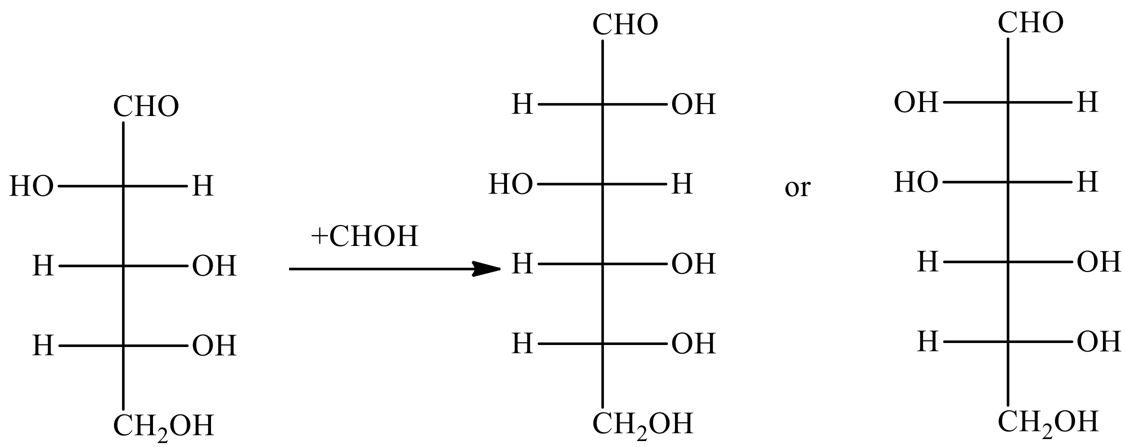
From A From B

2. D-Arabinose has configuration II or IV. Oxidation of D-arabinose with nitric acid oxidizes the terminal CHO and CH_2OH groups yielding two optically active dicarboxylic acids. The forms II and IV can form two optically active diacids, while I and III can give meso acids only that have a plane of symmetry, therefore, D-arabinose is either II or IV.
3. Configyration II confirmed for D-arabinose. D-arabinose by Killiani-Fisher synthesis yields two epimeric aldohexoses, D-glucose and D-mannose. Thses of oxidation with nitric acid form two optically active dicarboxylic acids. This is theoretically possible only if D-arabinose has the configuration II and not IV.



Proceeding similarily, you will find that if D-arabinose had configuration IV, of the two dicarboxylic acids derived from it, one would be meso and one asymmetric. Hence D-arabinose has the configuration II.

4.Ruff degradation of D-glucose and D-mannose produces D-arabinose in each case. In ruff degradation the CHOH below CHO is destroyed. Therefore , the configuration of the two aldohexoses, D-glucose and D-mannose, can be derived by adding a new CHOH below CHO in form II of D-arabinose.



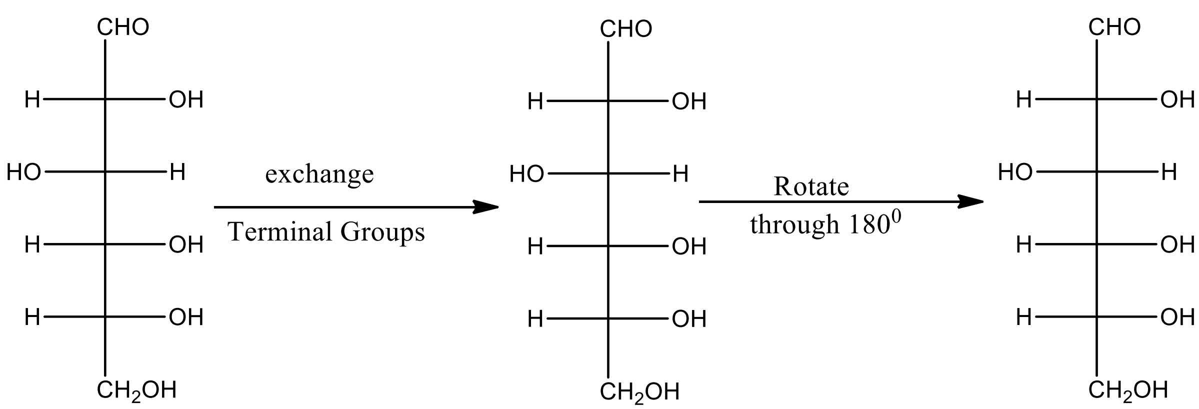
D-arabinose
II

V

VI

Hence D-glucose has configuration V or VI.

4. D-Glucose and L-Glucose yield the same dicarboxylic acid. This means thattwo sugars differ only in respect of the position of the terminal groups (CHO and CH_2OH). Therefore , the exchange of the terminal groups in D-glucose should be able to give a different aldohexose (L-glucose). Let us now examine configuration formula V and VI (one of which is D-glucose) from the angle.



V VI VII
Different from V

If VII is rotated through 180^0 in the plane of paper, it gives an aldohexose VII, different from V.a similar procedure with formula VI does not give rise to a different sugar.

From the above arguments it is evident that D-glucose has the configuration as shown by the form V.

Cyclic structure of D-Glucose:

The open chain structure of glucose explained most of its properties. However, it could not explain the following facts.

1. Despite having an aldehyde group, glucose does not undergo certain characteristic reactions of aldehyde,

(a) Glucose does not react with sodium bisulphate to form addition product.

(b) Glucose does not react with ammonia.

(c) Glucose does not give Schiff's test and 2, 4-DNP test like other aldehydes.

2. Glucose reacts with hydroxylamine to form an oxime but glucose pentaacetate does not react with hydroxylamine. This shows that –CHO group is not present in glucose pentaacetate.

3. **D (+)-Glucose exist in two stereoisomeric forms i.e., α- D (+)-Glucose and β- D (+)-Glucose.** These two forms are crystalline and have different m.p and optical rotations. When glucose was crystallized from a concentrated solution at 303 K, it gave α-form of glucose having m.p 419 K and $[\alpha]_D = +111^0$. On the other hand, the β-form of glucose is obtained on crystallization of glucose from a hot saturated solution of at a temperature above 371 K. The β-form of glucose has m.p 423 K and $[\alpha]_D = +19.2^0$.

4. **Mutarotation**. When either of two forms of glucose (α- D-glucose and β- D-glucose) are dissolved in water and allowed to stand, these get slowly converted into other form and a equilibrium mixture of both α- D-glucose (36 %) and β- D-glucose (about 64%) is forme The formation of equilibrium mixture can be explained as:

The α- D-glucose has a specific rotation of $+111^0$, while β- D-glucose has a specific rotation of $+19.2^0$. When α-form is dissolved in water, its specific rotation falls until a constant value of $+52.5^0$ is reached. On the other hand, when β-form is dissolved in water, its specific rotation increases and becomes constant at 52.5^0. This spontaneous change in specific rotation of an optically active compound with time to an equilibriumvalue is called mutarotation.(Latin, muto means to change).Thus, there is an equilibrium mixture of α- and β-forms in the solution

α-D-glucose	⇌	Open chain form	⇌	β-D-glucose
Sp.rotation $= +111^0$		Sp.rotation $= +52.5^0$		Sp.rotation $= +19.2^0$

5. Glucose forms isomeric methyl glucosides. When glucose is heated with methanol in the presence of dry HCl, it gives two isomeric monomethyl derivatives known as α-D-glucoside (m.p. = 438 K) and β-D-glucoside (m.p. 380 K).

$$\underset{\text{Glucose}}{C_6H_{11}O_5\,OH} + H\,OCH_3 \xrightarrow{\text{Dry HCl}} \underset{\text{Methyl glycoside}}{C_6H_{11}O_5OCH_3} + H_2O$$

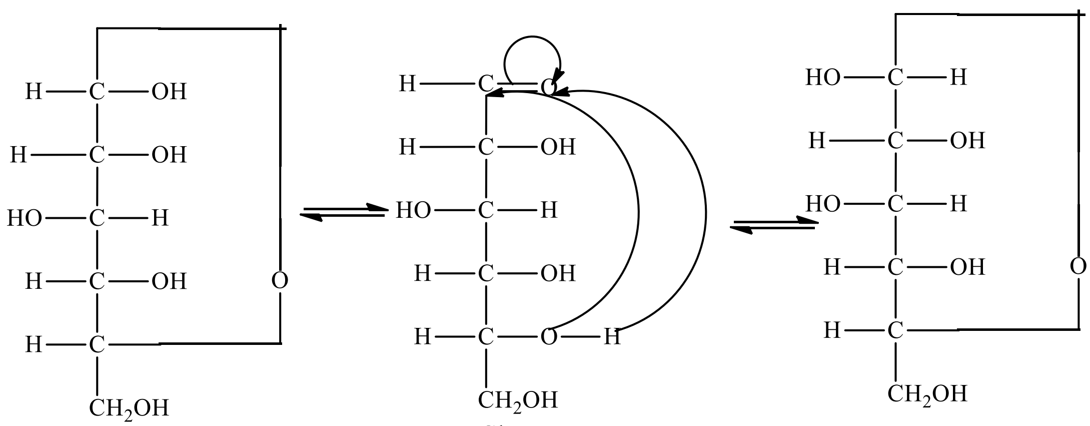
These two glucosides do not reduce Fehling's solution and also do not react with HCN or NH_2OH indicating that the free –CHO group is not present but it is converted to –COOH group.

Cyclic structure of Glucose

Anomers:

Glucose forms a hemiacetal between the –CHO group and the -OH group on the C_5 atom. As a result, of cyclisation, C_1 becomes asymmetric (chiral) and the newly formed –OH group may be either on the left or on the right in Fisher projection formulae. These results in the formation of two isomerswhich differ in the orientation of H and –OH groups around C1 atom. These isomers are known as α- D-glucose and β- D-glucose. The isomer having the –OH group on the right is called α- D-glucose and one having the –OH group on the left is called β- D-glucose. Such pairs of optical isomers which differ in the configuration only around C_1 atom are called anomers.

These two forms are not mirror image of each other, hence are not enantiomers. The C1 carbon is known as anomeric carbon or glycosidic carbon.

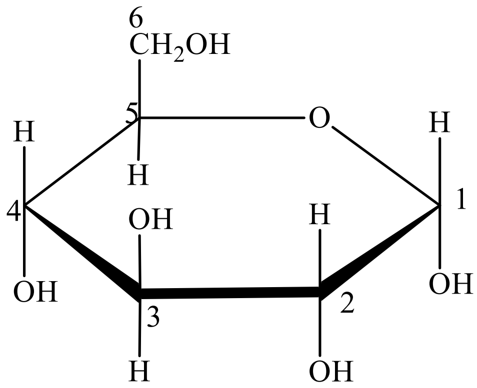


α-D-Glucose D-Glucose (open chain form) β-D-Glucose

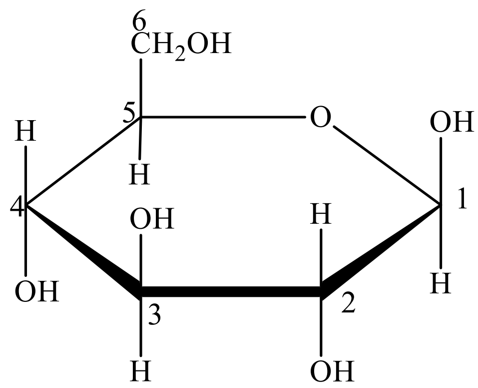
The above representations are called Fisher projection formulae.

Haworth projection formulae or pyranose structures of D-Glucose.

In Haworth structures drawn with the heterocyclic oxygen in the upper right corner, the α-form has the –OH group on C_1 pointing "down". The β-form has the same group pointing "up". For D-sugars, the free –CH2OH group of an aldohexose is drawn above the plane of ring when ring oxygen is in the upper right. The rest is the simple, the groups on the left of the Fisher projection are up and those on the right are down in the Haworth structure.



α-D-Glucose
or
α-D-Glucopyranose



β–D-Glucose
or
β-D-Glucopyranose

Fructose

Fructose is another commonly known monosaccharide having the same molecular formula as glucose. It is laevorotatory because it roatates plane polarized light towards the left. It is present abundantly in fruits. That is why it is called fruit-sugar also.

Physical properties

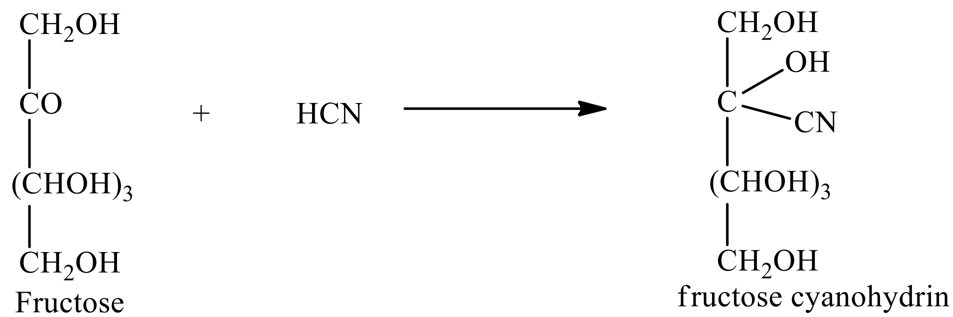
1. It is sweetest of all known sugars.
2. It is readily soluble in water, sparingly soluble in alcohol and insoluble in ether.
3. It is white crystalline solid with m.p. 375 K.
4. Fresh solution of fructose has a specific rotation -133^0.

Chemical properties of fructose

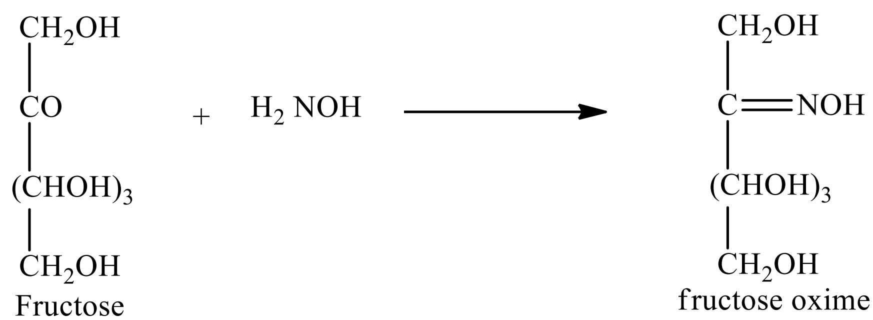
Chemical properties of fructose can be studied under the following heads:

(A) Reactions due to ketonic group

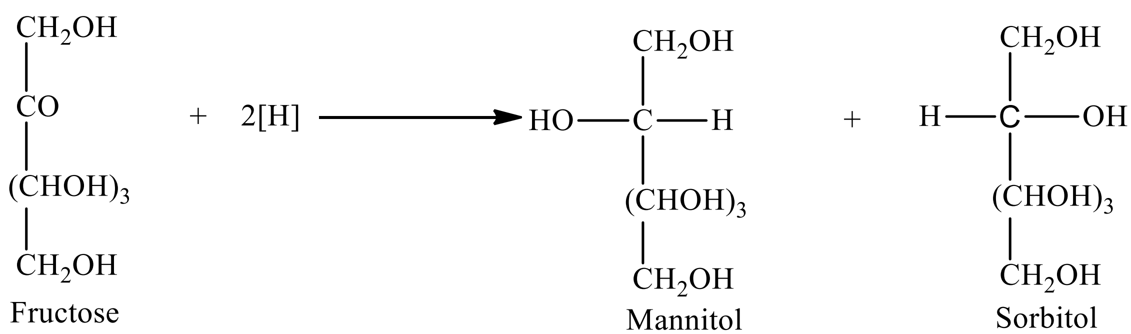
1. **Reaction with HCN**. Fructose reacts with HCN to form cyanohydrins.



2. **Reaction with hydroxylamine**. Fructose reacts with hydroxylamine to form an oxime.

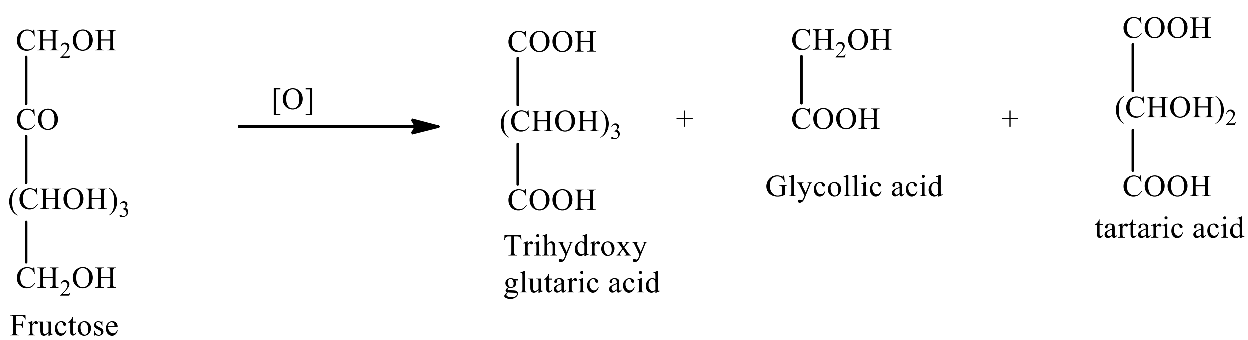


3. **Reduction**. Fructose gives a mixture of sorbitol and mannitol on reduction with Na-Hg and water or catalytic hydrogenation.



4. **Oxidation.** (i) there is no action of mild oxidizing agent like bromine water on fructose.

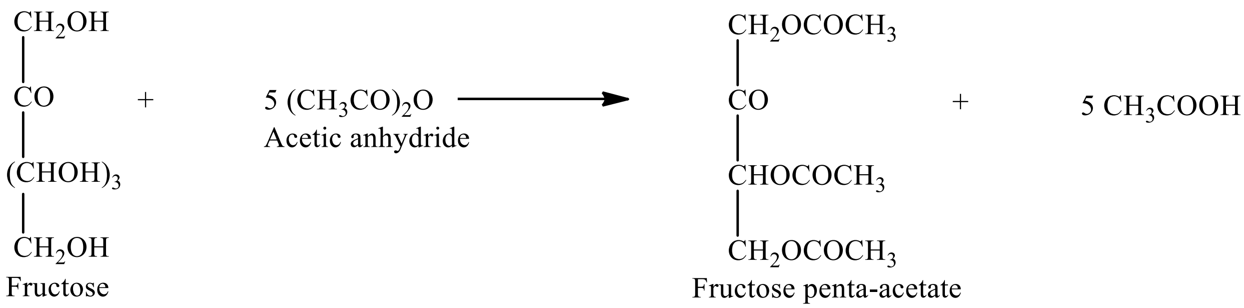
   (ii) Strong oxidizing agents like nitric acid oxidize fructose into a mixture of trihydroxy glutaric, glycolic and tartaric acids.



(i) Unlike other ketones, it reduces Tollen's reagent and Fehling solution. This is due to the presence of traces of glucose in alkaline medium.

[B] reactions of the alcoholic group

1. Acetylation . with acetic anhydride or acetyl chloride, fructose forms penta-acetate.



2. Reaction with methyl alcohol (glucoside formation). Fructose reacts with methyl alcohol in the presence of dry HCl gas forming methyl fructoside.

$$\underset{\text{Fructose}}{C_6H_{11}O_5\,OH} + H\,OCH_3 \xrightarrow{\text{Dry HCl}} \underset{\text{Methyl fructoside}}{C_6H_{11}O_5OCH_3} + H_2O$$

3. Reaction with metallic hydroxides (fructosate formation)

$$\underset{\text{Fructose}}{C_6H_{11}O_5\,OH} + \underset{\text{calcium hydroxide}}{H\,OCaOH} \longrightarrow \underset{\text{calcium-fructosate}}{C_6H_{11}O_5OCaOH} + H_2O$$

Structure of Fructose

1. Elemental analysis and molecular weight determination of fructose show that it ahs the molecular formula $C_6H_{12}O_6$.

2. Fructose on reduction gives sorbitol which on reduction with HI and red P gives a mixture of n-hexane and 2-Iodohexane. This reaction indicates that six carbon atoms in fructose are in a straight chain.

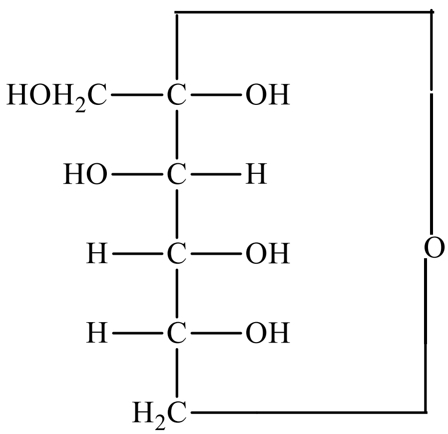
3. Fructose reacts with hydroxylamine, HCN and phenylhydrazine. It shows the presence of _CHO or C=O group in the molecule of fructose.

4.On treatment with bromine water , no reaction takes palce. This rules out the possibility of presence of –CHO group.

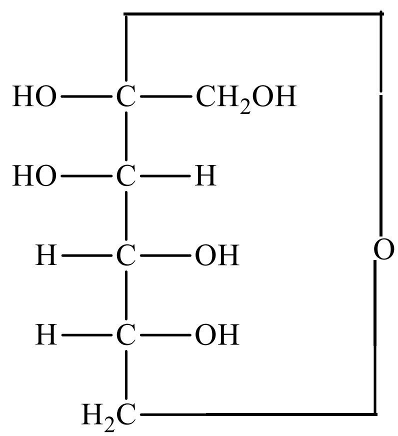
5.On oxidation with nitric acid, it gives glycollic acid and tartaric acids which contain smaller number of carbon atoms than fructose. This shows that a ketonic group is present at position 2. It is at this point that the molecule is broken.

Cyclic structure of D-Fructose

Fructose shows the property of mutarotation. This means that it exists in two forms α-fructose and β-fructose which are cyclic in structure and change into each other via the open chain structure. The cyclic and pyranose structures of α-D-fructose and β-D-fructose are represented below:

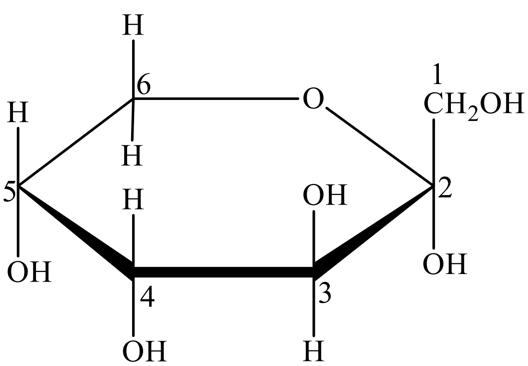


α-D-fructose

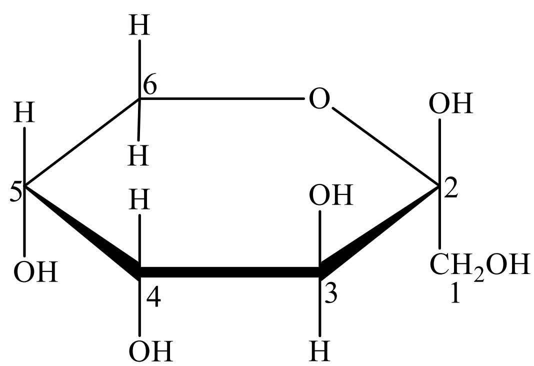


β-D-fructose

Haworth Pyranose structure

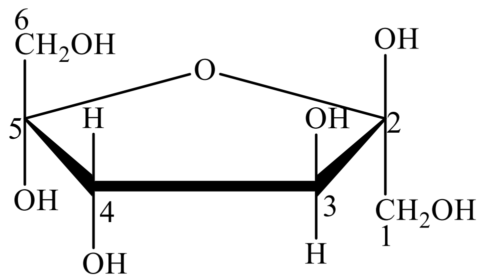


α-D-fructopyranose



β-D-fructopyranose

However, when fructose is linked to glucose in a sucrose molecule, it has the furanose structure as shown below:



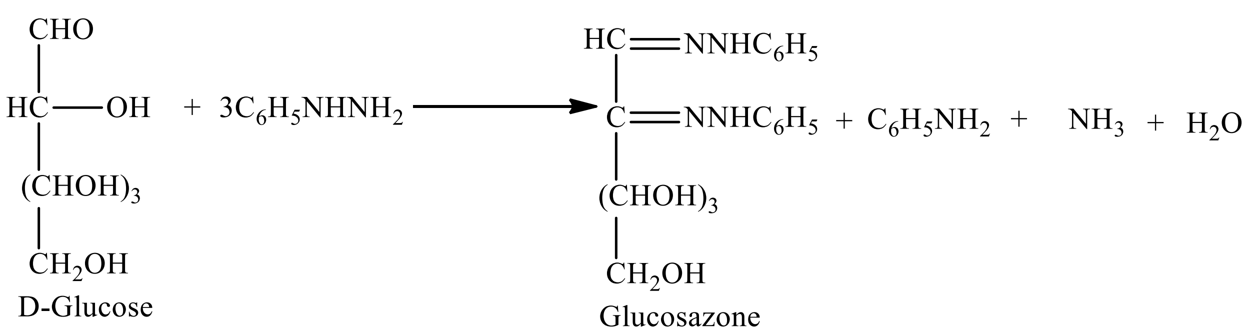
β-D-fructofuranose

1.5 MECHANISM OF OSAZONE FORMATION

Glucose and fructose react with one equivalent of phenylhydrazine, forming phenylhydrazone. In contrast, α-

hydroxy carbonyl compounds react with three equivalents of phenylhydrazine to form bis-phenylhydrazones,

commonly called osazones.

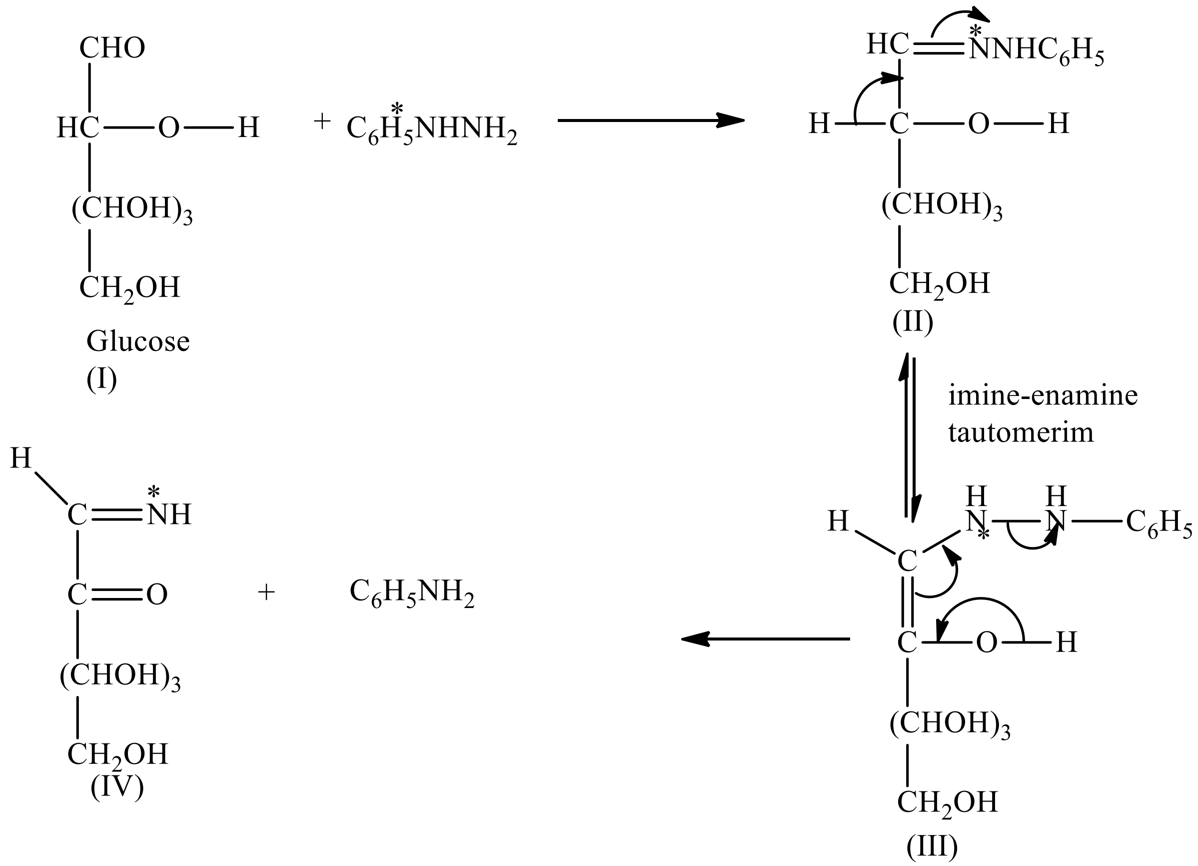


Phenylosazones crystallize readily and are useful derivatives for identifying sugars.

Mechanism: the first equivalent of phenylhydrazine forms phenylhydrazone with the aldehyde or ketone

group as expected. Phenylhydrazone the ungergoes the rearrangement , known as Amadori rearrangement,

to give α-iminoketone (IV) with the loss of aniline.

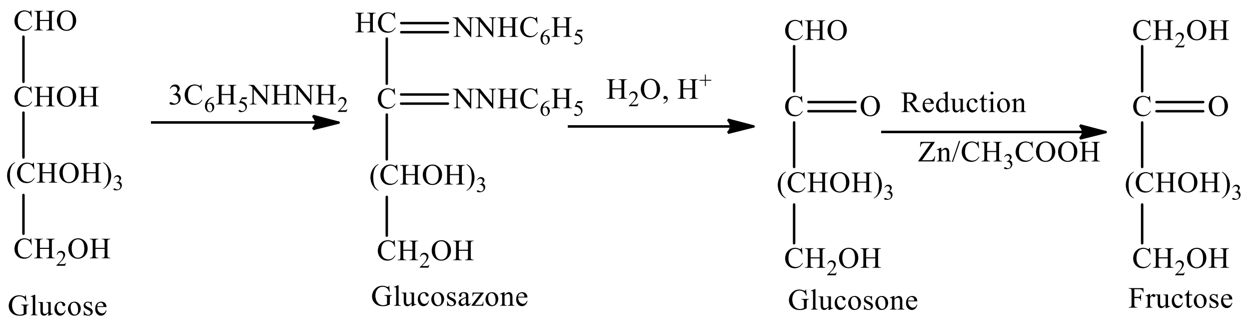


Subsequent attack of two moles of phenylhydrazine on the iminoketone (scheme-a) or on the ketoaldehyde (scheme-b) results in the formation of osazone accompanied by the elimination of ammonia.

The given mechanism is supported by the observation that when phenyl hydrazone prepared by the reaction of glucose with N^{15} (N^*) labeled phenylhydrazine is treated with ordinary phenylhydrazine, unlabelledosazone is obtained accompanied by the expulsion of labelled ammonia.

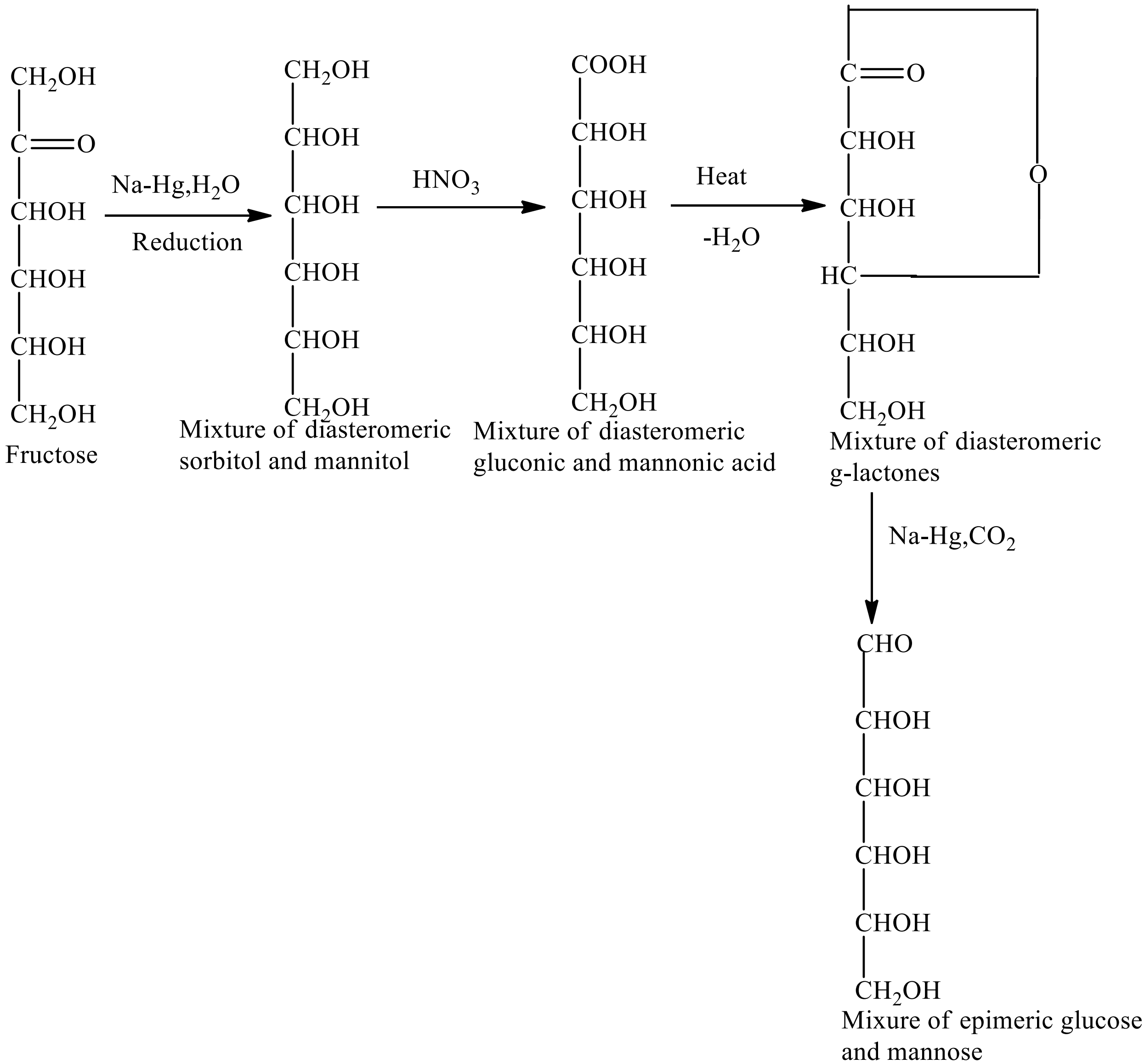
1.6 INTERCONVERSION OF GLUCOSE AND FRUCTOSE

(a) Conversion of an aldose into an isomeric ketose. The procedure used for this purpose may be illustrated by taking into account the conversion of glucose into fructose.



(b) Conversion of ketose into an isomeric aldose. The procedure used here may be illustrated by taking

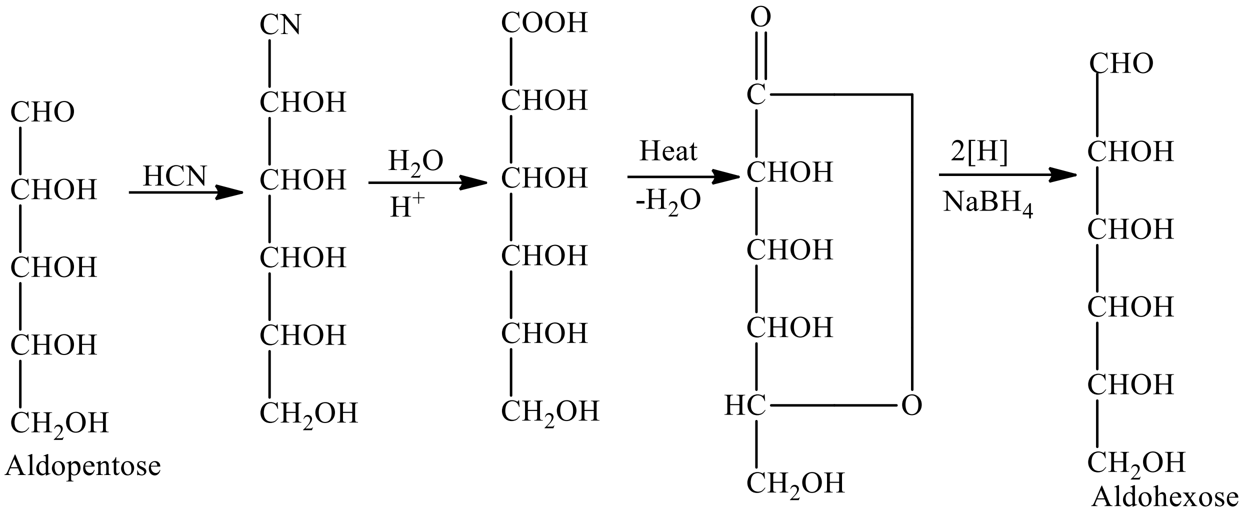
into account the conversion of fructose into a mixture of epimeric aldoses, viz., glucose and mannose.



1.7 CHAIN LENGTHENING AND CHAIN SHORTENING OF ALDOSE

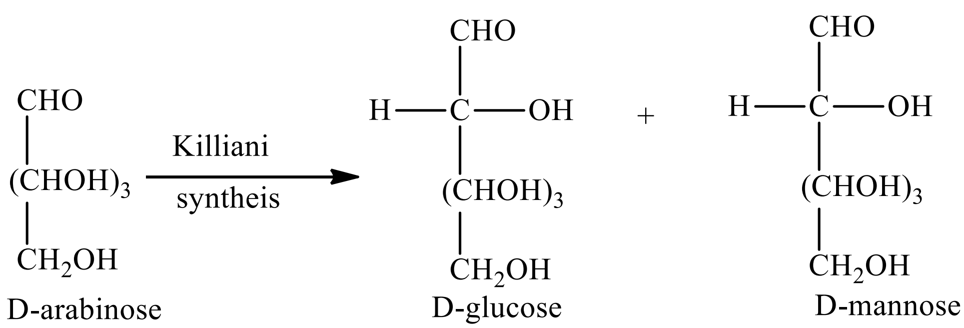
(a) Lengthening of aldoses: Killiani-Fisher synthesis

The aldose chains may be lengthened by one carbon atom by a procedure known as **Killiani-Fisher synthesis.** Thus an aldose may be converted to the next higher member by the following steps: (1) Formation of cyanohydrins; (2) hydrolysis of –CN to –COOH, giving aldonic acid; (3) conversion of aldonic acid to lactone by heating; (4) reduction of lactone with sodium borohydride, $NaBH_4$, to get higher aldose. For illustration, the overall change is the creation of an asymmetric centre at C-2 where a new CHOH has been added. Therefore their result two aldoses with one carbon more and differing only in configuration at C-2.



Taking a specific example, D-arabinose by killiani-Fisher synthesis gives two isomeric aldohexoses,

D-glucose and D-mannose which differ only in the configuration at C-2



Such sugars which differ in configuration only at one asymmetric centre (C-2) are called Epimers.

(b) Shortening of aldoses

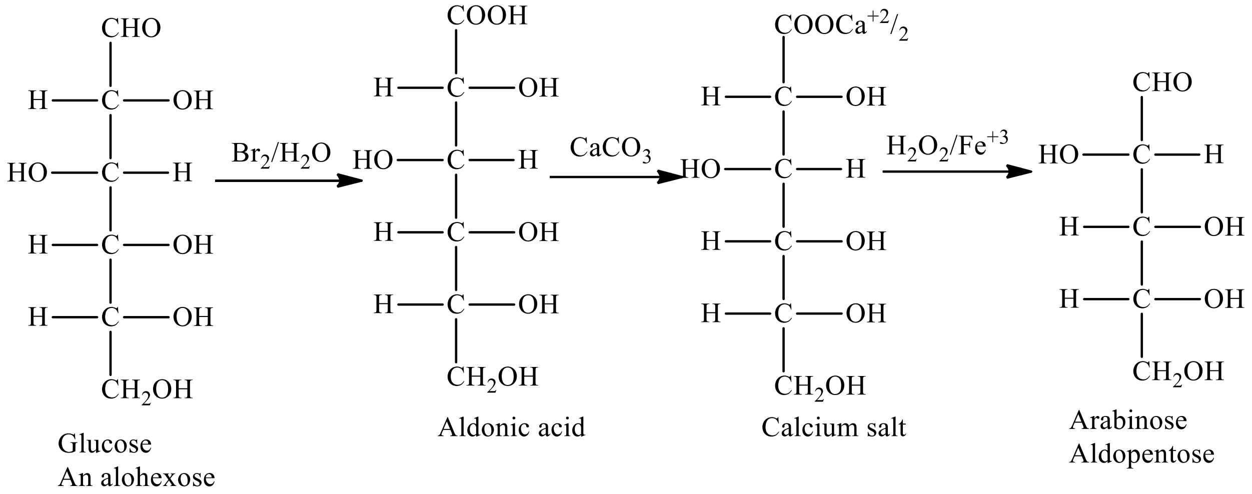
(1) Ruff degradation. An aldose may be converted into a lower aldose having one carbon atom less, i.e.,

the carbon chain may be shortened by Ruff degradation.

The method involves the oxidation of starting aldose into the corresponding aldonic acid. The acid is

converted into its calcium salt which is treated with Fenton’s reagent (H2O2 in presence of Fe^{+3} ion)

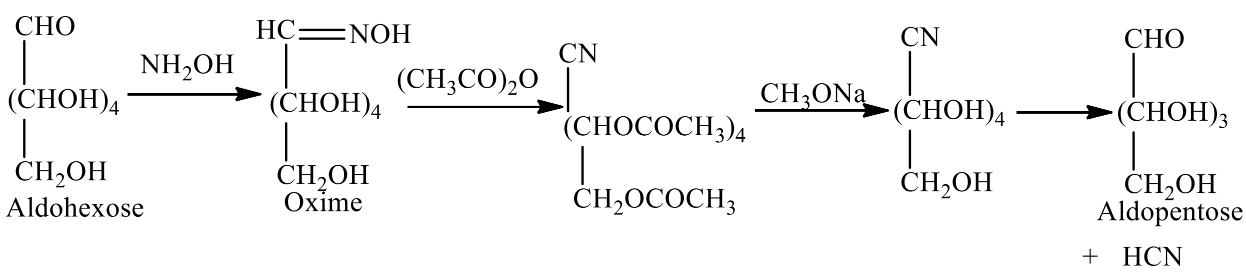
to get the lower aldose. This method is illustrated as follows:

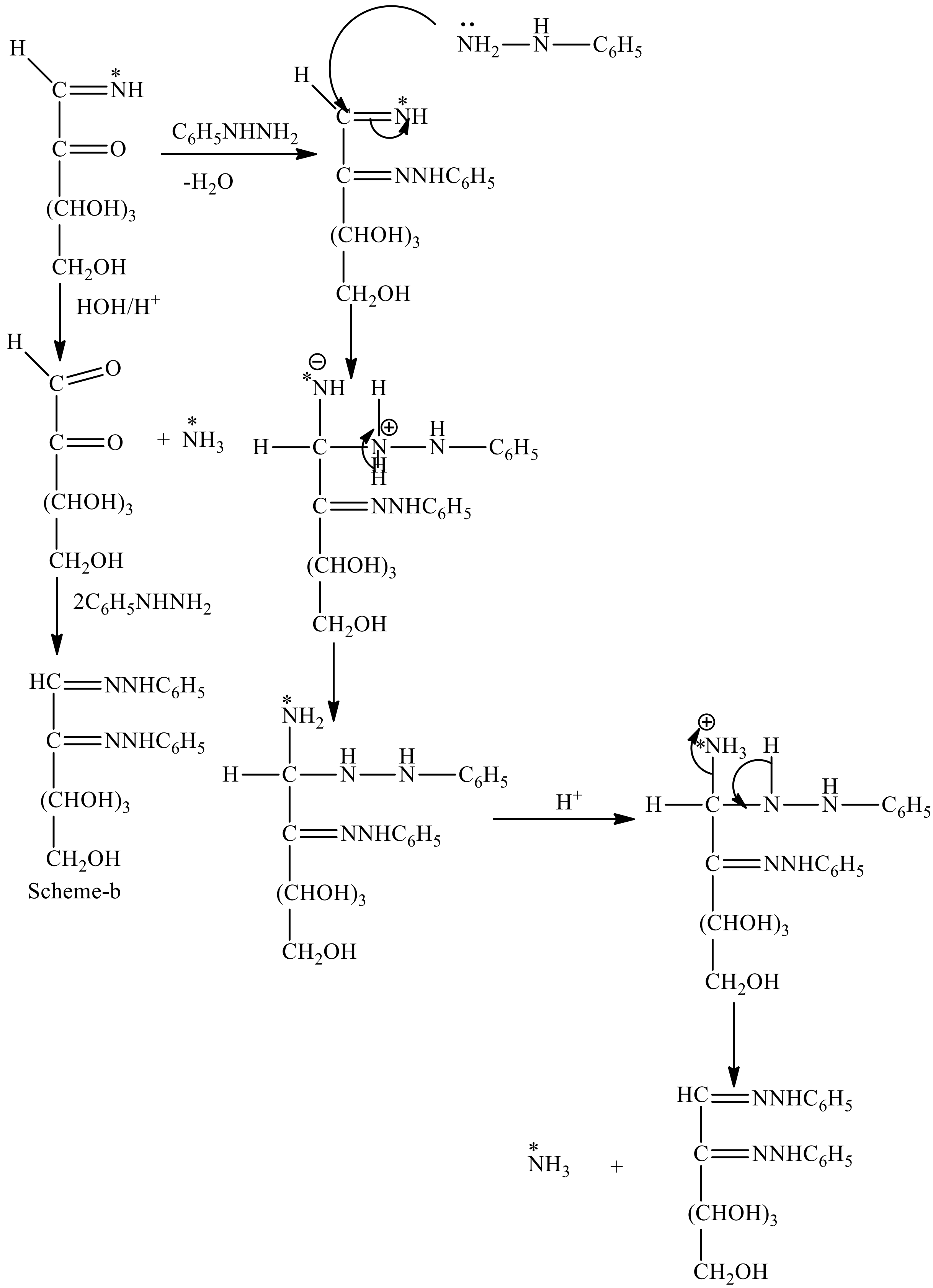


(2) Wohl's degradation for chain shortening in aldoses

In this degradation, the aldose is converted into its oxime by treatment with hydrgradazoxylamine.

The oxime is treated with acetic anhydride when the oxime is dehydrated to nitrile. The nitrile is then treated with sodium methoxide. The cyanohydrin obtained undergoes degradation to a lower aldose. The reaction are written as under.

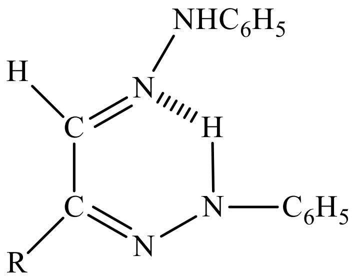




Scheme-b

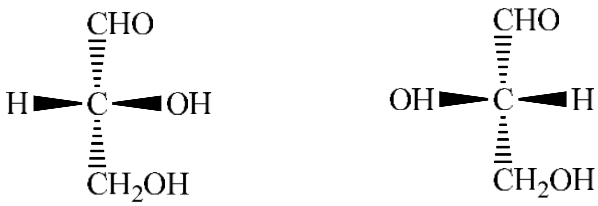
Scheme-a

The osazone so formed does not undergo further amadori rearrangement. This is the reaction with phenylhydrazine stops at this stage; thus further reaction at C-3 –OH group dost not occur. This is because the osazone so formed, does not react further via intramolecular Amadori rearrangement involving C-3 –OH group because of the intramolecular hydrogen bomding as shown below:



1.8 CONFIGURATION OF MONOSACCHARIDES

In early days of development of stereochemistry of organic compounds, it was not possible to determine the absolute configurations. The chemists were only interested in knowing the relative configurations. To decide about configurations, Emil Fisher in 1885 chose glyceraldehyde ($CHOCHOHCH_2OH$) as the standard substance and fixed its relative configurations arbitrarily. This compound exists in two enantiomeric forms, as given below:



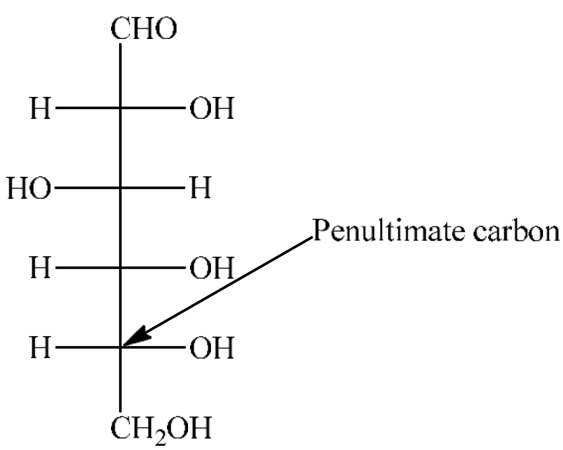
D(+)-Glyceraldehyde (I)

L(-)-Glyceraldehyde (II)

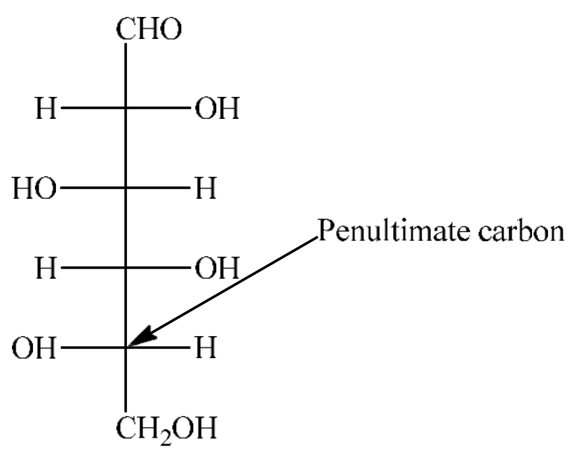
Compound I was found to be dextrorotatory and compound II was found to be laevorotatory. The difference between configuaration of the two compounds is that in compound (I), -H is located on the L.H.S and –OH is located on the R.H.S. of the Fisher projection formula while in compound (II), this is in reverse order.Configuration of other compounds was then assigned by relating their configuration to that of D- or L-Glyceraldehyde.

In 1951 Bijvoet using x-ray crystallography established that the arbitrarily assigned configurations of glyceraldehydes actually represented their correct absolute configurations. Thus, if the configuration of glyceraldehydes were correct, the derived relative configurations of other compound must also be their correct absolute configuration.

Thus D- and L- glyceraldehydes serve as reference molecule for all the monosaccharides. A monosaccharide whose penultimate carbon (farthest chiral carbon atom from most oxidizing end i.e, -CHO) has the same configuration as D-Glyceraldehyde has L-configuration. Similarily , amonosaccharide whose penultimate carbon has the same configuration as L-Glyceraldehyde has L-configuration. This is illustrated with the help of following examples.



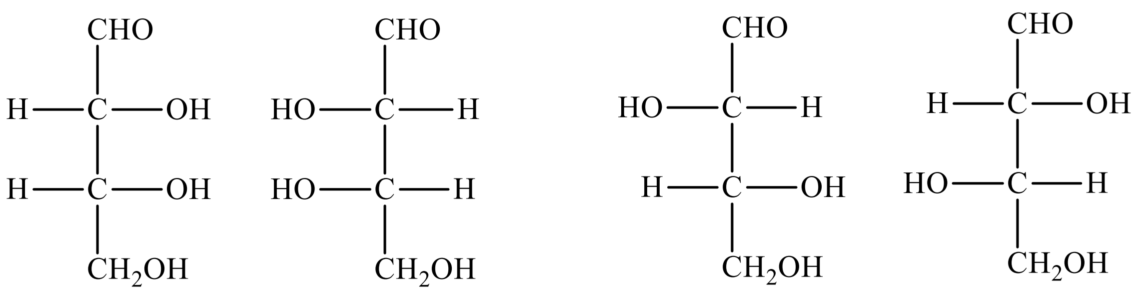
D-configuration
(because the configuration at penultimate carbon is the same as that of D-Glyceraldehyde



L-configuration
(because the configuration at penultimate carbon is the same as that of L-Glyceraldehyde

1.9 ERYTHRO AND THREO DIASTEROMERS CONVERSION OF GLUCOSE

Erythro and Threo system of nomenclature is used only in aldotetroses. Aldotetrose have two chirality centres and therefore four stereoisomers. Two of the stetreoisomers are D-sugars and two are L-sugars. When fisher projections are drawn for stereoisomers with two adjacent chirality centres, the pair of enantiomers with similar groups on the same side of the carbon chain is called the erythreo enantiomers. The pair of enantiomers with similar groups on opposite sides are called the threo enantiomers. The names of erythreo and threo pairs of enantiomers in fact, originated from the name of aldotetroses, erythreose and threose.



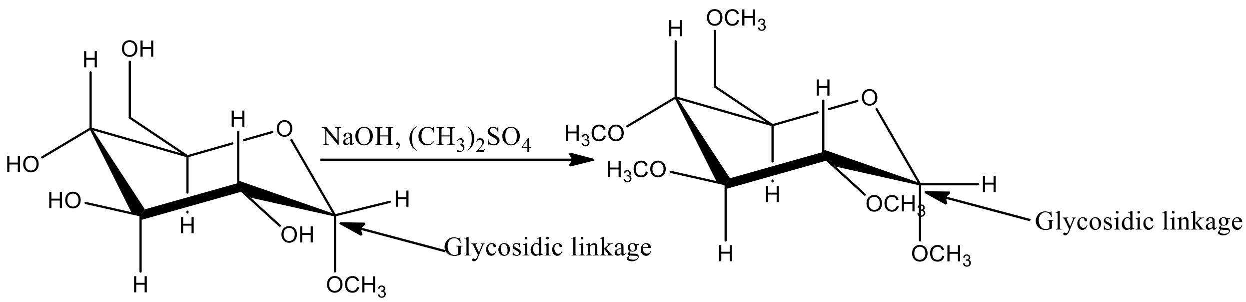
D-Erythreose L-Erythreose D-Threose L-Threose

Erythreose and threose are diastereomers.

1.10. ETHERS AND ESTERS

(a) Formation of ethers

It is possible to convert the –OH groups attached to carbons other than anomeric carbon into alkyl derivatives having ordinary ether C-O-C linkages. For example methyl glucoside can be converted into pentamehyl derivative by treatment with excess dimethyl sulphate in aqueous sodium hydroxide. The function of sodium hydroxide is to convert hydroxyl groups into alkoxide ions which then react with dimethyl sulphate by an S_N2 reaction to form methyl ethers.



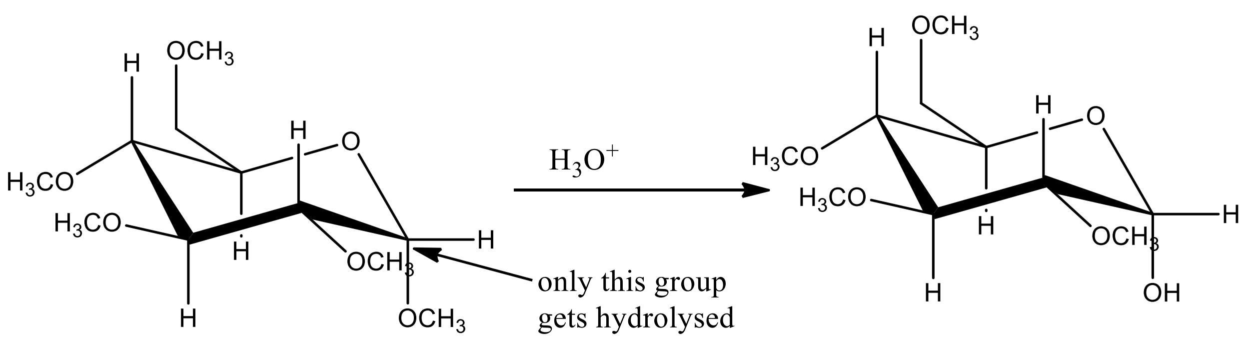
Methyl α-D-glucopyranoside

Methyl2,3,4,6-tetra-O-methyl α-D-glucopyranoside

Since all the –OH groups are converted into-OCH3 groups, the process is called exhaustive methylation or permethylation.

For naming these compounds, each –OCH3 group except that of glycosidic linkage is named as an O-methyl group.

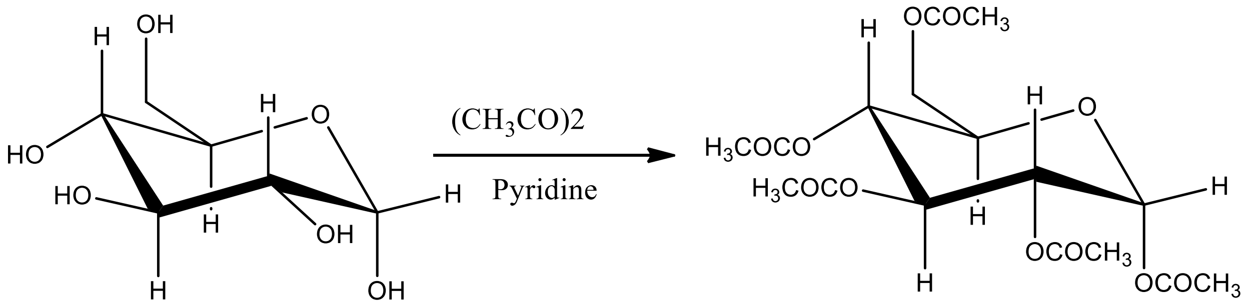
When permethylated glycoside is treated with dilute aqueous acid, the methyl glycoside bond gets hydrolysed (since acetals are hydrolysed in acidic solution). But the other methyl groups remain unaffected. This is because ordinary ether groups are stable in dilute aqueous acids. This is shown as under:



The process of permethylation of glycosides followed by acidic hydrolysis of glycosidic linkage forms an important method for decctermining the ring size of monosaccharides. This has been illustrated in the case of cyclic structure of glucose.

(b) Formation of esters

Monosaccharides on treatment with acetic anhydride are converted into ester derivatives which are very useful crystalline compounds. The monosaccharide is treated with acetic anhydride and pyridine when all the hydroxyl groups are converted to ester groups. When carried out at low temperature (273 K), the reaction takes place stereospecifically, α-aomer gives the α-acetate and the β-anomer gives the β-acetate. For example:

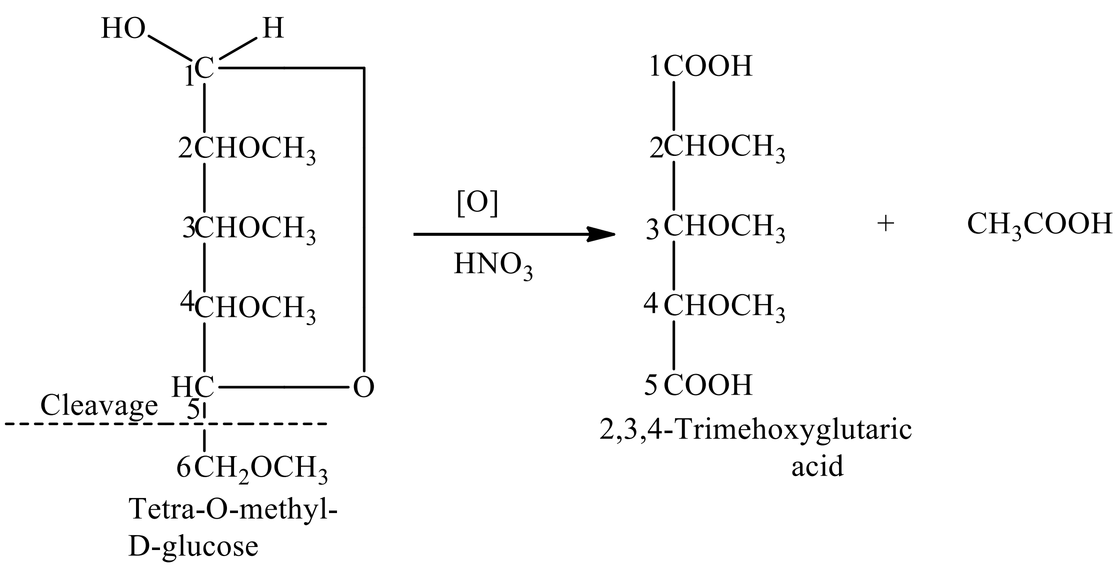


α-D-glucopyranose Penta-O-acetyl-α-D-glucopyranoside

1.11DETERMINATION OF RING SIZE OF MONOSACCHARIDES

So far we have represented structure of cyclic hemiacetals or anomers of D-glucose as having a ring of six me zmbers, five carbons and one oxygen. This has been proved to be correct and a five membered ring has been ruled out.

Hirst (1926) prepared tetra-O-methyl-D-glucose with dimethyl sulphate and subsequent acid hydrolysis of the pentamethyl derivative formed. The oxidation of tetra-O-methyl-D-glucose with nitric acid yielded trimethoxyglutaric acid.



Obviously, the two carboxylic carbons (1, 5) of the trimethoxyglutaric acid are the one's originally involved in ring formation. Hence, there must have existed an oxide ring between C-1 and C-5. Tracing back the reaction sequence, it stands proved that D-glucose has a six membered ring. The presence of a 6-membered ring in D-glucose has also been confirmed by X-ray analysis.

1.12 CYCLIC STRUCTURE OF D-GLUCOSE

The open chain structure of glucose explained most of its properties. However, it could not explain the following facts.

2 Despite having an aldehyde group, glucose does not undergo certain characteristic reactions of aldehyde,

(d) Glucose does not react with sodium bisulphate to form addition product.

(e) Glucose does not react with ammonia.

(f) Glucose does not give Schiff's test and 2, 4-DNP test like other aldehydes.

3 Glucose reacts with hydroxylamine to form an oxime but glucose pentaacetate does not react with hydroxylamine. This shows that –CHO group is not present in glucose pentaacetate.

4 **D (+)-Glucose exist in two stereoisomeric forms i.e., α- D(+)-Glucose and β-D(+)-Glucose.** These two forms are crystalline and have different m.p and optical rotations. When glucose was crystallized from a concentrated solution at 303 K, it gave α-form of glucose having m.p 419 K and $[\alpha]_D$= +111^0. On the other hand, the β-form of glucose is obtained on crystallization of glucose from a hot saturated solution of at a temperature above 371 K. The β-form of glucose has m.p 423 K and $[\alpha]_D$= +19.2^0.

5 **Mutarotation**. When either of two forms of glucose (α- D-glucose and β- D-glucose) are dissolved in water and allowed to stand, these get slowly converted into other form and a equilibrium mixture of both α- D-glucose (36 %) and β- D-glucose (about 64%) is formed.

The formation of equilibrium mixture can be explained as:

The α- D-glucose has a specific rotation of +111^0, while β- D-glucose has a specific rotation of +19.2^0. When α-form is dissolved in water, its specific rotation falls until a constant value of +52.5^0 is reached. On the other hand, when β-form is dissolved in water, its specific rotation increases and becomes constant at 52.5^0.

This spontaneous change in specific rotation of an optically active compound with time to an equilibrium value is called mutarotation.(Latin, muto means to change).

Thus, there is an equilibrium mixture of α- and β-forms in the solution

$$\underset{\text{Sp.rotation} = +111^0}{\alpha\text{-D-glucose}} \rightleftharpoons \underset{\text{Sp.rotation} = +52.5^0}{\text{Open chain form}} \rightleftharpoons \underset{\text{Sp.rotation} = +19.2^0}{\beta\text{-D-glucose}}$$

6 Glucose forms isomeric methyl glucosides. When glucose is heated with methanol in the presence of dry HCl, it gives two isomeric monomethyl derivatives known as α-D-glucoside (m.p. = 438 K) and β-D-glucoside (m.p. 380 K).

$$\underset{\text{Glucose}}{C_6H_{11}O_5\,OH} + H\,OCH_3 \xrightarrow{\text{Dry HCl}} \underset{\text{Methyl glycoside}}{C_6H_{11}O_5OCH_3} + H_2O$$

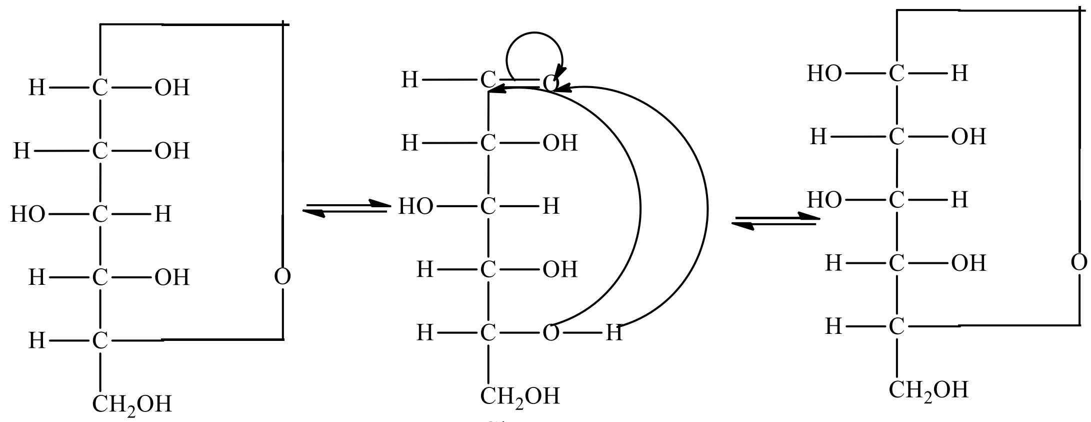
These two glucosides do not reduce Fehling's solution and also do not react with HCN or NH_2OH indicating that the free –CHO group is not present but it is converted to –COOH group.

Cyclic structure of Glucose

Anomers.

Glucose forms a hemiacetal between the –CHO group and the -OH group on the C_5 atom. As a result, of cyclisation, C_1 becomes asymmetric (chiral) and the newly formed –OH group may be either on the left or on the right in Fisher projection formulae. This result in the formation of two isomerswhich differs in the orientation of H and –OH groups around C1 atom. These isomers are known as α- D-glucose and β- D-glucose. The isomer having the –OH group on the right is called α- D-glucose and one having the –OH group on the left is called β- D-glucose. Such pairs of optical isomers which differ in the configuration only around C_1 atom are called anomers.

These two forms are not mirror image of each other, hence are not enantiomers. The C1 carbon is known as anomeric carbon or glycosidic carbon.

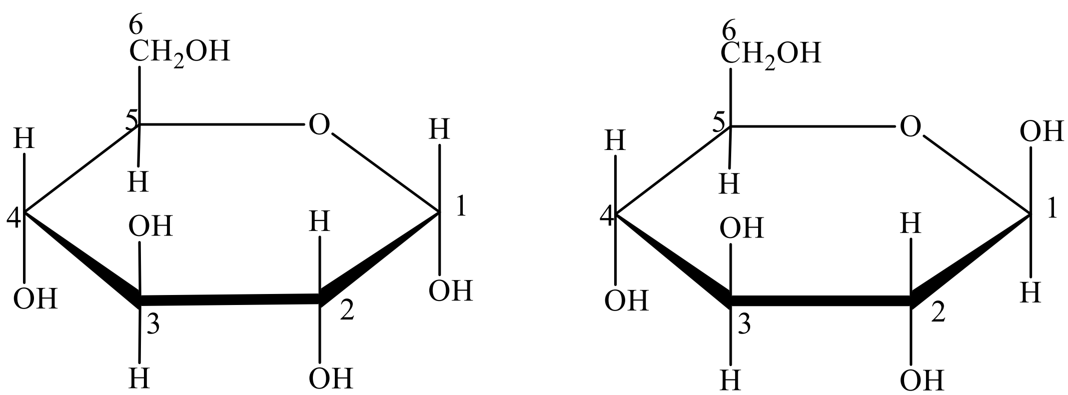


α-D-Glucose — D-Glucose (open chain form) — β-D-Glucose

The above representations are called Fisher projection formulae.

Haworth projection formulae or pyranose structures of D-Glucose.

In Haworth structures drawn with the heterocyclic oxygen in the upper right corner, the α-form has the –OH group on C_1 pointing "down". The β-form has the same group pointing "up". For D-sugars, the free $–CH_2OH$ group of an aldohexose is drawn above the plane of ring when ring oxygen is in the upper right. The rest is the simple, the groups on the left of the Fisher projection are up and those on the right are down in the Haworth structure.

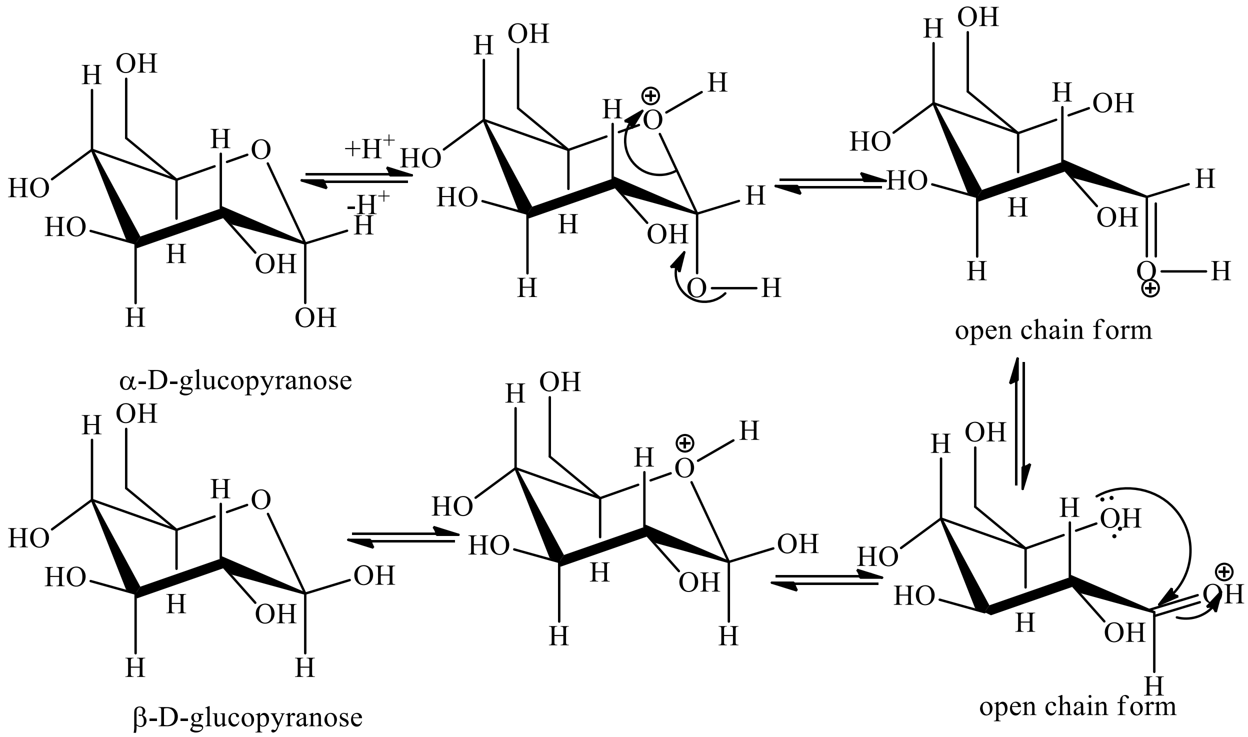


α-D-Glucose or α-D-Glucopyranose — β–D-Glucose or β-D-Glucopyranose

1.13 MECHANISM OF MUTAROTATION

Mutarotation occurs by opening of the ring to the free carbonyl form. The mechanism shown in Scheme I begin as the reverse of hemiacetal (or hemiketal) formation. An 180^0 rotation about the bond to the carbonyl group permits attack of the hydroxyl group at C-5 on the opposite face of the carbonyl carbon. Hemiacetal formation then gives the other anomer. Mutarotation is catalysed by both acid and base.

Thus, the easy opening and closing of hemiacetal or hemiketal linkage is responsible for mutarotation.



Scheme I. Acid catalysed mechanism of mutarotation

1.14. GENERAL STUDY OF DISACCHARIDES

Disaccharides are the carbohydrates which on hydrolysis give two same or different monosaccharides. Their general formula is $C_{12}H_{22}O_{11}$. The important members belonging to disaccahrides are sucrose, maltose, and lactose. On hydrolysis with dilute acids or enzymes these give the following two molecules of monosaccharides.

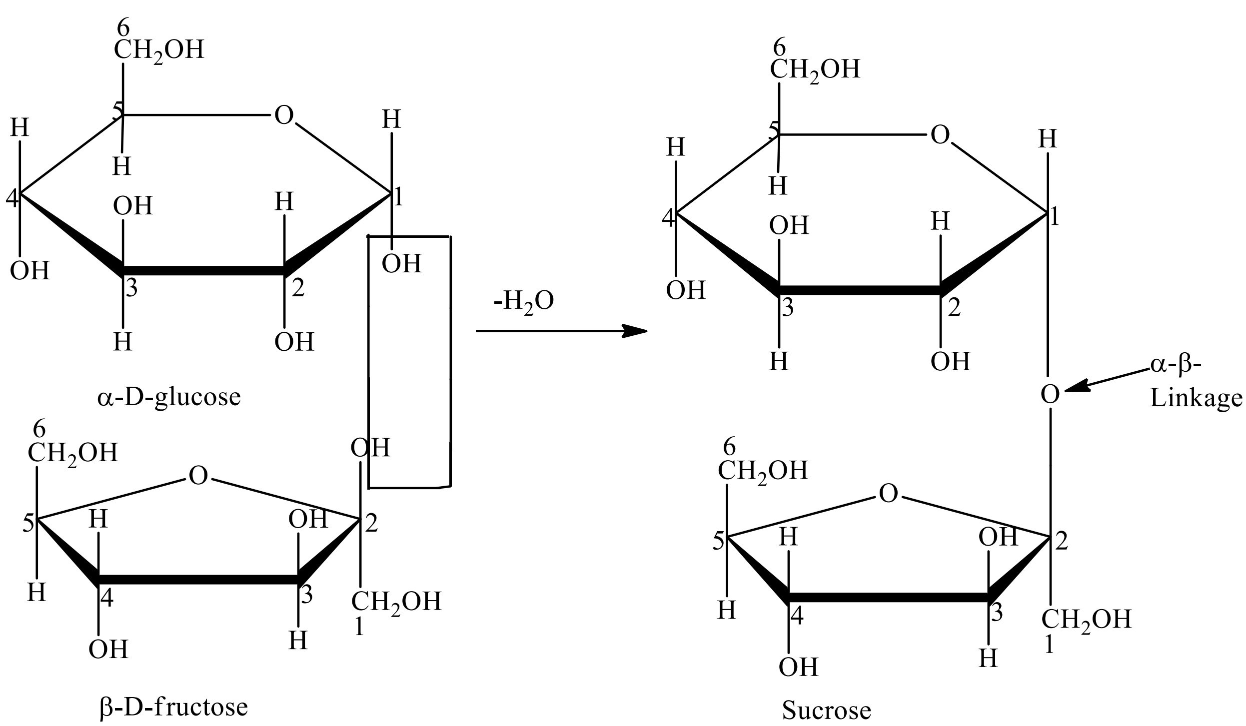
$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

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

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

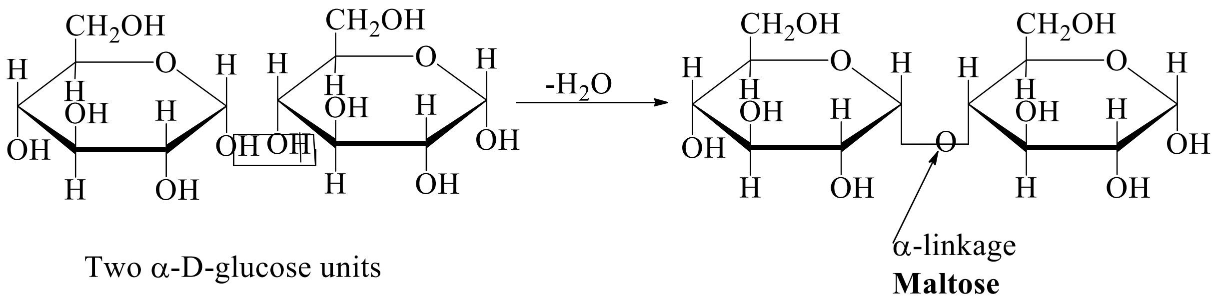
In disaccharides, the two monosaccharides are joined together by acetal or glycosidic formation. The hemiacetal OH of one monosaccharide and an OH of second monosaccharide, dehydrate to establish the bond (called glycosidic bond) between the two monosaccharides. That is, disaccharides are composed of two units of monosaccharides joined by glycosidic linkage.

Sucrose (Cane Sugar). Sucrose is ordinary table sugar. It is obtained from cane sugar. Sucrose is composed of α-D-glucose and β-D-fructose unit. These units are joined by α,β-glycosidic linkage between C-1 of glucose and C-2 of fructose unit.



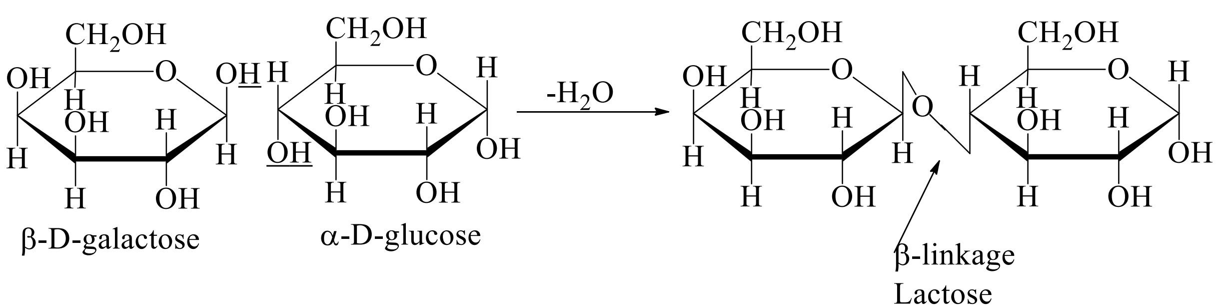
Notice that in the above structure of sucrose, hemiacetal structure is missing. That is why sucrose: (a) does not form an osazone with phenylhydrazine (b) does not reduce Tollen's reagent or Fehling's solution (sucrose is a non reducing sugar) (c) does not exhibit mutarotation.

Maltose: It is obtained from starch. It is composed of two α-D-glucose units joined by a α-glycosidic linkage between C-1 of one unit and C-4 of the other unit.



Notice that C-1 of the second glucose unit in the maltose structure is a hemiacetal carbon. Consequently, it is in equilibrium with the open chain aldehyde form. Thus maltose can exist in α and β forms. Since it has a potential aldehyde group, maltose shows mutarotation, forms osazone and reduces Fehling's solution (Maltose is a reducing sugar).

Lactose (Milk Sugar). It is found in milk of all animals. Cow's milk contains 4-5 % and human milk 6-7 % lactose. Lactose is composed of β-D-galactose unit and α-D-glucose unit joined by β-D-glycosidic linkage between C-1 of the galactose and C-4 of the glucose unit.

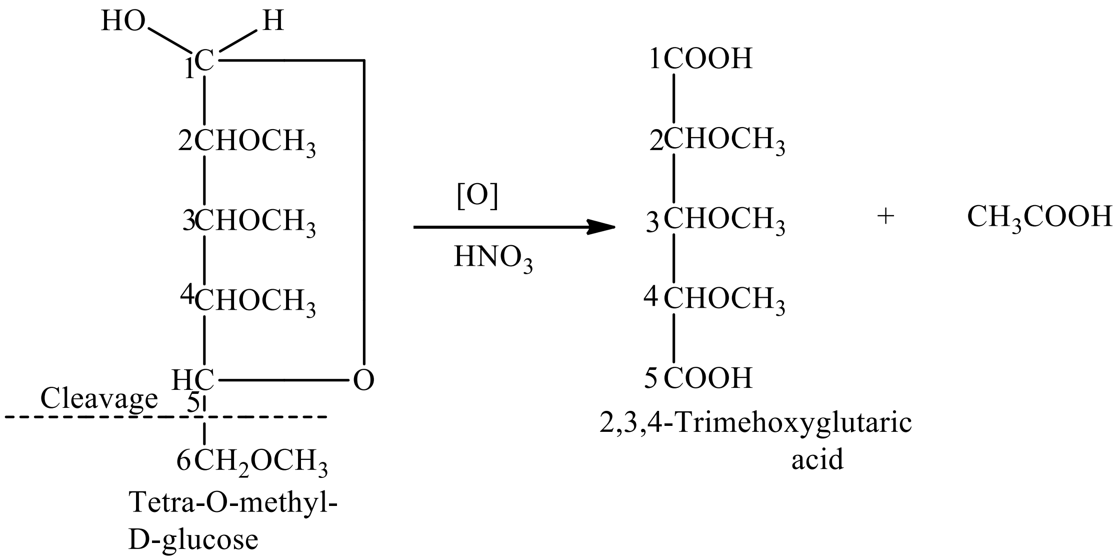


Like maltose, lactose can also exist in α and β forms. Lactose is a reducing sugar and shows mutarotation. It reacts with Tollen's reagent and Fehling's solution.

Determination of ring size of monosaccharides:

So far we have represented structure of cyclic hemiacetals or anomers of D-glucose as having a ring of six me zmbers, five carbons and one oxygen. This has been proved to be correct and a five membered ring has been ruled out.

Hirst (1926) prepared tetra-O-methyl-D-glucose with dimethyl sulphate and subsequent acid hydrolysis of the pentamethyl derivative formed. The oxidation of tetra-O-methyl-D-glucose with nitric acid yielded trimethoxyglutaric acid.



Obviously, the two carboxylic carbons (1,5) of the trimethoxyglutaric acid are the one's originally involved in ring formation. Hence, there must have existed an oxide ring between C-1 and C-5. Tracing back the reaction sequence, it stands proved that D-glucose has a six membered ring. The presence of a 6-membered ring in D-glucose has also been confirmed by X-ray analysis.

SUCROSE, Cane Sugar, ($C_{12}H_{22}O_{11}$):

Sucrose is ordinary table sugar. It occurs chiefly in sugar cane and sugar beets. In smaller amounts it is present in maple sap, honey, and several fruits.

Manufacture of Sucrose (Table Sugar):

In India and other tropical countries, the main source of sucrose is sugar cane. The modern method for the manufacture of 'Direct Consumption' sugar from cane consists of the following steps. (Fig 8.1).

(1) Juice Extraction. The crushed cane is passed through a roller mill to squeeze out juice. The partially exhausted 'cane mat' emerging from the mill is passed on to a tank, called Diffuser, by a chain conveyer. Here the maximum extraction of sucrose is done by washing with hot water and dilute juice on counter-current principle. This technique gets sugar extraction upto 98%. The cellulosic material discharged from the diffuser is called Bagasse and is used as fuel under boilers.

(2) Juice Purification: The raw juice contains 14-25% sucrose and much impurity such as organic acids, inorganic salts. Proteins and colouring matter. It is purified by the operations listed below:

(i) Defecation: The juice is heated with high pressure steam and treated with 2-3 % lime in a steel tank. This operation called defecation throws out organic acids as insoluble calcium salts, coagulated protein and colouring matter. The precipitate is removed by filtration.

(ii) Carbonation: Through the filtered juice is then CO_2. This operation known as carbonation, removes the excess, of lime as calcium carbonate which entraps colouring matter, colloidal and some inorganic salts. The 'mud' that settles is separated by filtration.

(iii) Decolorisation: In India, the clarified juice is decolorized by treating with SO_2. This operation called Sulphitation while it bleaches the brown colour of the juice, completes the neutralization of lime. The insoluble calcium sulphite is removed by filtration.

(3) Concentration and Crystallisation: The clear solution is then concentrated by boiling under reduced pressure in Multiple Effect Evaporators. In these, the steam produced in the first evaporator is used to boil the juice in the second maintained at a lower pressure; the second being used to boil the juice in the third kept at a still lower pressure; and son on.

The concentrated juice is finally passed to the Vacuum Pan where further evaporation reduces the water content to 6-8%. Here partial separation of crystals takes place. The mixture of syrup and crystals, known as Massecuite, is then discharged into a large tank, the Crystallising Tank, fitted with cooling pipes. The crystals grow and form a thick crop.

(4) Separation of Crystals by Centriguagation, and Drying. The massecuite is then sent to centrifuges wherby sugar crystals are separated from the syrup. The crystals are here sprinkled with a little water to wash any syrup sticking to the surface. The wet sugar is dried by passing down a rotating drum with stream of hot air flowing counter-current to it. The residual mother liquor, from which the crystals have been removed, is called molasses. In India, it is valuble raw material for alcohol manufacture by fermentation.

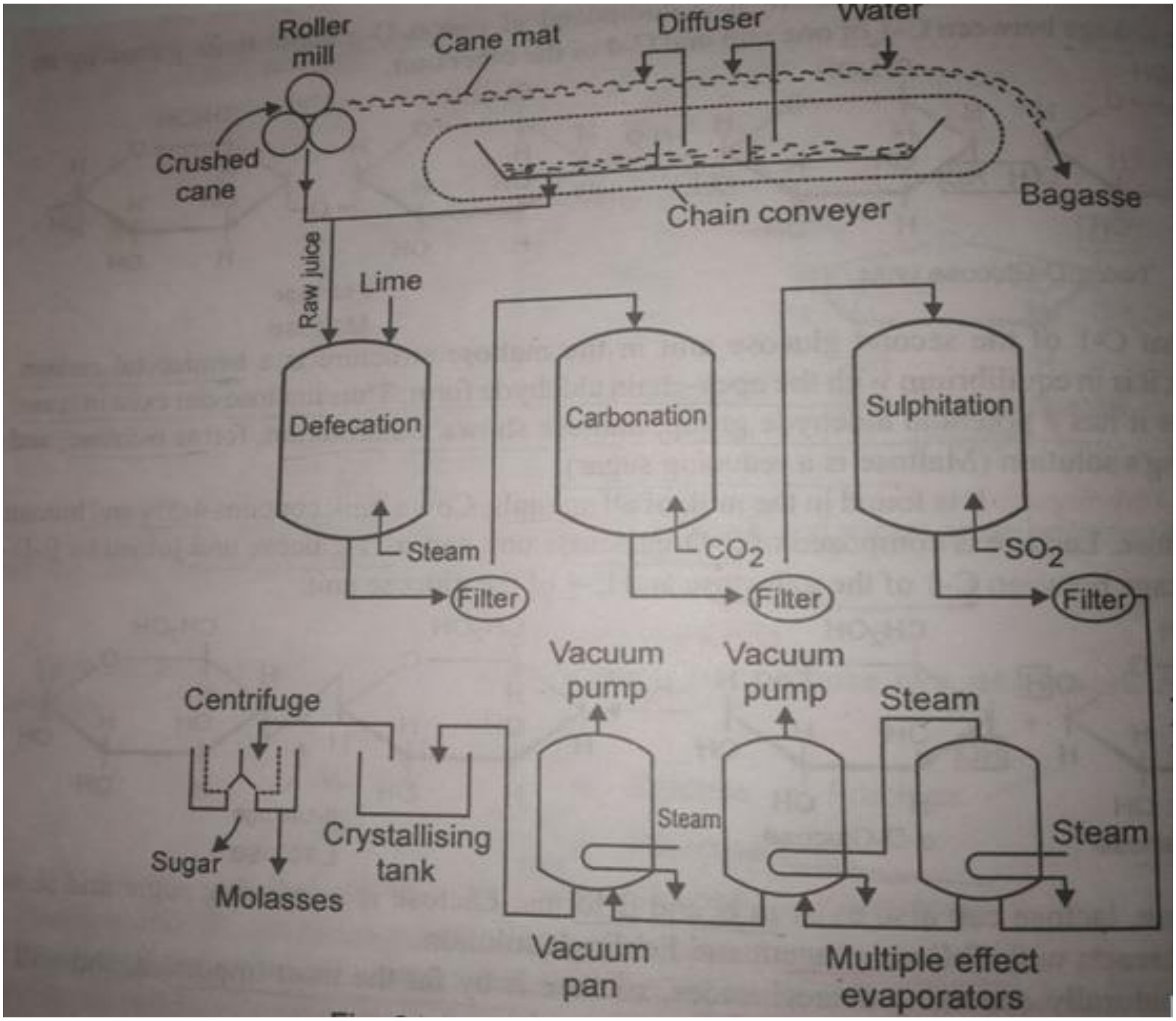


Fig .sugar manufacture (Flow sheet)

Properties of Cane Sugar, $C_{12}H_{22}O_{11}$:

1. It is colourless, crystalline substance, sweet in taste. It is very soluble in water and the solution is dextrorotatory $[\alpha]_D = +66.5$.

2. Effect of heat. Sucrose on heating slowly and carefully melts and then if allowed to

cool, it solidifies to pale-yellow glassy mass called 'barley sugar'.

When heated to 473K, it loses water to form a brown amorphous mass called caramel. On strong heating it chars to almost pure carbon giving characteristic smell of burnt sugar.

3. Hydrolysis or Inversion of Sucrose (Sugar). Sucrose when boiled with mineral acids, or by the enzyme invertase, yields an equimolar mixture of glucose and fructose.

$$\underset{\substack{\text{Cane sugar} \\ [\alpha]_D = +66.5}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Inversion}} \underset{\substack{\text{Glucose} \\ [\alpha]_D = +52.7}}{C_6H_{12}O_6} + \underset{\substack{\text{Fructose} \\ [\alpha]_D = -92.4}}{C_6H_{12}O_6}$$

Invert Sugar $[\alpha]_D = -20$

Sucrose is dextrorotatory and on hydrolysis produces dextrorotatory glucose and laevorotatory fructose. With greater laevorotation of fructose the mixture is laevorotatory. Thus, there is a change (inversion) in the direction of rotation of the reaction mixture from dextro to laevo. This phenomenon is called inversion and the enzyme which brings about this inversion is called invertase.

4. **Formation of Sucrosates:** Sucrose solution reacts with calcium, barium and strontium hydroxides to form sucrosates.

$$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}} + 3Ca(OH)_2 \longrightarrow \underset{\text{Calcium sucrosate}}{C_{12}H_{22}O_{11.3}(CaO)} + 3H_2O$$

The sucrosate decomposes when carbon dioxide is passed in the solution.

5. **Action of nitric acid:** Concentrated nitric acid oxidizes cane sugar to oxalic acid.

$$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}} + \underset{\text{From } HNO_3}{18O} \longrightarrow 6 \underset{\text{Oxalic acid}}{\begin{array}{c} COOH \\ | \\ COOH \end{array}} + 5H_2O$$

6**. Fermentation:** Fermentation of Sucrose is brought about by yeast when the enzymes invertase hydrolysed sucrose to glucose and fructose and zymase converts them to ethyl alcohol.

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

$$C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2C_2H5OH + 2CO_2$$

1.15 GENERAL INTRODUCTION OF STRUCTURE OF RIBOSE AND DEOXYRIBOSE

Ribose and deoxyribose are two well known aldopentoses. Their structures are discussed as under.

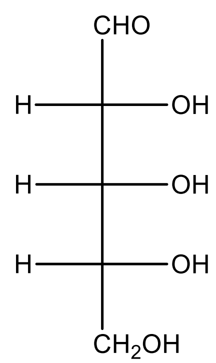
Structure of D-(+)- Ribose:

D-(+)- Ribose occurs naturally in plant nucleic acids and in liver and pancreas nucleic acids. It gives properties similar to glucose.

Ribose has the molecular formula ($C_5H_{10}O_5$) and shows the presence of an aldehyde group, four hydroxyl groups (one primary and three secondary) and a straight chain of carbon atoms. Therefore, it was assigned an open chain formula as given below:

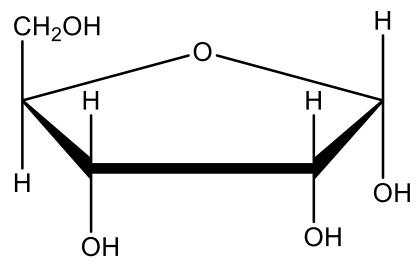
$$^5CH_2OH\text{-}^4CHOH\text{-}^3CHOH\text{-}^2CHOH\text{-}^1CHO$$

The configuaration of D-ribose has been established as follows.

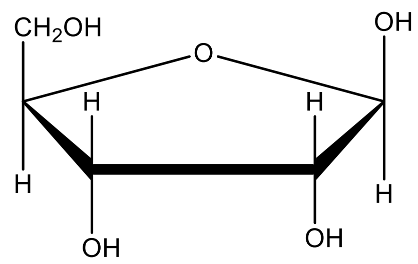


D-(+)-ribose

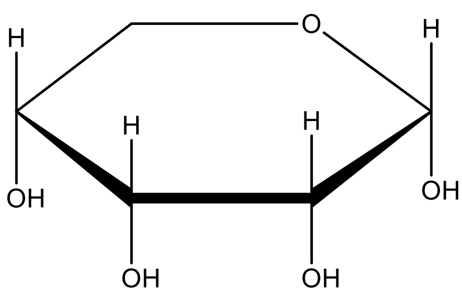
As in the case of glucose, D-ribose is now assigned a ring structure and is known to exist both in furanose and pyranose forms as depicted below:



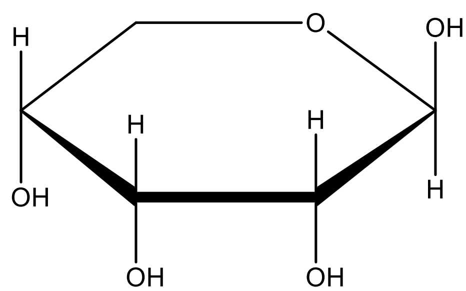
α-D-(-)-Ribofuranose



β-D-(+)-Ribofuranose



α-D-(-)-Ribopyranose



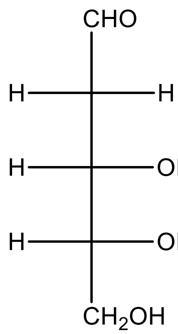
β-D-(+)-Ribopyranose

Pyranose form is more stable than the furanose form. Equilibrium mixture of ribose contains 56% β-D-ribopyranose 20% α-D-ribopyranose, 18% β-D-ribofuranose and 6% α-D-ribofuranose. In RNA ribose is present in furanose form.

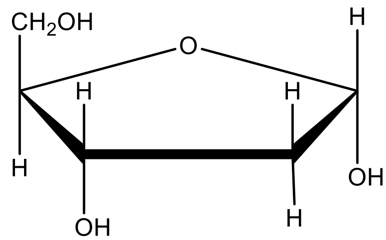
Structure of deoxyribose:

In this aldopentose the hydroxyl group at C-2 of ribose has been replaced by hydrogen. That is why it is named as deoxyribose. It is fundamental constituent of deoxyribonucleic acid (DNA).

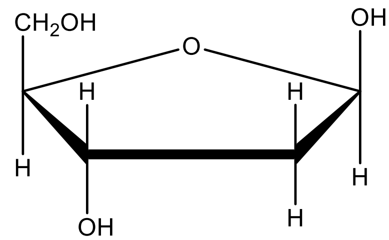
The structure of D-2-deoxyribose is derived from that of D-ribose and may be represented in the open chain and ring forms as follows.



Open chain form of D-2-deoxyribose



α-D-2-deoxyribofuranose



β-D-2-deoxyribofuranose

1.16SUMMARY

- Carbohydrates are poly hydroxy aldehydes and ketones.
- Monosaccharides containing an aldehyde group are called aldoses and those with a keto group are called ketoses.
- Carbohydrates can also be classified as disaccharides, oligosaccharides, and polysaccharides consist of monosaccharides linked by glycosidic bonds.
- The most abundant monosaccharide in nature is 6- carbon sugar, D-glucose. It exists as α and β anomers with different optical rotations.
- If two monosaccharides isomers differ in configuration around one specific carbon atom [With exception of carbonyl carbon] they are called epimers of each other.
- Glyceraldehydes are the simplest carbohydrate and it serves as a reference molecule to write the configuration (D and L) of all other monosaccharides.
- The pair of enantiomers with similar groups on the same side of the carbon chain is called the erythreo enantiomers while pair of enantiomers with similar groups on opposite sides is called the threo enantiomers.
- Mutarotation is defined as the interconversion of and β anomeric forms with the change in the optical rotation.
- Disaccharides are the carbohydrates which on hydrolysis give two same or different monosaccharides.
- Disaccharides are composed of two units of monosaccharides joined by

glycosidic linkage.

- Polysaccharides are neutral polymeric compounds in which hundreds or even thousands of monosaccharide units are joined by glycosidic linkages.

1.17*MODEL EXAMIONATION QUESTIONS*

1.Define and classify carbohydrates with suitable examples.

2.Explain kiliani-Fisher synthesis and Ruff's degradation.

3.Explain the limitations of open chain D-glucose structure.

4.Establish the structure of glucose and fructose.

5.How will you convert glucose into fructose?

6.Discuss the mechanism of mutarotation.

7.How is sucrose manufactured from sugar cane.

8.Discuss the structure of sucrose, lactose and maltose.

9.Write a short note on polysaccharides

1.18 REFERENCES

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3. Organic chemistry, Vol.III, Jagdamba singh and L.D.S Yadav, Prgati Prakashan.
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UNIT-2 AMINO ACIDS, PEPTIDES, PROTEINS

CONTENTS:

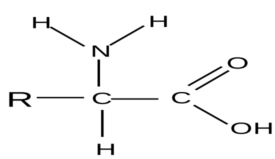
2.1 OBJECTIVE

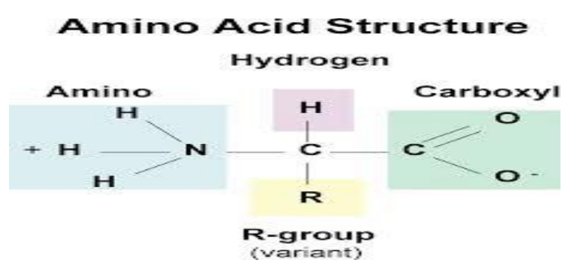
- After completion of this unit, the student should be able to:
- Define terms associated with amino acids and protein.
- Classification of Amino Acids
- Explain the difference between essential and nonessential amino acids.
- Acids and Bases behaviour of an amino acid.
- Classification of protein.
- Structure of protein.
- Functions of protein.

- Describe the biological value of protein
- Enzymes, Coenzymes, Cofactors and Vitamins

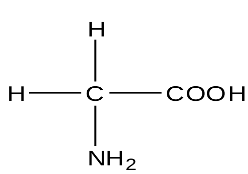
2.2 INTRODUCTION

Proteins are very big molecules made up of smaller units known as 'amino acids'. Amino acids are organic molecules that contain an amino group and a carboxylic acid group. All amino acids have a simple chemical backbone with an amine group (the nitrogen containing part) at one end. At the other end is the acid part. This backbone is the same for all amino acids. The difference between them depends on a distinctive structure, the chemical side chain that is attached to the backbone. It is the nature of the side chain that gives identity and chemical nature to each amino acid. There are about 20 different naturally occurring amino acids that combine to form proteins of all living tissue. The amino acids that make up proteins differ from fats and carbohydrates in that they contain the element nitrogen. The amino acids in proteins are called alpha (α)-amino acids because the amino group is attached to the -α carbon. A carbon connected to any carboxylic acid carbon is termed a □-carbon. Amino acids as are generally represented using the following formula:

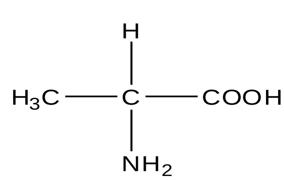




'R' varies from one amino acid to another. The NH_2 part is the amino group and COOH the acid group. The simplest amino acid is glycine, where 'R' is a hydrogen atom. In alanine, 'R' is CH_3, known as the methyl group.



Glycine



Alanine

All amino acids (except proline) contain –H, $-NH_2$, and –COOH bound to the □-carbon. They are differentiated by the side chains (called R-groups) also bound to the □-carbon. Amino acids occur widely in nature and have a number of uses in the human body.

2.3 CLASSIFICATION OF AMINO ACIDS

The difference between amino acids depends on their side-chain R groups because this is the only point of difference (all amino acids contain a carboxyl group, an amino group, and an H). The most important characteristic of R groups is polarity. As a result, amino acids are classified into four groups: nonpolar, polar acidic, polar basic, and polar-neutral amino acids. Amino acids are known by common names and each is abbreviated using a three-letter code.

The 20 amino acids commonly used to make proteins in the human body are listed in the following table. Essential amino acids cannot be made in the body and must be obtained in the diet. Non-essential amino acids are needed but don't have to be obtained from the diet because the body produces them.

Essential Amino Acids:

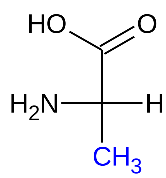
- Histidine
- Isoleucine
- Leucine
- Lysine
- Methionine
- Phenylalanine
- Threonine
- Tryptophan
- Valine

Non-Essential Amino Acids:

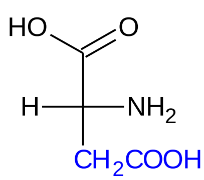
- Alanine
- Arginine
- Asparagine

- Aspartic Acid
- Cysteine
- Glutamic Acid
- Glutamine
- Glycine
- Proline
- Serine
- Tyrosine

You need all of the essential amino acids in adequate amounts in order for protein synthesis to occur in the body. If one essential amino acid is not present, the protein cannot be made.



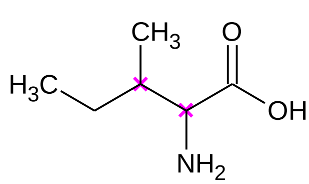
Alanine(Ala)



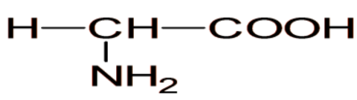
Aspartic Acid (Asp)

1. Name an amino acid besides threonine = Thr that has more than one asymmetric center.

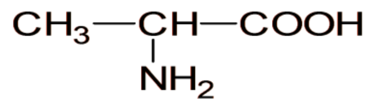
   Isoleucine = Ile



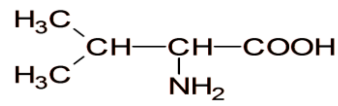
Ile



Glycine



Alanine



Valine

2.4 STRUCTURE AND STEREOCHEMISTRY OF AMNO ACIDS

In amino acid, there is a central carbon atom attached to hydrogen, a carboxylic acid group, an amine group and an alkyl group. Amino acids are thus all chiral except for glycine, in which the R is another H atom.

Optical activity:

• All amino acids except glycine are optically active due to asymmetric α-C atom.

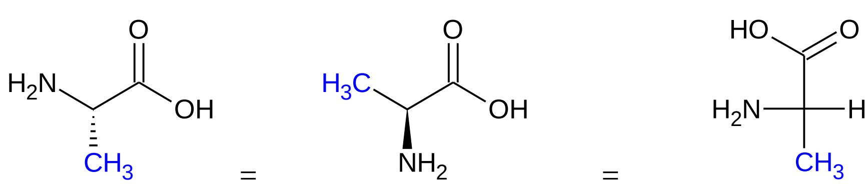
• They occur in D and L forms the naturally occurring amino acids in proteins are of the L-α amino acid form. D-amino acids are found in some antibiotics and bacteria.

All α -amino acids, except glycine, are **chiral** because the α -carbon is bound to *four different* groups. Glycine is exempt because it has two hydrogen atoms attached to the α - carbon (recall chiral carbons must have four different groups attached).

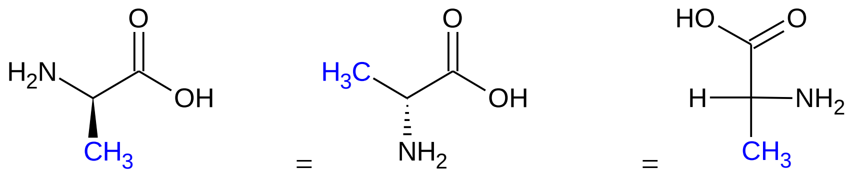
As chiral molecules, amino acids can exist as D or L isomers. When writing Fischer projections for amino acids, the -COOH group is always written at the top and the R group at the bottom. If the NH_2 is on the Left we have the L- isomer, if it is on the right, we have the D- isomer. In biological systems, only L isomers are found in proteins.

An example: L-Alanine, and D-Alanine

2.

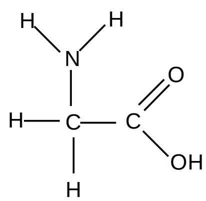


(S)-Ala **(L)-Ala (naturally occurring)**



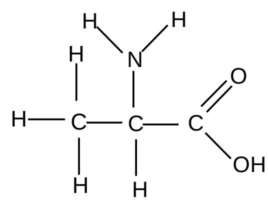
(R)-Ala **(D)-Ala**

Some simple examples are:



glycine

aminoethanoic acid



alanine

2-aminopropanoic acid

2.5 ACIDS AND BASES BEHAVIOUR

Amino acids contain an acidic group (-COOH) and a basic group (NH_2). The carboxylic acid (COOH) has a tendency to donate H+ and the amine group (NH_2) has a tendency to accept H+.

The product of this “internal” acid-base reaction is a dipolar ion (two poles) called a *zwitterion* (from the German meaning “double ion”). When the carboxylic acid donates H+ it becomes carboxylate (COO-). Therefore, the name indicates whether H+ is present (carboxylic acid) or absent (carboxylate).

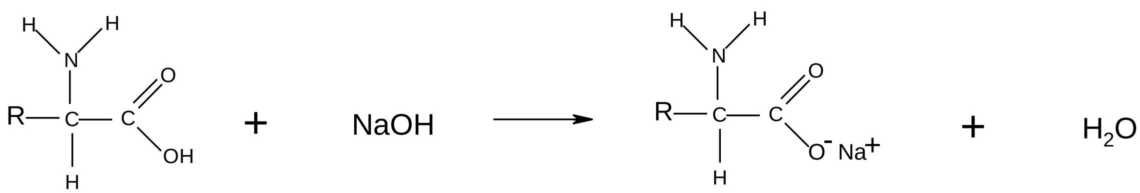
For example: glutamic acid (H^+ present on carboxylic acid) and glutamate (H^+ absent).

Zwitterion:

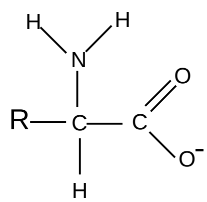
Every amino acid has a carboxyl group and an amino group, and each group can exist in an acidic form or a basic form, depending on the pH of the solution in which the amino acid is dissolved. Zwitterions are simultaneously electrically charged and electrically neutral. They contain positive and negative charges that cancel resulting in a net charge of zero. A **zwitterion** is a compound that has a negative charge on one atom and a positive charge on a nonadjacent atom. (The name comes from *zwitter*, German for “hermaphrodite” or “hybrid.”). Zwitterions are the neutral form of the amino acid despite the presence of “ion” in the name.

Zwitterions gain H^+ in acidic solutions and lose H^+ in basic solutions. Carboxylic acids have acidic properties and react with bases. Amines have basic properties and react with acids. It therefore follows that amino acids have both acidic and basic properties.

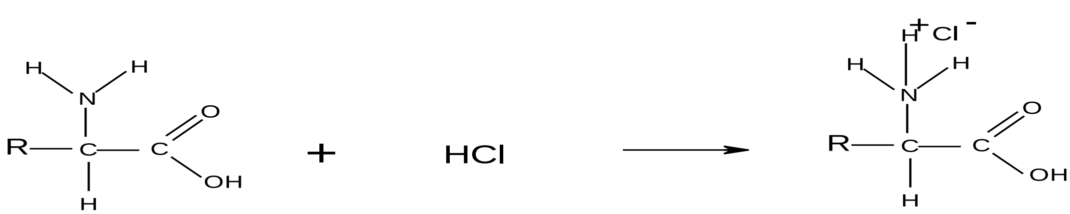
i) Reaction with bases: Amino acids react with strong bases such as sodium hydroxide:



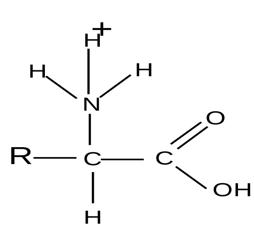
In **high pH**, therefore, amino acids exist in anionic form:



ii) Reaction with acids: Amino acids react with strong acids such as hydrochloric acid:



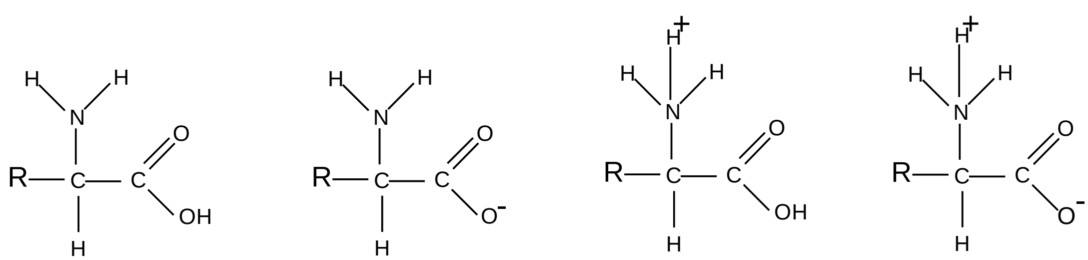
In **low pH**, therefore, amino acids exist in cationic form:



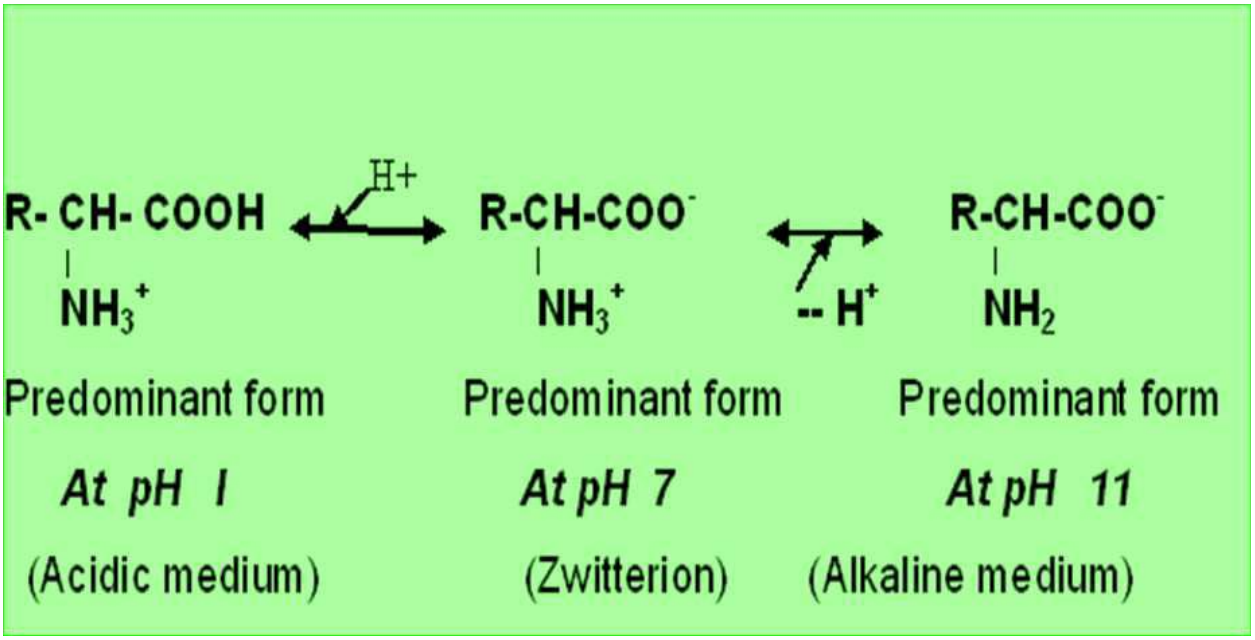
iii) Reaction with itself: Since amino acids have a proton donating group and a proton accepting group on the same molecule, it follows that each molecule can undergo an acid-base reaction with itself:

The double ion that is formed as a result of this reaction is called a **Zwitterion**. This reaction happens in the solid state. In the solid state, therefore, amino acids are ionic. This explains why they are solids with a high melting point.

iv) Summary: Amino acids can exist in molecular form, in cationic form, in anionic form or in Zwitterion form depending on the environment:



in neutral solution in alkaline solution in acidic solution in the solid state



Since amino acids can react with acids and alkalis, they make very effective **buffer solutions**.

2.6 ISOELECTRIC POINT AND ELECTROPHORESIS

The **isoelectric point** (pI) of an amino acid is the pH at which it has no net charge. It is the pH at which the protein carries equal positive and negative charges i.e. electrically neutral i.e. protein molecule occurs as a zwitterion. In other words, it is the pH at which the amount of positive charge on an amino acid exactly balances the amount of negative charge:

pI (isoelectric point) = **pH at which there is no net charge**

At some intermediate pH, the amino acid is present in an electrically neutral form. At this pH, called the isoelectric point (plI, the amino acid exists almost exclusively in the dipolar form. The isoelectric point depends on the structure of an amino acid. Neutral amino acids have isoelectric points in the pH range of 5.

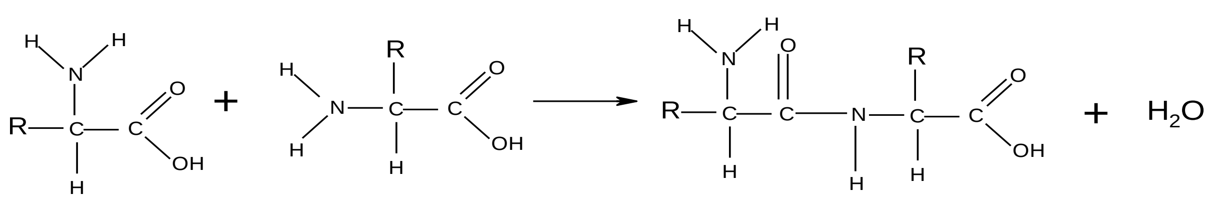
Aspartic and glutamic acids contain an extra carboxyl group and at neutral pH values they are mainly present in anionic form. To convert this anion into a neutral dipolar ion (in other words to reach the p~ some quantity of an acid must be added. Thus, the isoelectric point of dicarboxylic amino acids is in the range of 3.

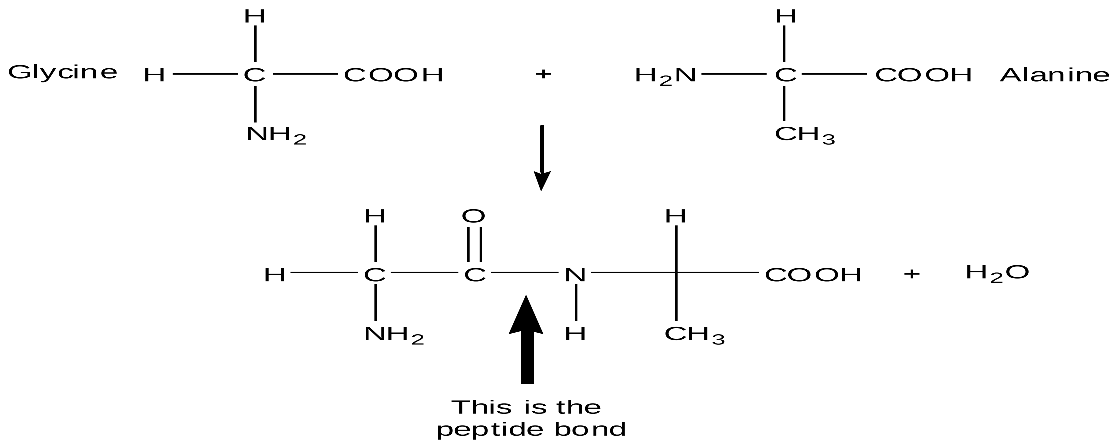
For a similar reason, the isoelectric points of basic amino acids are in the basic region of pH. Due to amphoteric nature of amino acids they are able to neutralize small quantities of acids or bases, thus maintaining a constant pH of the solution. Such compounds are termed buffers and are used in biochemical investigations.

A mixture of amino acids can be separated by e**lectrophoresis method,** which separates amino acids on the basis of their isoelectric point values. In this method, a few drops of a solution of an amino acid mixture are applied to the middle of a piece of filter paper or to a gel. When the paper or the gel is placed in a buffered solution between two electrodes and an electric field is applied, an amino acid with a pI greater than the pH of the solution will have an overall positive charge and will migrate toward the cathode (the negative electrode). The farther the amino acid's pI is from the pH of the buffer, the more positive the amino acid will be and the farther it will migrate toward the cathode in a given amount of time. An amino acid with a pI less than the pH of the buffer will have an overall negative charge and will migrate toward the anode (the positive electrode). If two molecules have the same charge, the larger one will move more slowly during electrophoresis because the same charge has to move a greater mass.

Peptide bond

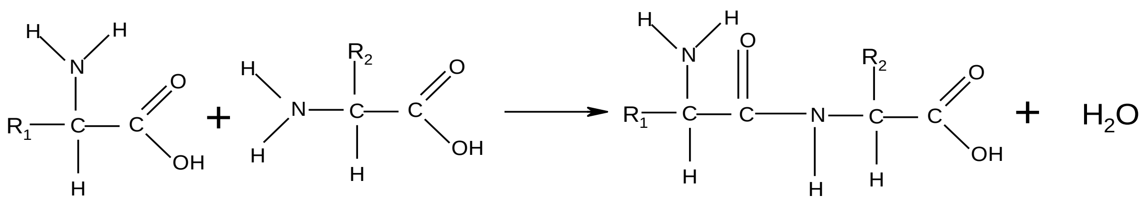
Since amino acids have both acid and amine groups, two molecules can therefore react with each other to form a molecule containing a peptide or amide link. Amino acids can link together to form chains of variable length. To do this, the acid group of one amino acid interacts with the amino group of an adjacent amino acid. The linkage formed is known as a peptide bond. Peptide bond is formed between the amino group of one amino acid and the carboxylic group of another amino acid with the removal of water. Two amino acids are linked together they form a dipeptide; if 3 they form tripeptides and so on. Polypeptides may contain more than 10 and up to 100 amino acid residues, while peptides containing more than 100 amino acid residues are called proteins.



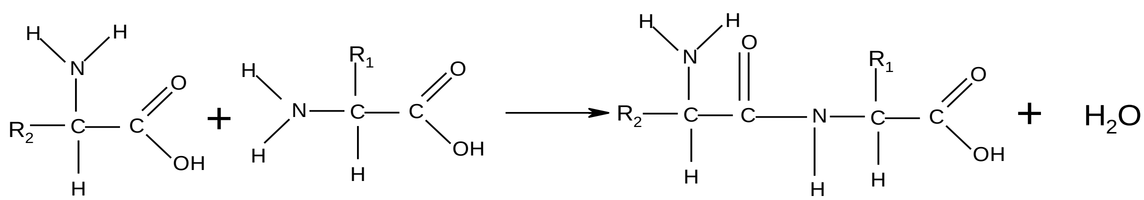


This dipeptide (two amino acids linked together) is known as glycylalanine and is represented as Gly-Ala using the three-letter amino acid coding system. This reaction is called a condensation reaction because two amino acid molecules join together and one molecule of water is eliminated.

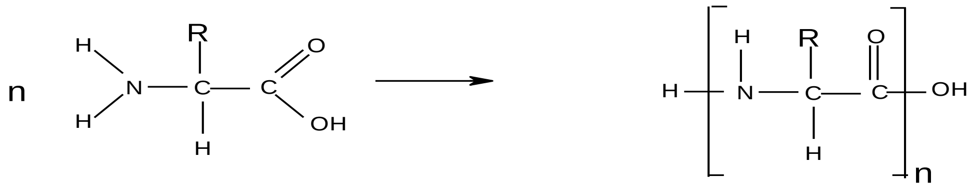
Dipeptides can also be formed by the condensation of two different amino acids. In this case two different molecules can be formed:



or



Since the resulting dipeptides also have both amine groups and carboxylic acid groups, they can undergo further condensation reactions, eventually forming polymers:



PROTEINS

The word protein is derived from the Greek word proteios, meaning″protein″ a″ first. The word indicates the importance of these substances. Proteins are formed of amino acid residues linked together by peptide bonds. The resulting polymer is called a **protein**, and is an essential component of living organisms.

Proteins are naturally occurring polyamides formed by the condensation of many amino acid molecules under carefully controlled conditions. Proteins are naturally occurring polymers of amino acid monomer units joined by a peptide bond. Chemically, polymerization of amino acids into protein is a dehydration reaction. They are of high molecular weight (more than 5000), colloidal in nature, non dialysable and heat labile.

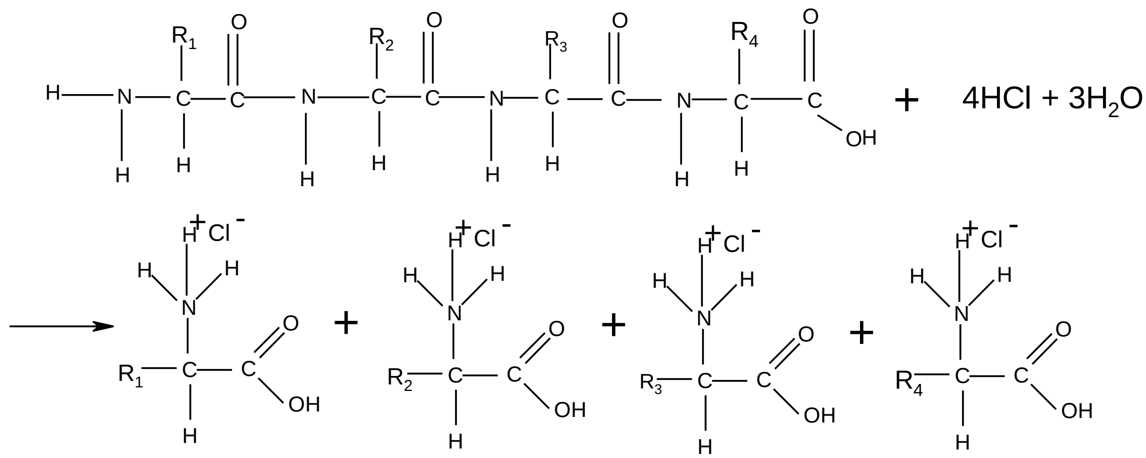
Proteins are naturally occurring organic polymers that are composed of monomer units called amino acids. Amino acids contain a carbon atom with two functional groups, an amino group, (NH_2), and a carboxylic acid group, (COOH) attached. This central carbon atom also has a hydrogen atom and another organic group, an "R" group, attached. The identity of the R group determines the identity of the amino acid.

Proteins play an important role in a variety of biological systems, i.e.: oxygen transport, components of skin and hair, muscle movement, as biological catalysts (enzymes), regulate metabolic processes (hormones), and the list goes on and on and on. Proteins are large complex polymers of amino acids, the monomeric unit of proteins. Amino acids are connected by an amide linkage called a peptide bond. Our study of proteins begins with a survey of amino acids commonly found in proteins. It has been estimated that about 18% of the human body is made up of protein. Like carbohydrates and fats, proteins are made up of the elements carbon (C), hydrogen (H) and (O) but they also contain nitrogen (N).

The sequence of the amino acids dictates the properties of a protein. Examples of proteins include keratin in hair, hemoglobin, insulin, antibodies, and enzymes.

2 .7 SELECTIVE HYDROLYSIS OF PEPTIDES AND PROTEINS

The peptide link in proteins is the same as the peptide link in N-substituted amides. As a result it can be broken by heating in strong acid or strong alkali. Proteins can thus be broken down into their constituent amino acids by heating in strong acid or strong alkali; in practice 6 mol dm^{-3} HCl is generally used. This reaction is an example of a hydrolysis reaction. In acidic conditions the amino acids are produced in cationic form:



This hydrolysis reaction enables chemists to deduce which amino acids are present in a sample of protein. The different amino acids can be identified by chromatography. If a sample of the amino acid mixture is placed onto chromatography paper and allowed to separate, it is possible to identify the different amino acids present in the sample by comparing their R_f values (the distance each amino acid moves up the paper compared to the solvent) with those of known amino acids.

2.8 LEVEL OF PROTEINS STRUCTURE

Proteins differ from each other in the sequence of the amino acids that form a particular chain. They also differ in the way that the protein chain (also called a peptide chain) is linked, coiled, or twisted. Protein molecules are described by several levels of structure. It can be explained under four headings.

2.8.1 Primary structure: refers to sequence of amino acids in a poly peptide chain.If this sequence changes then nature and function of protein changes. The sequence of amino acids in a protein is known as the **primary** structure of the protein. It varies from protein to protein, depending on the function that the protein needs to perform.

Eg: gly – ala – leu – iso – gln

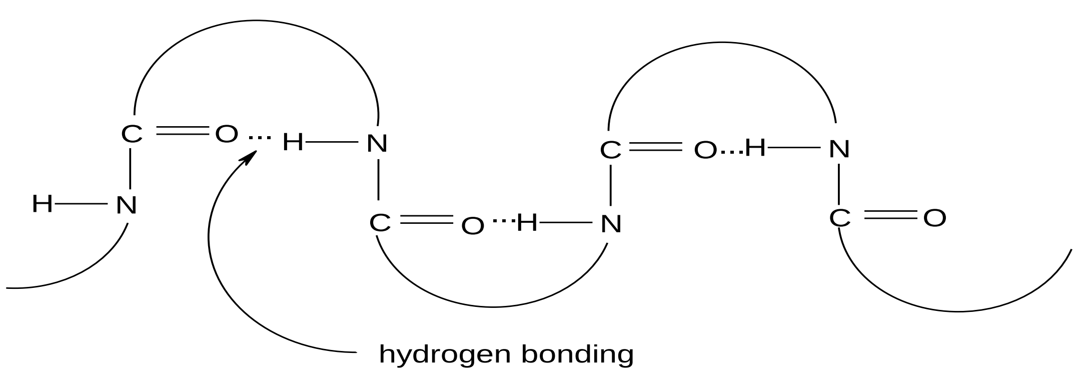
(each of these three–letter symbols is the code for an amino acid)

A protein can have several thousand amino acids, all arranged in a specific order.

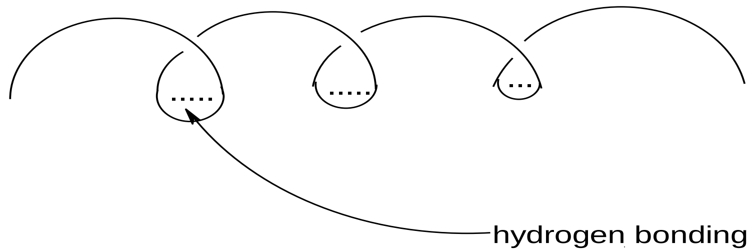
Chemically, the backbone of every chain is -C-C-N-. This backbone is also called a peptide chain. If two amino acids join in a chain, it is called a dipeptide. A number of amino acids in a chain are called polypeptide. Molecules of water bind to both the backbone and polar groups of proteins. Polypeptide and proteins are formed from amino acids by a condensation reaction in which one amino acid loses -OH from -COOH and another loses -H from -NH2 to form a peptide bond. Repetition of this reaction (polymerization) converts dipeptide to polypeptide and these in turn to proteins. A strand formula for an amino acid, with the variable group R, has been used in the diagram. Breakdown of proteins to polypeptide to amino acids is the reverse process, an enzyme-catalyzed hydrolysis.

2.8.2. Secondary structure: *Secondary structure* refers to the shape in which a long polypeptide chain can exist. This describes the conformation of segments of the backbone chain of a peptide or protein.This structure is resulted due to regular folding of long polypeptide chain. This folding is caused due to H-bonding between H atom of -NH group and oxygen atom of CO group of different amide same or different polypeptide chain. To minimize energy, a polypeptide chain tends to fold in a repeating geometric structure such as an α- or a β-sheet Chain exists in two different forms.

Protein molecules are not straight as there is hydrogen bonding within the molecule; the hydrogen atom on one peptide link can form a hydrogen bond with the nitrogen or oxygen atoms on another peptide link; causing the structure to coil up:

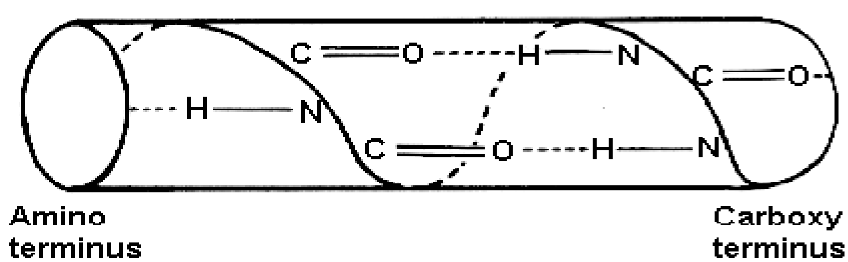


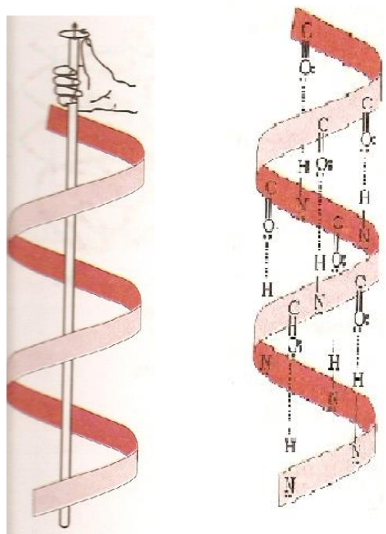
The result of this coiling is a helical structure known as the **secondary** structure of the protein:



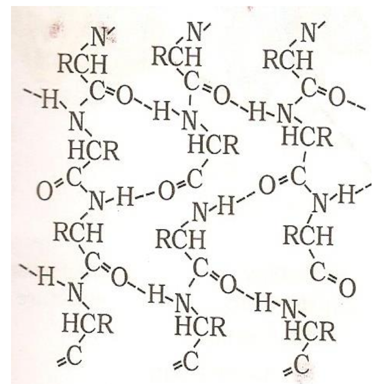
(i) **α –helix structure**: a structure resulted due to twisting of polypeptide chain into a right handed screw (helix). In this case –NH group of each amino acid residue is hydrogen bonded to the CO of an adjacent turn of helix. The structure repeats itself every 5.4 Å along the helix axis, i.e. we say that the α-helix has a pitch of 5.4 Å. α-helices have 3.6 amino acid residues per turn, i.e. a helix 36 amino acids long would form 10 turns. The separation of residues along the helix axis is 5.4/3.6 or 1.5 Å, i.e. the α-helix has a rise per residue of 1.5 Å. Every main chain C=O and N-H group is hydrogen-bonded to a peptide bond 4 residues away (i.e. O_i to N_{i+4}). This gives a very regular, stable arrangement. The peptide planes are roughly parallel with the helix axis and the dipoles within the helix are aligned, i.e. all C=O groups point in the same direction and all N-H groups point the other way. Side chains point outward from helix axis and are generally oriented towards its amino-terminal end.

Toilet roll representation of the main chain hydrogen bonding in an alpha-helix.





α–helix structure



β- pleated structure

A human hair strand is made up of many alpha helices. As the diagram below shows, three alpha helices are interwoven to make a protofibril. Eleven protofibrils are bonded and coiled together to make a microfibril. Hundreds of these microfibrils are combined together into an irregular bundle called a macrofibril. These, in turn, are mixed with dead and living cells to make a complete strand of hair. Fibroin is a fibrous protein found in silk. It has a pleated sheet structure in which polypeptide chains line up in a parallel arrangement and are held together by hydrogen bonds.

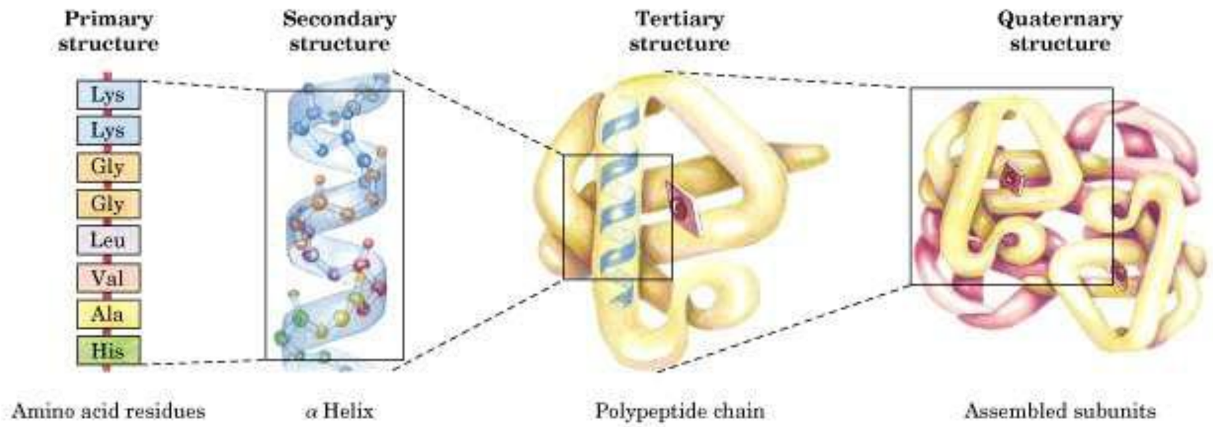
(ii) **β- pleated structure**: Structure of protein in which polypeptide chains are stretched out to nearly maximum extension and then laid side by side and held together by hydrogenbond. In a **β** -sheet two or more polypeptide chains run alongside each other and are linked in a regular manner by hydrogen bonds between the main chain C=O and N-H groups. Therefore all hydrogen bonds in a α-sheet are between different segments of polypeptide. This contrasts with the α-helix where all hydrogen bonds involve the same element of secondary structure. The R-groups (side chains) of neighbouring residues in a □-strand point in opposite directions. The axial distance between adjacent residues is 3.5 Å. There are two residues per repeat unit which gives the **β**-strand a 7 Å pitch. This compares with the α-helix where the axial distance between adjacent residues is only 1.5 Å. Clearly, polypeptides in the **β**-conformation are far more extended than those in the α-helical conformation.

(iii) **Tertiary structure**: This structure of a protein is the three-dimensional arrangement of all the atoms in the protein. Proteins fold spontaneously in solution in order to maximize their stability. Every time there is a stabilizing interaction between two atoms, free energy is released. The more free energy released, the more stable the protein. So a protein tends to fold in a way that maximizes the number of stabilizing interactions. It refers to overall folding of polypeptide chain i.e. further folding of 20 structures. 2^o and 3^o structures are stabilized by

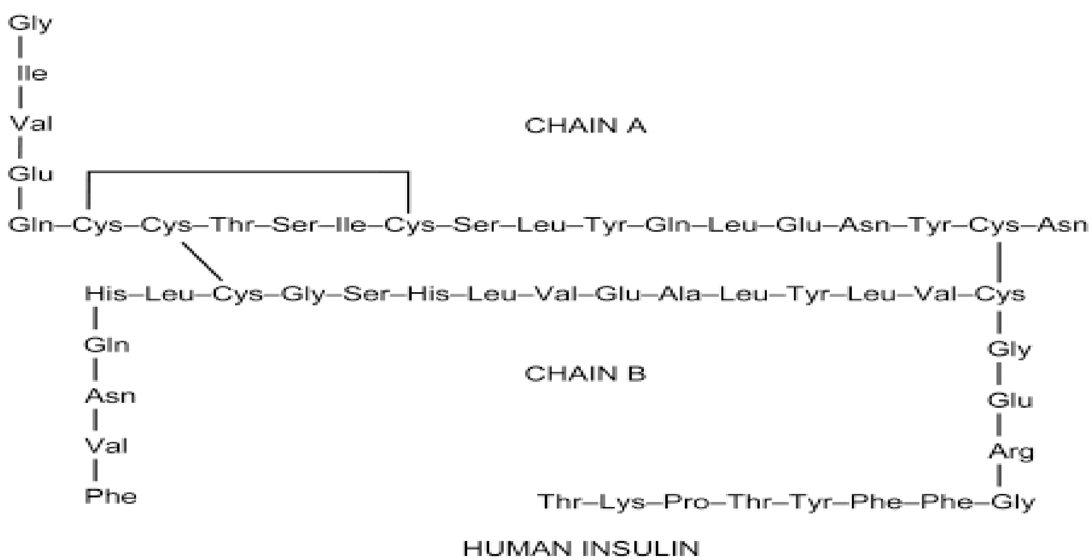
- H –bonding
- Disulphide linkage
- Vander Wall's force
- Electrostatic force

Tertiary structure describes the folding of the polypeptide chain to assemble the different secondary structure elements in a particular arrangement. As helices and sheets are units of secondary structure, so the domain is the unit of tertiary structure. In multi-domain proteins, tertiary structure includes the arrangement of domains relative to each other as well as that of the chain within each domain.

(iv) **Quarternary structure**: It refers to spatial arrangement of two ro more polypeptide chains i.e sub-units with respect to each other. The quaternary structure is that level of form in which units of tertiary structure aggregate to form homo- or hetero- multimers. Proteins that have more than one peptide chain are called **oligomers**. The individual chains are called **subunits**. A protein with a single subunit is called a monomer, one with two subunits is called a dimer; one with three subunits is called a trimer, and one with four subunits is called a tetramer. Hemoglobin is an example of a tetramer. It has two different kinds of subunits and two of each kind. The subunits are held together by the same kinds of interactions that hold the individual protein chains in a particular three-dimensional conformation: hydrophobic interactions, hydrogen bonding, and electrostatic attractions. This is found to be remarkably common, especially in the case of enzymes.



Insulin is a protein hormone that is involved in maintaining blood sugar levels. It consists of 51 amino acids organised into two chains that link into a 3D structure.



Classification of proteins: Various classifications are used.

I- According to shape

II- According to the biological value

III- According to structure

I- According to shape: On the basis of axial ratios of proteins (the ratios of length to breadth) and their three dimensional shape two classes of proteins are found:

(a) Fibrous – consisting of polypeptide chains arranged side by side. They have an axial ratio of more than 10 e.g. keratin, myosin, fibrin and collagen.

Keratin is a protein found in hair and skin. It is a fibrous protein and has a coiled structure similar to that of a telephone cord. The structure is described as an alpha helix. This confers on it properties such as toughness, rigidity, and water insolubility.

(b) Globular – consisting of coiled polypeptide chains that form compact roughly spherical shapes. They have an axial ratio of less than 10 (usually about 3 or 4) *e.g. plasma albumins and globulins* and many enzymes. They have spheroidal shape. Insulin is a globular protein with a roughly spherical shape that is soluble in water.

II- According to the biological value:

(a) Proteins of high biological value: i.e. contain all the essential amino acids. e.g. animal proteins as albumin and globulins in milk and in egg-white.

(b) Proteins of low biological value: i.e. deficient in one or more essential amino acid. e.g. plant proteins as Zein in maize.

III- According to structure:

1- Simple proteins: Formed only of amino acids

2- Conjugated proteins (compound proteins)

3. Derived proteins

1- Simple proteins:

a- Protamines and histones: These are water soluble basic proteins rich in histidine, arginine and lysine. They are present in nucleoproteins. Protamines are present in fish and histones are present in plants and animals. Globin; the protein moiety of Hb and myoglobin is considered as histone.

b- Albumins and globulins: These are heat coagulable. Globular proteins have high biological value. Globulins have larger molecular weight compared to albumins. They are present mainly in blood plasma, egg white and milk.

c- Scleroproteins (ALBUMINOIDS): These are fibrous structural proteins.

• They are insoluble in most protein solvent

• They include:

i. Keratins (epidermal proteins).

They are rich in sulphur containing amino acid (Cysteine).

They are the proteins of the outer surface of the skin, hair and nails.

It is an α-helical polypeptide chain.

ii. Collagen:

It is present mainly in skin, cartilage, tendons and ligaments (hard tissues). It has a special structure; the unit structure of its fibers is the tropocollagen. The tropocollagen is formed of three polypeptide chains; each chain is in a helical conformation different from the α-helix in that:

a. It is left handed of three residues per turn.

b. No hydrogen bonds in each helix while the three helices are hydrogen bonded to each other. In each polypeptide chain glycine occurs in 3rd position, the other amino acids are mainly proline and hydroxyproline, also lysine and hydroxylysine are present.

iii. Elastin: Found in yellow elastic tissue.

iv. Ossein: The main protein of bone and teeth.

4. Gliadin and glutelin: are plant proteins of low biological value e.g. protein of maize and wheat.

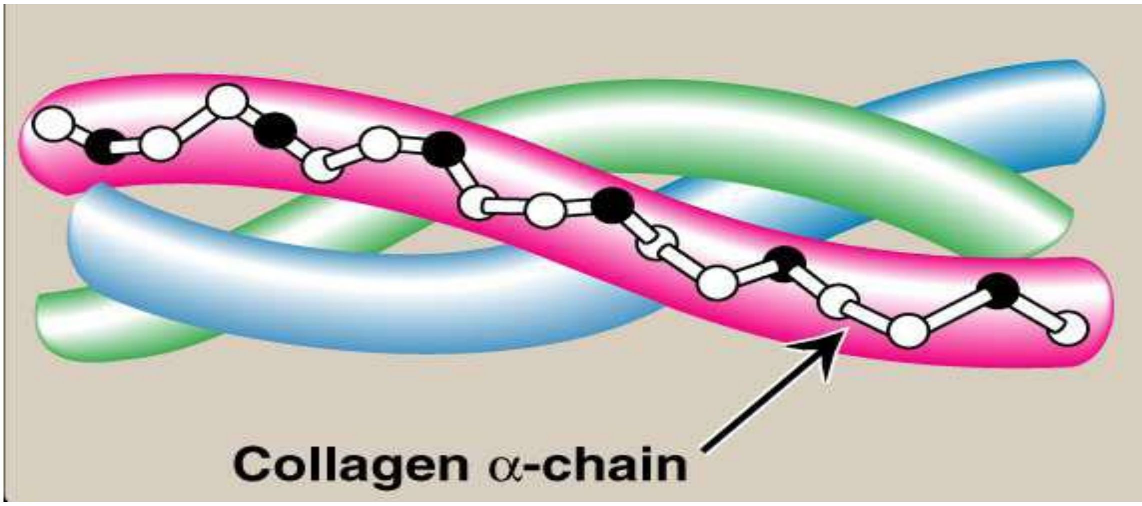


Fig: Collagen

2- Conjugated proteins (compound proteins): Those contain in addition to the protein moiety some other groups called the prosthetic group attached by covalent bonds. According to the prosthetic group; they are classified into:

a. Phosphoproteins: They contain *phosphoric acid* as prosthetic group; conjugated to hydroxyl group of *serine or threonine.* They are of animal origin *e.g. caseinogen* of milk and *vitellin* of egg yolk. Caseinogen is converted by rennin to soluble casein which is precipitated by Ca as Ca caseinate (cheese).

b.Glycoproteins: They are proteins that have carbohydrates (glycan) covalently attached to their polypeptide backbones.

c. Lipoproteins: These are combinations of proteins with lipids. They are present in *cell membranes and plasma lipoproteins.*

d. Nucleoprotiens: They contain nucleic acids (DNA or RNA) as prosthetic groups attached to *protamines or histones*. They are found in cell nuclei and also in cytoplasm.

e. Chromoproteins: These are proteins that contain colored prosthetic groups Haemoglobin is composed of globin and haem (red), (myoglobin is similar to Hb, but present in skeletal muscle). Rhodopsin is composed of opsin (protein) and 11-cis retinal. It gives purple color (visual purple). It is present in retina and responsible for vision in dim light.

f. Metalloproteins: They contain metals as prosthetic groups.

e.g.: Hb and ferritin contain iron.

Ceruloplasmin contains copper.

Carboxypeptidase and carbonic anhydrase contain zinc

3. Derived Proteins: They are hydrolytic products of proteins as a result of acids, alkalis or enzymes.

According to molecular weight they are classified into:

a. Metaproteins.

b. Proteoses.

c. Peptones.

Where metaproteins have the higher molecular weight, while peptones have the smallest Molecular weight Gelatin which is a hydrolytic product of collagen is considered as a proteose. It is poor in essential amino acids, but it is used as a supplementary protein as it is easily digested.

Functions of proteins:

I. Dynamic functions include:

1. Transport molecules or ions across membrane or between cells. e.g.:

• Albumin carries **calcium, free fatty acid and bile pigment.**

• Haemoglobin carries **oxygen**.

2. Catalytic role: chemical reactions are carried by enzymes (protein).

3. Metabolic regulations are carried by some protein hormones e.g. Insulin.

4. Contraction of muscles produced by myosin and actin.

5. Protection:

• Immunoglobulins act against invasion by bacteria and viruses.

• Blood clotting factors protect against hemorrhage.

• Mucin protects the respiratory and gastrointestinal tracts.

6. Fluid balance

7. Acid/base balance

8. Immune function

9. Enzymes

10. Cells in intestine replaced, skin cells, red blood cells

11. Tendons, bones, skin teeth - collagen

12. Fluids - albumin keeps balance between cells extracellular fluid and intracellular and BLOOD VESSELS - or else swelling

13. Can lower or raise pH - and act as buffers

14. Immune - antibodies, mucus - kill pathogens

15. Enzymes - lactose intolerance

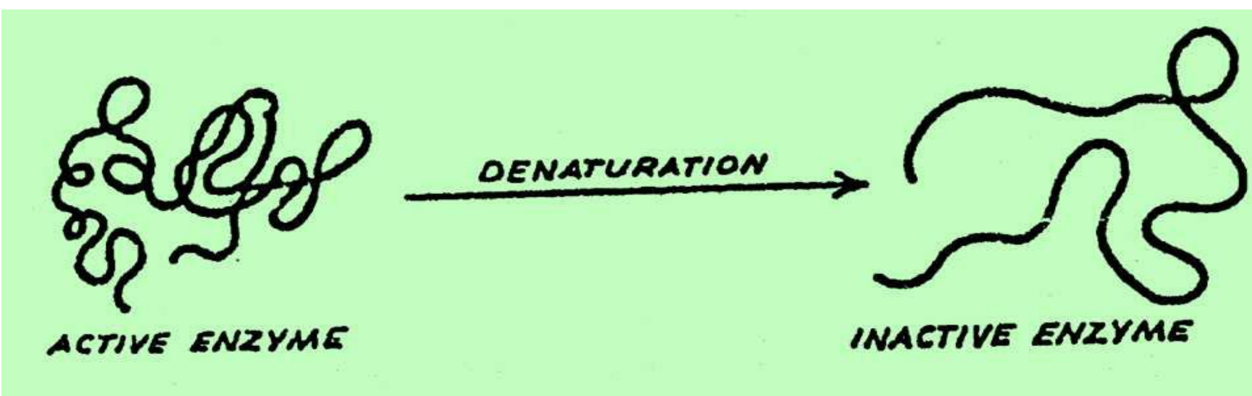
16. Hormones- like insulin

II. Structural functions: (static function)

1. Proteins are structural components of cell membrane, cytoplasm, cell organelles and nuclei.
2. Mechanical support: collagen and elastin enter in the structure of ligaments, tendons and blood vessels. Keratin has an essential structural role in skin, hair and nail. Ossein enters in the structure of bone.

2.9 PROTEIN DENATURATION

The tertiary structure of a globular protein is the result of many intramolecular attractions that can be disrupted by a change of the environment, causing the protein to become denatured. Destroying the highly organized tertiary structure of a protein is called **denaturation**. A change in the secondary, tertiary and quaternary structure of proteins is due to ***rupture of the non-covalent bonds (hydrogen bonds, hydrophobic bonds and electrostatic bond.*** Anything that breaks the bonds responsible for maintaining the three-dimensional shape of the protein will cause the protein to denature (unfold). Because these bonds are weak, proteins are easily denatured. The totally random conformation of a denatured protein is called a **random coil**. Denaturation disrupts all orders of protein structure except primary structure.



Representation of denaturation of a protein.

Solubility is drastically decreased as in heating egg white, where the albumins unfold and coagulate. Enzymes also lose all catalytic activity when denatured.

Causes of denaturation: The following are some of the ways that proteins can be denatured:

1. Physical agents:

• Heating above 70ºC. Heating increase molecular motion, which can disrupt the attractive forces. A well-known example is the change that occurs to the white of an egg when it is heated or whipped.

• Vigorous shaking

• Stirring

• Repeated freezing and thawing

• Ultraviolet rays

• X-rays.

2. Chemical agents:

• Salts of heavy metals as Mg^{2+} and Pb^{2+} disrupt ionic bonds

• Strong acids and bases (extreme pH). Changing the pH denatures proteins because it changes the charges on many of the side chains. This disrupts electrostatic attractions and hydrogen bonds.

• Sulfhydral reagents e.g. mercaptoethanol (destroys S-S bonds by reduction).

• Alkaloidal reagents e.g. picric acid and phosphotungestic acid

• Alcohol.

• Certain reagents such as urea and guanidine hydrochloride denature proteins by forming hydrogen bonds to the protein groups that are stronger than the hydrogen bonds formed between the groups.

• Detergents such as sodium dodecyl sulfate denature proteins by associating with the nonpolar groups of the protein, thus interfering with the normal hydrophobic interactions.

• Organic solvents denature proteins by disrupting hydrophobic interactions.

Effects of denaturation

1. Physical changes:

- Decreased solubility (due to exposure of internal non-polar groups) and decreased rate of diffusion through membranes.
- Increased viscosity of proteins (due to unfolding of chains and increase of their molecular size).

2. Chemical changes:

- Rupture of non- covalent bonds (and may be disulfide bonds).
- Exposure of some groups which are present in the interior of the protein molecule e.g. – SH.

3. Biological changes:

- Loss of biological activity of enzymes and protein hormones.
- Changes of antigenic property of proteins.
- Denatured proteins are easily digested due to unfolding of the peptide chains.

2.10 ENZYMES, COENZYMES, COFACTORS AND VITAMINS

Enzymes are Biomolecules that catalyze, increase the rates of chemical Reactions. Almost all enzymes are proteins. In enzymatic reactions, the molecules at the beginning of the process are called substrates, and the enzyme converts them into different molecules, the products.

Almost all processes in a biological cell need enzymes in order to occur at significant rates.

- Most enzyme reaction rates are millions of times faster than those of comparable un catalyzed reactions.
- However, enzymes do differ from most other catalysts by being much more specific.
- Activators are molecules that increase activity. Many drugs and poisons are enzyme inhibitors.
- Activity is also affected by temperature, chemical environment (e.g. pH).
- Some enzymes are used commercially, for example, in the synthesis of antibiotics.
- In addition, some household products use enzymes to speed up biochemical reactions.

Naming of Enzymes

Enzymes are usually named according to the reaction they carry out. Typically the suffix *-ase* is added to the name of the substrate (*e.g.*, lactase is the enzyme that cleaves lactose) or the type of reaction (*e.g.*, DNA polymerase forms DNA polymers).

Specificity

Enzymes are usually very specific as to which reactions they catalyze and the substrates that are involved in these reactions.

"Lock and key" model

Enzymes are very specific, because both the enzyme and the substrate possess specific complementary geometric shapes that fit exactly into one another. This is often referred to as "the lock and key" model.

However, while this model explains enzyme specificity, it fails to explain the stabilization of the transition state that enzymes achieve.

Induced fit model

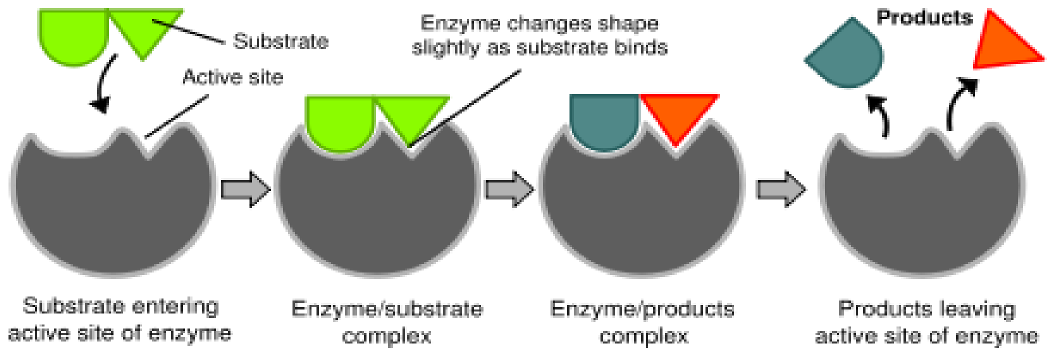


Fig: Diagrams to show the induced fit hypothesis of enzyme action.

Cofactors and coenzymes:

Cofactors

- Some enzymes do not need any additional components to show full activity.
- However, others require non-protein molecules called cofactors to be bound for activity.
- Cofactors can be either inorganic (*e.g.*, metal ions and iron-sulfur clusters) or organic compounds, (e.g., flavin and heme).

Organic cofactors can be either:

Most cofactors are not covalently attached to an enzyme, but are very tightly bound. However, organic prosthetic groups can be covalently bound.

Coenzymes

Coenzymes are small organic molecules that transport chemical groups from one enzyme to another. Some of these chemicals such as riboflavin, thiamine and folic acid are vitamins, (acquired).

“Cofactor” usually refers to a substance that is noncovalently bound to the enzyme; “coenzyme” usually refers to a covalently bound substance.

Enzyme Deficiency

A variety of metabolic diseases are now known to be caused by deficiencies or malfunctions of enzymes. **Albinism**, for example, is often caused by the absence of tyrosinase, an enzyme essential for the production of cellular pigments. The hereditary lack of phenylalanine hydroxylase results in the disease phenylketonuria (PKU) which, if untreated, leads to severe mental retardation in children.

Enzyme Inhibitors:

Competitive Inhibitors: Are molecules that are chemically similar to the substrate and can compete with the substrate for access to the active site (like putting the wrong key in a lock, blocking the correct key but not destroying the keyhole).

Noncompetitive Inhibitors: Are substances that chemically interact with the protein that the enzyme is made of, altering the enzymes chemical structure and destroying the active site's ability to bind to its substrate. A noncompetitive inhibitor may acts on a part of the enzyme other than its active site (like hitting a lock with a sledgehammer, bending the keyhole out of shape so that the key doesn't fit any more).

Vitamins: These are a group of Organic compounds required in small quantities of a variety of biological functions, for proper metabolism; protect helth, for normal growth and activity of the body.

Vitamins are also required for the prevention of a number of diseases. Most vitamins cannot be synthesized by the body. They must be supplied in the diet. Vitamins are usually classified as water soluble or fat soluble.

Types of Vitamins:

1. **Fat-Soluble Vitamins:**

Properties:

- Fat soluble vitamins often have very specialized functions
- Necessary for the function or structural integrity of specific body tissues and membranes.
- Can be retained in the body, and are not leached out quickly.
- Apolar hydrophobic compounds that can only be absorbed efficiently when there is normal fat absorption.
- Unlike water soluble vitamins, an excess of a fat soluble vitamin can be just as harmful as a deficiency

2. **Water-Soluble Vitamins**:

Properties:

- Act as catalysts and enzyme cofactors in metabolic processes and energy transfer.
- Are not stored in the body (excreted fairly rapidly) and must be replaced each day.
- These vitamins are easily destroyed or washed out during food storage and preparation (overcooking)
- Water soluble vitamins do not accumulate in the body, so regular supplies are necessary

FAT – SOLUBLE VITAMINS

Vitamin A: Vitamin A is also known as retinol

Vitamin A Sources:

- Commonly found in cod liver oil, green vegetables, fruit dairy products, eggs, and liver
- Carrots indirectly serve as a source of vitamin A since they contain b carotene which the body readily converts to vitamin A

Vitamin A Functions:

- Role in aiding in night vision.
- Retinol is oxidized to retinal, which combines with the protein opsin to form rhodopsin. Rhodopsin is the active agent which converts light signals to electrical impulses that the optic nerve transmits to the brain

Vitamin A Deficiencies:

- A deficiency in vitamin A results in night blindness.
- The most serious deficiency results in a condition known as Xeropthalmia, a severe form of conjunctivitius or blindness.

Excess of Vitamin A:

- Carotenemia; Bleeding; Hepatosplenomegaly (rare)

2-Vitamin D (Calciferol)

Sources:

- Dairy products, eggs, Fish liver oils. Synthesized by sunlight action on skin.
- Unlike other vitamins, the body synthesizes vitamin D in the skin through the action of ultraviolet light on 7-dehydrochlosterol

Vitamin D Functions:

- Vitamin D is an important regulator of calcium metabolism.
- It is involved in the uptake of calcium and phosphate ions from food into the body.
- It is necessary for the proper formation of bone structures and teeth.

Vitamin D Deficiencies:

- Rickets (children)
- Osteomalacia (adults)

Excess of Vitamin D :

- Hypercalcemia leading to metastatic calcification and renal damage (rare).

3- Vitamin K:

Function:

- Blood clotting, Required for synthesis of Prothrombin (II) and clotting factors VII, IX and X.

Sources:

- Green leafy vegetables, liver; Naturally produced by bacteria in the intestine.

Deficiencies:

- Hemorrhagic disease

Water-Soluble Vitamins:

1- **B12 (Cyanocobalamin)**

Food source:

Red meats, Liver, eggs, dairy products and fish

Function:

Nucleic acid production

Deficincy:

Megaloblastic anemia (Pernicious anemia);neuropathy.

2- **Vitamin C (Ascorbic Acid)**

Sources:

- Citrus fruits, green leafy vegetables, tomatoes

Function:

- Collagen formation in teeth, bone, and connective tissue of blood vessels
- May help in resisting infection
- Absorption of iron, calcium, folacin
- Ascorbic acid is a great antioxidant
- Works with vitamin E as a free-radical scavenger.

Deficincy:

- Scurvy (breakdown of skin, blood vessels, and teeth)
- Impaired wound healing.
- *Vitamin C deficiency- often results secondary to hyperparathyroidism

Excess:

- None known, minimal-possibly urinary calculi, gastrointestinal complaints including diarrhea, nausea and abdominal cramps

3. Folic Acid (Folacin)

Source:

Whole-wheat foods, green vegetables, legumes, organ meats, fish, citrus fruits.

Function:

Nucleic acid metabolism

Deficiency:

Megaloblastic anemia (Pernicious anemia)

Other vitamins:

1. **Vitamin P** (bioflavonoids, citrin):
    a. Helps increase strength of capillaries found in the mesocarp (tasteless, spongy, white layer beneath the rind) of lemon fruit.

2. **Vitamin F** (unsaturated fatty acids):
   a. Is important in respiration of vital organs.
      i. -helps maintain resilience and lubrication of cells.
      ii. -helps regulate blood coagulation.
      iii. -is essential for normal glandular activity.

3. **Vitamin B13** (Orotic acid):
   a. is needed for the metabolism of some B-vitamins

   b. **Vitamin B15** (Pangamic acid): Helps eliminate hypoxia helps promote CHON metabolism stimulates nervous and glandular system
4. **Vitamin B17** (Laetrile): has been linked to cancer prevention

2.11 SUMMARY

Peptides and proteins are polymers of amino acids linked together by peptide (amide) bonds. A dipeptide contains two amino acid residues, a tripeptide contains three, an oligopeptide contains three to 10, and a polypeptide contains many amino acid residues. Proteins have 40 to 4000 amino acid residues. The amino acids differ only in the substituent attached to the Most amino acids found in nature have the L configuration. The carboxyl groups of the amino acids have values of and the protonated amino groups have values of At physiological pH, an amino acid exists as a zwitterion. A few amino acids have side chains with ionizable hydrogens. The isoelectric point (pI) of an amino acid is the pH at which the amino acid has no net charge. A mixture of amino acids can be separated based on their pI's by electrophoresis or based on their polarities by paper chromatography or thin-layer chromatography.

The amide bonds that link amino acid residues are called peptide bonds. A peptide bond has about 40% double bond character. By convention, peptides and proteins are written with the free amino group (the N-terminal amino acid) on the left and the free carboxyl group (the C-terminal amino acid) on the right. The primary structure of a protein is the sequence of its amino acids and the location of all its disulfide bridges. The secondary structure of a protein describes how local segments of the protein's backbone folds. A protein folds so as to maximize the number of stabilizing interactions: covalent bonds, hydrogen bonds, electrostatic attractions (attraction between opposite charges), and hydrophobic interactions (interactions between nonpolar groups). An α and β-helix and a coil conformation are types of secondary structure. The tertiary structure of a protein is the three-dimensional arrangement of all the atoms in the protein. Proteins with more than one peptide chain are called oligomers. The individual chains are called subunits. The quaternary structure of a protein describes the way the subunits are arranged with respect to each other in space.

Enzymes are biological substances that regulate the rates of the chemical reactions in living organisms; most enzymes are proteins (covered in some detail later in this course).

2.12 TERMINAL QUESTIONS

1. Define the following terms used in relation to proteins:
 (i) Denaturation (ii) Peptide linkage (iii) Primary
2. What are nucleotides and nucleotides?
3. Define the following terms (i) Essential amino acids (ii) Non- essential amino acids
4. Enumerate the structural difference between DNA and RNA.Write down the structure of sugar present in DNA.
5. Where does the water present in the egg go after boiling the egg?
6. Define the following as related to proteins (i) peptide linkage (ii) Primary structure(iii) Denaturation
7. What are the common types of secondary strcture of proteins?
 (i) α –helix structure (ii) β - pleated structure
8. What type of bonding helps in stabilizing the α - helix structure of protein?
9. Differentiate between globular and fibrous proteins. How do you explain the amphoteric behaviour of amino acids.
10. What is the effect of denaturation on the structure of proteins?
11. What are nucleic acids? Mention their two important functions.
12. Write the important structural and functional differences between DNA and RNA.
13. Protein requirements are higher for athletes than for non-athletes: True/False

MCQ: Choose the correct answer:

1. Proteins

(a) are macromolecules whose name means first or foremost.

(b) constitute 50% or more of the dry weight of the cell.

(c) are hundreds of different molecules in the living tissue.

(d) all the above

2- An average protein is how many folds larger than a glucose molecule?

(a) 2-10. (b) 10-20. (c) 20-50. (d) More than 500.

3- Diet proteins are important because they are the main source of

(a) carbon. (b) carbon and hydrogen. (c) hydrogen and oxygen. (d) nitrogen and sulfur.

4- Complex proteins may include

(a) glycoproteins and lipoproteins. (b) hemeproteins and nucleoproteins.

(c) phosphoproteins and metalloproteins. (d) all the above.

5- Aminoacids of proteins

(a) have the amino group and the carboxyl group attached to the same carbon atom.

(b) have the amino group attached to the alpha-, beta-, or gamma-carbon.

(c) both (a) and (b).

(d) neither (a) nor (b).

6- How many aminoacids share in the biosynthesis of all known proteins?

(a) 10 (b) 20 (c) 30 (d) 50

7- Alpha-aminoacids of proteins

(a) all have the D configuration. (b) all have the L configuration.

(c) have D or L configuration. (d) None of the above is true.

8- Regarding aminoacids that share in protein structure,

(a) all have optical activity. (b) all contain at least one asymmetric carbon atom.

(c) both (a) and (b). (d) neither (a) nor (b).

9- Proteins differ from each other in

(a) the number of forming aminoacids. (b) the types of forming aminoacids.

(c) the sequence of forming aminoacids. (d) all the above.

10- Which of the following statements best describes the difference between essential and non-essential aminoacids?

(a) Essential aminoacids should be supplied in the diet.

(b) Non-essential aminoacids should be avoided in the diet.

(c) Essential aminoacids are important for body function, while non-essential aminoacids are not.

(d) Non-essential aminoacids can be synthesized in the body, while the essential aminoacids cannot.

11- High biological value proteins

(a) contain some of the essential aminoacids. (b) come from animal source only.

(c) are hard to digest and metabolize. (d) are necessary in the diet, especially for children and pregnant women.

12- High biological value proteins are those proteins that

(a) contain all the essential aminoacids. (b) have high caloric value.

(c) are not hydrolyzed by digestive enzymes. (d) are obtained usually from plants.

13- Metabolic classification of aminoacids dictates that

(a) the majority of aminoacids are ketogenic.

(b) leucine and lysine are purely glucogenic aminoacids.

(c) isoleucine, threonine, phenyl alanine, tyrosine, and tryptophan are mixed.

(d) all the above.

14- Regarding the solubility of aminoacids in the plasma,

(a) all are soluble.

(b) only the aminoacids with charged groups are soluble.

(c) the aminoacids with non-polar groups need a carrier.

(d) the aminoacids with charged or polar groups are the only soluble ones.

15- Aminoacids are amphoteric molecules, so they

(a) have both acidic and basic groups.

(b) can react with acids or alkalis, forming salts in either case.

(c) can act as buffers at more than one pH.

(d) all the above.

16- Isoelectric point is

(a) acidic pH for basic aminoacids. (b) alkaline pH for dicarboxylic aminoacids.

(c) neutral pH for neutral aminoacids. (d) the pH at which the aminoacid carries no net charge.

17- Isoelectric point is defined as

(a) the pH at which the aminoacid or protein carries no net charge.

(b) the pH at which the aminoacid or protein does not migrate in a direct current electric field.

(c) both (a) and (b).

(d) neither (a) nor (b).

18- At isoelectric point, an aminoacid carries

(a) one or more positive charges. (b) one or more negative charges.

(c) equal positive and negative charges. (d) no electric charges.

19- At a pH above its isoelectric point, an aminoacid

(a) migrates towards the anode. (b) migrates towards the cathode.

(c) does not migrate in either direction. (d) migrates according to the charge on the amino group.

20- Zwitter ion is

(a) an aminoacid carrying one positive and one negative charges.

(b) an aminoacid at its isoelectric point.

(c) an aminoacid not migrating in direct current electric field.

(d) all the above.

21- A peptide bond

(a) results as a condensation reaction between the α -carboxyl group of one aminoacid and the α -amino group of another aminoacid.

(b) can be formed by the reaction of a non-carboxyl group.

(c) both (a) and (b).

(d) neither (a) nor (b).

22- Arrangement of chemical groups around a peptide bond is usually

(a) Cis. (b) Trans.

(c) Either cis or trans. (d) Neither cis or trans since the peptide bond is not a double bond.

23- A tripeptide is

(a) a molecule formed by three peptide bonds. (b) a molecule formed by three aminoacids.

(c) a molecules formed of three chains of aminoacids. (d) none of the above.

24- Hydrophobic bonds

(a) are not true bonds, which are created by the presence of hydrophobic molecules in an aqueous medium.

(b) result from association of water molecules, which pushes away any hydrophobic groups in the medium.

(c) are of extreme importance for the structure of proteins and biological membranes.

(d) all the above.

25- Van der Waals forces

(a) are non-specific weak attraction between close atoms.

(b) decrease greatly as the distance between the two atoms increases.

(c) turn to repulsion when the two atoms are closer than the critical distance.

(d) all the above

26- Hydrogen bond

(a) is a strong attraction between a hydrogen atom, already linked covalently to an oxygen or a nitrogen atom, and another oxygen or nitrogen atom.

(b) is necessary for determining the primary structure of protein molecules.

(c) can be seen in the α -helix of protein between the hydrogen of a peptide N and the carbonyl O of the residue fourth in line behind.

(d) all the above.

27- Regarding protein structure,

(a) Only peptide bonds are necessary for the proper biological function of a protein.

(b) Peptide bonds can be broken by acid hydrolysis or by the proteolytic action of proteases.

(c) Disulfide bond is a strong covalent bond which cannot be broken by oxidation or reduction in the lab.

(d) None of the above is true.

28- Primary structure of a protein

(a) is the number, types, and order of aminoacids. (b) is maintained by peptide bonds.

(c) Cannot be disrupted by heating or mild acid treatment. (d) all the above.

29- Regarding secondary structure of a protein,

(a) it is the folding of the polypeptide chain in the form of α-helices, β-pleated sheets or nonrepetitive elements.

(b) It is maintained entirely by the disulfide bonds.

(c) α-helix, β-pleated sheets, and non-repetitive elements cannot exist together in the same molecule.

(d) All the above.

30- Tertiary structure of a protein

(a) Gives the tridimensional shape of a protein.

(b) Describes the relationship between different domains of the molecule.

(c) Brings together aminoacids far apart in the primary structure.

(d) All the above.

31- Quaternary structure

(a) Is seen only in some proteins, which are called oligomeric proteins, e.g. hemoglobin.

(b) Is the aggregation of two or more polypeptide chains called monomers, protomers, or subunits held together by covalent bonds.

(c) Both (a) and (b).

(d) Neither (a) nor (b).

32- Hemoglobin is

(a) a pentamer. (b) a homodimer.

(c) a homotetramer. (d) none of the above.

33- Intra-chain hydrogen bonds may not stabilize which of the following?

(a) Alpha helix. (b) Beta-pleated sheets.

(c) Tertiary structure. (d) Quaternary structure.

34- The final shape of a protein is determined by

(a) the aminoacid sequence.

(b) the disulfide and non-covalent forces between aminoacid residues.

(c) the steric hindrance and electrostatic repulsion exerted by side groups of aminoacids.

(d) all the above.

35. When a peptide bond is formed there is removal of:

(a) CO_2 (b) H_2O (c) NH_3 (d) H^+

36. All amino acids are optically active except:

(a) Glycine (b) Serine (c) Threonine (d) Tryptophan

37. The major linkage between amino acids in protein is the:

(a) Hydrogen bond (b) Ionic bond (c) Sulphide bond (d) Peptide bond

38. Essential amino acids are so named because:

(a) They are essential for life process (b) Cannot be synthesized in the body

(c) Deficiency leads to genetic diseases (d) Important in cell growth

6.13 ANSWERS

1- d; 2- d; 3- d; 4- d; 5- a; 6- b; 7- d; 8- d; 9- d; 10- a; 11- d; 12- a; 13- c; 14- a; 15- d; 16- d; 17- c; 18- c; 19- a; 20- d; 21- c; 22- b; 23- b; 24- d; 25- d; 26- c; 27- b; 28- d; 29- a; 30- d; 31- a; 32- d; 33- d; 34- d; 35-b; 36-a; 37- d; 38- b.

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