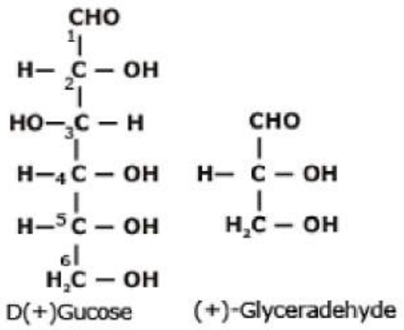
Chapter 13

Biomolecules

Structure of Glucose

6. Configuration* of Glucose:

Since the above structure possesses four asymmetric carbon atoms (shown by asterisks), it an exist in $2^4 = 16$ optically active forms, i.e., eight pairs of enantiomers. All these are known and correspond to the D-and L-forms of glucose, mannose, galactose, allose, glucose, idose and talose.
Naturally occurring glucose is the dextrorotatory glucose (+), one of the 16-stereoisomers.



Notations D- and L- for denoting configuration were given by Rosanoff; according to this convention, any compound whose bottom asymmetric carbon atoms has the configuration similar to the configuration of dextrorotatory glyceraldehyde (drawn above, i.e. the bottom carbon atom has -OH to the left and H to the right is given L-configuration. Remember that the symbols D-and L- have no relation with the specific rotation value, i.e., with (+) or (-) value. For example, the natural (-) fructose belongs to D-series, i.e., it is D(-)-fructose).

7. Objections to open-chain structure of glucose:

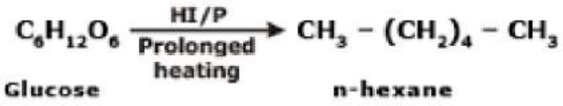
Even though the open chain structure of (+) glucose explains most of its reactions, it fails to explain the following facts about it.
i) Glucose does not restore Schiff's reagent colour.

ii) Glucose does not form a bisulphite and aldehyde-ammonia compound.
iii) Glucose forms two isomeric pent-acetates neither of which reacts with carbonyl reagents.
iv) The existence of the two isomeric glucose and the change in specific rotation (mutarotation) is not explained by an open-chain formula.
v) Glucose reacts with methanol in presence of dry HCl gas to form two isomeric glucosides.
Since glucose is less soluble in ethanol, it separates out on cooling the reaction mixture. Commercially, it is obtained by the hydrolysis of starch which is available from relatively inexpensive source such as maize, potatoes and rice.

Constitution of Glucose:

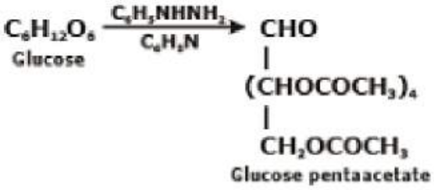
1. Molecular Formula: By the usual analytical methods, the molecular formula glucose is found to be $C_6H_{12}O_6$.

2. Straight Chain of six carbon atoms:
i) Reduction of glucose with conc. HI and phosphorus gives 2-iodohexane and n-hexane. This indicates that six carbon atoms in glucose are present in a straight chain.



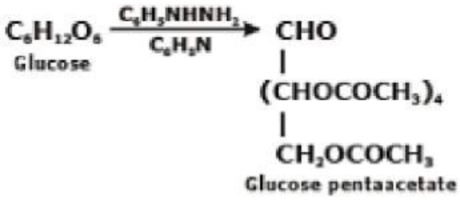
$$\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow[\text{Prolonged heating}]{\text{HI/P}} \underset{\text{n-hexane}}{CH_3-(CH_2)_4-CH_3}$$

ii) Glucose when oxidized with bromine water gives gluconic acid which when reduced with excess of HI gives n-hexanoic acid, $CH_3.(CH_2)_4.COOH$ confirming the presence of a straight chain of six carbon atoms in glucose.



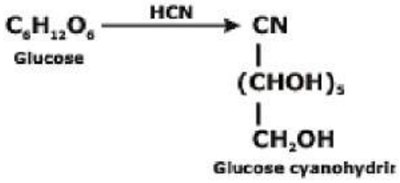
$$\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow[C_5H_5N]{C_6H_5NHNH_2} \underset{\text{Glucose pentaacetate}}{\begin{array}{c} CHO \\ | \\ (CHOCOCH_3)_4 \\ | \\ CH_2OCOCH_3 \end{array}}$$

3. Presence of five hydroxyl groups: When treated with acetic anhydride, glucose forms pent-acetate indicating the presence of 5 -OH groups and since glucose is a stable compound, the five -OH groups must be attached to 5 different carbon atoms.



$$\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow[C_5H_5N]{C_6H_5NHNH_2} \underset{\text{Glucose pentaacetate}}{\begin{array}{c} CHO \\ | \\ (CHOCOCH_3)_4 \\ | \\ CH_2OCOCH_3 \end{array}}$$

4. Presence of an aldehydic groups:
i) Glucose forms a cyanohydrin with hydrogen cyanide and a mono-oxime with hydroxylamine suggesting the presence of a carbonyl group.



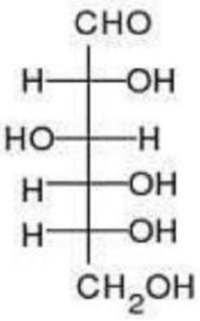
$$\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow{HCN} \underset{\text{Glucose cyanohydrir}}{\begin{array}{c} CN \\ | \\ (CHOH)_5 \\ | \\ CH_2OH \end{array}}$$

ii) Glucose reduces Fehling's solution and Tollen's reagent indicating that the carbonyl group is aldehydic in nature.
iii) The presence of aldehydic gruop in glucose is confirmed by its oxidation to gluconic acid having the same number of carbon atoms.

$$\underset{\text{Glucose}}{C_5H_{11}.\,CHO} + (O) \xrightarrow{Br_2} \underset{\text{Gluconic acid}}{C_5H_{11}O_5.\,COOH}$$

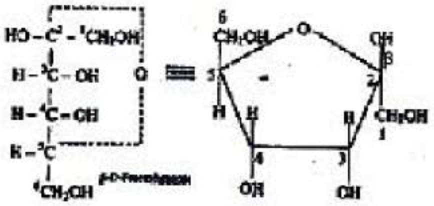
Now since aldehydic group is monovalent, it must be present on the end of the chain.

5. Open chain structure: On the basis of the above points, glucose may be assigned following prt structure orientation shown in the a anomer has the -OH trans to the -CH2OH group and the b anomer has the -OH cis to the -CH2OH group.

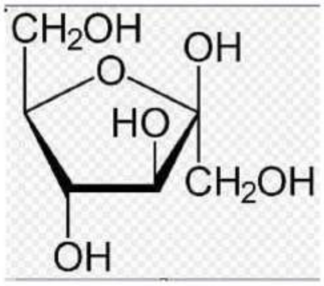


Cyclic structure of Fructose:

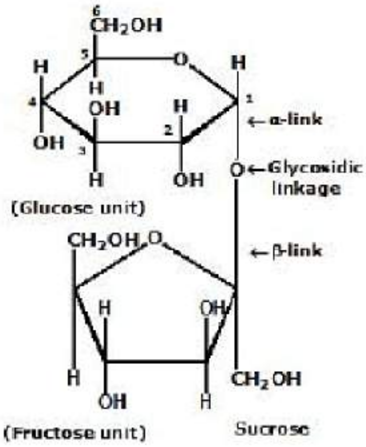
Like glucose, fructose also has a cyclic structure. Since fructose contains a keto group, it forms an intramolecular hemiketal. In the hemiketal formation, C5-OH of the fructose combines with C2-keto group. As a result, C2 becomes chiral and thus has two possible arrangements of CH_2OH and OH group around it. Thus,



D-fructose exists in two stereoisomeric forms, i.e., α-D-fructopyranose and β-D fructopyranose. However in the combined state (such as sucrose), fructose exists in furanose form as shown below:



Hydroylsis of Sucrose:



(Invert Sugar or Invertose). Hydrolysis of sucrose with hot dilute acid yields D-glucose and D-fructose.

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

Sucrose D ()-glucose D (-)-Fructose
$[a]_D = 66.5°$ $[a]_D = 53°$ $[a]_D = -92°$
Invert Sugar:
$[a]_D = (53°) - (-92°) = 39°$

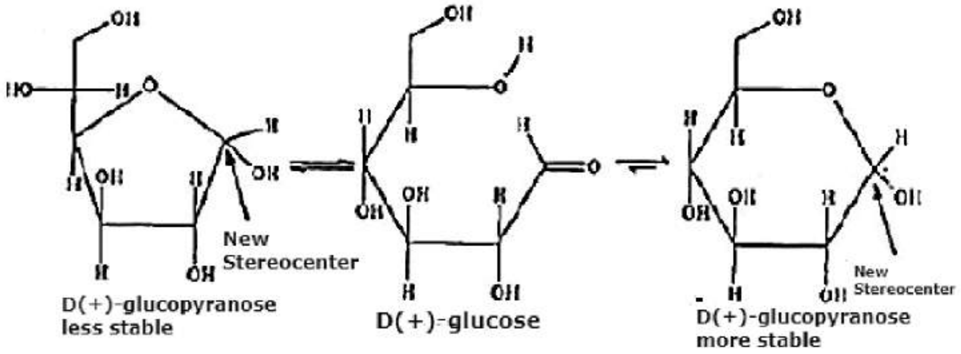
Surose is dextrorotatory, its specific rotation being 66.5%, D-glucose is also dextrorotatory, $[a]_D = 53°$, but D-fructose has a large negative rotation, $[a]_D = -92°$. Since D-fructose has a greater specific rotation than D-glucose, the resulting mixture is laevorotatory. Because of this the hydrolysis of sucrose is known as the inversion of sucrose, and the equimolecular mixture of glucose and fructose is known as invert sugar or invertose.

Solved Subjective Problems: Biomolecules & Polymers

SOLVED Subjective PROBLEMS

Problem 1: Write the hemiacetal formation for glucose.

Solution:



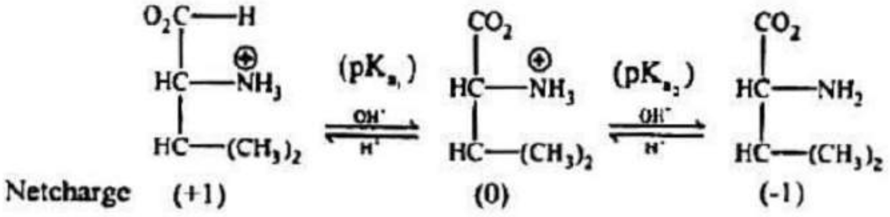
Problem 2: The pKa of the carboxyl group in an amino acid valine, $(CH_3)_2CHCH(NH_2)(COOH)$ is 2.31 and the pKa for the amino group of the same amino acid is 9.69. Compute the Isolectric point (pI) for valine and draw the structure of this amino acid when the pH of the solution equals to p1. Also draw the structures of valine that predominate at pH =2 and pOH =2.

Solution: The isoelectric point (pI) is the pH at which the amino acid exists only as a dipolar ion with net charge zero.

At isoelectric point, for a neutral amino acid,

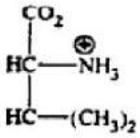
$$pI = \frac{\left(pK_{a_1} + pK_{a_2}\right)}{2}$$

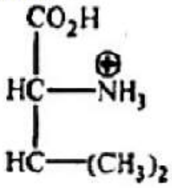
The dissociation of cationic form of valine can be represented as:

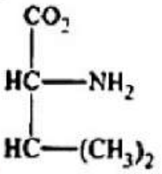


The species with zero net charge exists between species with (+I) and (—I) net charges.

$$pI = \frac{(pK_{a_1} + pK_{a_2})}{2} = \frac{9.69 + 2.31}{2} = 6$$

When the p_1-I of the solution equals to p_1, the structure of valine is 

When the pH of the solution is two, the structure of valine is 

When the pH of the solution is 12, the structure of valine is 

Problem 3*:* Sucrose on hydrolysis yields a mixture which is

(a) Optically inactive (b) Dextrorotatory (c) Laevorotatory (d) Racemic

Solution: ***(c)*** Sucrose on hydrolysis yields equimolar mixture of D-(—)-fructose and D-(+)glucose. Since specific rotation of D(—)-fructose is greater than (+)-glucose D, the mixture is laevorotatory.

Problem 4: A high molecular weight molecule which does not contain repeating structural units is called a
(a) Polymer (b) Macromolecule (c) Both (a) and (b) (d) None of these

Solution: (b) A polymer has always repeating structural units derived from monomer. For example proteins and nucleic acid are regarded as macromolecules, but not polymers because their molecules do not contain repeating structural units. All polymers are macromolecules, but all macromolecules are not polymers.

Problem 5: The force of attraction between the neighbouring peptide chains is (a) van der Waal's force (b) Covalent bond (c) Hydrogen bond (d) Peptide linkage

Solution*:* (c) Neighbouring peptide chains are held by hydrogen bonds between —CO— and — NH—.

Problem 6: **Peptides on hydrolysis give**

(a) Ammonia (b) Amines (c) Amino acids (d) Hydroxy acids

Solution*:* (c) Peptides are formed by condensation of a-amino acids. Therefore, on hydrolysis they yield a-amino acids.

Problem 7*:* An example of a condensation polymer is

(a) PVC (b) terylene (c) polypropylene (d) polystyrene

Solution: (b) In condensation polymerization, a series of condensation reactions between the (generally two) monomers containing atleast two functiønal groups each occur with the loss of a small molecule such as H_2O, CH_3OH or HX (X = halogen). Terylene is a condensation polymer of ethylene glycol and terephthalic acid.

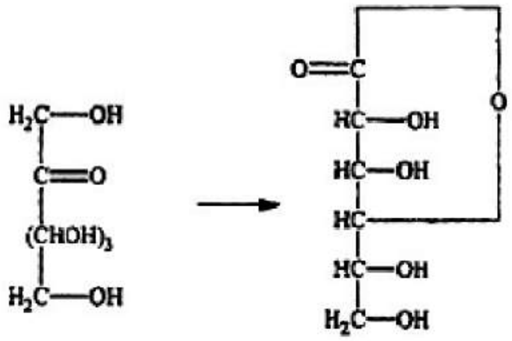
Problem 8: Although both polymers are prepared by free radical processes, poly (vinyl chloride) is amorphous and poly (vinylidene chloride) (saran) is highly crystalline. How do you account for the different (vinylidene chloride is 1,1-dichloroethene).

Solution: As poly (vinyl chloride) is able to show stereoisomerism and further it is formed by a free radical process, it is atactic (chlorine atoms (distributed randomly), the molecules fit together poorly.
Poly (vinylidene chloride) has two identical substitutents on each carbon and the chains fit together well.

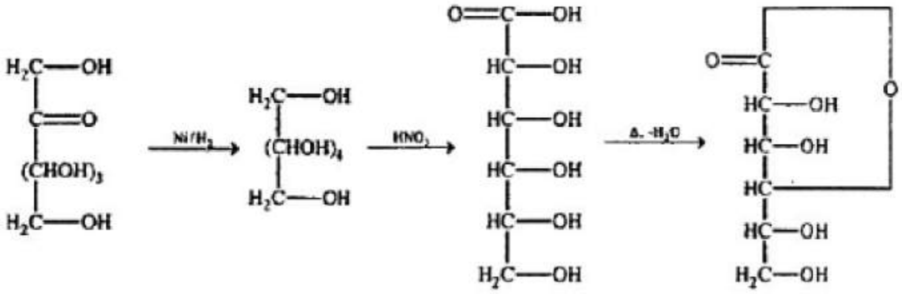
Problem 9: Compound A $C_5H_{10}O_4$, is oxidized by Br_2-H_2O to the acid, $C_5H_{10}O_5$. (A) Forms a triacetate (Ac_2O) and is reduced by HI to n-pentane. Oxidation of (A) with HIO_4 gives, among other product, 1 molecule of CH_2O and 1 molecule of HCO_2H. What are the possible strcutures of (A) and how could you distinguish between them?

Solution: (A) is an aldehyde, contains three hydroxyl groups and the carbon skeleton consists of five carbon atoms in a straight chain. Also, the formula $C_5H_{10}O_4$ therefore suggests that (A) is a deoxy-sugar. If we now try to work out the possibilities based directly on the periodic oxidation of (A), we shall find it.

Problem 10: Convert

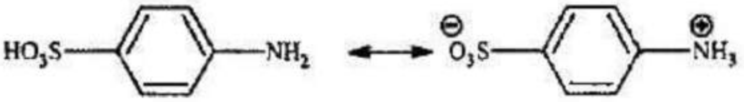


Solution:



Problem 11: i) Sulphanilic acid although has acidic as well as basic group, it is soluble in alkali but insoluble in mineral acid.
ii) Sulphanilic acid is not soluble in organic solvents.

Solution: i) Sulphanic acid exist as Zwitter ion.

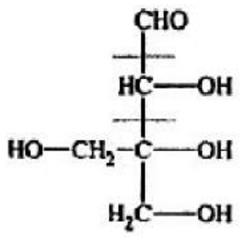


The weakly acidic $-NH_3$ transfers H to OH_- to form a soluble salt, $P-NH_2-C_6H_4-SO_3-Na$ on the other hand $\_SO_{3-}$ is too weakly basic to accept H from strong acids.

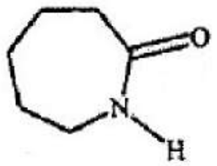
iii) Due to its ionic character it is insoluble in organic solvents.

Problem 12: Compound (A) $C_5H_{10}O_5$, give a tetra-acetate with Ac_2O and oxidation of (A) with Br_2 _ H_2O gives an acid, $C_5H_{10}O_6$. Reduction of (A) with HI and red phosphorous gives 3-methylbutane. What is structure of (A)?

Solution: The formation of tetracetate indicates of 4OH group and oxidation with bromine water indicates presence of CHO group. Reduction with red phosphorous and HI indicates presence of one carbon in the side chain. Thus, the structure of (A) would be

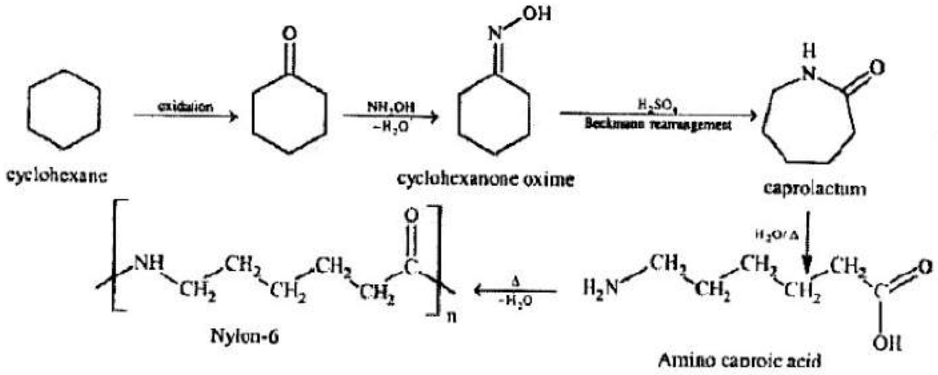


Problem 13*:* What is the structure of nylon-6, made by alkaline polymerisation of caprolactum?



Solution: The configuration of these carbons which are unchanged in the reactions, must be identical in order to get the same osazone.

a) **Nylon-6:** Another polymer of this class is nylon-6. It is a monomer of caprolactum which is obtained from cyclohexane.



It used for making tyre cords, fabrics and ropes.
b) **Nylon-6, 10:** A polymer of hexamethylene diamine (six carbon atoms) and sebacic acid (ten carbon atoms).

$$\underset{\text{hexamethylene diamine}}{nNH_2-(CH_2)_6-NH_2}+\underset{\text{sebacic acid}}{nCOOH-(CH_2)_8-COOH}\xrightarrow{-2n\,H_2O}$$

$$\underset{\text{Nylon-6,10}}{(-CO-(CH_2)_8-CO-NH-(CH_2)_6-NH-CO-(CH_2)_8-CO-)_n}$$

These polymers are formed by the condensation of two or more monomers with the elimination of simple molecules like H_2O, NH_3, ROH etc.

Problem 14: Supply structures for H through K. Given :

$$\textit{An Aldohexose}\xrightarrow{NH_2OH/base}H\xrightarrow{Ac_2O/NaOAc}I$$

$$I\xrightarrow{-HOAC}J\xrightarrow{NaOMe/MeOH}K.$$

(b) Explain the last step (c). What is net structural change (d) Name this overall method. (c) Discuss the possibility of epimer formation.

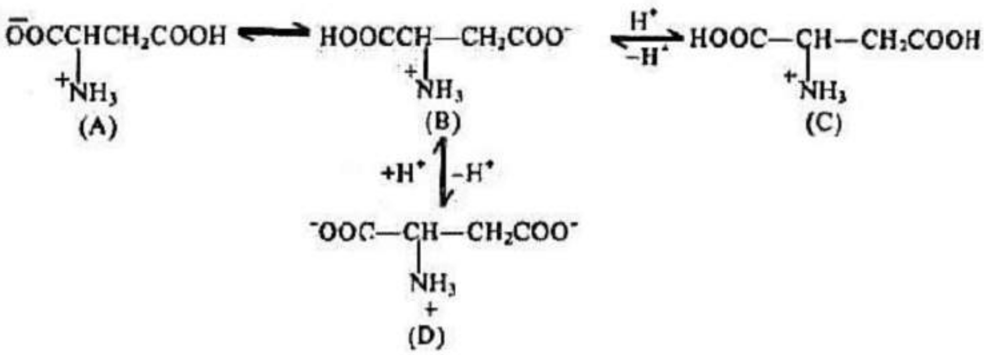
Solution: a) H is an oxime $HOCH_2(CHOH)_4CH = NOH$; is the completely acetylated oxime, $AcOCH_2(CHOH)_4CH = NoAc$ that loses 1 mole of HOAc to form J, $AcOCH_2(CHOAc)_4$ C _ N; K is an aldopentose, $HOCH_2(CHOH)_3CHO$.
b) The acetates undergo trans-esterification to give methyl acetate freeing all the sugar OH's. This is followed by reversal of HCN addition.
c) There is loss of one C from the carbon chain.
d) Wohl Degradation.
e) The -CHOH becomes the -CH = O without any configurational changes of the other chiral carbons. Thus, no epimers are formed.

Problem 15*:* Glycine exists as ($H_3N\ CH_2COO^-$) while anthranilic acid (P - NH_2 - C_6H_4 - COOH) does not exist as dipolar ion.

Solution: -COOH is too weakly acidic to transfer H to the weakly basic -NH_2 attached to the electron withdrawing benzene ring. When attached to an aliphatic carbon, the -NH_2 is sufficiently basic to accept H from -COOH group.

Problem 16: **Why should isoelectric point for Aspartic acid (2.98) be so much lower than that of leucine?**

Solution: This may be explained by considering following ion equilibrium

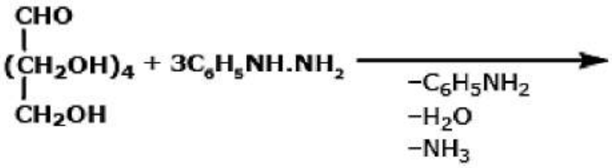


It is apparent that ions (A) and (B) are neutral, while (C) is a cation and (D) is dianion. In species (D), the anion is derived from the second -COOH group present in aspartic acid and is not possible in leucine. At neutral pH a significant concentration of (D), will be present in aqueous solution. It will therefore, be necessary to decrease the pH of such a solution if the formation of (D) is to be suppressed to a stage where anions and cations are present in equal concentration (the isoelectric point).

Problem 17*:* (a) Show how an aldohexose can be used to synthesize 2-ketohexose.

(b) Since glucose is converted to fructose by this method, what can you say about the configuration of C_3, C_4 and C_5 in the sugars.

Solution:



$$\begin{matrix}\text{CHO}\\ |\\ (\text{CH}_2\text{OH})_4\\ |\\ \text{CH}_2\text{OH}\end{matrix} + 3C_6H_5NH.NH_2 \xrightarrow[\begin{matrix}-C_6H_5NH_2\\ -H_2O\\ -NH_3\end{matrix}]{}$$

Here aldohexose reacts with one molecule of phenylhydrazine which condenses with the aldehyde group to give phenylhydrazone. When warmed with excess of phenyl hydrazine, the secondary alcoholic group adjacent to the aldehyde group is oxidised by another molecule of phenylhydrazine, to a ketonic group. With this ketonic group, the third molecule of phenylhydrazine condenses to given osazone. The phenylhydrazinyl group is transferred from osazone to C_6H_5CHO giving $C_6H_5CH = N.NHC_6H_5$ and a dicarbonyl compound called Osone. The more reactive aldehyde group of the osone is reduced, not the less reactive keto group and it gives 2-ketohexose.

Problem *18:* Starch is polymer of:

(a) Fructose (b) Glucose (c) Lactose (d) None

Solution: (b) Starch is homopolysaccharide of glucose having 24 — 30 glucose units.

Problem 19: The commonest disaccharide has the molecular formula

(a) $C_{10}H_{18}O_9$ (b) $C_{10}H_{20}O_{10}$ (c) $C_{11}H_{22}O_{11}$ (d) $C_{12}H_{22}O_{11}$

Solution: (d) The most common disaccharide is sucrose, whose molecular formula is $C_{11}H_{22}O_{11}$.

Problem 20: The structure of glycine (amino acid) is $H_3N\ CH_2\ COO^-$ (Zwitter Ion.)

Select the correct statement of the following.

(a) Glycine, as well as other amino acids are amphoteric.
(b) The acidic functional group in amino acids is — NH_3
(c) The basic functional group in amino acids is —CO_2^-
(d) All the statements are correct

Solution: (d) Glycine and all other amino acids are amphoteric because of the presence of NH_2 and CO_2H group both. The amino acid exists as Zwitter ion and acidic group is —NH_3 while basic group is —CO_2^-

Problem 21: Sugars are characterised by the preparation of osazone derivatives. Which sugar have identical osazones.

(a) Glucose and lactose
(b) Glucose and fructose
(c) Glucose and arabinose
(d) Glucose and maltose

Solution: (b) The reaction with phenyl hydrazone gives same osazone because glucose and fructose differ only on carbon atoms 1 and 2 which are involved in osazone formation.

Problem 22: Cane sugar on hydrolysis yields

(a) Glucose and maltose
(b) Glucose and lactose
(c) Glucose and fructose
(d) Only glucose

Solution: (c) $C_{12}H_{22}O_{11} \xrightarrow[H^+]{HOH} C_6H_{12}O_6 + C_6H_{12}O_6$

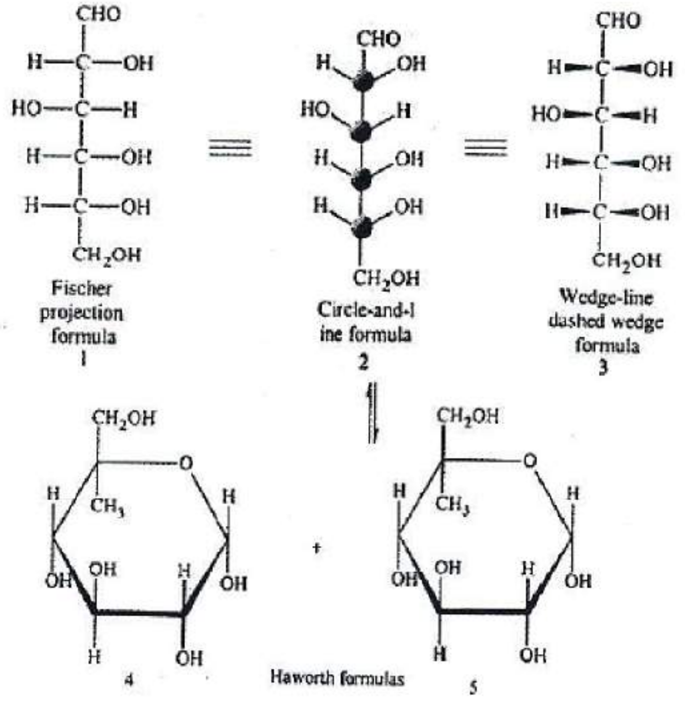
Glucose and Fructose

The process is known as inversion of cane sugar.

Structure Formulas for Monosaccharides

Structure Formulas for Monosaccharides:

Although many of the properties of D (+)-glucose can be explained in terms of an open-chain structure (1, 2, or 3), a considerable body of evidence indicates that the open-chain structure exists, primarily, in equilibrium with two cyclic forms. These can be represented by structures 4 and 5 or 6 and 7. The cyclic forms of D(+)-glucose are hemiacetals formed by an intramolecular reaction of the -OH group at C5 with the aldehyde group. Cyclization creates a new stereogenic centre at C1, and this stereogenic centre explains how two cyclic forms are possible. These two cyclic forms are diastereomers that are different only in the configuration of C1. In carbohydrates, chemistry diastereomers of this type are called anomers, and the hemiacetal carbon atom is called the anomeric carbon atom.

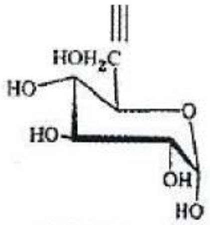


Fischer projection formula 1

Circle-and-line formula 2

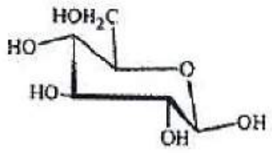
Wedge-line dashed wedge formula 3

4 Haworth formulas 5



a-D-(+)-Glucopyranose
6

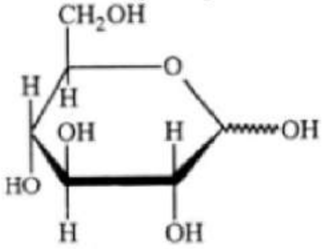
+

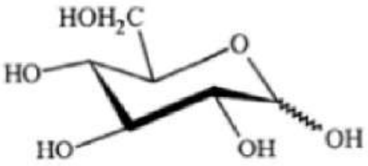


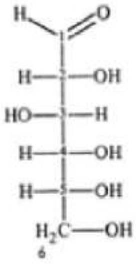
b-D-(+)-Glucopyranose
7

Structures 4 and 5 for the glucose anomers are called Haworth formulas and, although they do not give an actual picture of the shape of the six-membered ring, they have many practical uses. Demonstrates how the representation of each stereogenic centre of the open-chain form can be correlated with its representation in the Haworth formula.

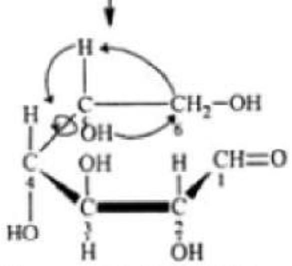
Each glucose anomer is designated as an a anomer or a b anomer depending on the location of the -OH group of Cl. When we draw the cyclic forms of a D sugar:



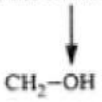


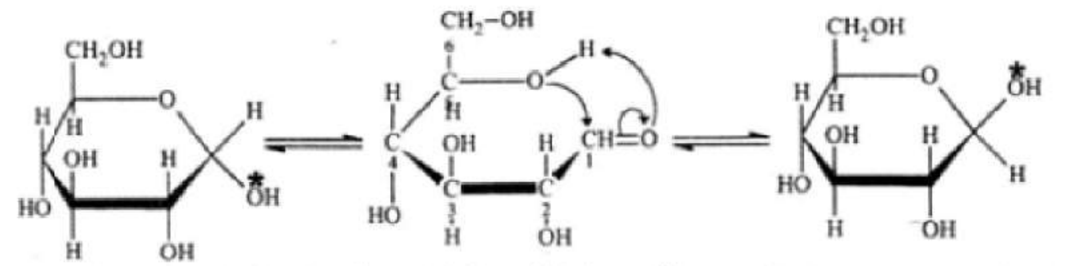


Glucose
(Plane projection formula) When a model of this is made it will coil as follows:



If the group attached to C4 is pivoted as the arrows indicate, we have the structure below.





α-D-(+)-Glucopyranose (Starred —OH) is the hemiacetal —OH, which in α-glucose is on the opposite side of the ring from the —CH$_2$OH group at C5.

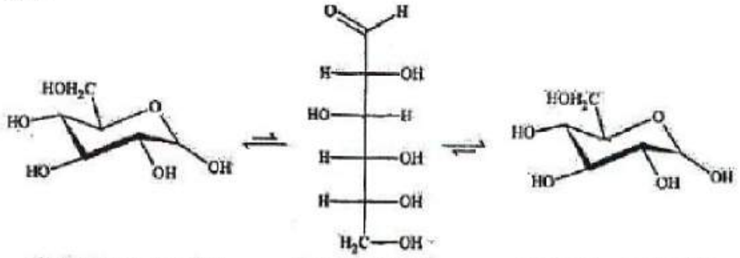
Open-chain form of D-glucose (The proton transfer step occurs between separate molecules. It is not intramolecular or concerted.)

β-D-(+)-Glucopyranose (Starred —OH) is the hemiacetal —OH, which in β-glucose is on the same side of the ring as the —CH$_2$OH group at C5)

Mutarotation:

Ordinary D (+)-glucose has a melting point of 146°C. However, when D (+)-glucose is crystallized by evaporating an aqueous solution kept above 98°C, a second form of D(+)-glucose with a melting point of 150°C can be obtained. When the optical rotations of these two forms are measured, they are found to be significantly different, but when an aqueous solution of either form is allowed to stand, its rotation changes. The specific rotation of one form decreases and the rotation of the other increases, until both solutions show the same value. A solution of original D-(+) glucose (mp: 146°C) has an initial specific rotation of 112°, but, ultimately, the specific rotation of this solution falls to 52.7°. A solution of second form of D (+) glucose (mp: 150°C) has an initial specific rotation of 18.7°, but slowly, the specific rotation of this solution rises to 52.7°. This change in rotation towards an equilibrium value is called mutarotation.

The explanation for this mutarotation lies in the existence of an equilibrium between the open-chain form of D(+) glucose and the a and b forms of the cyclic hemiacetals.



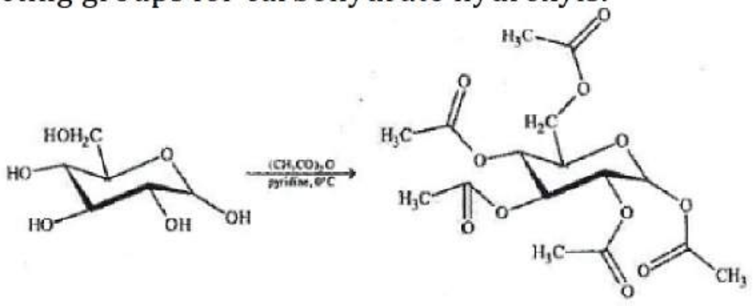
α-D-(+)-Glucopyranose (mp 146°C; $[\alpha]_D^{25} = +112°$)

Open-chain form of D-(+)-glucose

β-D-(+)-Glucopyranose (mp 150°C; $[\alpha]_D^{25} = +18.7°$)

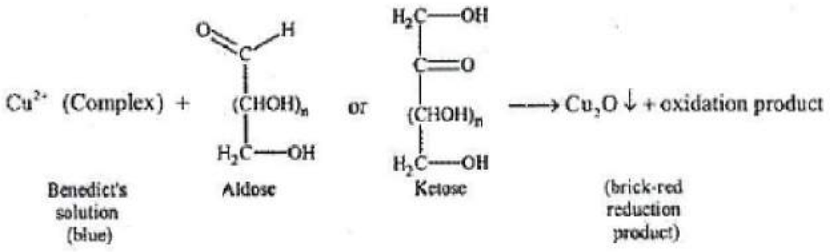
Conversion to Esters:

Treating a monosaccharide with excess acetic anhydride and a weak base (such as pyridine or sodium acetate) converts all of the hydroxyl groups, including the anomeric hydroxyl, to ester groups. If the reaction is carried out at a low temperature (e.g., 0°C), the reaction occurs stereospecifically; the α-anomer gives the a-acetate and the β-anomer gives the b-acetate. Acetate esters are common protecting groups for carbohydrate hydroxyls.



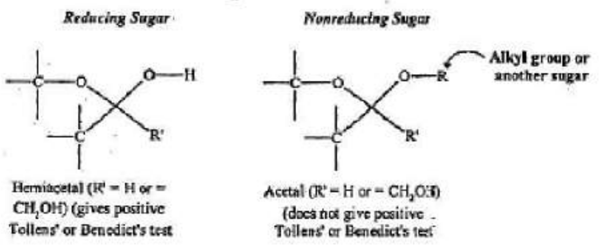
BENEDICT'S OR TOLLENS' REAGENTS: REDUCING SUGARS

Benedict's reagent (An alkaline solution containing a cupric citrate complex ion) and Tollen's solution $[Ag\ (NH_3)_2OH]$ - oxidize and thus give positive tests with aldoses and ketoses. The tests are positive even though aldoses and ketoses exist primarily as cyclic hemiacetals.



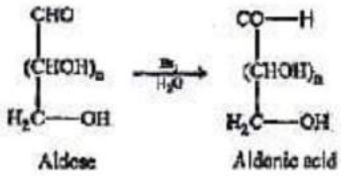
Sugars that give positive tests with Tollen's or Benedict's solutions are known as reducing sugars, and all carbohydrates that contain a hemiacetal group give positive tests. In aqueous solution these hemiacetals exist in equilibrium with relatively small, but not insignificant, concentration of noncyclic aldehydes or α-hydroxy ketones. It is the latter two that undergoes the oxidation until one reactant is exhausted.

Carbohydrates that contain only acetal groups do not give positive tests with Benedict's or Tollen's solutions, and they are called non-reducing sugars. Acetals do not exist in equilibrium with aldehydes or α-hydroxy ketones in the basic aqueous media of the test reagents.

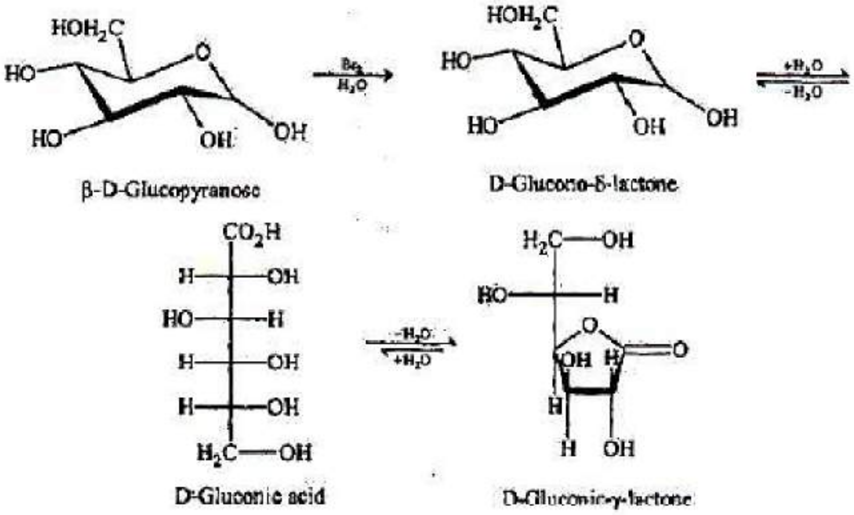


Bromine Water: The synthesis of Aldonic Acid

Monosaccharides do not undergo isomerization and fragmentation reactions in mildly acidic solution. Thus, a useful oxidizing reagent for preparative purposes is bromine in water (pH 6.0). Bromine water is a general reagent that selectively oxidizes the -CHO group to a $-CO_2H$ group. It converts an aldose to an aldonic acid.

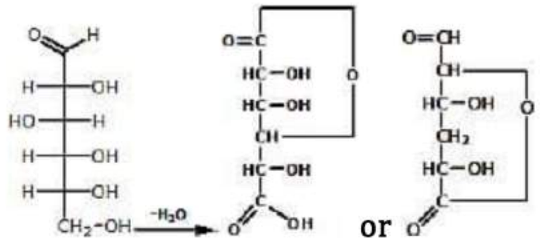


Experiments with aldopyranoses have shown that the actual course of the reaction is somewhat more complex than we have indicated above. Bromine water specifically oxidizes the β anomer, and the initial product that forms is a d-aldonolactone. This compound may then hydrolyze to an aldonic acid, and the aldonic acid may undergo a subsequent ring closure to form a γ-aldonolactone:



NITRIC ACID OXIDATION: ALDARIC ACID

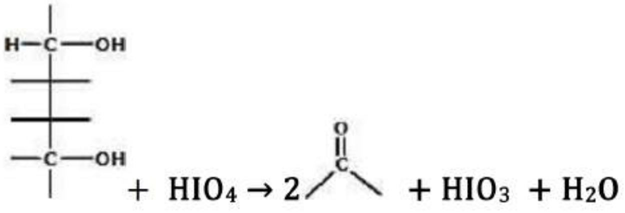
Dilute nitric acid -a stronger oxidizing agent than bromine water oxidizes the both -CHO group and the terminal $-CH_2OH$ group of an aldose to $-CO_2H$ groups. These dicarboxylic acids are known as aldaric acids:



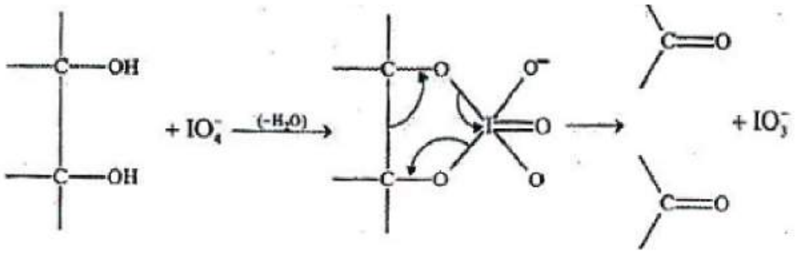
This aldaric acid obtained from D-glucose is called D-glucoaric acid.

PERIODATE OXIDATION: OXIDATIVE CLEAVAGE OF POLYHYDROXY COMPOUNDS

Compounds that have hydroxyl groups on adjacent atoms undergo oxidative cleavage when they are treated with aqueous periodic acid (HIO_4). The reaction breaks carbon-carbon bonds and produces carbonyl compounds (aldehydes, ketones, or acids).

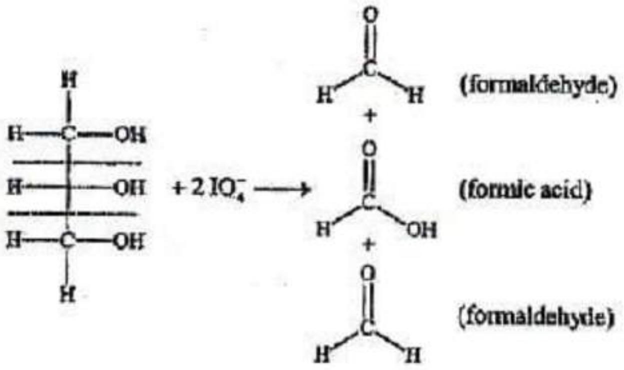


Since the reaction usually takes place in quantitative yield, valuable information can often be gained by measuring the number of molar equivalents of periodic acid that is consumed in the reaction as well as by identifying the carbonyl products.
Periodate oxidation are though to take place through a cyclic intermediate:

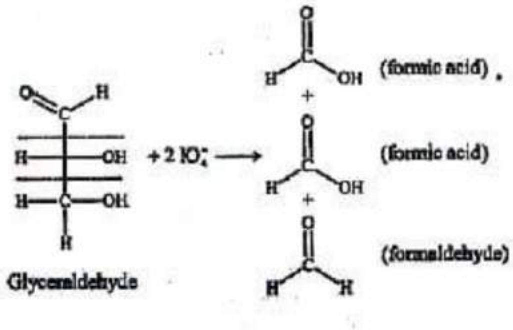


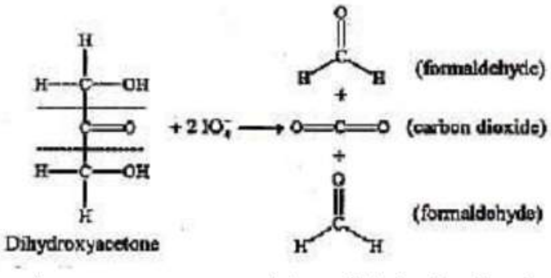
Before we discuss the use of periodic acid in carbohydrate chemistry, we should illustrate the course of the reaction with several simple examples. Notice in these periodate oxidation that for every C - C bond broken, a C - O bond is formed at each carbon.

1. When three or more -CHOH groups are continuous, the internal ones are obtained as formic acid. Periodate oxidation of glycerol, for example, gives two molar equivalents of formaldehyde and one molar equivalent of formic acid.

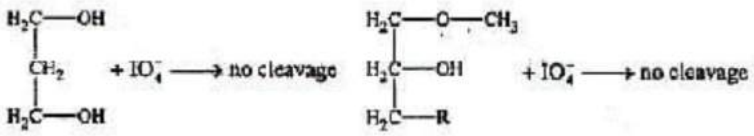


2. Oxidative cleavage also take place when an - OH group is adjacent to the carbonyl group of an aldehyde or ketone (but not that of an acid or an ester). Glyceradehyde yields two molar equivalents of formic acid and one molar equivalent of formaldehyde, while dihydroxyacetone gives two molar equivalents of formaldehyde and one molar equivalent of carbon dioxide.



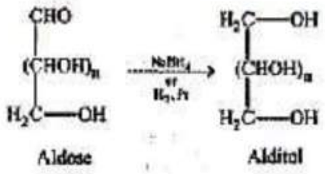


Periodic acid does not cleave compound in which the hydroxyl groups are separated by an intervening -CH_2 group, nor those in which a hydroxyl group is adjacent to an ether or acetal.



REDUCTION OF MONOSACCHARIDES: ALDITOLS

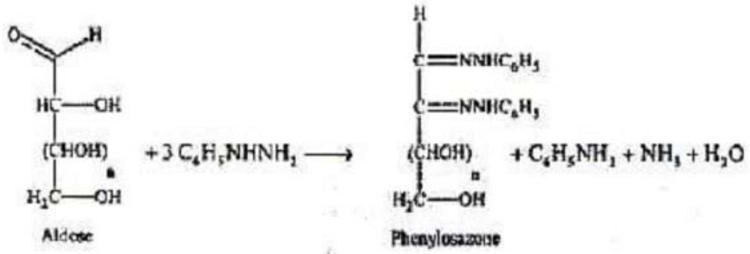
Aldoses (and ketoses) can be reduced with sodium borohydride to compounds called alditols:

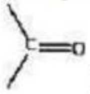


Reduction of D-glucose, for example, yields D-glucitol.

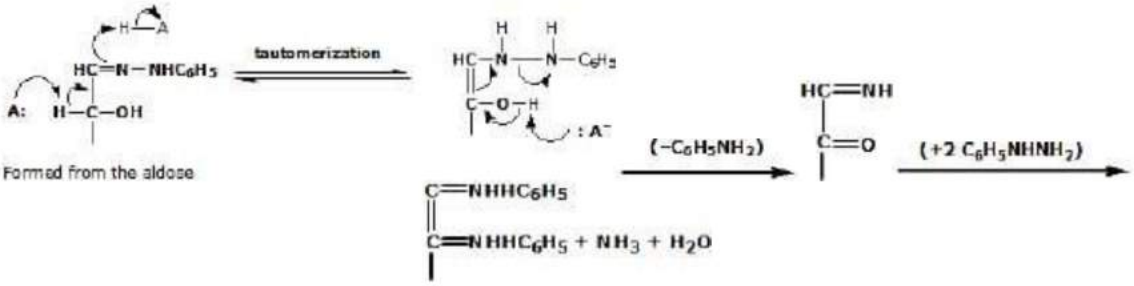
REACTIONS OF MONOSACCHARDIES WITH PHENYLHYDRAZINE: OSAZONES

The aldehyde group of an aldose reacts with such carbonyl reagents as hydroxylamine and phenylhydrazine. With hydroxylamine, the product is the expected oxime. With enough phenylhydrazine, however, three molar equivalents of phenylhydrazine are consumed and a second phenylhydrazeone group is introduced at C2. The product is called a phenylosazone. Phenylosazones crystallize readily (unlike sugars) and are useful derivatives for identifying sugars.

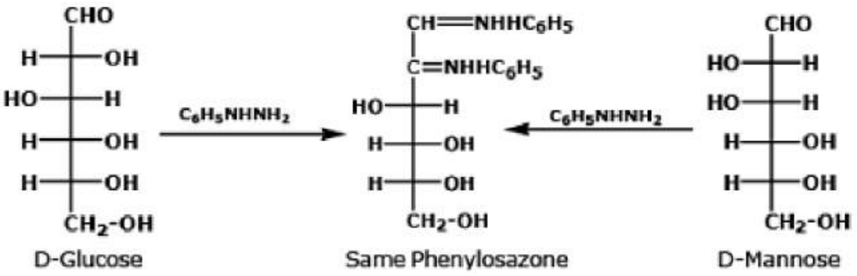


The mechanism for osazone formation probably depends on a series of reaction in which it behaves very much like  in giving a nitrogen version of an enol.

A Mechanism for the Reaction-
Phenylosazone Formation:



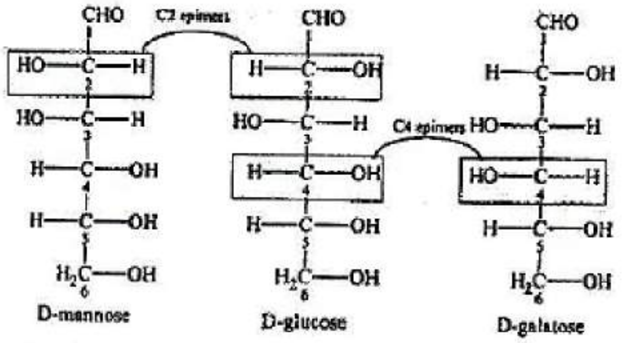
Osazone formation results in a loss of the stereogenic centre at C2 but does not affect other stereogenic carbons; D-glucose and D-mannose, for example, yield the same phenylosazone:

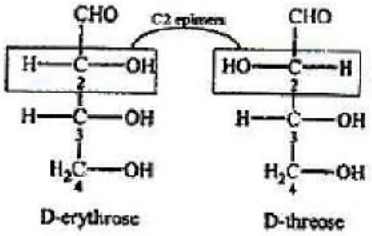


This experiment, first done by Emil Fischer, established that D-glucose and D-mannose have the same configuration about C3, C4 and C5. Diastereomeric aldoses that differ in configuration at only one carbon (such as D-glucose and D-mannose) are called epimers. In general, any pair of diastereomers that differ in configuration at only a single tetrahedral stereogenic carbon can be called as epimers.

Epimers:

Many common sugars are closely related, differing only by the stereochemistry at a single carbon atom. For example, glucose and mannose differ only at C2, the first asymmetric carbon atom. Sugars that differs only by the stereochemistry at a single carbon are called ***epimers*** and the carbon atom where they differ is generally stated. If the number of a carbon atom is not specified, it is assumed to be C_2. Therefore, glucose and mannose are "C2 epimers" or simply "epimers". The C4 epimer of glucose is galactose and the C_2 epimer of erythrose is threose.





Carbohydrates & Their Classification

CARBOHYDRATES:

1. Introduction:

Carbohydrates received their name becasue of their general formula $C_x(H_2O)_y$, according to which they appear to be hydrates of carbon.

$$xCO_2 + yH_2O \xrightarrow{\text{Sunlight, chlorophyl}} C_x(H_2O)_y + xO_2$$

Photosynthesis:

$$6CO_2 + 6H_2O + 18\ ATP \xrightarrow{\text{Sunlight, chlorophyl}} C_6H_{12}O_6 + 6O_2$$

Cellular Respiration:

$$C_6H_{12}O_6 + 6O_2 \xrightarrow{\text{Enzymes}} 6CO_2 + 6H_2O + 38\ ATP\ (36\ ATP\ \text{net gain})$$

2. Classification and structure of Carbohydrates:

Carbohydrates are polyhydroxy aldehydes and ketones and substances which hydrolyse to polyhydroxy aldehydes and ketones.
The simplest carbohydrates are called ***sugars*** or ***saccharides***, (Latin: Saccharum, sugar). Carbohydrates can be classified as **monosaccharides, oligosaccharides** *and* **polysaccharides.**

3. General Characteristic of Monosaccharides:

The important characteristics of monosaccharides as follows:

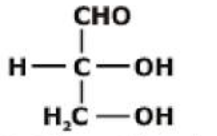
(i) All monosaccahrides are water soluble due to the presence of hydrogen bonding between the different OH groups and surrounding water molecules.

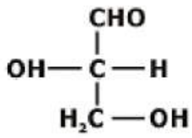
(ii) Monosaccharides have sweet taste and dependent upon heating they get charred and give the smell of burning sugar.

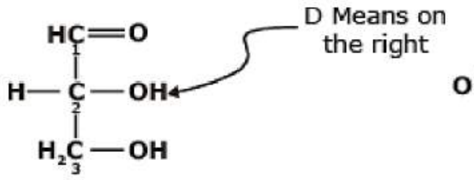
(iii) Monosaccharides are optically active in nature due to the presence of chiral carbon atoms.

(iv) The chemical characteristics of monosaccharides are due to OH groups and carbonyl group which may be either aldehydic or ketonic group.

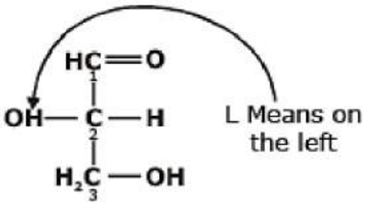
Glyceraldehyde contains one asymmetric carbon atom (marked by an astrisk) and can thus exist in two optically active forms, called the D-form and the L-form. Clearly, the two forms are mirror images that cannot be superimposed, that is they are **enantiomers**.


D-Glyceraldehyde


L-Glyceraldehyde

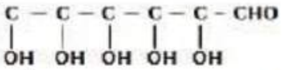


D-Glyceraldehyde



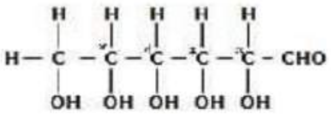
L-Glyceraldehyde

All four isomers have been prepared synthetically. The D-and L-erythrose are mirror images, that is, they are enantiomers. They have exactly the same degree of rotation but in opposite directions. Equal amounts of the two would constitute a racemic mixture, that is a mixture that would allow a plane-polarised light to pass through the solution unchanged.



$$\underset{\mathrm{OH}}{\mathrm{C}}-\underset{\mathrm{OH}}{\mathrm{C}}-\underset{\mathrm{OH}}{\mathrm{C}}-\underset{\mathrm{OH}}{\mathrm{C}}-\underset{\mathrm{OH}}{\mathrm{C}}-\mathrm{CHO}$$

Supplying hydrogen atoms to the five carbon atoms to satisfy their tetravalency, following structure (open chain) may be assigned to glucose: (* indicates assymetric carbon atom).



$$\mathrm{H}-\overset{\mathrm{H}}{\underset{\mathrm{OH}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{OH}}{{}^{*}\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{OH}}{{}^{*}\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{OH}}{{}^{*}\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{OH}}{{}^{*}\mathrm{C}}}-\mathrm{CHO}$$

Enzymes & Mechanism of Enzyme Action

Enzymes

Proteins which are used as a catalyst in biochemical reaction are known as biocatalysts.

Specific characteristics

Enzymes have following two specific characters as :
(i) Specificity (ii) Efficiency

Specificity of enzymes

(a) Generally, one enzyme can catalyze only one biochemical reaction.
(b) It can increase the rate of reaction upto 10^{20} times.
(c) In some cases one enzyme can catalyze more than one reaction and one reaction can be catalyzed by more than one enzyme. eg. Enzymes present in Yeast (Zymase) can ferment both glucose and fructose into alcohol and also cane-sugar can be hydrolysed by invertase and sucrase enzymes.

Efficiency of enzymes:

(a) One molecule of enzyme can convert millions of substrate molecules into product per second.
eg. Carbonic anhydrase enzyme present in red blood cells has the highest turn over number.
(b) With having tertiary structure it can be collected as crystals.
Enzymes are denatured at higher temperatures.
(c) Enzymes can be stored at low temperature as they are inactivated.

Importance of enzymes

In the thousands of enzymes present in body if even a single enzyme would be absent or damaged then complex disease results in.
eg. Scarcity of **Phenylalanine** hydroxylase enzyme in human body results in **Phenylketonuria** disease.

Factors affecting enzyme action:

(i) **Optimum temperature and pH**. Enzyme catalysed reactions have maximum rate at physiological pH of around 7.4 and human body temperature of 37ºC (310 K) under one atmosphere pressure.

In fact, as the temperature or pH is increased, the rate rises to a maximum (at 37ºC or pH = 7.4) and then falls off.

(ii) **Enzyme activators (coenzymes).** The activity of certain enzymes is increased in the presence of certain substances, called co-enzymes. It has been observed that if a protein contains a small amount of vitamin as the non-protein part, its activity is enhanced considerably. The activators are generally metal ions such as Na , Mn^{2+} , Cu^{2+} , Co^{2+} etc. These metal ions are weakly bonded to the enzyme molecules and increase their catalytic activity. For example, the enzyme, amylase in presence of NaCl, which provides Na^+ ion, shows a very high catalytic activity.

(iii) **Enzyme inhibitors and poisons.** Just as in the case of catalysts, the activity of enzyme is slowed down in the presence of certain substance. Such substances are called inhibitors or poisons. They act by combining with the active functional group thereby reducing or completely destroying the catalytic activity of the enzymes. The use of many drugs is on account of their action as enzyme inhibitors in our body.

Nutrients:

Sodium, Potassium and Chlorine

(i) $Na^+$is the principal mineral cation in the extracellular fluid.
(ii) K^+ is the principal cation inside the cell.
(iii) Cl^- is the principal mineral anion in the ECF.
(iv) Na^+ and K^+ are essential to the maintenance of water balance and acid-base balance.
(v) Na^+ and K^+ are important in nerve impulse transmission.

Calcium and Phosphorus

(i) Calcium and phosphorus are deposited in bones and teeth to give them strength and rigidity.
(ii) $Ca^{2+}$is also essential for blood coagulation, neuromuscular function, cardiac function and actions of many enzymes and hormones.
(iii) Phosphorus enters into many compounds such as nucleic acids and phospholipids, many co-enzymes and high energy compounds like ATP.
(iv) Calcium plays an essential role in sustaining intestinal peristalsis and growth of body tissues.

Iron
(i) Iron is required for haemoglobin synthesis.

(ii) Iron is essential both for transportation of oxygen to tissues and for operation of oxidative systems within the tissue cells.

Magnesium-

(i) Magnesium is required as a catalyst for many intracellular enzymatic reactions, particularly those relating to carbohydrate metabolism.

(ii) Mg is the central metal atom in chlorophyll.

Iodine-

Iodine is used in the synthesis of thyroid hormones.

Zinc-

(i) Zinc is a constituent of carbonic anhydrase, present in RBCs helping in CO_2 transport.

(ii) Zinc is a component to lactic dehydrogenase, important for the interconversion between pyruvic acid and lactic acid.

(iii) Zinc is a component part of some peptidases and therefore is important for digestion of proteins in the alimentary canal.

Cobalt-

(i) Cobalt helps in erythropoiesis and in the activities of some enzymes.

(ii) It is present in vitamin B_{12}.

Copper-

(i) Copper helps in the utilisation of iron.

(ii) Copper deficiency may produce anaemia because of failure in iron utilisation.

Molybdenum-

(i) Molybdenum is a constituent of oxidase enzymes **(xanthine oxidase).**

(ii) Molybdenum plays an important role in biological **nitrogen** fixation.

Fluorine-

(i) Fluorine maintains normal dental enamel and prevents dental caries.

(ii) Excessive intake of fluorine cause fluorosis characterized by mottled teeth and enlarged bones.

Vitamins

It has been observed that certain organic compounds are required in small amounts in our diet but their deficiency causes specific diseases. These compounds are called vitamins.

Classification of Vitamins-
Vitamins are classified into two groups depending upon their solubility in water or fat.

(i) Fat soluble vitamins:
Vitamins which are soluble in fat and oils. But insoluble in water are kept in this group. These are vitamins A, D, E and K. They are stored in liver and adipose (fat storing) tissues.

(ii) Water soluble vitamins:
B group vitamins and vitamin C are soluble in water so they are grouped together. Water soluble vitamins must be supplied regularly in diet because they are readily excreted in urine and can not be stored (except vitamin B_{12}) in our body.
Some important vitamins, their sources and diseases caused by their deficiency are listed in table.

Sr. No.	Name of Vitamins	Source	Deficiency Diseases
1	Vitamin A (Retinol)	Fish liver oil, carrots, butter and milk	Xerophthalmia (hardening of cornea of eye) Night blindness
2	Vitamin B_1(Thiamine)	Yeast, milk, Green Vegetables and cereals and grams	Beri beri (loss of appetite, retarded growth)
3	Vitamin B_2 (Riboflavin)	Milk, egg white, liver, Kidney	Cheilosis (fissuring at corners of mouth and lips), digestive disorders and burning sensation of the skin
4	Vitamin B_6 (Pyridoxine)	Yeast, milk, egg yolk, cereals and grams	Convulsions
5	Vitamin B_1 (Cyanocobalamine)	Meat, fish, egg and curd	Pernicious anaemia (RBC deficient in haemoglobin)
6	Vitamin C (Ascorbic acid)	Citrus fruits, amla and	scurvy (bleeding gums)

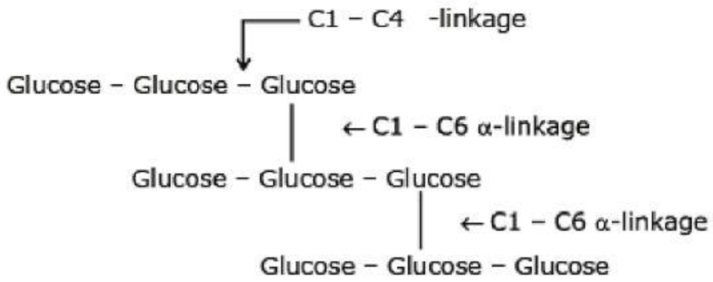
		green leafy vegetables	
7	Vitamin D (Calciferol)	Exposure to sunlight, fish and egg yolk	Rickets (bone deformities in children) and osteo-malacia (soft bones and joint pain in adults)
8	Vitamin E or Tocopherol (α, β and γ) or Anti Sterility factor	Eggs, Milk, Fish, Wheat germ oil cotton seed oil etc.	Sterility (loss of sexual power and reproduction)

Polysaccharides: Starch, Cellulose & Glycogen

POLYSACCHARIDES

Polysaccharides are the polymers of monosaccharides. The natural polysaccharides generally contain about 100-3000 monosaccharide units. The three most abundant natural polysaccharides-cellulose, starch and glycogen are derived from the same monomer, i.e., glucose.

Starch: It is a polymer of glucose. Its molecular formular is $(C_6H_{10}O_5)_n$ where the value of n(200 - 1000) varies from source to source. It is the chief food reserve material or storage polysaccharide of plants and is found mainly in seeds, roots, tubers, etc. Wheat, rice, potatoes, corn, bananas etc., are rich source of starch.
Starch is not a single compound but is a mixture of two components - a water soluble component called amylose (20%) and a water insoluble component called amylopectin (80%). Both amylose and amylopectin are polymers of α-D glucose.
Amylose is a linear polymer of α-D glucose. It contains about 200 glucose units which are linked to one another through a-linkage involving C_1 of one gluose unit with C_4 of the other.
Amlopectin, on the other hand, is a highly branched polymer. It consists of a large number (several branches) of short chains each containing 20-25 glucose units which are joined together through α-linkages involving C1 of one glucose unit with C4 of the other. The C1 of terminal glucose unit in each chain is further linked to C_6 of the other glucose
unit in the next chain through C1-C6 α-linkage. This gives amylopectin a highly branched structure as shown below:



Hydrolysis:

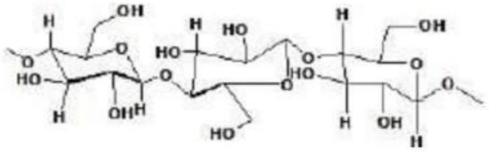
Hydrolysis of starch with hot dilute acids or by enzmyes give dextrins of varying complexity, maltose and finally D-glucose. Starch does not reduce Tollen's reagent and Fehling's solution.

Uses:

It is used as a food. It is encountered daily in the form of potatoes, bread, cakes, rice etc. It is used in coating and sizing paper to improve the writing qualities. Starch is used to treat textile fibres before they are woven into cloth so that they can be woven without breaking. It is used in manufacture of dextrins, glucose and ethyl alcohol. Starch is also used in manufacture of starch nitrate, which is used as an explosive.

Cellulose:

Cellulose is the chief component of wood and plane fibres; cotton, for instance, is nearly pure cellulose. It is insoluble in water and tasteless; it is a non-reducing carbohydrate. These properties, in part at least, are due to extremely high molecular weight.



Cellulose

Cellulose has the formula $(C_6H_{10}O_5)_n$. Complete hydrolysis by acid yields D ( )-glucose as the monosaccharide. Hydrolysis of completely methylated cellulose gives a high yield of 2, 3, 6-tri-O-methyl-D-glucose. Like starch, therefore, cellulose is made up of chains of D-glucose units, each unit joined by a glycoside linkage of C-4 of the next.

Cellulose differs from starch, however, in the configuration of the glycoside linkage. Upon treatment with acetic anhydride and sulphuric acid, cellulose yields octa-O-acetylcholine, there is evidence that all glycoside linkages in cellulose, like the one in ( ) cellobiose, are *beta* linkages.

Physical methods give molecular weights for cellulose ranging from 250000 to 1000000 or more; it seems likely that there are at least 1500 glucose units per molecule. End group analysis by both methylation and periodic acid oxidation gives a chain length of 1000 glucose units or more. X-ray analysis and electron microscopy indicate that these long chains lie side by side in bundles, undoubtedly held together by hydrogen bonds between the numerous neighbouring -OH groups. These bundles are twisted together to form.

Rope like structure which themselves are grouped to form the fibers we can see. In wood, these cellulose "ropes" are embedded in lignin to give a structure that has been linked to reinforced concrete.

Properties of Cellulose:

We have seen that the glycoside linkages of cellulose are broken by the action of acid, each cellulose molecule yielding many molecules of D(+)-glucose. Now let us look briefly at reactions of cellulose in which the chain remains essentially intact. Each glucose unit in cellulose contains three free -OH groups; these are the positions at which reactions occur.

These reactions of cellulose, carried out to modify the properties of a cheap, available ready-made polymer, are of tremendous industrial importance.

Like any alcohol, cellulose forms ***esters***. Treatment with a mixture of nitric and sulphuric acid converts cellulose into *cellulose nitrate*. The properties and uses of the product depend upon the extent of nitration. *Guncotton*, which is used in making smokeless powder, is very nearly completely nitrated cellulose, and is often called cellulose trinitrate (three nitrate groups per glucose unit). *Pyroxylin* is less highly nitrated material containing between two and three nitrate groups per glucose unit. It is used in the manufacture of plastics like celluloid and collodion, in photographic film, and in lacquers. It has the disadvantage of being flammable, and forms highly toxic nitrogen oxides upon burning.

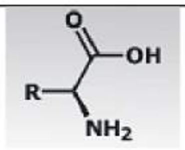
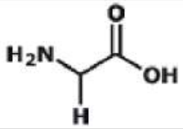
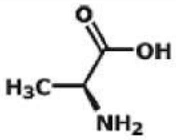
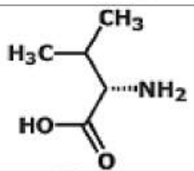
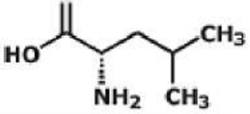
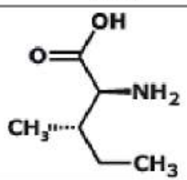
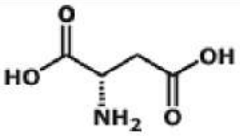
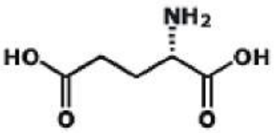
Industrially, cellulose is alkylated to ***ethers*** by the action of alkyl chlorides (cheaper than sulfates) in the presence of alkali. Considerable degradation of the long chain is unavoidable in these reactions. Methyl, ethyl, and benzyl others of cellulose are important in the production of textiles, films, and various plastic objects.

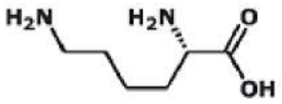
Amino Acids & Their Classification

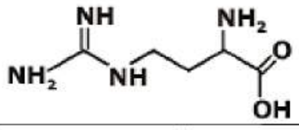
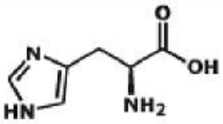
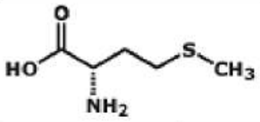
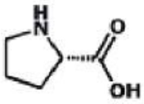
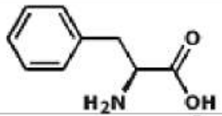
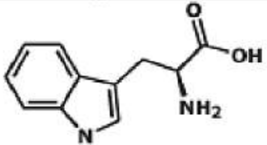
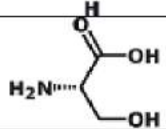
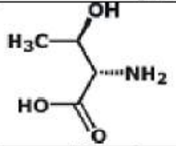
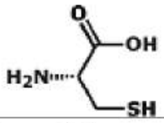
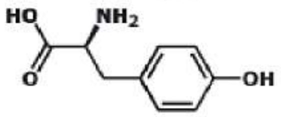
Amino Acids

1. Intorudction:

Amino acids are the compounds which contain both an amino group and a carboxy group in their molecules. They constitute a particularly imortant class of difunctional compounds as they are the building blocks of proteins.
While several hundred different amino acids are known to occur naturally, 20 of them deserve special mention as they ae preesent in proteins. These amino acids are listed in Table. As given in this table, for amino acids trivial names are common. The convention to use a three letter code, as an abbreviation, for each amino acid is also given in the table. These abbreviations are particularly useful in designating the sequence of amino acids in peptides and proteins which your will study.

Nature of amino acid	E/N.E		Name	Abbreviation
Neutral amino acid	NE		Glycine	Gly
Neutral amino acid	NE		Alanine	Ala
Neutral amino acid	E		Valine	Val
Neutral amino acid	E		Leucine	Leu
Neutral amino acid	E		Isoleucine	Ile
Acidic amino acid	NE		Aspartic Acid	Asp
Acidic amino acid	NE		Glutamic Acid	Glu

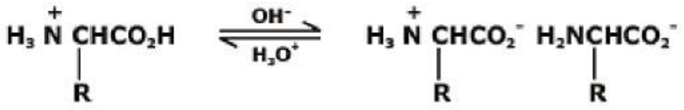
Basic amino acid	E		Lysine	Lys

Basic amino acid	NE		Arginin	Arg
Basic amino acid	NE		Histidine	His
Neutral amino acid	E		Methionine	Met
Neutral amino acid	NE		Proline	Pro
Neutral amino acid	E		Phenylalanine	Phe
Neutral amino acid	E		Tryptophan	Trp
Neutral amino acid	NE		Serine	Ser
Neutral amino acid	E		Threonine	Thr
Neutral amino acid	NE	threonine 	Cysteine	Cys
Neutral amino acid	NE		Tyrosine	Tyr

E = essential amino acid **NE** = Non essential amino acid

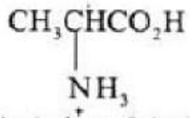
AMINO ACID AS DIPOLAR IONS:

Amino Acids contain both a basic group ($-NH_2$) and an acidic group ($-COOH$). In the dry solid state, amino acids exist as dipolar ions, a form in which the carboxyl group is present as a carboxylate ion, $-CO_2^-$, and the amino group is present as an aminium ion, $-NH_3$ (Dipolar ions are also called zwitter ions.) In aqueous solution, an equilibrium exists between the dipolar ion and the anionic and cationic forms of amino acids.



$$H_3\overset{+}{N}\underset{\displaystyle R}{CH}CO_2H \underset{H_3O^+}{\overset{OH^-}{\rightleftharpoons}} H_3\overset{+}{N}\underset{\displaystyle R}{CH}CO_2^- \; H_2N\underset{\displaystyle R}{CH}CO_2^-$$

If alanine is dissolved in a strongly acidic solution (e.g. pH 0), it is present in mainly a net cationic form. In this state, the amine group is protonated (bears a formal 1 charge) and the carboxylic acid group is neutral (has no formal charge). As is typical of α-amino acids, the pK_a for the carboxylic acid hydrogen of alanine is considerably lower (2.3) than the pK_a of an ordinary carboxylic acid (e.g., propanoic acid, pK_a= 4.89):



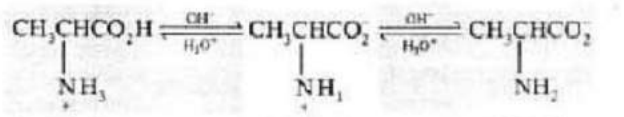
$$CH_3\underset{\displaystyle \overset{+}{N}H_3}{C}HCO_2H$$

Cationic formof alanine
$pK_{a_1} = 2.3$

$CH_3CH_2CO_2H$
Propanoic acid
$pK_a = 4.89$

The reason for this enhanced acidity of the carboxyl group in an α-amino acid is the inductive effect of the neighbouring aminium cation, which helps to stabilize the carboxylate anion formed when it loses a proton. Loss of proton from the carboxyl group in a cationic α-amino acid leaves the molecule electrically neutral (in the form of a dipolar ion). This equilibrium is shown in the red-shaded portion of the equation below.

The protonated amine group of an α-amino acid is also acidic, but less so that the carboxylic acid group. The pK_a of the animium group in alanine is 9.7. The equilibrium for loss of an aminium proton is shown in the blue-shaded portion of the equation below. The carboxylic acid proton is always lost before a proton from the aminium group in an α-amino acid.



$$CH_3\underset{\displaystyle \overset{+}{N}H_3}{C}HCO_2H \underset{H_3O^+}{\overset{OH^-}{\rightleftharpoons}} CH_3\underset{\displaystyle \overset{+}{N}H_3}{C}HCO_2^- \underset{H_3O^+}{\overset{OH^-}{\rightleftharpoons}} CH_3\underset{\displaystyle NH_2}{C}HCO_2^-$$

Cationic form
$pK_{a_1} = 2.3$

Dipolar ion
$pK_{a_2} = 9.7$

Anionic form

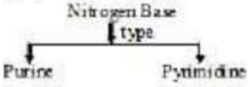
The state of an a-amino acid at any given pH is governed by a combination of two equilibrium, as shown in the above equation for alanine. The isoelectric point (pI) of an amino acid such as alanine is the average of pKa_1 and pKa_2;
pI = ½ (2.3 9.7) = 6.0 (isoelectric point of alanine)
When a base is added to a solution of the net cationic form of alanine (initially at pH 0, for example), the first proton removed is the carboxylic acid proton, as we have said. In the case of alanine, when a pH of 2.3 is reached, the acid proton will have been removed from half of the molecules. This pH represents the pK_a of the alanine carboxylic acid proton, as can be demonstrated using the Henderson-Hasselbalch equation. The Henderson - Hasselbalch equation shows that for an acid (HA) and its conjugate base (A^-),
$pK_a = pH + \log [HA]/[A^-]$
When the acid is half neutralized,
b) Co-polymers are another type of polymers. These contain more than one sub-unit (or monomer).
Example:
In the above example, styrene and maleic anhydride monomers laternate. Co-polymer can be a block co-polymer.
Example:
Co-polymers can be random as well.
— B - A - A - B - A - B - B - A - B - A -B - B - A —
A and B are monomers.
6. There are many polymers in nature.
Example: Cellulose, starch, pepsin, insulin, egg albumin, rubber, DNA (Deoxyribonucleic acid) etc. These are called Biopolymers.
Man made polymers are, Nylon, Terylene, Polythene, Polystyrene, PVC (Polyvinyl chloride), Bakelite, Perspex, Polysiloxane etc.
7. The properties of a polymer solution are strikingly different from those of a true solution. For example, when polyvinyl alcohol is added to water, it swells.
a) Its shape gets distorted and after a long time it dissolves.
b) When more of polymer is added to a given solvent, saturation point is not reached. The mixture of polymer and solvent assumes a soft dough-like consistency.
8. Addition polymers and condensation polymers are two important types of polymers.
9. Polymer can be described as linear, branched and network.

Nucleic Acids: Chemical Composition & Structure

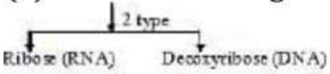
Nucleic Acid

(a) These are special type of acids which are present in nucleus & cytoplasm.
(b) Control the metabolic activities of cell.
(c) They are also found in Mitochondria, centriole and chloroplast.

Types → These are of 2 types:
DNA-Deoxyribonucleic acid
RNA- Ribonucleic acid
(d) **Fischer** discovered Nitrogen bases in 1888.

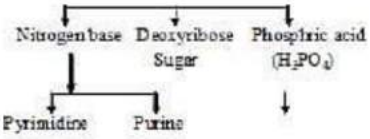


(e) **Levan** found sugar.



Deoxyribonucleic Acid (D.N.A.):

(a) It is found in Nucleus.
(b) They are on pneumococcus bacteria.
(c) DNA made up of 3 units-



(i) Thymine (i) Adenine
(ii) Cytosine (ii) Guanine
(d) Nucleoside
When nitrogen base is combined with deoxyribose sugar, it constitutes a nucleoside.

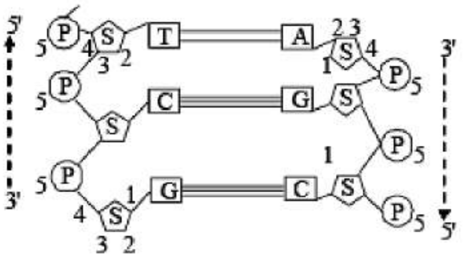
Deoxyribonucleoside:

Adenine Deoxyribose → Deoxyadenosine
Guanine Deoxyribose → Deoxyguanosine
Cytosine Deoxyribose → Deoxycytidine
Thymine Deoxyribose → Deoxythymidine

(i) Nucleotide
(a) Nitrogen base Sugar Phosphate → Nucleotide.
(b) Nucleotide is a unit of DNA.
(c) All nucleotides combined and form a chain called polynucleotides by which RNA and DNA are formed.

Structure of DNA-

(a) Double Helical model of DNA was proposed by biochemist **J.D.Watson**, British chemist **FHC Crick** in 1953.



(b) DNA in double stranded structure is made up of two chains of polynucleotides.
(c) DNA is a polymer of Nucleotide.
(d) Nucleotide are joined by 3' → 5' phosphodiester bonds.
(e) Sugar and phosphorous are alternately arranged.
(f) In both chains, in between A and T, 2 Hydrogen bonds are present while in C and G, 3H bonds are present. (A = T) (C º G)
(g) A always attaches with T while C always attaches with G.
(h) Purine and pyrimidine are found in ratio 1 : 1 cells.
(i) DNA is attached with histone protein.
(j) In prokaryotic cell and mitochondria, circular DNA is present.

Function of DNA:

(i) Self - Replication or self -Duplication

DNA has the property of self - replication. It is therefore a reproducing molecule. This unique property of DNA is at the root of all reproduction. Through its replication, DNA acts as the key to heredity. In the replication of DNA, the two strands of a double helix unwind and separate as a template for the formation of a new complementary strand.

(ii) Protein Synthesis

The specific sequence of base pair in DNA represents coded information for the manufacture of specific proteins. These coded instructions first are transcribed into the matching nitrogen-base sequences within mRNA and the instructions in such RNA subsequently are translated into particular sequence of amino acid units within the polypeptide chains and proteins.
The major steps in the utilization of the genetic information can be represented as :

$\text{D N A} \xrightarrow{\text{Replication}} \text{D N A} \xrightarrow{\text{Transcription}} \text{R N A} \xrightarrow{\text{Transcription}} \text{Protein}$

Ribonucleic Acid (RNA):
⇒ Found in cytoplasm as well as in nucleus.
Cytoplasm → In the ribosome (higher amount).

Chemical Nature:

⇒ Ribonucleic acid is a polymer of purine and pyrimidine ribonucleotides linked by 3' → 5' phosphodiester bridges. The number of nucleotides in RNA ranges from as few as 75 to many thousands. Although sharing many features with DNA, RNA possesses several specific differences.
⇒ As indicated by its name, sugar in RNA to which the phosphate and nitrogen-bases are attached is ribose rather than the deoxyribose of DNA.
⇒ Although RNA contains the ribonucleotides of adenine, guanine, and cytosine, it does not posses thymine. Instead of thymine, RNA contains the ribonucleotides of uracil. Thus, the pyrimidine components of RNA differs from those of DNA.
⇒ RNA exists basically as a single-stranded molecule rather than as a double - stranded helical molecule, as does DNA. However the single strand of RNA is capable of folding back on itself like a hairpin and thus acquiring double-stranded characteristics. In these regions, A pairs with U and G pairs with C.
Thus a given segment of a long RNA molecule might, for example, be represented as follows:

```
P–R–P–R–P–R–P–R–P–R
  |   |   |   |   |
  A   U   G   G   C
```

⇒ where R stands for ribose ; A, U, G, and C for Adenine, Uracil, Guanine and Cytosine respectively.

Types of RNA and their Functions:

There are 3 main types of RNA molecules:
(i) Messenger RNA (mRNA)
(ii) Transfer RNA (tRNA)
(iii) Ribosomal RNA (rRNA)

(i) Messenger RNA (mRNA)

⇒ This type of RNA consists of **single strand** of variable length and serves as a template for protein synthesis. Code is in the chromosomes.
⇒ mRNA forms complementary copy of DNA as it carries chemical messages in the form of nitrogen-base sequence from the nucleus to the ribosomes, i.e. from DNA to

cytoplasm where proteins are synthesized. Therefore, it is called messenger RNA or mRNA.
⇒ mRNA is sythesised from DNA in the nucleus.
⇒ It is called **transcription**.

(ii) Ribosomal RNA
⇒ A ribosome is a cytoplasmic nucleoprotein structure which serves as the organellar machinery for protein synthesis from mRNA templates.
⇒ On the ribosome, the mRNA and tRNA molecules interact to translate into a specific protein molecule the information transcribed from the DNA.
⇒ rRNA constitutes the largest part of total RNA (Highest) - 80%

(iii) Transfer RNA (RNA)

⇒ These are also called **Soluble RNA**.
⇒ Single stranded.
⇒ 10-15% of the total RNA.
⇒ **Size - Smallest:** 75 - 80 nucleotides only.
⇒ **Synthesis** - Within **nucleus** from **DNA**.
Function- It transports amino acid from cytoplasm to the site of protein synthesis.