



NATIONAL OPEN UNIVERSITY OF NIGERIA

SCHOOL OF SCIENCE AND TECHNOLOGY

COURSE CODE: BIO 216

COURSE TITLE: Chemistry of Carbohydrates, Lipids and Nucleic Acid

MODULE 1: CARBOHYDRATES.**UNIT 1: CARBOHYDRATES: PHYSICAL PROPERTIES AND FUNCTIONS.**

- 1.0 Introduction.
- 2.0 Objectives.
- 3.0 Definitions of Carbohydrates.
 - 3.1 Classification of Carbohydrates.
 - 3.2 Function/Role of Carbohydrates.
 - 3.3 Physical property of Carbohydrates.
 - 3.4 Stereochemistry of Carbohydrates.
 - 3.5 Self Assessment Exercises.
- 4.0 Conclusions.
- 5.0 Summary.
- 6.0 Tutor Marked Assignment (TMA)
- 7.0 References and Further Readings .

1.0 INTRODUCTION

The term 'Carbohydrates' describes a group of organic compounds, ranging from simple sugars through polysaccharides, which form some of the important structures in the biosphere. Carbohydrates are the most abundant biomolecules on earth. Thus the term "carbohydrates" includes compounds such as simple sugars (glucose and galactose), storage carbohydrates (starch and glycogen) and complex carbohydrates (cellulose and a bacterial cell wall peptidoglycans). In this unit you are going to study carbohydrates, their physical property, classification, functions and stereochemistry.

2.0 OBJECTIVES

By the end of this unit you are expected to know:

- What carbohydrates are;
- The various classification of carbohydrates;
- Physical property of carbohydrates;
- Different roles played by carbohydrates in living system;
- Stereochemistry of carbohydrates.

3.0 DEFINITION OF CARBOHYDRATES

Carbohydrates can be defined as polyhydroxy aldehydes or ketones, or as substance that yield one of these compounds on hydrolysis. Many but not all carbohydrates have the empirical formula $(\text{CH}_2\text{O})_n$, where n is three (3) or greater than three. However, this formula does not fit in for all carbohydrates because some carbohydrates have been found to contain nitrogen, phosphorus or sulfur while some are deoxysugars eg deoxyribose.

The occurrence of the ratio of one molecule of water to one atom of carbon led to the name "hydrates of carbon" or "carbohydrates". However this name is not applicable to all carbohydrates because of the aforementioned reason of the presence of nitrogen, phosphorus or sulfur.

3.1 CLASSIFICATION OF CARBOHYDRATES

Carbohydrates are classified into (3) three major classes. These are: Monosaccharides, Oligosaccharides and Polysaccharides. The word "saccharide" is derived from the Greek word "sackaron" meaning sugar.

Monosaccharides are simple sugars consisting of single polyhydroxy aldehyde or ketone unit. The most abundant monosaccharide in nature is the six-carbon sugar D-glucose. Other monosaccharides include: Mannose, Galactose and Fructose.

Oligosaccharides consists of short chains of monosaccharide units or residues joined by characteristic linkage called glycosidic bonds. The most abundant ones are the disaccharides which contain two monosaccharide units joined together by the glycosidic bond. Typical example is sucrose which consists of two six carbon sugars, D-glucose and D-fructose.

Polysaccharides are sugar polymers that occur in a continuous range of sizes, they usually contain more than 20 monosaccharide units. Polysaccharides may have hundreds and thousands of monosaccharides units joined together by glycosidic bonds.

3.2 FUNCTIONS / ROLES OF CARBOHYDRATES

- One of the primary role/function of carbohydrates is that they serve as nutrients to cells e.g glucose
- Carbohydrates also functions as form by which energy is stored in cells e.g. glycogen is the storage form of energy in animal cell while cellulose is the storage form of energy in plant cells.
- Carbohydrates function in serving as structural components of cells and tissue e.g chitin found in insects and cellulose found in plants.
- Carbohydrates like peptidoglycans serve as 'ground substance' in connective tissues (a gelly-like material) that is very important to the proper functioning of the tissue).
- Carbohydrates e.g. Hyaluronic acid can also serve as lubricants due to their viscosity in joint.
- Carbohydrates e.g. Oligosaccharides serve as components of glycoprotein where they are involved cellular/molecular recognition.
- Carbohydrates e.g. Galactose and fucose also function as antigenic determinant of blood group (ABO) system.
- Carbohydrates, e.g. Sialic acid serve protecting roles, they shield oligosaccharides of glycoconjugates from the action of hydrolytic enzymes.
- Carbohydrates, e.g. glycolipids play role in infection in that they serve as site or recognition by toxins such as cholera toxins and pertusis toxin.

3.3 PHYSICAL PROPERTY OF CARBOHYDRATES

- Carbohydrate e.g. monosaccharides are soluble in water but insoluble in organic solvents eg chloroform. Polysaccharides like cellulose are insoluble in water but will dissolve in ammoniacal solution of cupric salts.
- Carbohydrates including monosaccharides, oligosaccharides and polysaccharides are solid at room temperature.
- Most monosaccharides and some diasaccharides e.g. sucrose are sweet to taste.
- Carbohydrates e.g. monosaccharides are colourless crystalline solids.
- Monosaccharides, diasaccharides and polysaccharides are odourless.

3.4 STEREOCHEMISTRY OF CARBOHYDRATES

Carbohydrates, as organic compounds exhibit stereoisomerisms, different molecule in which the order of bonding is the same but the spatial relationship among the atoms is different.

Enantiomers are stereoisomers that are non super imposible mirror images of each other. The concept of enatiomerism requires the presence of a chiral carbon atom. A chiral carbon (also called asymmetric atom) is one that is attached to four different groups:



Enantiomers

The structure of D and L Glyceraldehyde Enantiomers was obtained from Lehninger's Principles of Biochemistry.

Enantiomers will be distinguished from each other by designations D for dextrorotatory and L for levorotatory. The maximum number of stereoisomers possible is 2^n , where n is the number of chiral carbon atoms. In sugars, what determines whether it is a D or L is the position of $-\text{OH}$ group on the carbon atom adjacent or next to the carbon atom that is most distant from the aldehyde or ketone functional group in the sugar.

Diastereoisomers are stereoisomers that are not mirror images of each other and need not contain chiral atoms. Epimers are diastereoisomers that contain more than one chiral carbon and differ in configuration about only one asymmetric carbon. e.g. of epimers include: glucose, galactose and mannose. Epimers therefore exhibit the concept of epimerism (differing around only one chiral carbon atom)

Anomers are a special form of carbohydrate stereoisomers in which the difference is specifically about the anomeric carbon. Carbohydrates that exhibit difference around the anomeric carbon atom are said to undergo anomerism e.g. of anomers are α and β - D-glucose. When the $-\text{OH}$ group on the anomeric carbon atom is down or below the plane, it is an alpha (α) anomer while $-\text{OH}$ group is up or above the plane, it is a beta (β) anomer.

3.6 SELF ASSESSMENT EXERCISES (SEA).

- 1.a. What is stereoisomerism?
- b. Using examples, distinguish between epimerism and anomerism.
2. State five(5) functions of carbohydrates.

4.0 CONCLUSION

Carbohydrates are organic compounds that are classified into different classes, have functions/roles in biological systems and exhibit stereochemistry.

5.0 SUMMARY

- Carbohydrates are defined as polyhydroxyaldehydes, polyhydroxy ketones or their derivatives.
- Carbohydrates functions include: surveying as energy source, structural importance, cellular recognition, antigenic determinants among other functions.
- Carbohydrates exhibit; anomerism, epimerism, enantiomerism and diastereoisomerism.

6.0 TUTOR MARKED ASSESSMENT

- 1(a) Define carbohydrates
- (b) Which classes of carbohydrates are you familiar with?
2. list the physical properties of carbohydrates.

7.0 REFERENCES/FURTHER READING.

- Elegbede J.A.(1990) Introductory Biochemistry (Chemistry of Macromolecules) .Institute of Education Press.
- Nelson L.,D., and Cox M.,M (2000) Lehninger's Principles of Biochemistry. New York. Worth Publishers.
- White A.,Handler P.,Smith E.,L., Hill R.,L., Lehman R.I.(1978). Principles of Biochemistry (6th.edition)Mc Graw Hill, Kogakusha.
- Devlin, T. (1986). Textbook of Biochemistry with Clinical Correlations.(2nd Edition) John Wiley and sons New York.

MODULE 1: CARBOHYDRATES**UNIT 2: MONOSACCHARIDES**

- 1.0 Introduction
- 2.0 Objectives
- 3.0 Structure of Glucose.
 - 3.1 Projection and Perspective Formula .
 - 3.2 Fischer's Projection Formula.
 - 3.3 Cyclisation of Fischer Projection Formula in Monosaccharides.
 - 3.4 Optical activity in Monosaccharides.
 - 3.5 Measurement of Optical Activity.
 - 3.6 Haworth Projection Formula.
 - 3.7 Self Assessment Exercises.
- 4.0 Conclusion
- 5.0 Summary
- 6.0 Tutor Marked Assignment
- 7.0 References and Further Reading

1.0 INTRODUCTION

Monosaccharides are the simplest carbohydrates that are also called simple sugars. They are the first of the three classes of carbohydrates characterized by being products of hydrolysis of non simpler sugars (Oligosaccharides and Polysaccharides). Monosaccharides consists of a single polyhydroxy aldehyde or ketone unit. The most abundant monosaccharides in nature is the six carbon sugar D-glucose, sometimes referred to as dextrose. Monosaccharides are of two families; those containing aldehyde functional group, called aldose and those with ketonic group are called ketoses, each having its own characteristic structure. In this unit you are going to study some aspects of monosaccharide (glucose) chemistry.

2.0 OBJECTIVES

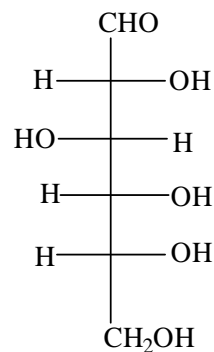
The objectives of this unit are:

- To study the structure of glucose;
- To study the perspective and projection formula of glucose;
- To study the Fisher and Haworth projection of glucose .

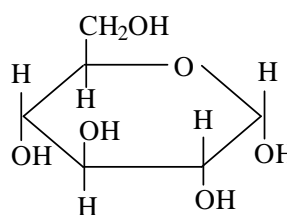
3.0 STRUCTURE OF GLUCOSE

The most abundant, naturally-occurring monosaccharide is D-glucose. D-glucose is a component of structures e.g. cellulose, glycogen, starch and important disaccharides such as sucrose, lactose and maltose.

Structurally glucose can be represented in a straight chain and a cyclic structure called Fisher and Haworth projection formulae of D-glucose respectively, these will be discussed in this unit



D Glucose

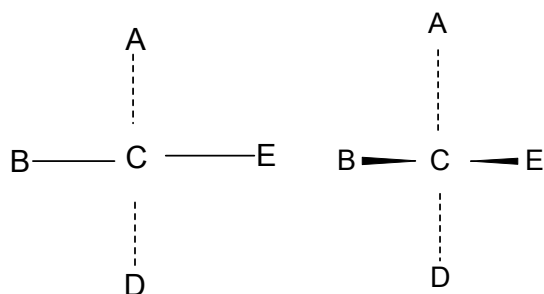


α - D- Glucose

3.1 PROJECTION AND PERSPECTIVE FORMULAS

The tetrahedral nature of carbon compounds presents a unique problem in writing the three dimensional structure of a compound on a two dimensional surface such as paper. This difficulty persisted until Emil Fischer introduced the projection formula in which 4 groups attached to a carbon atom are projected onto a plane. In Fischer's scheme, the horizontal bonds are understood to be in front of the

plane of the paper (i.e nearer to the reader or writer) and represented by solid lines while the vertical bonds are behind the plane of the paper (further away from the writer or reader) and represented by broken or dashed lines as below:



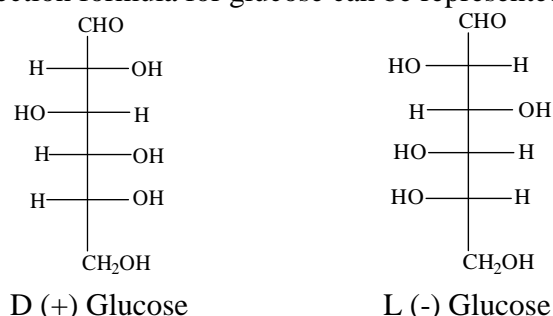
Projection formula

Perspective formula

This relationship is seen more clearly in the perspective formula where the vertical, dashed lines represent bonds behind the plane of the paper, and the horizontal solid wedges identify bonds in front of the plane of the paper.

3.2 FISCHER'S PROJECTION

Emil Fischer won the Nobel Prize in chemistry for elucidating the structure of glucose. From Fischer's work it has been possible to write the projection formula for glucose as well as the ball and stick formula for D and L glucose. The Fischer's projection formula for glucose can be represented.



D (+) Glucose

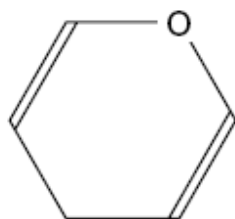
L (-) Glucose

3.3 CYCLISATION OF THE FISCHER PROJECTION FORMULA IN MONOSACCHARIDES.

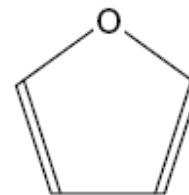
It has been shown that the two crystalline forms of glucose exist depending on the method of crystallization. These two forms of glucose are the α form and the β form. The observation of this observed behaviour for glucose is attributed to the fact that aldohexoses and other sugars react internally to form cyclic hemiacetals. The formation of cyclic hemiacetals is a characteristic reaction between aldehydes and alcohols while hemiketals are formed between ketones and alcohols.

In glucose, the hemiacetal reaction occurs between the alcoholic (-OH) group on carbon 5 and the aldehyde group on carbon 1, thus forming a 6-membered ring

(related structurally to pyran and therefore referred to as pyranose). When the –OH group on carbon 4 participates in the hemiacetal formation, a 5 – membered ring structure is formed (related structurally to furan, hence called furanose). The furanose form of glucose is less stable than the pyranose form in solution hence it is the pyranose form that usually exists. However, furanose forms of other monosaccharides e.g fructose are also stable and found in nature.



Pyran



Furan

The structures of Pyranose and Furanose rings above were obtained from Harper's Review of Biochemistry

The formation of pyranose rings confers some asymmetry on carbon atom 1 (Hemiacetal carbon) and hence optical activity. The α and β forms of D-glucose differ only in the configuration around the hemiacetal carbon. These two forms of glucose are called diastereo isomers or anomers. The term anomer is used to describe isomeric form of monosaccharides that differ each other only on their configuration about hemiacetal carbon atom such as α – D – glucose and β – D-glucose. The hemiacetal or carbonyl carbon is called the anomeric carbon.

3.4 OPTICAL ACTIVITY IN MONOSACCHARIDES

Optical activity is a concept exhibited by organic compounds e.g. glucose having an anomeric carbon atom or chiral centre to rotate the path of plane-polarized light in a polarimeter. If the path of the plane polarized light is rotated clockwise it is called (+) Dextrorotatory and if anticlockwise it is called (-) or Laevorotatory denoted by D and L respectively.

3.5 MEASUREMENT OF OPTICAL ACTIVITY

Specific rotation is a quantitative measurement of the optical activity of a stereoisomer. It is determined from measurement of the degree of rotation of a solution of a pure stereoisomer at a given concentration in a tube of a given length in a polarimeter. The specific rotation is calculated as:

$$[\alpha]_D^{25^{\circ}} = \frac{\text{Observed rotation in degrees}}{\text{length of tube, (dm) x concentration (g/ml)}}$$

Where dm = decimeter (0-1m)

D = Line of sodium (indicating light at wavelength of 589nm)

25⁰C = Temperature of measurement

(α) = Specific Rotation

3.6 HAWORTH'S PROJECTION FORMULA

The English chemist W.H. Haworth proposed that the ring forms of monosaccharides should be represented by a hexagonal ring consisting of carbon atoms C-1 to C – 5 and the oxygen atoms of glucopyranose in a plane perpendicular to the plane of the paper. The side nearer the reader should be represented by thickened lines while the substituents on the carbon atoms in the ring will extend above or below the plane of the hexagonal ring for example the C-6, which is substituent on C-5 will be above the plane of the ring as shown below. Contrary to the implication of the Haworth projection formula the hexagonal ring of pyranose is not planar. In most monosaccharides, it exists as the chair conformation though in some may exist as the boat conformation.

3.7 SELF ASSESSMENT EXERCISES(SEA)

- 1.(a) Describe the projection and perspective formula for glucose.
- (b) Briefly describe optical activity in monosaccharides.

4.0 CONCLUSION

Monosaccharides e.g. glucose can structurally exist in straight and cyclic forms (α - and β anomeric forms). These two anomeric forms exhibit optical activity and their specific rotations can be measured.

5.0 SUMMARY

- Straight chain structure of glucose can cyclise into the pyranose and furanose rings.
- The Fischer's projection formula of glucose is more clearer when represented in the perspective formula.
- The α and β anomeric forms of glucose are optically active.
- Haworth projection formula is another way of representing glucose structure.

6.0 TUTOR MARKED ASSESSMENT (TMA)

- 1a. Describe the Fischer's projection formula for glucose
- b. How do monosaccharides e.g. glucose cyclize?
- 2a. How is optical activity measured in monosaccharides?
- b. What is the Haworth projection formula?

7.0 REFERENCES AND FURTHER READING.

- Elegbede J.A.(1990) Introductory Biochemistry (Chemistry of Macromolecules) .Institute of Education Press.
- Nelson L.,D., and Cox M.,M (2000) Lehninger's Principles of Biochemistry. New York. Worth Publishers.
- White A.,Handler P.,Smith E.,L., Hill R.,L., Lehman R.I.(1978). Principles of Biochemistry (6th.edition)Mc Graw Hill, Kogakusha.
- Devlin, T. (1986). Textbook of Biochemistry with Clinical Correlations.(2nd Edition) John Wiley and sons New York.

MODULE 1: CARBOHYDRATES**UNIT 3: STRUCTURE OF OTHER MONOSACCHARIDES AND PROPERTIES**

- 1.0 Introduction
- 2.0 Objectives
- 3.0 Structure of Monosaccharides with 3 and 4 carbon atoms (Trioses Tetroses)
 - 3.1 Structure of monosaccharides with more than 4 carbon atoms.
 - 3.2 Structure of Derived Monosaccharides.
 - 3.2.1 Sugar Acids.
 - 3.2.2 Deoxy Sugars.
 - 3.2.3 Amino Sugars.
 - 3.3 Properties of Monosaccharides.
 - 3.3.1 Mutarotation.
 - 3.3.2 Reducing Property.
 - 3.3.3 Glycoside Formation.
 - 3.3.4 Ester Formation.
 - 3.3.5 Dehydration.
 - 3.3.6 Rearrangement in Alkaline Solution.
 - 3.3.7 Reduction of Monosaccharides.
 - 3.4 Self Assessment Exercises (SAE).
- 4.0 Conclusion.
- 5.0 Summary.
- 6.0 Tutor Marked Assignment.
- 7.0 References and Further Reading

1.0 INTRODUCTION

Apart from the monosaccharide glucose, other monosaccharides units do exist. Trioses (3) three carbon containing sugars and Tetroses (4) four carbon containing sugars which are monosaccharides that have only straight chain structures. Monosaccharides having (5) five carbon atoms or more do exist usually in cyclic or ring structures in solution. In such ring structures, the carbonyl group is not free but would form a covalent bond with one of the hydroxyl groups in the chain (intramolecular hemiacetal or hemiketal formation). In this unit you shall study other structures of monosaccharide types and their properties.

2.0 OBJECTIVES

In this unit we are expected to:

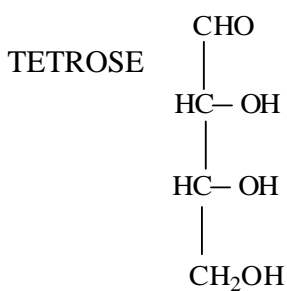
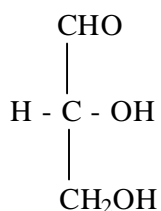
- Study the structure of other monosaccharides units with 3 and 4 carbon atoms.
- Study the structure of monosaccharides with more than 5 carbon atoms.
- Study the properties of monosaccharides.

3.0 STRUCTURE OF MONOSACCHARIDES WITH THREE (3) CARBON AND FOUR (4) CARBON ATOMS (TRIOSES AND TETROSES)

Monosaccharides containing 3 and 4 carbon atoms usually exist in straight chain forms. They do not form pyran or furan rings. Trioses (3C) sugars and tetroses (4C) sugars are very important monosaccharides.

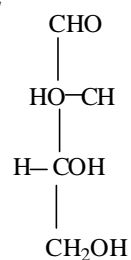
TRIOSE

D-Glyceraldehyde



D- Erythrose

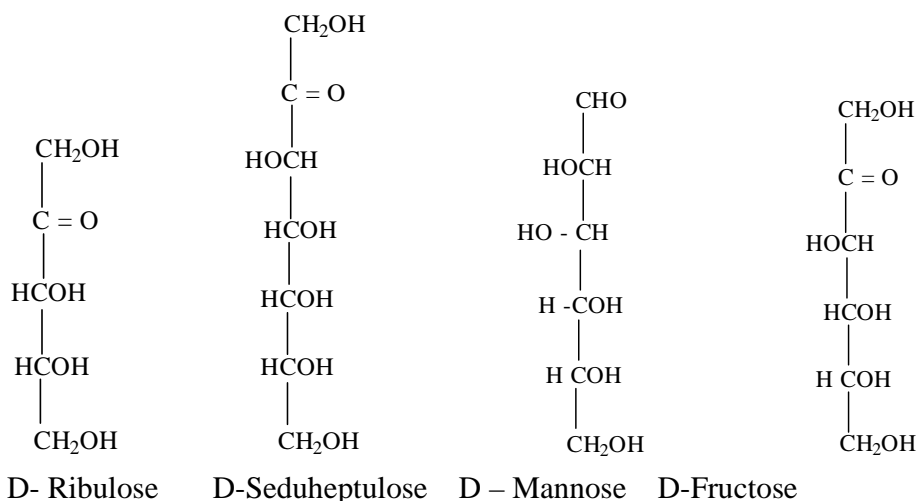
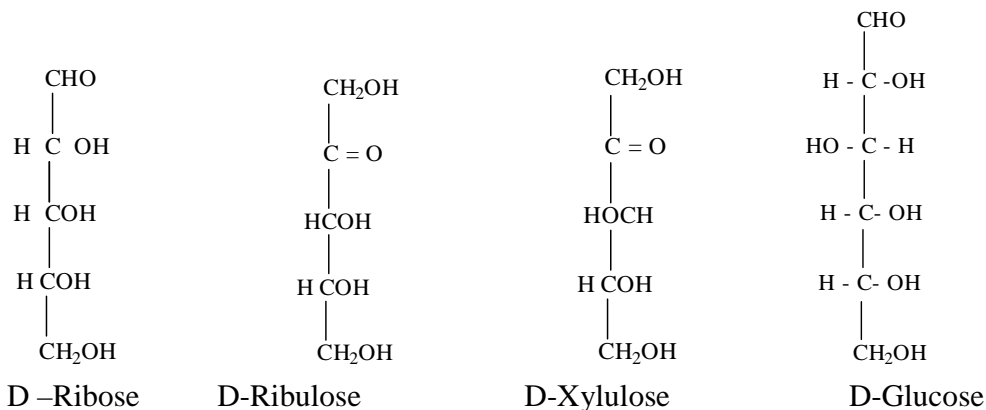
TETROSE



D – Threose

3.1 STRUCTURE OF MONOSACCHARIDES WITH MORE THAN FOUR (4) CARBON ATOMS

PENTOSE

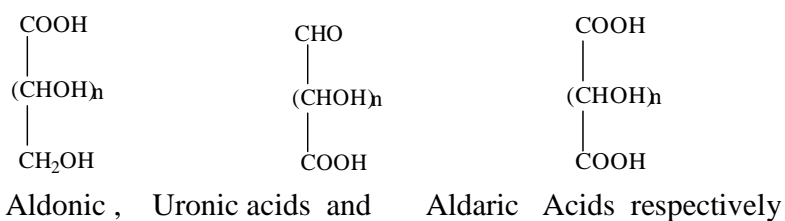


3.2 STRUCTURE OF DERIVED MONOSACCHARIDES

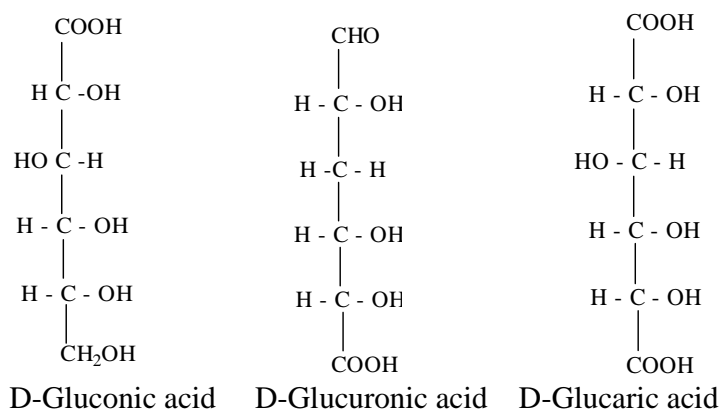
Many derivatives of monosaccharides are constituents of living things. Among the more important are the sugar acids, the amino sugars and the deoxy sugars.

3.2.1 SUGAR ACIDS

The most common compounds of this group are formed by oxidation of aldoses to carboxylic acids at either C – 1 aldehyde carbon, the C-6 hydroxymethyl carbon, or both. These acids have the generic names aldonic, uronic acid and aldaric acid, respectively and the general structures.

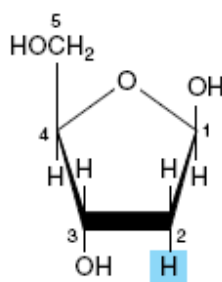


Oxidation of glucose gives rise to the following acids



3.2.2 DEOXY SUGARS

These sugars include compounds with one or more hydroxyl groups on the pyranose or furanose rings replaced by hydrogen. An example is 2 – Deoxyribose which is a component of the repeating unit in the polymeric deoxyribonucleic acids (DNA).

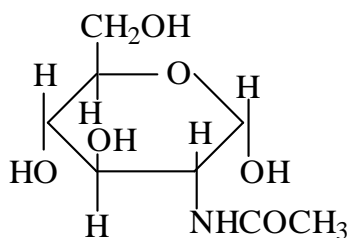


2- Deoxyribose

The structure of 2-deoxy ribose was obtained from Harper's Review of Biochemistry

3.2.3 AMINO SUGARS

In these compounds, a hydroxyl group on one of the pyranose – ring carbon atoms is replaced by an amino group. These compounds are widely distributed in plants and animals. Example of amino sugars are *N*-acetyl D-glucosamine and *N*-acetyl D-galactosamine.



(N-acety - D-glucosamine)

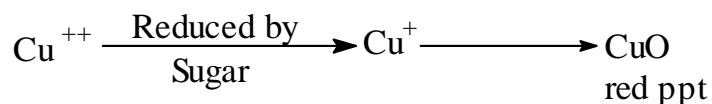
3.3 PROPERTIES OF MONOSACCHARIDES

3.3.1 MUTAROTATION

Isomeric forms of monosaccharides that differ only in their configuration about a hemiacetal or hemketal carbon atom (anomers) have the capability to undergo mutarotation. Mutarotation is a phenomenon where α and β anomers of D-glucose interconvert in aqueous solution.

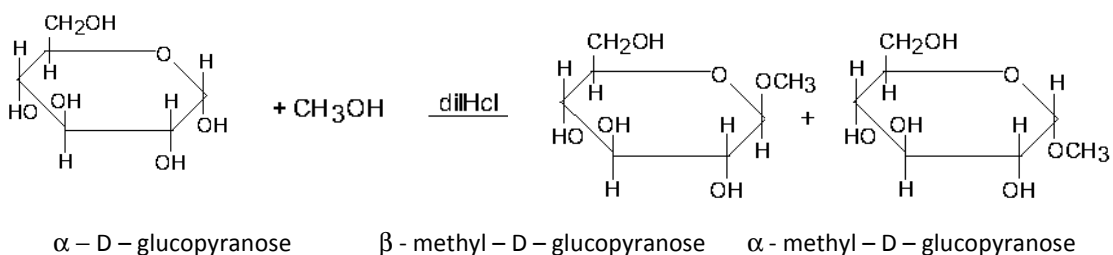
3.3.2 REDUCING PROPERTY

Monosaccharides readily reduce oxidizing agents such as (Cu^{2+}) cupric ions and hydrogen peroxide (H_2O_2). Glucose and other sugars capable of reducing oxidizing agents are called reducing sugars. E.g. Benedict's solution which contains Cu^{2+} in alkaline medium is a common reagent used for detecting reducing sugars by its ability to be converted to brick-red colour by reducing sugars..



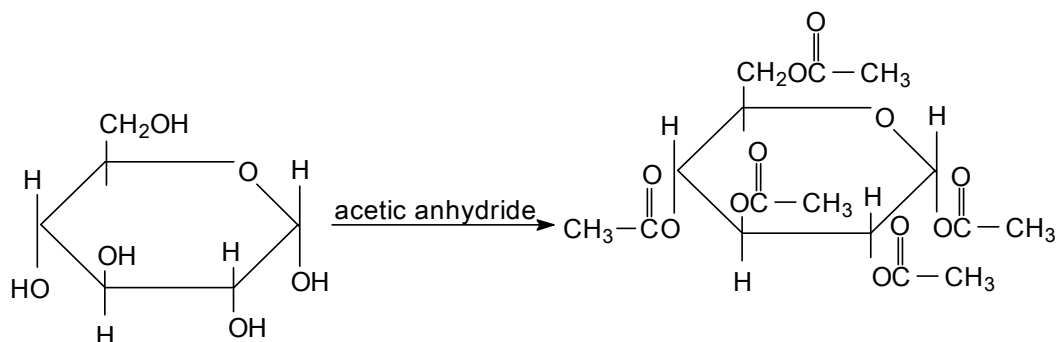
3.3.3 GLYCOSIDE FORMATION

Monosaccharides have the capacity to form acetals or glycosides when glucose solution is exposed to methanol in the presence of dilute HCl. Two compounds are formed, methyl - β - D- glucopyranoside and methyl- α - D glycopyranoside (Glycosides). Glycosides are not reducing sugars and does not show the phenomenon of mutarotation.

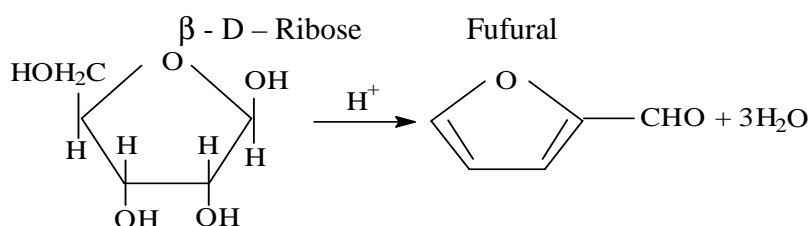


3.3.4 ESTER FORMATION

Another important property of monosaccharides is formation of esters. If α - D-glucopyranose is treated with acetic anhydride, all the -OH groups become acetylated to yield penta - O- acetyl glucose. This function is useful in structural elucidation of sugars since acetyl groups can be hydrolysed in acid or alkali. One of the most important type of ester formation is the formation of phosphate esters of carbohydrates.

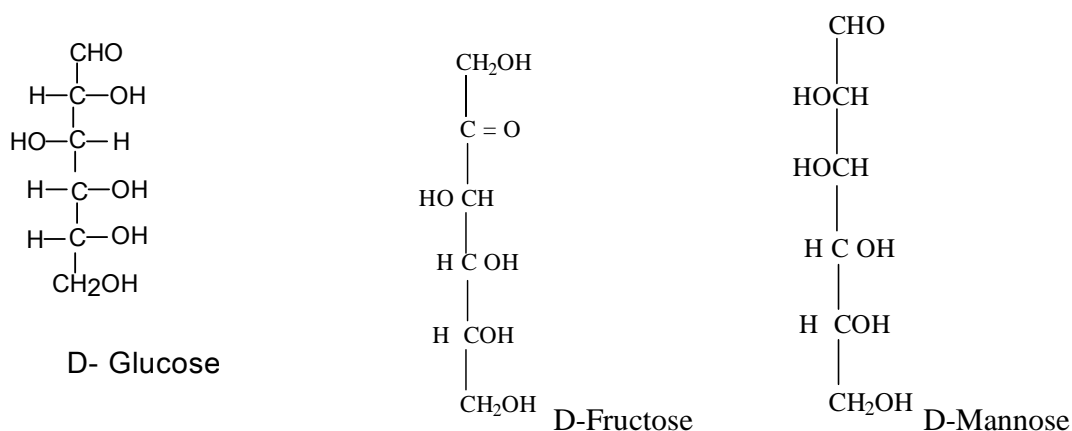


3.3.5 DEHYDRATION In strong mineral acid like HCl, pentoses and hexoses are dehydrated to form fufurals and hydroxymethylfurfural compounds respectively. This reaction is used in qualitative analysis of carbohydrates.



3.3.6 REARRANGEMENT IN ALKALINE SOLUTION

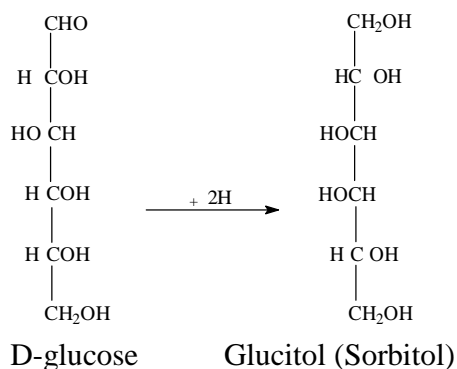
In cold, dilute alkaline solution, glucose forms both mannose and fructose. This interconversion is attributable to enolisation reaction that involves removal of hydrogen from carbon atom adjacent to the carbonyl group.



Source: Harper's Review of Biochemistry

3.3.7 REDUCTION OF MONOSACCHARIDES

D – glucose can be reduced by hydrogen gas and a suitable metal catalyst to give glucitol (sorbitol).



3.4 SELF ASSESSMENT EXERCISES(SEA).

- 1.(a) Draw the structure of any three (3) derived monosaccharides.
- (b) Describe the rearrangement of glucose in Alkaline solution.

4.0 CONCLUSION

Apart from glucose other monosaccharides like mannose, glyceraldehydes and Ribose do exist. Each of them has a characteristics structure and property.

5.0 SUMMARY

- Three (3) carbon and four (4) carbon atoms containing monosaccharides exist and they only have a straight chain structure .
- Monosaccharides containing more than four (4) carbon atoms have different structure from glucose and can be in straight as well as cyclic structure forms.
- Derived monosaccharides include: sugar acids, amino sugars and deoxy sugars.
- Monosaccharides have variety of properties which include: Reducing property, glycoside formation, ester formation among others.

6.0 TUTOR MARKED ASSIGNMENT (TMA)

- 1a. Draw the structure of a named 3 carbon and 4 carbon atom containing sugars.
- b. Draw the structure of any two of the following:
 - i. Mannose.
 - ii. Fructose .
 - iii. Seduheptulose.
- 2a. Describe the reducing property of monosaccharides .
- b. How do monosaccharides form glycosides.

7.0 REFERENCES AND FURTHER READING.

- Elegbede J.A.(1990) Introductory Biochemistry (Chemistry of Macromolecules) .Institute of Education Press.
- Nelson L.,D., and Cox M.,M (2000) Lehninger's Principles of Biochemistry. New York. Worth Publishers.
- White A.,Handler P.,Smith E.,L., Hill R.,L., Lehman R.I.(1978). Principles of Biochemistry (6th.edition)Mc Graw Hill, Kogakusha.
- Devlin, T. (1986). Textbook of Biochemistry with Clinical Correlations.(2nd Edition) John Wiley and sons New York

MODULE 1: CARBOHYDRATES
UNIT 4: OLIGOSACCHARIDES

- 1.0 Introduction.
- 2.0 Objectives.
- 3.0 Chemistry of Oligosaccharides.
 - 3.1 Types of Oligosaccharides.
 - 3.2 Maltose.
 - 3.3 Lactose.
 - 3.4 Sucrose.
 - 3.5 Trehalose.
 - 3.6 Properties of Oligosaccharides.
 - 3.7 Self Assessment Exercises.
- 4.0 Conclusion.
- 5.0 Summary.
- 6.0 Tutor Marked Assignment (TMA).
- 7.0 References and Further Reading .

1.0 INTRODUCTION

Oligosaccharides represent the second class of carbohydrates which consists of few (2 to 10) monosaccharide units or residues joined by characteristics linkages called glycosidic bonds. Oligosaccharides can be diasaccharides when they contain only (2) two units of monosaccharides, trisaccharides when they contain (3) three units of simple sugars, tetrasaccharides when they contain (4) four units of simple sugars, pentasaccharides, hexasaccharides or heptasaccharides. The most important Oligosaccharides are the diasaccharides which contain (2) two units of simple sugars. In this unit you are going to study the various types of diasaccharides.

2.0 OBJECTIVES

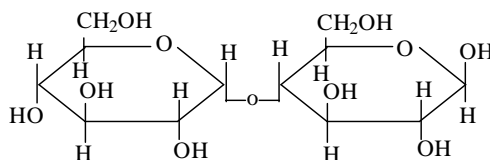
- To study chemistry of Oligosaccharides
- To study different types of important Oligosaccharides (diasaccharides)
- To learn the structure of different types of diasaccharides.

3.0 CHEMISTRY OF OLIGOSACCHARIDES

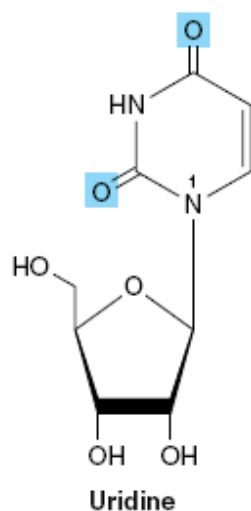
All common Oligosaccharides have names ending with suffix – ose. In cells, most Oligosaccharides having three or more units do not occur as free entities but are joined to non-sugar molecules (lipids or protein) in glycojugates.

Oligosaccharides are basically involved in (2) two different types of linkages *O* – glycosidic linkage and *N*-Glycosidic linkage.

The *O*-glycosidic linkage is more common in joining the monosaccharides unit together while *N*-glycosidic linkage usually links Oligosaccharides with other glycoconjugates like protein and nucleic acid. The *O*-glycosidic bonds joining monosaccharide units in Oligosaccharides can either be an α or β configuration. These configurations depend on the position of the –OH group of the anomeric carbon atom involved in the linkage. When the – OH group from the anomeric carbon atom involved in glycosidic linkage is below the plane, then it is called an alpha-*O*-glycosidic linkage and when it is above the plane it is called beta - *O*-glycosidic linkage. While writing the name of an Oligosaccharides, it is important to indicate the (2) two carbon atoms joined by the glycosidic linkage in parentheses, with an arrow connecting the two numbers for example (1 \rightarrow 4) shows that C – 1 of the first named sugar residue is joined to C – 4 of the second.



Example of *O*-glycosidic linkage holding the two glucose molecules in Maltose



Example of *N*-glycosidic linkage holding the ribose sugar and a base at the N-1 position of the base.

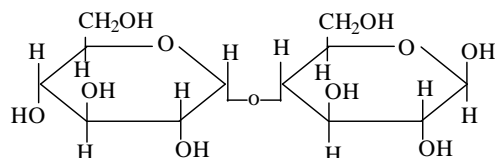
Source: Harper's Review of Biochemistry.

3.1 TYPES OF OLIGOSACCHARIDES (DIASACCHARIDES)

Different types of diasaccharides do exist and the differences in these diasaccharides are based upon the type of monosaccharides units contained in them (they are made up of). In addition, the orientation of the component monosaccharides units determines whether the diasaccharides is a reducing diasaccharide or a non – reducing one.

3.2 MALTOSE

The diasaccharide maltose contains (2) two D – glucose residues joined by a glycosidic linkage between C – 1 (the anomeric carbon atom) of one glucose residue and C – 4 of another. Due to the fact that the anomeric carbon (C – 1 of the glucose residue on the right) can reduce, maltose is a reducing diasaccharide. The configuration of the anomeric carbon atom is α .

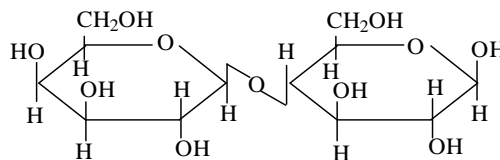


Maltose. α - D Glucopyranosyl (1 \rightarrow 4) D-glucopyranose.

Maltose is formed when – OH group of one glucose molecule (right) condenses with intermolecular hemiacetal of the other glucose molecule (left) with the elimination of water and formation of *O*-glycosidic bond (linkage).

3.3 LACTOSE

Lactose contains D – galactose and D – glucose units. Lactose occurs naturally only in milk. The anomeric carbon of glucose is available for oxidation and thus lactose is a reducing disaccharide. It is abbreviated as Gal (β 1 – 4) Glc.

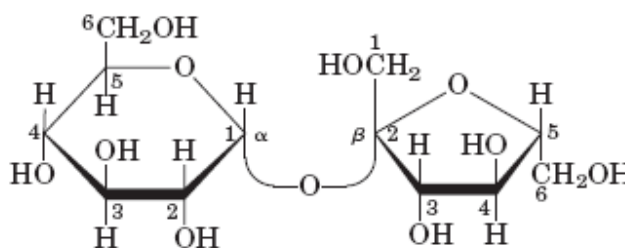


Lactose

β - D – galactopyranosyl (1 \rightarrow 4) β - D – glucopyranose

3.4 SUCROSE

The table sugar is sucrose and is a disaccharides of glucose and fructose. It is formed by plants but not by higher animals. In contrast to maltose and lactose, sucrose contains no free anomeric carbon atom. The anomeric units of both disaccharides are involved in glycosidic linkage. Sucrose is therefore not a reducing sugar. In the abbreviated nomenclature for sucrose, a double headed arrows in parenthesis are used instead of the single headed arrow, as in lactose and maltose, this is simply to indicate that it is the 2 (two) anomeric carbons that are involved in glycosidic bond.



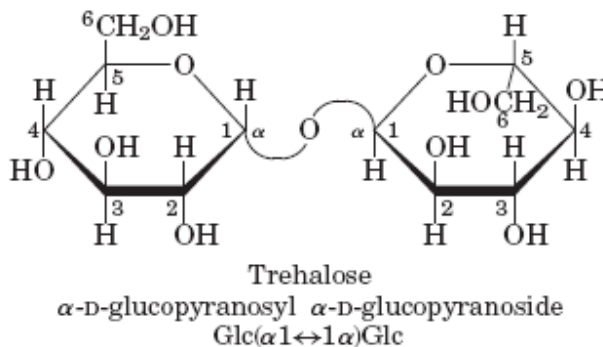
Sucrose

α -D-glucopyranosyl β -D-fructofuranoside
Glc(α 1 \leftrightarrow 2 β)Fru

Source: Lehninger's Principles of Biochemistry

3.5 TREHALOSE

Trehalose, Glc ($\alpha 1 \leftrightarrow 1 \alpha$) Glc is a disaccharide containing two glucose units joined by alpha 1 - 1 glycosidic bond. Like sucrose, trehalose is a non reducing disaccharide (sugar). It is a major constituent of circulating fluid (hemolymph) in insects where it serves in energy storage.



Source: Lehninger's Principles of Biochemistry

3.6 PROPERTIES OF OLIGOSACCHARIDES (DISACCHARIDES)

- Oligosaccharides can be hydrolyzed by acids or other hydrolytic enzymes to their monomeric units.
- Some Oligosaccharides can undergo mutarotation because they have reducing properties eg. lactose.
- Some Oligosaccharides e.g. maltose are reducing sugars while some are not eg sucrose.
- Oligosaccharides units are held together by glycosidic linkages

3.7 SELF ASSESSMENT EXERCISES(SMA)

- 1.(a) Describe the type of linkages present in any three named disaccharide.
- (b) Draw the structure of Trehalose.

4.0 CONCLUSION

Oligosaccharides contains fewer monosaccharides units joined together by glycosidic bond. The monosaccharides can be similar or different and could be reducing sugar or non-reducing sugar.

5.0 SUMMARY

- Oligosaccharides represent the second class of carbohydrates.
- There are different classes of oligosaccharides with the disaccharides being the most important class.
- Maltose and lactose are reducing disaccharides while sucrose and trehalose are non – reducing disaccharides.

- Oligosaccharides have *O*-glycosidic linkage joining their monosaccharide unit together and *N* – glycosidic linkages links oligosaccharides to other glycoconjugates like proteins and nucleic acids.

6.0 TUTOR MARKED ASSESSMENT

- 1 (a) What are Oligosaccharides?
(b) Give 3 characteristic of Oligosaccharides.
2. (a) How are monosaccharide units of Oligosaccharides linked?
(b) Draw the structure of the following: Maltose, Sucrose and Lactose.

7.0 REFERENCES AND FURTHER READING.

- Elegbede J.A.(1990) Introductory Biochemistry (Chemistry of Macromolecules) .Institute of Education Press.
- Nelson L.,D., and Cox M.,M (2000) Lehninger's Principles of Biochemistry. New York. Worth Publishers.
- White A.,Handler P.,Smith E.,L., Hill R.,L., Lehman R.I.(1978). Principles of Biochemistry (6th.edition)Mc Graw Hill, Kogakusha.
- Devlin, T. (1986). Textbook of Biochemistry with Clinical Correlations.(2nd Edition) John Wiley and sons New York

MODULE 1: CARBOHYDRATES
UNIT 5: POLYSACCHARIDES

- 1.0 Introduction.
- 2.0 Objectives.
- 3.0 Types of Polysaccharides.
 - 3.1 Homopolysaccharides.
 - 3.1.1 Cellulose.
 - 3.1.2 Starch.
 - 3.2 Heteropolysaccharides.
 - 3.2.1 Pectin.
 - 3.2.2 Hyaluronic acid.
 - 3.3 Self Assessment Exercises.
- 4.0 Conclusion .
- 5.0 Summary.
- 6.0 Tutor Marked Assignment (TMA)
- 5.0 References and Further Reading.

1.0 INTRODUCTION

Most carbohydrates found in nature occur as polysaccharides. They represent the third class of carbohydrate types also called glycans. Hydrolysis of polysaccharides yields exclusively monosaccharides or products related to monosaccharides, most frequently D-Glucose. However, D-mannose, D-galactose, D-fructose, D – arabinose as well as D-glucuronic acid, D. galacturonic acid, D – glucosamine, sialic acids and uronic acids also occur as constituents of polysaccharides. The various polysaccharides differ not only in constituent monosaccharide composition but differ also in molecular weight and other structural features. Thus, some polysaccharides are linear while some are highly branched. In this unit we are going to study the different types of polysaccharides, their chemical compositions and structures.

2.0 OBJECTIVES

The objectives of this unit are:

- To study the classification of polysaccharides.
- Study the chemical composition of each type of polysaccharide.
- To learn the structure of polysaccharides.

3.0 TYPES OF POLYSACCHARIDES

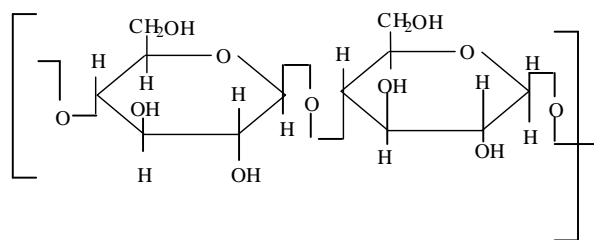
Although there are various indices that can be used in classifying polysaccharides, the most widely used index is the product of hydrolysis of the polysaccharides, whether they are similar in which case they are called homopolysaccharides or whether the products of hydrolysis are different in which case called heteropolysaccharides.

3.1 HOMOPOLYSACCHARIDES

These are polysaccharides that upon hydrolysis, give only one type of monomeric units. There are various types of homopolysaccharides which include: cellulose, starch and glycogen.

1.1 CELLULOSE

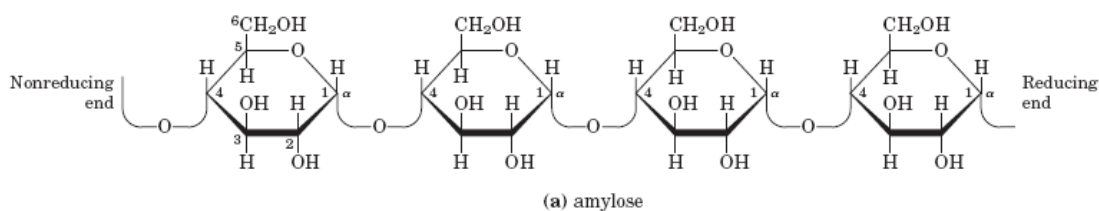
Cellulose is unquestionably the most abundant carbohydrate and the most abundant organic compound in the world, constituting 50% or more of all the carbon in vegetation. It is a linear homopolysaccharide composed of D-glucopyranose units linked by β (1-4) linkages. On partial hydrolysis of cellulose, a disaccharide cellobiose is produced while on complete hydrolysis of cellulose, glucose units are produced.



Repeating cellobiose unit of cellulose

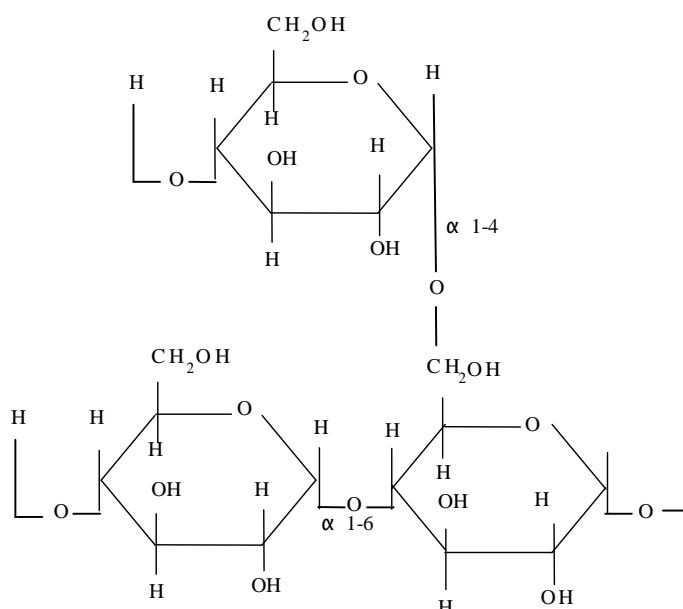
3.1.2 STARCH

Starch is a polymer of glucose units linked in α 1 – 4 linkages. It serves as nutritional reservoir in plants. The repeating disaccharide unit in starch therefore is maltose.



Repeating Unit of Starch (Amylose Unit) containing two Maltose Units.
The structure was obtained from Lehninger's's Principles of Biochemistry.

Native starches are a mixture of two compounds that are separable from each other, Amylose and Amylopectin. Amylose is a component that is believed to be a long unbranched chain of glucose joined together by α 1-4 bonds and amylopectin which is a branched chain polysaccharide. The glucose residue that is situated at each point of branching is substituted on carbon 4 and carbon 6. The isolation of α 1 – 6 disaccharide, isomaltose, from the products of incomplete hydrolysis of amylopectin proves the substitution of the branch points.



Repeating Unit of Starch (Amylopectin Unit)

3.1.2 GLYCOGEN

Glycogen is another homopolysaccharide of glucose. It is also a storage polysaccharide of animals that serves as a source of fuel, serving similar purpose as starch. It is similar to amylopectin in that it is a branched polysaccharide. It is however different from amylopectin in that its branch point occurs every 8 – 10 units of glucose. Glycogen is hydrolysable by α and β - amylases to yield glucose, maltose and limit dextrins.

3.2 HETEROPOLYSACCHARIDES

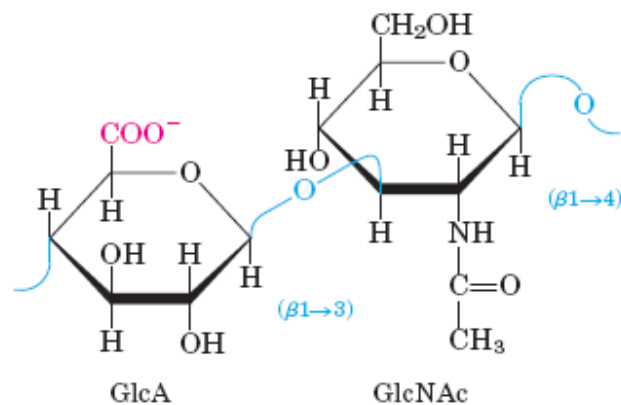
These are class of carbohydrate composed of repeating monomeric unit that are different. Many types of heteropolysaccharides do exist.

3.2.1 PECTINS

These are heteropolysaccharides consisting of arabinose, galactose and galactouronic acid.

3.2.2 HYALURONIC ACID

This is a heteropolysaccharide consisting of repeating units of D-glucuronic acid and N-acetyl D glucosamine. The monosaccharides are linked together by $\beta(1 - 3)$ bonds to form a disaccharides which is linked by $\beta(1 - 4)$ bond to the next repeating unit. It is soluble in water and form viscous solution.

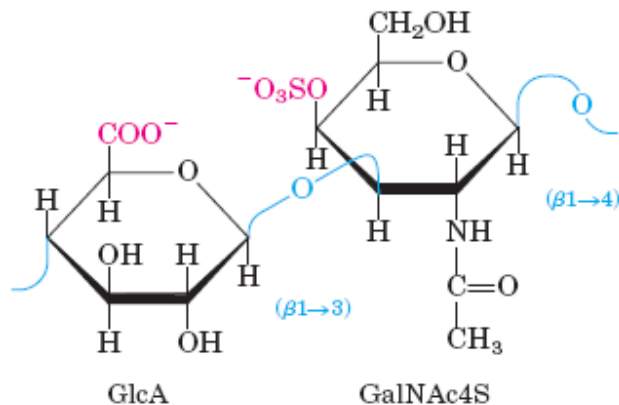


Repeating unit of hyaluronic acid obtained from Lehninger's's Principles of Biochemistry

3.2.3 CHONDROITIN

This is also a heteropolysaccharide similar to hyaluronic acid in composition except that the amino sugar is N-acetyl D-galactosamine not N-acetyl D-

glucosamine sulfate esters are found at C-4 or C-6 of the amino sugar of chondroitin making it chondroitin-4-sulfate or chondroitin-6-sulfate respectively.



The structure of chondroitin-4-sulfate was obtained from Lehninger's's Principles of Biochemistry.

3.3 SELF ASSESSMENT EXERCISES(SAE)

- 1.(a) What are polysaccharides?
- (b) How are polysaccharides classified?

4.0 CONCLUSION

Polysaccharides are the third class of carbohydrates that is usually a polymer of same monomeric unit of simple sugars or different monomeric units of simple sugar.

5.0 SUMMARY

- Polysaccharides are the most abundant class of carbohydrates that on hydrolysis yields monosaccharides or monomeric units of sugars.
- Polysaccharides can be classified into homo and heteropolysaccharide.
- Different polysaccharides contain different type of monomeric composition .
- Homopolysaccharides includes: Starch, Glycogen, Cellulose e.t.c. while heteropolysaccharides are: Hyaluronic acid, Pectin, chondroitin sulfate e.,t.c.

6.0 TUTOR MARKED ASSESSMENT

1. (a) Differentiate between homopolysaccharides and heteropolysaccharides
- (b) Draw the structure of the repeating unit of a named homopolysaccharide
2. (a) Draw the structure of chondroitin sulfate
- (b) Distinguish between hyaluronic acid and chondroitin sulfate.

7.0 REFERENCES AND FURTHER READING

Elegbede J.A.(1990) Introductory Biochemistry (Chemistry of Macromolecules) .Institute of Education Press.

- Nelson L.,D., and Cox M.,M (2000) Lehninger's Principles of Biochemistry. New York. Worth Publishers.
- White A.,Handler P.,Smith E.,L., Hill R.,L., Lehman R.I.(1978). Principles of Biochemistry (6th.edition)Mc Graw Hill, Kogakusha.
- Devlin, T. (1986). Textbook of Biochemistry with Clinical Correlations.(2nd Edition) John Wiley and sons New York

MODULE 2: LIPIDS**UNIT 1: CHEMISTRY OF LIPIDS**

- 1.0 Introduction.
- 2.0 Objective
- 3.0 Chemistry composition of lipids.
 - 3.1 Types of Fatty acids .
 - 3.2 Properties of fatty acids in lipids .
 - 3.2.1 Physical property of Fatty acids.
 - 3.2.2 Chemical property of fatty acids.
 - 3.3 Nomenclature of fatty acids.
 - 3.4 Self Assessment Exercises.
- 4.0 Conclusion.
- 5.0 Summary.
- 6.0 Tutor Marked Assignment (TMA).
- 7.0 Further Reading and References.

1.0 INTRODUCTION

Lipids are a group of compounds that are insoluble in water but soluble in organic solvents. Lipids are usually oily or greasy organic substances extractable from cells and tissues using solvents like chloroform or ether. The most abundant type of lipid is the triglyceride (Triacylglycerol). In this unit we shall discuss the chemistry of these organic substances called lipids.

2.0 OBJECTIVES

By the end of this unit you are expected to know

- The building blocks of most lipids (fatty acids) ;
- The various types of fatty acids;
- Structure and nomenclature of fatty acids;
- Properties of fatty acids;
- Reaction of fatty acids.

3.0 CHEMICAL COMPOSITION OF LIPIDS

Majority of lipids have fatty acids as their building blocks. Fatty acids are long-chain organic acids (carboxylic acids). They have carbon atoms from 4 – 36, a single (-COOH) carboxyl group and a long non-polar tail which is responsible for water – insolubility and oily or greasy nature of most lipids.

3.1 TYPES OF FATTY ACIDS

The hydrocarbon tail of fatty acids may be either saturated, contain one double bond (monounsaturated) or more (up to six) double bonds (polyunsaturated fatty acids). The double bonds are nearly always in *cis*-configuration in unsaturated fatty acids. In polyunsaturated fatty acids the double bonds are never conjugated (-CH - CH - CH = CH -), rather they are separated by methylene group (-CH = CH = CH₂- CH = CH -). This arrangement is called pentadiene structure.

Table 1.0 shows some naturally occurring fatty acids.

Carbon skeleton	Structure*	Systematic name [†]	Common name (derivation)	Melting point (°C)	Solubility at 30 °C (mg/g solvent)	
					Water	Benzene
12:0	CH ₃ (CH ₂) ₁₀ COOH	<i>n</i> -Dodecanoic acid	Lauric acid (Latin <i>laurus</i> , "laurel plant")	44.2	0.063	2,600
14:0	CH ₃ (CH ₂) ₁₂ COOH	<i>n</i> -Tetradecanoic acid	Myristic acid (Latin <i>Myristica</i> , nutmeg genus)	53.9	0.024	874
16:0	CH ₃ (CH ₂) ₁₄ COOH	<i>n</i> -Hexadecanoic acid	Palmitic acid (Latin <i>palma</i> , "palm tree")	63.1	0.0083	348
18:0	CH ₃ (CH ₂) ₁₆ COOH	<i>n</i> -Octadecanoic acid	Stearic acid (Greek <i>stear</i> , "hard fat")	69.6	0.0034	124
20:0	CH ₃ (CH ₂) ₁₈ COOH	<i>n</i> -Eicosanoic acid	Arachidic acid (Latin <i>Arachis</i> , legume genus)	76.5		
24:0	CH ₃ (CH ₂) ₂₂ COOH	<i>n</i> -Tetracosanoic acid	Lignoceric acid (Latin <i>lignum</i> , "wood" + <i>cera</i> , "wax")	86.0		
16:1(Δ ⁹)	CH ₃ (CH ₂) ₅ CH=CH(CH ₂) ₇ COOH	<i>cis</i> -9-Hexadecenoic acid	Palmitoleic acid	1-0.5		
18:1(Δ ⁹)	CH ₃ (CH ₂) ₇ CH=CH(CH ₂) ₇ COOH	<i>cis</i> -9-Octadecenoic acid	Oleic acid (Latin <i>oleum</i> , "oil")	13.4		
18:2(Δ ^{9,12})	CH ₃ (CH ₂) ₄ CH=CHCH ₂ CH=CH(CH ₂) ₇ COOH	<i>cis</i> -, <i>cis</i> -9,12-Octadecadienoic acid	Linoleic acid (Greek <i>linon</i> , "flax")	1-5		
18:3(Δ ^{9,12,15})	CH ₃ CH ₂ CH=CHCH ₂ CH=CHCH ₂ CH=CH(CH ₂) ₇ COOH	<i>cis</i> -, <i>cis</i> -, <i>cis</i> -9,12,15-Octadecatrienoic acid	α-Linolenic acid	-11		
20:4(Δ ^{5,8,11,14})	CH ₃ (CH ₂) ₄ CH=CHCH ₂ CH=CHCH ₂ CH=CHCH ₂ CH=CH(CH ₂) ₃ COOH	<i>cis</i> -, <i>cis</i> -, <i>cis</i> -, <i>cis</i> -5,8,11,14-Icosatetraenoic acid	Arachidonic acid	-49.5		

Table 1.0 was Obtained from Lehninger's's Principles of Biochemistry.

3.2 PROPERTIES OF FATTY ACIDS.

Like any other organic compound, fatty acids also have their physical and chemical properties which is dependent on the chemical nature of the fatty acids.

3.2.1 PHYSICAL PROPERTY OF FATTY ACID.

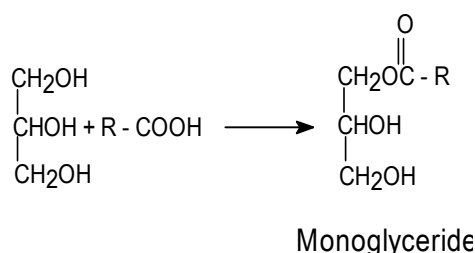
Physical property of fatty acids are largely determined by the length of the fatty acid and the degree of unsaturation of the hydrocarbon chain. The non polar hydrocarbon chains accounts for the poor solubility of fatty acids in water. The longer the hydrocarbon chain and the fewer the double bonds the lower the solubility of fatty acids, eg. Lauric acid with 12 carbon atoms has greater solubility than Palmitic acid with 16 carbon atoms.

Melting points are also influenced by the length and the degree of unsaturation of hydrocarbon chain. At room temperature (25°C), the saturated fatty acids from 12 carbon to 24 carbon atoms have a waxy nature, whereas unsaturated fatty acids of these chain length are oily liquids. This difference in melting points is due to difference in degree of packing of the fatty acid molecules. For a given fatty acid chain, melting point decreases as the number of double bond increases.

3.2.2 CHEMICAL PROPERTIES OF FATTY ACID.

- Ester bond formation:- The carboxyl group ($-\text{COOH}$) in fatty acids can react with hydroxyl groups ($-\text{OH}$) of compounds like Glycerol to form ester. This type of reaction leads to the formation of triacylglycerides and phospholipids.

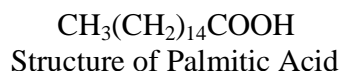
Glycerol + Fatty Acid = Mono, Di or Triglyceride,
depending on the number of fatty acids



- The methyl group of the non-conjugated pentadiene structure in polyunsaturated fatty acids can be directly attacked by O_2 to form free radicals.

3.3 NOMENCLATURE OF FATTY ACIDS

A general rule in the nomenclature of fatty acids first considers the number of carbon atoms, then the number of double bonds if any and finally the position of the double bonds counting from $-\text{COOH}$ carbon as carbon number 1. For example, palmitic acid, $\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$, a saturated fatty acid is written as 16:0, which means the fatty acid has 16 carbon atoms and no double bonds .



Oleic acid, $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$, is a monounsaturated fatty acid is written as 18 : 1 (Δ^9) which means the fatty acid has 18 carbon atoms and one double bond or carbon atom number 9. The notation (Δ) simple mean carbon

atom number. For polyunsaturated fatty acid (PUFA) arachidonic acid, its nomenclature is written as 20:4 ($\Delta^{5,8,11,14}$), meaning that it's a 20 carbon atom fatty acid with double bond at positions/carbon atoms 5,8,11 and 14. It is important to note that generally the cis configuration of double bonds in fatty acids are assumed when their nomenclatures are written.

3.4 SELF ASSESSMENT EXERCISES(SAE).

- 1.(a) Draw the structure of two (2) named saturated fatty acids.
- (b) Give two physical properties of fatty acids.

4.0 CONCLUSION

The chemistry of lipids is simply based on the nature of fatty acids contained in them and these fatty acids have their inherent physicochemical properties.

5.0 SUMMARY

- Fatty acids are the building blocks of majority of lipids which can either be saturated or unsaturated.
- Physical properties of fatty acids include differential solubility and melting points determined by chain length and degree of unsaturation.
- Chemical properties of fatty acids include ability to form ester linkage, free radicals on oxidation e.t.c.
- In naming fatty acids, the numbers of carbon atoms is considered first, followed by of double bonds.

6.0 TUTOR MARKED ASSESSMENT

1. (a) What are the factors that determine the physical property of lipids.
- (b) Write the structures of fatty acids with 12, 14 and 16 carbon atoms.
2. (a) Give any two reaction of fatty acids
- (b) Give the nomenclature of a polyunsaturated fatty acid with double bonds at position 9, 12 and 15 in cis configuration.

7.0 REFERENCES AND FURTHER READING

- Elegbede J.A.(1990) Introductory Biochemistry (Chemistry of Macromolecules) .Institute of Education Press.
- Nelson L.,D., and Cox M.,M (2000) Lehninger's Principles of Biochemistry. New York. Worth Publishers.
- White A.,Handler P.,Smith E.,L., Hill R.,L., Lehman R.I.(1978). Principles of Biochemistry (6th.edition)Mc Graw Hill, Kogakusha.
- Devlin, T. (1986). Textbook of Biochemistry with Clinical Correlations.(2nd Edition) John Wiley and sons New York

MODULE 2: LIPIDS**UNIT 2: CLASSIFICATION OF LIPIDS**

- 1.0 Introduction .
- 2.0 Objectives.
- 3.0 Classification of lipids.
 - 3.1 Acylglycerols .
 - 3.2 Phosphoacylglycerols.
 - 3.3 Sphingolipids.
 - 3.3.1 Sphingomyelins.
 - 3.3.2 Glycosphingolipids.
 - 3.3.3 Gangliosides.
 - 3.4 Waxes.
 - 3.5 Steroids.
 - 3.6 Terpenes ..
 - 3.7 Self Assessment Exercises.
- 4.0 Conclusion
- 5.0 Summary
- 6.0 Tutor Marked Assignment (TMA)
- 7.0 References and Further Reading.

1.0 INTRODUCTION

Lipids have been classified and subclassified into different types. The indices upon which these classifications are made is basically due to their composition and properties. The classification enables one to easily categorize a lipid which could be isolated from plant or animal tissue. In this unit you will learn the various classes of lipids and their structures.

2.0 OBJECTIVES

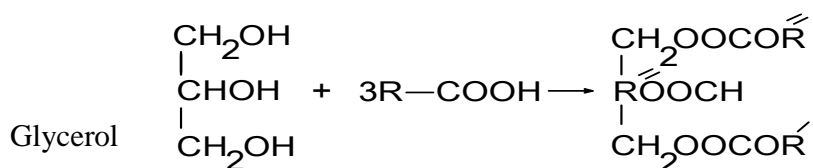
- To study the various classes of lipids .
- To learn the structures of lipids present in various classes.

3.0 CLASSIFICATION OF LIPIDS

Lipids have been broadly classified into saponifiable and non saponifiable lipids. Saponifiable lipids are those lipids that yield salt of fatty acids upon alkaline hydrolysis while non saponifiable lipids are not usually subjected to hydrolysis. Example of saponifiable lipids includes: Acylglycerols, Phosphoacylglycerols, Sphingolipids and Waxes. While example of non-saponifiable lipids are Terpenes, Steroids, Prostaglandins and related compounds.

3.1 ACYLGLYCEROLS

These are the most abundant and widespread of all lipids, they are also called neutral lipids. Acylglycerols are compounds in which one or more of the three hydroxyl groups (OH) is esterified to fatty acids. Acylglycerols can either be mono when only one –OH group is esterified, diacylglycerol when two of the three hydroxyl groups are esterified to fatty acid or triacylglycerol when all three –OH groups of the glycerol are esterified to fatty acids. Triacylglycerols also called triglycerides are the form in which lipids is a good storage form of energy and the form in which lipid is stored in adipose tissues. They are produced from the reaction.

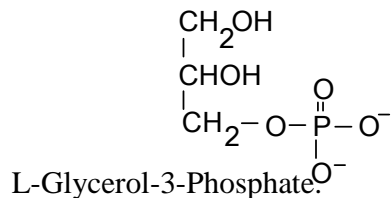


The R' and R'' may be the same or different fatty acids.

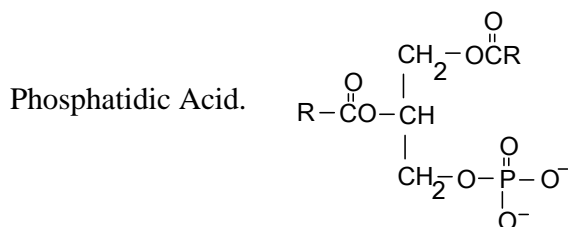
Triacylglycerols are hydrophobic and do not form stable micelles. They may be hydrolysed to glycerol and 3 fatty acids by enzymes (lipases) or strong alkali. The properties of triacylglycerol are determined to a great extent by the those fatty acids contained in it.

3.2 PHOSPHOACYLGLYCEROLS

Phosphoacylglycerols are derivatives of (L – Glycerol – 3 – phosphate)

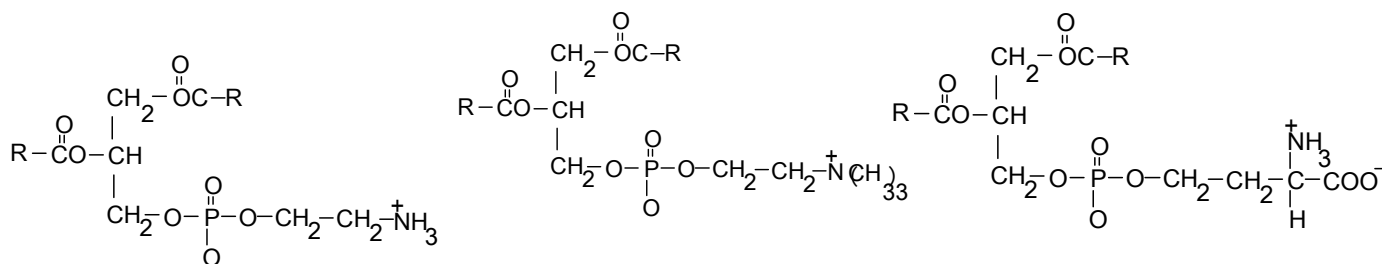


The parent compound of phosphoacylglycerols, (phosphatidic acid) is derived from L-glycerol – 3- phosphate by esterification of its two –OH groups.



All phosphoacylglycerols (phosphoglycerides) or phospholipids have negative charge around pH 7. They are amphipathic (possessing a polar head group and non polar hydrophobic tails).

Examples of phosphoacylglycerols include phosphatidylcholine (lecithine), phosphatidylethanolamine, phosphatidylinositol and phosphatidylserine.



Phosphatidylethanolamine

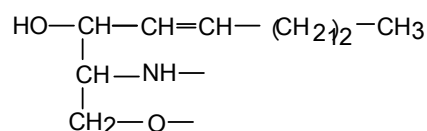
Phosphatidylcholine

Phosphatidylserine

In phospholipids, when the –OH group on the first carbon atom is in ether linkage to a fatty acid rather than ester linkage, a specific type of phospholipids called plasmalogens are formed. Other types of phospholipids include cardiolipin.

3.3 SPHINGOLIPIDS

Sphingolipids are the second largest class of membrane lipids. They are a complex lipids composed of long chain fatty acids one molecule of long chain amino alcohol or its derivative called sphingosine and a polar head alcohol. Sphingolipids contain no glycerol backbone and are of 3 types.



Sphingosine

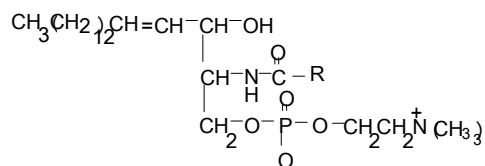
Structure of Sphingosine (Parent compound of Sphingolipids)

In ceramides, a long chain fatty acid in amide linkage to sphingosine

3.3.1 SPHINGOMYELINS

These are the most common class of sphingolipids. In sphingomyelins the –OH group at C-1 of sphingosine is esterified to phosphocholine or phosphoethanolamine while one of the H atoms of the –NH₂ group attached to C – 2 of sphingosine is linked to a fatty acid.

Sphingomyelins resemble phosphatidylcholines in general properties and three dimensional structures.



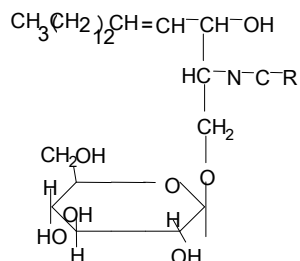
Structure of Sphingomyelin (Note, R in the structure of the fatty acid molecule.)

3.3.2 GLYCOSPHINGOLIPIDS

These are type of sphingolipids that occur largely on the outer surface of plasma membranes. They have head groups with one or more sugars attached directly to the – OH at C - 1 of the sphingosine moiety. They do not contain phosphate. Cerebrosides are example of Glycosphingolipids which have a single sugar linked to sphingosine.

Globosides are other example of sphingolipids that are neutral (uncharged) with two or more sugars usually D – glucose, D – gatalactose or N-acetyl neuraminic

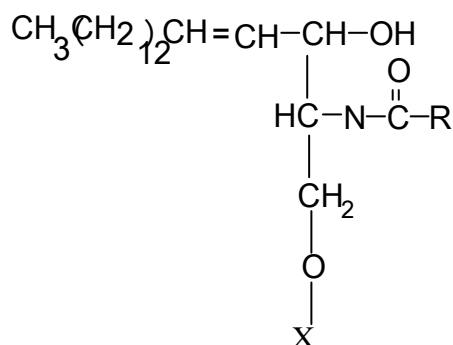
acid. Cerebrosides and globosides are usually called neutral glycolipids as they have no charge at pH 7.0.



Glucosylceramide (glucocerebroside)

3.3.3 GANGLIOSIDES

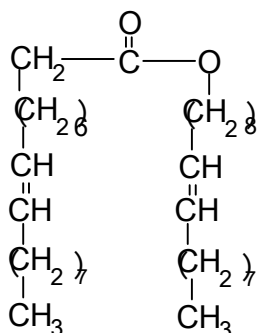
These are perhaps the most complex of all the phospholipids. They have oligosaccharides as their polar groups and one or more residues of *N* - acetylneuraminic acid also called sialic acid.



X is oligosaccharide containing sialic acid

3.4 WAXES

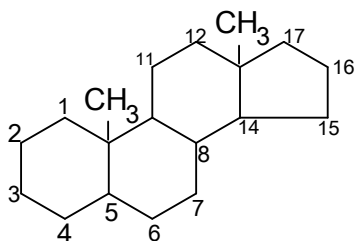
These class of saponifiable lipids are esters of long chain fatty acids (14 – 36 Carbon atoms) and long chain monohydric alcohols (16 – 22 atoms). They are highly insoluble in water and are chemically inert.



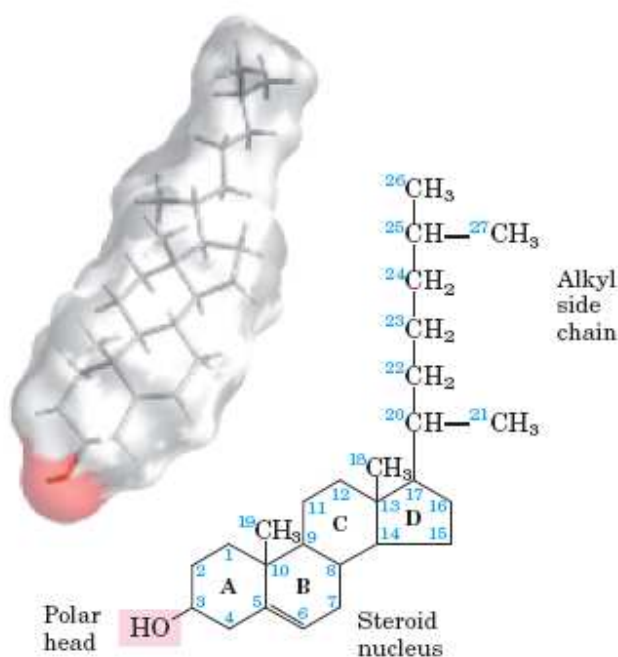
Structure of Biological wax

3.5 STEROIDS

These are non-saponifiable lipids that are derivatives of cyclopentanoperhydroxyphenanthrene (steroid nucleus). The steroid nucleus is essentially planar, rigid consisting of four (4) fused rings. Most steroids in humans have methyl groups at position 10 and 13 and frequently a side chain at position 17.



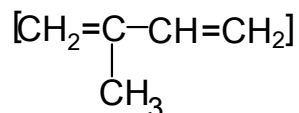
Sterols contain steroid nucleus with one or more (-OH) groups free or esterified to fatty acids. The most abundant sterol in animal tissue is the cholesterol which has the structure.



Structure of Cholesterol obtained from Lehninger's's Principles of Biochemistry.

3.6 TERPENES

Terpenes are other examples of non-saponifiable lipids that are composed of two or more isoprene units. Isoprene is a 5 carbon compound with the structure.



Structure of Isoprene unit

Terpenes are basically hydrocarbons found in plants. Isoprene units are combined in head – to – tail fashion to form variety of compounds which include: β - carotene, rubber, carotenoids, limonene etc.

3.7 SELF ASSESSMENT EXERCISES.

- 1.(a) What are saponifiable lipids?
- (b) Draw the structure of the parent compound of sphingolipids.

4.0 CONCLUSION

There are 2 broad classes of lipids: Saponifiable and nonsaponifiable lipids, each having its own sub-classes and structures.

5.0 SUMMARY

- Saponifiable lipids are those lipids that can undergo alkaline hydrolysis.
- Example of saponifiable lipids are: Triacylglycerols, Waxes, Phospholipids and Sphingolipids.
- Non saponifiable lipids are lipids that cannot undergo alkaline hydrolysis.
- Examples of non saponifiable lipids include: Steroids, Terpenes, Prostaglandins, Thromboxanes e.t.c.

6.0 TUTOR MARKED ASSESSMENT

- 1 (A) What is the basis of lipid classification?
- (B) Draw the structure of (2) two named saponifiable lipids.
- 2 (a) Distinguish between steroids and sterols.
- (b) Draw the structure of isoprenoid unit.

7.0 REFERENCES AND FURTHER READING.

- Elegbede J.A.(1990) Introductory Biochemistry (Chemistry of Macromolecules) .Institute of Education Press.
- Nelson L.,D., and Cox M.,M (2000) Lehninger's Principles of Biochemistry. New York. Worth Publishers.
- White A.,Handler P.,Smith E.,L., Hill R.,L., Lehman R.I.(1978). Principles of Biochemistry (6th.edition)Mc Graw Hill, Kogakusha.
- Devlin, T. (1986). Textbook of Biochemistry with Clinical Correlations.(2nd Edition) John Wiley and sons New York

MODULE 2: LIPIDS**UNIT 3: PROPERTIES & METHOD OF ANALYSIS OF LIPIDS**

- 1.0 Introduction.
- 2.0 Objectives .
- 3.0 Physical Properties of lipids.
 - 3.1 Chemical Properties of Lipids.
 - 3.1.1 Acid Value
 - 3.1.2 Iodine Value
 - 3.2 Function of lipids.
 - 3.3 Analysis of Lipids
 - 3.3.1 Extraction of lipids.
 - 3.3.2 Quantitative/Qualitative Analysis of Lipids.
 - 3.4 Self Assessment Exercises.
- 4.0 Conclusion
- 5.0 Summary
- 6.0 Tutor Marked Assignment (TMA)
- 7.0 Reference & Further Reading

1.0 INTRODUCTION

Like other macromolecules, lipids have their physicochemical properties and can be analysed qualitatively or quantitatively. The physical and chemical properties of lipids are basically as a result of the composition of the lipids. The insolubility of lipids in water makes it have a special approach to isolation/extraction different from other macromolecules like, carbohydrates and proteins. In this unit we shall discuss the physicochemical properties of lipids and their methods of analysis.

2.0 OBJECTIVES

At the end of this chapter we are expected to know :

- Physical properties of fatty acids ;
- Chemical properties of fatty acids;
- How to extract and analyse lipids.

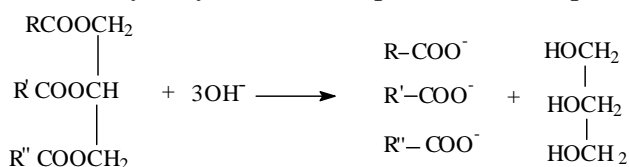
3.0 PHYSICAL PROPERTIES OF LIPIDS

1. Lipids are insoluble in water but are soluble in organic solvents e.g. ether and chloroform.
2. They are oily or greasy organic substances .
3. Lipids are found in plant and animal tissues where they can be extracted from.
4. Lipids can be solid or liquid at room temperature.
5. They have characteristics melting point which is influenced by the nature of fatty acids contained in a lipid. The more the C-chain length and degree of saturation of a fatty acid, the higher its melting point.

3.1 CHEMICAL PROPERTIES OF LIPIDS

Lipids e.g. (Neutral fats) are susceptible to acid, alkaline or enzyme hydrolysis. The enzymes that catalyse the hydrolysis of lipids are called esterases or lipases.

Alkaline hydrolysis of these lipids is called saponification



The reaction is irreversible and therefore the carboxylate ions combine with sodium (Na) or potassium (K) salt of the alkali to form soap. Saponification of lipids is measured by its saponification value which is the number of milligram of KOH required to saponify 1 gram of fat.

Polar lipids e.g. (phospholipids) are amphipathic (contains a charged head group and hydrophobic tail) as such in aqueous systems polar lipids spontaneously disperse to form micelles in which the hydrophobic tails are tucked or hidden inside the micelle structure and the polar heads are exposed to the aqueous environments.

3.1.1 ACID VALUE.

The acid value of fat can be defined as the number of milligram of KOH required to neutralize the free fatty acids present in 1gram of fat. Each lipid sample has a characteristic acid value which is defined by the number of and type of fatty acid contained in it.

3.1.2 IODINE VALUE.

Iodine value is another property of lipids which is defined as the number of grams of iodine absorbed by 100g of lipid. A molecule of iodine adds across each double bond of the unsaturated fatty acid. Iodine value gives a measure of the degree of unsaturation of a lipid.

3.2 FUNCTIONS OF LIPIDS

- Lipids are stored in tissues largely in a water free state and therefore serve as reservoirs of energy.
- Some lipids serve as structural components of membranes e.g. phospholipids.
- Some lipids act as intracellular signals e.g. (phosphatidylinositols).
- Lipids e.g. biological waxes play important role in providing a water barrier for insects, birds and other animals like sheep. Biological waxes find a variety of application in pharmaceutical, cosmetic and other industries
- Lipids e.g Gangliosides form a very important components of specific receptor sites on the surfaces of cell membranes.
- Lipids (phospholipids) play significant roles in the architectures of membranes.
- Lipids serve as good sources of fat soluble vitamins: A, D, E and K.

3.3 ANALYSES OF LIPIDS

Due to the fact that lipids are insoluble in water, their extraction and subsequent fractionation requires the use of organic solvents and some techniques not commonly in used in the purification of water soluble molecules such as proteins and carbohydrates.

3.3.1 EXTRACTION OF LIPIDS

Neutral lipids (triacylglycerols, waxes, pigments) are readily extracted from tissues with ethylether, chloroform or benzene. A commonly used extractant is a mixture of chloroform, methanol and water. Initial volume proportions (1:2:0.8) that are miscible are used in the homogenization of tissues to extract all lipids. The lipids remain in chloroform layer and more polar molecules such as protein and sugar partition into the methanol/water layer.

3.3.2 QUALITATIVE/QUANTITATIVE ANALYSES OF LIPIDS.

One very important way of qualitatively analysis for lipids is by the use of Thin-layer Chromatography (TLC) using silica gel or silicic acid. A thin layer of silica gel is spread onto a glass plate, to which it adheres. A small sample of lipids dissolved in chloroform is applied near one edge of the plate, which is dipped into

a shallow container of an organic solvent or solvent mixture. All of which is enclosed within a chamber saturated with the solvent vapour. As solvent rises on the plate by capillary action, it carries lipids with it. The less polar lipids move farthest, as they have less tendency to bind to the silica gel. The lipids can then be detected after separation by spraying the plate with a dye (rhodamine) that fluoresces when associated with lipids, or by exposing the plate to iodine fumes which gives a yellow or brown colour with lipids containing unsaturated fatty acids. Other chromatographic techniques e.g. High Performance Liquid Chromatography (HPLC), Gas Liquid Chromatography (GLC) can be employed in both quantitative and qualitative analysis of lipids. Colorimetry, techniques that involve the use of chromogenic reagents that could complex with lipids to give coloured complex that can be measured by the use of colorimeters are also available for quantitative estimation of lipids.

3.4 SELF ASSESSMENT EXERCISES.

1.(a) State the functions of lipids .

(b) How can you qualitatively and quantitatively analyse lipids.

4.0 CONCLUSION

Lipids are of variety of physical and chemical properties. They have different roles and can be analyzed both qualitatively and quantitatively.

5.0 SUMMARY

In this unit we have learnt that:

- Physical properties of lipids include: Insolubility in water, oily in nature, can be solid or liquid at room temperature etc.
- Chemical properties of lipids include: susceptibility to hydrolysis, ability to form micelles in aqueous solution by (polar lipids) e.t.c)
- Lipids serve as source of energy, thermal insulation as intracellular signals, source of vitamins A,D,E and K, serve as specific receptor sites e.t.c.
- Lipids can be analyzed by chromatographic techniques and colorimetric procedures can be used to quantitatively analyze lipids.

6.0 TUTOR MARKED ASSESSMENT.

1.(a). Outline the physical properties of lipids.

(b). Give a reaction for the alkaline hydrolysis of lipids.

2. (a). What is iodine value of a lipid?

(b). Describe the term acid value of lipids.

7.0 REFERENCES AND FURTHER READING

- Elegbede J.A.(1990) Introductory Biochemistry (Chemistry of Macromolecules) .Institute of Education Press.
- Nelson L.,D., and Cox M.,M (2000) Lehninger's Principles of Biochemistry. New York. Worth Publishers.
- White A.,Handler P.,Smith E.,L., Hill R.,L., Lehman R.I.(1978). Principles of Biochemistry (6th.edition)Mc Graw Hill, Kogakusha.
- Devlin, T. (1986). Textbook of Biochemistry with Clinical Correlations.(2nd Edition) John Wiley and sons New York

MODULE 2: LIPIDS**UNIT 4: LIPOPROTEINS**

- 1.0 Introduction.
- 2.0 Objectives.
- 3.0 Definition of Lipoproteins.
 - 3.1 Types/Classification of Lipoproteins.
 - 3.2 Function of Lipoproteins .
 - 3.3 Self Assessment Exercises.
- 4.0 Conclusion.
- 5.0 Summary.
- 6.0 Tutor Marked Assignment (TMA).
- 7.0 References and Further Reading .

1.0 INTRODUCTION

In as much as most lipid are insoluble in aqueous media the transport of these substances in the blood plasma is accomplished differently from water soluble molecules. Lipids are not transported in the free form in the blood but bound to protein in the form of lipoprotein. The lipoproteins are lipids associated with specific proteins. These lipoproteins are of different characteristics, types and chemical composition. In this unit we are going to study what lipoprotein are, their chemical composition, types and function.

1.0 OBJECTIVES

The objectives of this unit are:

- To teach you what lipoprotein are;
- To teach you the chemical composition of different types/classes of lipoproteins;
- To teach you the functions of lipoproteins;

2.0 DEFINITION OF LIPOPROTEINS

A lipoprotein is a multicomponent complex of protein and lipids of characteristic density, molecular weight, size and chemical composition. These complexes of protein and lipids are held together by non covalent forces. While a certain typical chemical composition and molecular weight exists for each type of lipoprotein complex, there may exist no exact stoichiometry among the components of the complex.

3.1 CLASSIFICATION OF LIPOPROTEINS (PLASMA)

The classification of plasma lipoproteins is difficult as the physical and chemical characteristics of these complexes are often heterogenous. However, the most popular system for classification of plasma lipoprotein particles is based on criterion of density which is a reflection of their lipid content.

Four density classes of plasma lipoprotein are know widely in humans. They includes the high density lipoproteins (HDL) the low density lipoproteins (LDL) the very low density lipoproteins (VLDL) and the chylomicrons. The LDL is further categorized into LDL₁ and LDL₂ or Intermediate density lipoproteins (IDL) and the chylomicrons.

(Table 1.0) Table of the four different classes of lipoproteins and their densities.

Lipoprotein	Density (g/ml)
Chylomicrons	< 1.006
VLDL	.95 – 1.006
LDL	1.006 – 1.063
HDL	1.063 – 1.210

Table 1.0 was obtained from Text book of Biochemistry with Clinical Correlations by Thomas Devlin.

3.2 COMPOSITION OF LIPOPROTEINS (PLASMA)

The lipid fraction of the plasma lipoproteins contains significant amount of triacylglycerols, phospholipids, free cholesterols, and cholesterol esterified with long chain fatty acids and other lipids present in small amount.

When protein components of lipoprotein are separated from their lipid components by extraction of the lipid with an organic solvent, the isolated protein (apolipoproteins) can be shown by immunological and chemical characterization to be at least seven distinct types. The apolipoprotein isolated from plasma HDL is majorly apolipoprotein A. Apolipoprotein B (ApoB) is the major protein for LDL fraction . A third, apolipoprotein C (Apo C), is found predominately in VLDL. Other chemically distinct apolipoprotein are the apolipoproteins D & E (ApoD) and (ApoE). ApoD is found in HDL, where it is a minor component. Apo E is found in chylomicrons, also in a low concentration. Other types/subtypes of apolipoprotein are also available and are described in the table below.

Table 2.0 Apolipoprotein of Human Plasma Lipoproteins

Apo A - I	HDL
Apo A – II.....	HDL
Apo A – IV.....	HDL, chylomicrons
Apo B – 48.....	VLDL, LDL
Apo B – 100.....	Chylomicrons
Apo C I.....	VLDL, HDL
Apo C II.....	VLDL HDL, Chylomicrons
Apo C III.....	VLDL HDL, Chylomicrons
Apo D.....	HDL
Apo E	Chylomicrons and VLDL

Table 2.0 above was obtained from Text book of Biochemistry with Clinical correlations by Thomas Devlin.

3.2.1 SOME PROPERTIES OF PLASMA LIPOPROTEINS

Some properties of apolipoproteins in human plasma is described in the Table 3.0 below.

Apolipoprotein	Molecular weight	No of amino acids
Apo A – I	28,300	243
Apo A – II	17,380	Dimer of two 77 amino acid chains
Apo B	8,000 – 550,000	-
Apo C – I	6,600	57
Apo C – II	8,800	78
Apo C – III	8,700	79
Apo D	20,000	-
Apo E	33,000	-
Apo F	30,000	-
Apo G	72,000	-

Table 3.0 was Obtained from Text book of Biochemistry with Clinical Correlations by Thomas Devlin.

3.3 STRUCTURE OF LIPOPROTEINS

The structure of lipoprotein molecules have been investigated with a wide range of methods including electron microscopy, X-ray diffraction and spectrophotometric techniques. Although these techniques were unable to give a definitive structures of plasma lipoproteins.

The structure of lipoproteins can be easily visualized as a complex of organic matter containing a composite of lipids and proteins with the polar side of the complex facing outside towards water solvents and the apolar parts embedded inside the complex

3.4 FUNCTION OF LIPOPROTEINS

Each class of lipoprotein has a specific function, determined by its point of synthesis, lipid composition and apolipoprotein content. Chylomicrons are involved in the movement of dietary triacylglycerols from the intestine to other tissues, they are the largest but least in density and contain high proportion of triacylglycerols.

VLDL. When diet contains more fatty acids than are needed immediately as fuel, they are converted to triacylglycerols and exported from the liver as VLDL. In addition, VLDL contain some cholesterol, cholesteryl ester.

LDL. The loss of triacylglycerol converts some VLDL to VLDL remnants (also called IDL) and with further removal of triacylglycerols, to LDL. LDL is very rich in cholesterol and cholesteryl esters and therefore transports cholesterol to extrahepatic tissues that have specific plasma membrane receptors.

HDL. The fourth class of major lipoprotein is the HDL which basically picks up cholesterols stored in extrahepatic tissues and carry it to the liver. It can also pick up cholesterol from the liver for conversion into bile salts. In addition HDL

particles converts cholesterol and phosphatidylcholine of chylomicron and VLDL remnants to cholesteryl esters.

3.5 SELF ASSESSMENT EXERCISES(SAE).

- 1.(a) Describe the composition of lipoproteins.
- (b) What are the functions of lipoproteins.

4.0 CONCLUSION

Lipids are transported in the blood as lipoproteins which are of different types, each containing a specific apolipoprotein which has a characteristic lipid it transports.

5.0 SUMMARY

At the end of this unit we have learnt that:

- Lipoproteins are multicomponent of complex of proteins and lipids of characteristic density, molecular weight, size and chemical composition.
- Lipoproteins are classified based on their densities into four different classes namely: LDL, VLDL, HDL and Chylomicrons.
- Lipoproteins are composed of different type of apoproteins/apolipoproteins of varying molecular weight.
- Each lipoprotein has a particular type of lipid it majorly contains as such has a characteristics function.

6.0 TUTOR MARKED ASSIGNMENT

- 1(a) Classify lipoprotein based on their densities
- (b) Give some characteristics of lipoproteins
- 2 (a) Describe lipoproteins structurally
- (b) State the function of HDL and VLDL

7.0 REFERENCES AND FURTHER READING.

- Elegbede J.A.(1990) Introductory Biochemistry (Chemistry of Macromolecules) .Institute of Education Press.
- Nelson L.,D., and Cox M.,M (2000) Lehninger's Principles of Biochemistry. New York. Worth Publishers.
- White A.,Handler P.,Smith E.,L., Hill R.,L., Lehman R.I.(1978). Principles of Biochemistry (6th.edition)Mc Graw Hill, Kogakusha.
- Devlin, T. (1986). Textbook of Biochemistry with Clinical Correlations.(2nd Edition) John Wiley and sons New York

MODULE 2: LIPIDS**UNIT 5: MEMBRANES AND MEMBRANE STRUCTURE**

- 1.0 Introduction.
- 2.0 Objectives.
- 3.0 Chemical Composition of Membranes.
 - 3.0.1 Lipids of membrane.
 - 3.0.2 Membrane Proteins.
 - 3.0.3 Carbohydrate of Membranes.
- 3.1 Molecular Structure of Membranes.
- 3.2 Properties of Biological Membranes.
- 3.3 Function of Membranes.
- 3.4 Self assessment Exercises.
- 4.0 Conclusion
- 5.0 Summary
- 6.0 Tutor Marked Assignment (TMA)
- 7.0 References and Further Reading

1.0 INTRODUCTION

Living cells, whether prokaryotic or eukaryotic do have biological membranes which could serve as a barrier between cellular components and the entire extracellular environment. Biological membranes have trilaminar appearance when viewed under the microscope, with two dark bands on each side of the light band. The overall width of various mammalian membranes is 7 – 10nm, some membranes have smaller widths especially the intracellular ones. Even though, electron microscopy has provided us with a very static picture of the membranes, membranes are very dynamic with a movement that permits cellular and subcellular structures in eukaryotic cells to adjust their shape and move. In this unit we shall discuss the chemistry, component and other properties of membranes.

2.0 OBJECTIVES

- To study the chemical composition of membranes.
- To know the structure of biological membranes.
- To study the properties of biological membranes.
- To study the function of biological membranes.

3.0 CHEMICAL COMPOSITION OF BIOLOGICAL MEMBRANES

Lipids and proteins are the two (2) major components of all membranes but the amount varies greatly between different membranes. Intracellular membranes are known to have some proportion of protein because of the greater enzymatic activity of these membranes. Membranes also contain high amount of various polysaccharide (sugars) in the form of glycoprotein and glycolipid. Free carbohydrates do not exist in membranes.

3.0.1 LIPIDS OF MEMBRANE.

The three major lipid components of membranes are phosphoglycerides, sphingolipids and cholesterol. Individual cellular membranes also contain small quantities of other lipids such as triacylglycerol and diol derivatives. The percentage of each of the major lipids varies significantly in different membranes and is presumably related to specific roles of individual membranes.

3.0.2 MEMBRANE PROTEINS

Membrane proteins are classified into two (2). The peripheral membrane proteins (or extrinsic) which easily isolated from the membranes by treatment of the membrane with salt solution of low or high ionic strength, or extremes of pH or the name is used to imply a physical location on the surface of the membrane. Peripheral protein many with enzymatic activity are usually soluble in water and free of lipids.

Integral (or intrinsic) proteins require rather drastic treatment such as use of detergent or organic solvents to be extracted from the membrane. They usually contain tightly bound lipid, which if removed leads to denaturation of the protein and loss of its biological function. Removal of integral proteins leads to disruption

of the membrane where as peripheral proteins can be removed with little or no change in the integrity of the membrane.

3.0.3 CARBOHYDRATE OF MEMBRANES

Carbohydrates present in membranes are exclusively in the form of oligosaccharides covalently attached to proteins to form glycoproteins and to a lesser amount of lipids to form glycolipids. The sugars found in glycoproteins and glycolipids include Glucose, Mannose, Galactose, Fucose, N-acetylglucosamine, N-acetylgalactosamine and Sialic acid.

3.1 MOLECULAR STRUCTURE OF MEMBRANES

The basic structural characteristic of all membranes is derived from physicochemical properties of the major lipids components, the phosphoglycerides and sphingolipids. These are amphipathic compounds with a hydrophilic head and hydrophobic tail .

These amphipathic compounds due to their low solubility in water react in a unique fashion in aqueous systems. Under proper condition these lipids molecules will come together to form spheres termed micelles with the hydrophobic tails interacting to exclude water and the charged polar groups on the outside. The specific concentration of lipid required for micelle formation is called critical micelle concentration.

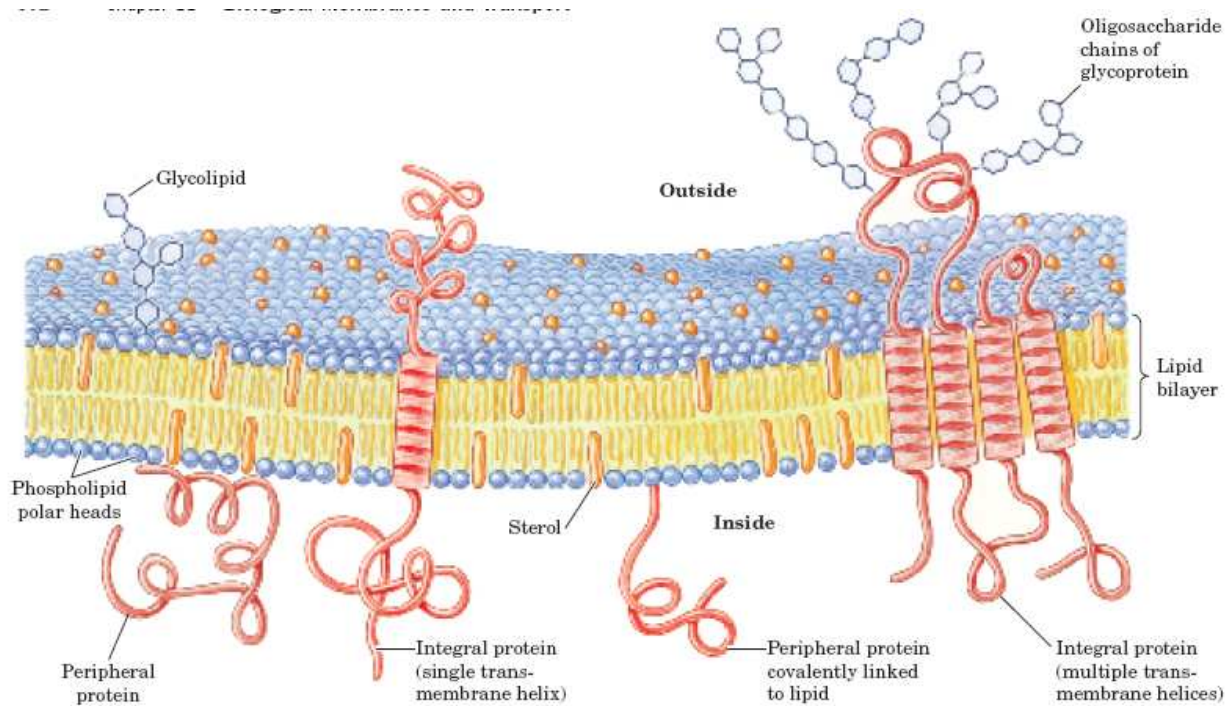
Also, depending on the condition, the amphipathic lipids will interest to form a bimolecular leaf structure with two layers of lipid in which the polar group are at the interface between the aqueous medium and the lipid while the hydrophobic tails react to form an environment that excludes water. This bilayer conformation is the basic lipid structure of all biological membranes. Lipids bilayers are extremely stable structures. A lipid bilayer can close in on itself, forming a spherical vesicle separating the external space from an internal compartment. These vesicle are termed liposomes.

Based on the physicochemical properties of lipids, their biochemical and electron microcopy investigations, knowledge of the structure of biological membrane evolved. The basic structure is a bimolecular leaf arrangement of lipids in which the phosphoglycerides, sphingolipids and cholesterol are oriented so that the hydrophobic portions of the molecules interact to minimize their interaction with water or other polar lipids. The polar heads of the amphipathic compounds are at the interface with the aqueous environment. This arrangement of lipids is same as that if synthetic phospholipids, liposomes. A major problem to resolve, however has been to explain the interaction of integral and peripheral proteins with the lipid bilayer.

A number of models for biological membrane structure have been proposed dating back to 1935 by H Davson and Danielle which was refined by J.D. Robertson later.

In early 1970s, G.L. Nichoson and S.J. Singer proposed Mosaic model for membranes in which it was suggested that proteins are on the surface as well as on the lipid bilayer. Some proteins could span the lipid bilayer with their polar groups in contact with the aqueous environment on both sides and hydrophobic

portions interacting with the lipids in the interior of the membrane. This model has been extensively refined and is referred to as fluid mosaic model to indicate the movement of both lipids and proteins in the membrane.



The Fluid Mosaic Model of Biological Membrane Structure: Obtained from Lehninger's Principles of Biochemistry.

3.2 PROPERTIES OF BIOLOGICAL MEMBRANES

- Biological membranes have fluidity (both lipids and protein more) and the degree of fluidity is dependent on temperature and composition of the membrane. At low temperatures, the lipids are in a gel crystalline state and as the temperature increases, there is a phase transition into liquid – crystalline state.
- They possess specific recognition sites e.g receptors.
- There is an asymmetric distribution of lipid components across biological membranes. Each layer of the bilayer of lipids has a different composition with respect to individual phosphoglycerides and phospholipids.
- There is an asymmetric distribution of lipid components across biological membranes. Each layer of the bilayer of lipid has a different composition with respect to individual phosphoglycerides and phospholipids.
- They contain electrically charged surface groups which support a different electrical potential across membrane structure.
- Biological membranes allow diffusion of solute molecules through them.

3.3 FUNCTION OF MEMBRANES

- Recognition of certain molecular signals.
- They serve as components of nerve cells.
- They control movement or translocation of molecules in and out of the cell.
- They serve as receptors for hormones.

3.4 SELF ASSESSMENT EXERCISES(SEA)

- 1.(a) What are the functions of membranes?
- (b) Outline the properties of membranes.

4.0 CONCLUSION

Biological membranes contain lipids, proteins and carbohydrates that confer some physicochemical properties that defines its structure, property and function.

5.0 SUMMARY

In this unit we learnt that:

- Membranes are structures found in prokaryotic and eukaryotic organisms.
- Proteins and lipids form major chemical composition of membranes .
- The structure of the biological membranes is basically derived from lipid bilayer and the fluid mosaic model of membrane structure is the most thermodynamically stable.
- Biological membranes have properties which include: Fluidity asymmetry, presence of recognition sites etc.
- Biological membranes functions in transport of solutes, conditions of impulses and recognition of some molecules any others.

6.0 TUTOR MARKED ASSIGNMENT (TMA)

- 1(a) Describe the lipid composition of membranes
- (b) Describe the fluid mosaic model structure of biological membranes
- 2 Relate the function of membranes to its property.

7.0 REFERENCES AND FURTHER READING.

- Elegbede J.A.(1990) Introductory Biochemistry (Chemistry of Macromolecules) .Institute of Education Press.
- Nelson L.,D., and Cox M.,M (2000) Lehninger's Principles of Biochemistry. New York. Worth Publishers.
- White A.,Handler P.,Smith E.,L., Hill R.,L., Lehman R.I.(1978). Principles of Biochemistry (6th.edition)Mc Graw Hill, Kogakusha.
- Devlin, T. (1986). Textbook of Biochemistry with Clinical Correlations.(2nd Edition) John Wiley and sons New York

MODULE 3: NUCLEIC ACID
UNIT 1: CHEMISTRY OF NUCLEOSIDES

- 1.0 Introduction.
- 2.0 Objectives.
- 3.0 Definition of Nucleosides.
 - 3.1 Components of Nucleosides.
 - 3.1.1 Nitrogenous Bases and Their Structures.
 - 3.1.2 Pentose Sugars and Their Structures.
 - 3.1.3 Linkages between Pentose Sugars and Nitrogenous Bases.
 - 3.2 Some Common Purines and Pyrimidine Bases and Their Structures.
 - 3.3 Nomenclature of Nucleosides.
- 3.4 Self Assessment Exercises.
- 4.0 Conclusion
- 5.0 Summary
- 6.0 Tutor Marked Assignment
- 7.0 References and Further Reading

1.0 INTRODUCTION

The association of nitrogenous bases and pentose sugars gives a compound called nucleoside which is a component of nucleotides (the monomeric units of nucleic acids). Based on the type of nitrogenous base and the types of sugar it is linked to, different types of nucleotides are formed each having its own characteristic and structure.

2.0 OBJECTIVES

The objectives of this unit include:

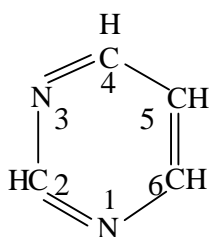
- To know what are nucleosides;
- To know the different components present in nucleosides;
- To know the structure of different type of nucleosides;

3.0 DEFINITION OF NUCLEOSIDES

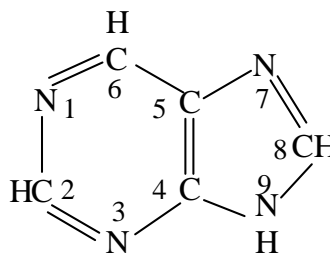
Nucleosides are organic compounds containing pentose sugars and nitrogenous base linked together by *N*- β -glycosidic bond. The sugar can either be a ribose sugar or a deoxyribose sugar while the nitrogenous bases are: Adenine, Guanine, Cytosine, Thymine or Uracil etc.

3.1 COMPONENTS OF NUCLEOSIDE.

The components of nucleosides are basically nitrogenous bases and pentose sugars.



Pyrimidine

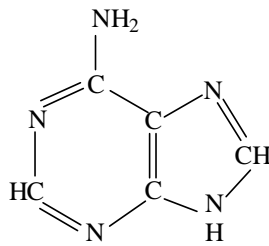


Purine

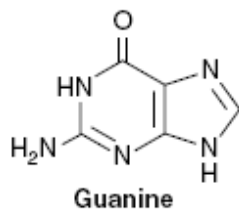
3.1.1 NITROGENOUS BASES AND THEIR STRUCTURES

The nitrogenous bases present in nucleosides are either purines or pyrimidines and are given below. The purine bases contain the purine ring (double ring system) while the pyrimidine base contain pyrimidine ring (single ring structure). The purine bases are:

- Adenine denoted by A and has the structure:

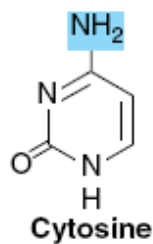


- Guanine denoted by G and has the following structure:



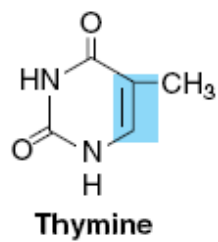
Source: Harper's Review of Biochemistry

- The pyrimidine bases are cytosine, thymine and uracil
Cytosine denoted by C and has the following structure



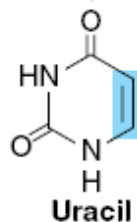
Source: Harper's Review of Biochemistry

- Thymine denoted by T and has the structure below



Source: Harper's Review of Biochemistry

- Uracil, denoted by U and has the structure below:

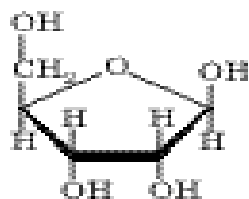


Source: Harper's Review of Biochemistry

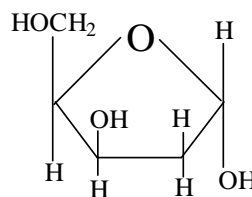
In addition to the purine bases A and G other unusual purine bases do exist and they include: hypoxanthine, 1 methylguanine, 1 methylhypoxanthine etc. Unusual pyrimidine bases also exist and they are derived from the cytosine, thymine and uracil and they include: 5-methylcytosine, Thiouracil etc.

3.1.2 PENTOSE SUGARS AND THEIR STRUCTURES

The pentose (5 carbon) sugars of nucleosides are basically ribose or (ribofuranose) 2' deoxyribose (2' deoxyribofuranose). The 2' deoxyribose sugar is found in deoxyribonucleic acid (DNA) while the ribose sugar is found in ribonucleic acid (RNA).



α - D – Ribofuranose
(Ribose sugar)



2 – Deoxy - α - D- ribofuranose
(Deoxyribose sugar structure)

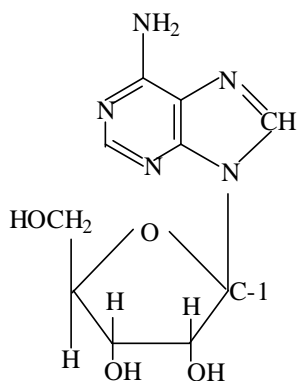
Source: Lehninger's's Principles of Biochemistry

3.1.3 LINKAGES BETWEEN PENTOSE SUGARS AND NITROGENOUS BASES IN NUCLEOSIDES

In nucleosides, nitrogenous bases are joined to pentose sugar through the hemiacetal hydroxyl group on the C-1 (first carbon atom of the sugar). Generally, the purines are attached to the sugar through the *N*-9 nitrogen atom while pyrimidine are attached through the *N*-1 nitrogen atom.

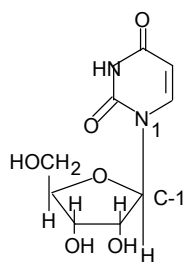
3.2 COMMON PURINE AND PYRIMIDINE NUCLEOSIDES AND THEIR STRUCTURES

Purine Nucleosides.

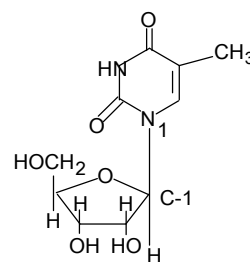


Adenosine

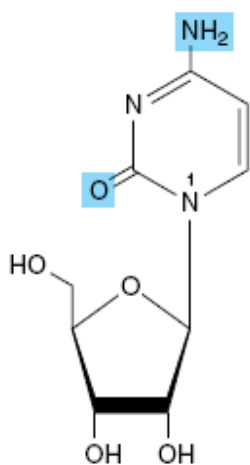
Pyrimidine Nucleosides



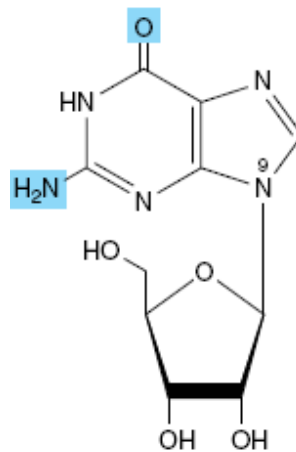
Uridine



Thymidine



Cytidine



Guanosine

Source:

Harper's Review of Biochemistry

Source: Harper's Review of Biochemistry.

3.3 NOMENCLATURE OF NUCLEOSIDES

Nucleosides are named based on the type of ribose sugar attached to the nitrogenous base and whether the base present in the nucleoside is a purine or pyrimidine.

All purine nucleoside names end with a suffix (-osine) added to the name of the purine base irrespective of whether it contains ribose or deoxyribose sugar. Examples include: Adenosine, guanosine, deoxynadenosine and deoxyguanosine. If the purine nucleoside contains a deoxyribose sugar then the prefix (-deoxy) is added to the name of its ribonucleoside counterpart example deoxyadenosine and deoxyguanosine are deoxyribonucleosides of adenosine and guanosine respectively.

For the naming of pyrimidine ribonucleoside the suffix (-idine) is added to the name of the base in the nucleoside. Example the ribonucleoside of uracil is named uridine, the (-acil) of uracil is replaced by (-idine). Cytosine ribonucleoside is named Cytidine while that of Thymine is Thymidine. On the other hand pyrimidine deoxyribonucleoside are named by adding a prefix 2' deoxy to the name of its pyrimidine ribonucleosides counterpart e.g. 2' deoxythymidine, 2' deoxycytidine, 2' deoxyadenosine, 2' deoxyguanosine and 2' deoxyuridine.

3.4 SELF ASSESSMENT EXERCISES.

- 1.(a) Draw the structure of purine and pyrimidine ring.
- (b) Draw the structure of two named purine and pyrimidine nucleosides.

4.0 CONCLUSION

Nucleosides are components of nucleotides which contain either purine or pyrimidine base. They also contain ribose or deoxyribose sugar.

5.0 SUMMARY

In this unit we have learnt that:

- Nucleoside is a compound containing pentose sugar and nitrogenous bases joined together via β -N- glycosidic linkage;
- The nitrogenous bases found in nucleosides are Adenine, Guanine, Cytosine, Uracil and Thymine.
- The purine bases are Adenine and Guanine while pyrimidine bases are Cytosine, Thymine and Uracil.
- Deoxyribonucleosides are named by adding the prefix -2'deoxy to the name of their ribonucleoside counterparts.

6.0 TUTOR MARKED ASSIGNMENT (TMA).

- 1(a) Define nucleosides.
- (b) Using the structure of a ribonucleoside, illustrate the type of linkage in nucleosides.

- 2(a) Draw the structures of a ribose and a 2' deoxyribose sugar.
(b) How do you name purine and pyrimidine deoxyribonucleosides?

7.0 REFERENCES AND FURTHER READING.

- Elegbede J.A.(1990) Introductory Biochemistry (Chemistry of Macromolecules) .Institute of Education Press.
Nelson L.,D., and Cox M.,M (2000) Lehninger's Principles of Biochemistry. New York. Worth Publishers.
White A.,Handler P.,Smith E.,L., Hill R.,L., Lehman R.I.(1978). Principles of Biochemistry (6th.edition)Mc Graw Hill, Kogakusha.
Devlin, T. (1986). Textbook of Biochemistry with Clinical Correlations.(2nd Edition) John Wiley and sons New York

MODULE 3: NUCLEIC ACIDS
UNIT 2: CHEMISTRY OF NUCLEOTIDES

- 1.0 Introduction.
- 2.0 Objectives.
- 3.0 Definition of Nucleotides.
 - 3.1 Components of Nucleotides.
 - 3.2 Nomenclature of Nucleotides.
 - 3.3 Structures of Some Common Nucleosides.
 - 3.4 Derivatives of Nucleotides.
 - 3.5 Functions/Roles of Nucleotides and Their Derivatives.
 - 3.6 Self Assessment Exercises.
- 4.0 Conclusion.
- 5.0 Summary.
- 6.0 Tutor Marked Assignment.
- 7.0 References and Further Reading..

1.0 INTRODUCTION

The monomeric units of nucleic acids (RNA & DNA) are nucleotides. These nucleotides are of different types and structures. They are also of physiological significance in cells and tissues where they are found. On partial hydrolysis of nucleic acids, nucleotides can be obtained. The structure of every protein, every biomolecule and cellular component is a product of information programmed into nucleotide sequences in form of genes. In this unit we are going to study the chemistry and roles of nucleotides.

2.0 OBJECTIVES:

The objectives of this unit include:

- To teach you what a nucleotide is and its components;
- To teach you the structures of different nucleotide types;
- To teach you the roles and functions of nucleotides;

3.0 DEFINITION

Nucleotides are phosphoric acid esters of nucleosides. They contain nitrogenous bases and sugars which are esterified to a phosphoric acid residue. The esterification could be either at positions (2, 3 or 5) in ribose and (3 or 5) in the deoxyribose where the ester bonds could be formed. In addition, the nucleotides could be in form of mono, di and triphosphates.

3.1 COMPONENTS OF NUCLEOTIDES

As mentioned earlier, nucleotides contain nitrogenous bases, sugars and phosphoric acids in ester linkage. Like nucleosides, the nitrogenous base, present in nucleotides are purines: Adenine and Guanine; pyrimidines: Cytosine, Thymine and Uracil. The uracil can only be found in ribonucleotides while thymine base can only be found in deoxyribonucleotides. The sugar in nucleotides is the pentose sugar which could be ribose and deoxyribose.

3.2 NOMENCLATURE OF NUCLEOTIDES

Nucleotides are strong acids and therefore are called adenylic acid, guanylic acid, thymidylic acid, cytidylic and uridylic acids. All the above mentioned nucleotides are monophosphate derivatives of their corresponding nucleotides and ribonucleotides as given in the table below.

Adenylic acid (Adenylate)	Adenosine 5' monophosphate
Guanylic acid (Guanylate)	Guanosine 5' monophosphate
Thymidylic acid (Thymidylate)	Thymidine 5' monophosphate
Cytidylic acid (Cytidylate)	Cytidine 5' monophosphate
Uridylic acid (Uridylate)	Uridine 5' monophosphate

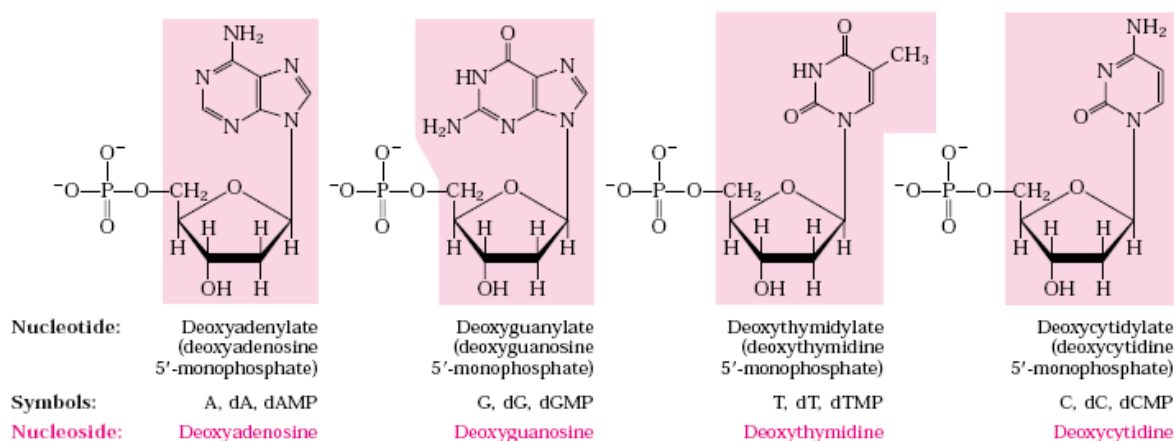
In all the examples given above, the phosphate groups are on position 5 of the sugar. However, the product of enzymatic or alkaline hydrolysis of RNA yields 2', 3' or 3', 5' monophosphates.

When the phosphate is on position 2, the nucleotide is named ribo nucleoside 2' monophosphate e.g. adenosine 2' monophosphate. When the phosphate is on

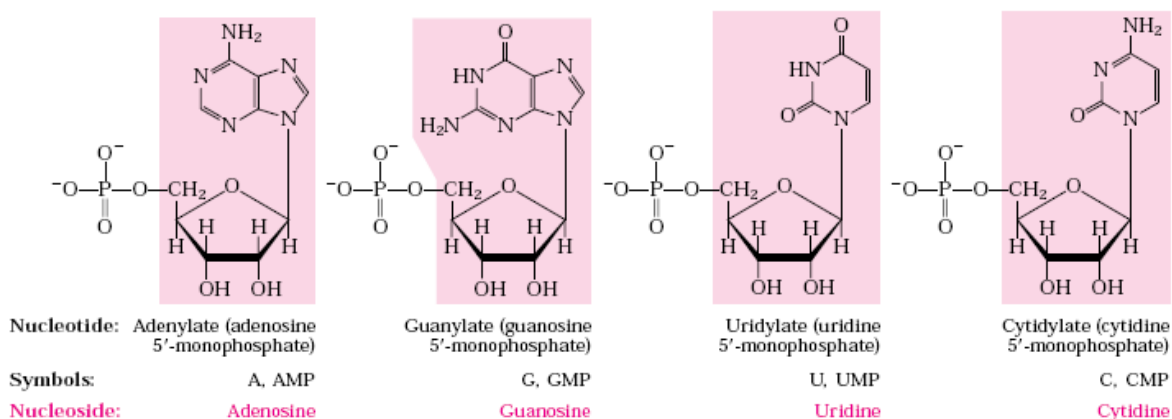
position 3, the nucleoside is called ribo nucleoside 3' the monophosphate. The ribonucleoside could be a cyclic monophosphate where a single phosphate is attached on carbon atoms or position 2' and 3' at the same time e.g Adenosine 2'3' cyclic monophosphate (cAMP).

When more than one phosphate is bonded to a nucleoside e.g. 2 or 3, the terms di and triphosphates are used respectively e.g. Adenosine diphosphate (ADP) and Adenosine triphosphate (ATP).

3.3 STRUCTURES OF SOME COMMON NUCLEOTIDES



(a) Deoxyribonucleotides



(b) Ribonucleotides

The structures of Nucleotides in above were obtained from Lehninger's Principles of Biochemistry.

3.4 DERIVATIVES OF NUCLEOTIDES

Nucleotide derivatives are compound that have their structures derived from some nucleotide structures. They contain nucleotide components and therefore nucleotide share close structural features. Different types of nucleotide derivatives do exist examples include: Nicotinamide Adenine dinucleotide (NAD), Nicotinamide Adenine dinucleotide phosphate (NADP), flavine adenine dinucleotide (FAD) among others.

3.5 IMPORTANCE/ROLE OF NUCLEOTIDES/NUCLEOTIDE DERIVATIVES

- Nucleotides play significant roles in cellular metabolism e.g. ATP which serves as energy currency of living cells. The energy used by cells is derived from this nucleotide molecule.
- Nucleotides also serve as coenzymes for important enzyme catalyzed reactions NAD and FAD are two coenzymes that are involved in oxidation-reduction reaction in living cells. Reactions of the Krebs's cycle involves these coenzymes.
- Nucleotide have also been found to play role in metabolic regulation. A derivative of AMP, cyclic AMP (cAMP) is directly involved in this process.
- Nucleotides also serve as source of electrons (H^+) in reductive biosynthetic pathways e.g. synthesis of cholesterol, $NADPH_2$ is very relevant in this process.

3.6 SELF ASSESSMENT EXAMINATION(SAE).

- 1(a). Draw the structures of two named ribonucleotides.
- (b). Draw the structures of Adenosinetriphosphate and Guanosine diphosphate .

4.0 CONCLUSION

Nucleotides are organic compounds that are monomeric units of nucleic acids, they are of different types and structures and have variety of physiological functions.

5.0 SUMMARY

- Nucleotides are phosphate esters of nucleotides.
- Nucleotides differ based on their nitrogenous base composition and pentose sugar.
- Nucleotides could be mono, dio or triphosphates.
- They have variety of roles they play in cellular and metabolic processes.

6.0 TUTOR MARKED ASSIGNMENT (TMA)

- 1(a) Describe the chemistry of a named nucleotide.
- (b) How are nucleotides named?
- 2(a) Distinguish between nucleosides and nucleotides.
- (c) What are the role(s) of nucleotides in cellular and metabolic processes?

7.0 REFERENCES AND FURTHER READING

- Elegbede J.A.(1990) Introductory Biochemistry (Chemistry of Macromolecules) .Institute of Education Press.
- Nelson L.,D., and Cox M.,M (2000) Lehninger's Principles of Biochemistry. New York. Worth Publishers.
- White A.,Handler P.,Smith E.,L., Hill R.,L., Lehman R.I.(1978). Principles of Biochemistry (6th.edition)Mc Graw Hill, Kogakusha.
- Devlin, T. (1986). Textbook of Biochemistry with Clinical Correlations.(2nd Edition) John Wiley and sons New York.

MODULE 3: NUCLEIC ACID**UNIT 3: CHEMISTRY OF NUCLEIC ACIDS**

- 1.0 Introduction.
- 2.0 Objectives.
- 3.0 Definition of Nucleic Acids.
 - 3.1 Characteristics of Nucleic Acids.
 - 3.2 Types of Nucleic Acids.
 - 3.2.1 mRNA
 - 3.2.2 rRNA
 - 3.2.3 tRNA
- 4.0 Conclusion.
- 5.0 Summary.
- 6.0 Tutor Marked Assignment.
- 7.0 Further Reading and References.

1.0 INTRODUCTION

The Chemistry of nucleic acids is basically about what nucleic acids are, the chemical groups that constitute them, the linkages in them and other chemical characteristics including their nomenclature and their structures. In this unit, you will study the basics about nucleic acids .

2.0 OBJECTIVES

By the end of this unit, you should be able to:

- Define nucleic acids;
- Know the basic constituents of nucleic acids;
- Draw each chemical constituent and label various atoms;
- Name nucleic acids.

3.0 DEFINITION OF NUCLEIC ACIDS.

Nucleic acids are macromolecules that are found in the cells and are responsible for storage and transmission of genetic information. Chemically, nucleic acids are polymers of nucleotides joined together by phosphodiester linkages (bonds). Nucleic acids are divided into two; Ribonucleic acid (RNA) which is single stranded containing Adenine (A), Uracil (U), Cytosine (C) and Guanine (G) ribonucleotides and deoxyribonucleic acid which is double stranded containing Adenine, Thymine (T), Cytosine and Guanine deoxyribonucleotides.

3.1 CHARACTERISTICS OF NUCLEIC ACIDS.

- **Linkage:** The components of nucleic acids are nucleotides joined by phosphodiester linkage to one another.
- **Component:** Based on the type of sugar in nucleic acids, nucleic acids can either be deoxyribonucleic acids in which case they contain deoxyribose sugar or ribonucleic acids when the sugar is a ribose one.
- **Denaturation:** Double stranded DNA or RNA can be denatured. DNA is highly viscous at pH 7.0 and room temperature (25⁰C). When such solution is subjected to extreme pH or temperature above 80⁰C, its viscosity decreases sharply indicating that DNA has undergone physical change. The denaturation of the double helical DNA is called melting of the double helical DNA as is associated with the disruption of hydrogen bonds between the paired bases in the DNA. When temperature is used to denature DNA, the temperature midpoint in the transition is called melting temperature (t_m) Renaturation of the DNA is a rapid one-step process which occurs when the temperature and pH is returned to the range in which the DNA is stable.
- **UV Absorption:** The conjugated system of purines and pyrimidines resulted in marked absorption in the ultraviolet (UV) region of the light spectrum with Absorption maxima near 260nm. Since proteins have a much weaker absorption in this region, the spectrum properties of nucleic acids have been useful in locating and estimating these substances in cells and tissues.

When a double stranded DNA is altered or denatured by change in temperature or pH, the close interaction between stacked bases in the nucleic acid is also affected because there is a decrease in the hydrogen bonding keeping both strands of the DNA together. This process is associated with a marked increase in absorption near the 260nm region, this phenomenon is called hyperchromic effect. The denatured form of DNA can therefore be detected by monitoring the absorption of UV light. Deoxyribonucleic Acids (DNA), when isolated, may be circular or linear, i.e. contain two ends. However, DNA exists in a highly condensed form within the chromosome. While the length of DNA in the largest human chromosome may be 8cm, it is condensed in a mitotic chromosome whose length is only 5 nm. In prokaryotes (bacteria or blue-green algae) the DNA is not associated with significant amount of protein while in eukaryotes, DNA is found in cytoplasmic organelles e.g. chloroplasts, mitochondria and chromosomes of the nucleic.

Nuclear DNA of plant and animal cell is associated with basic proteins, the histones, which are noncovalently bound to the DNA by ionic linkages. A DNA-histone complex is called chromatin. Ribonucleic acids (RNA) however are not associated with these proteins (histones).

- **Size of Nucleic Acids:** DNA and RNA molecules are long and unbranched. RNA molecules however have the capacity of forming secondary and tertiary structures which will be discussed in the next unit. Their size can be stated in three types of unit (length, number of base pairs and mass) thus 1nm (10^{-4} cm) of DNA contains 3,000 bases. The length of DNA molecules containing 300 to 300,000 base pairs can be measured directly by electron microscope. DNA was originally thought to be no longer than (5×10^{-4} cm) until it was discovered that it is very sensitive to hydrodynamic shear. When care is taken to avoid shear, considerable longer DNA molecules can be isolated. Sizes of DNA can be resolved using molecular-sieving effect of porous agarose gels and by sedimentation in a centrifugal field.

3.2 TYPES OF NUCLEIC ACIDS.

There are three different forms/types of DNA: The A form, B form and the Z form. The B form also known as B-DNA is the most stable. The structure of each form will be discussed in the next unit. There are 3 major types of RNA, namely (mRNA) messenger RNA, (tRNA) transfer RNA and rRNA (Ribosomal RNA) although more recently other RNA molecules do exist.

3.2.1 Messenger RNA (mRNA): This constitute of about 5-10% of total RNA in cell. Usually single stranded and their base sequence is usually complementary with that of DNA. mRNA is intimately involved in transcription and translation of information coded by DNA for protein synthesis.

3.2.2 Ribosomal RNA (rRNA):- These are found associated with large number of proteins in an ordered complex. Ribosomal RNA has a helical structure resulting from the folding back of a single stranded polymer, but may exist in several conformation ribosomal RNA constitute about 74-80% of total RNA in a cell.

3.2.3 Transfer RNA (tRNA). The tRNA comprises about 15% of the total cellular DNA. They are relatively small nucleic acids and range in length from 65-110 nucleotides the pairing of the bases in the DNA helix.

3.3 SELF ASSESSMENT EXERCISES(SAE)

1. (a) Describe the size of a DNA molecule.

(b) Explain the term DNA denaturation.

4.0 CONCLUSION

Conclusively, you have learnt what nucleic acids are . You have also learnt about its chemical composition and its types, DNA and RNA. Properties/characteristics of the nucleic acid types have also been studied.

5.0 SUMMARY

In this unit we have learnt that:

- Nucleic acids are polymers of nucleotides.
- There are two types of nucleic acids, DNA and RNA. The DNA is further subdivided into three (3) forms namely: A form, B form and Z form.
- DNA can be denatured and renatured .
- DNA is highly condensed in the chromosome and its size can be determined under centrifugal field.
- RNA has a primary,secondary and tertiary structures.

6.0 TUTOR MARKED ASSIGNMENT

1. (a) Define the term nucleic acids.

(b) Give three (3) Different properties of nucleic acids.

2. (a) How many types of RNA do you know?

(b) Chemically describe any named one.

7.0 REFERENCES AND FURTHER READING.

Elegbede J.A.(1990) Introductory Biochemistry (Chemistry of Macromolecules). Institute of Education Press.

Nelson L.,D., and Cox M.,M (2000) Lehninger's Principles of Biochemistry. New York. Worth Publishers.

White A.,Handler P.,Smith E.,L., Hill R.,L., Lehman R.I.(1978). Principles of Biochemistry (6th.edition)Mc Graw Hill, Kogakusha.

Devlin, T. (1986). Textbook of Biochemistry with Clinical Correlations.(2nd Edition) John Wiley and sons New York

MODULE 3: NUCLEIC ACIDS**UNIT 4: STRUCTURE OF NUCLEIC ACIDS**

- 1.0 Introduction
- 2.0 Objectives
- 3.0 Structure of DNA
- 3.1 Different forms of DNA
 - 3.1.1 A DNA
 - 3.1.2 B DNA
 - 3.1.3 Z DNA
- 3.2 Structure of RNA
- 3.3 Structure of Different forms of RNA
 - 3.3.1 Messenger RNA(mRNA)
 - 3.3.2 Transfer RNA(tRNA)
 - 3.3.3 Ribosomal RNA(rRNA)
- 3.4 Self Assessment Exercises.
- 4.0 Conclusion.
- 5.0 Summary.
- 6.0 Tutor Marked Assignment (TMA)
- 7.0 References and Further Reading.

1.0 INTRODUCTION

Nucleic acids comprising of both RNA and DNA as mentioned earlier have peculiar structures which are different from one another. The structure of nucleic acids are basically derived from the respective nucleotides for RNA, deoxyribonucleotides for DNA and the phosphate acid molecule embedded in the structure of the various types of nucleic acids and their properties.

2.0 OBJECTIVES

By the end of this unit, you should be able to:

- Describe the structure of nucleic acids;
- Draw the structure of DNA;
- Describe the structure of RNA;
- Explain the structure and properties of different types of RNA.

3.0 STRUCTURE OF DNA

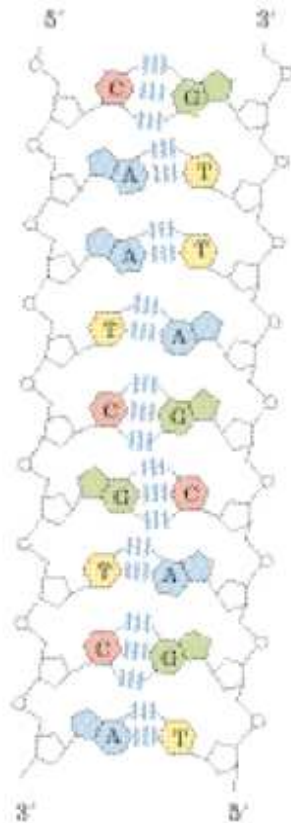
The structure of DNA was worked out by bringing together a number of observations from various sources. The following are some of the key observations.

- That DNA from different sources have remarkable similarity in their X-ray diffraction patterns; suggesting that DNA molecules have uniform molecular pattern and consists polynucleotide chains arranged in helical structure.
- That the ratio of the bases (A: T and C: G) is very close to one. The importance of this observation in working out the structure of DNA is that it suggests the pairing of bases in the DNA helix. It was then shown that A and T can be paired with a maximum of two hydrogen bonds between them while C and G will have a maximum of three bonds.
- The third observation was that of titration data which suggested that the long polynucleotide chains were held together through bonds between these residues.

Using these observations, Watson and Crick constructed a model of DNA structures in 1953.

The Watson - Crick Model consist of 2-deoxyribonucleotides joined together by phosphate diesters with the bases projecting perpendicularly from the chains into the central axis. For each adenine projecting inwards, there is a corresponding thymine from the other chain and for each cytosine, there is a guanine. Thus A-T and C-G are held together by two and 3 hydrogen bonds respectively.

The two chains are however not identical because of base pairings. The chains do not run in the same direction with respect to linkage between the nucleotides, rather they are antiparallel.



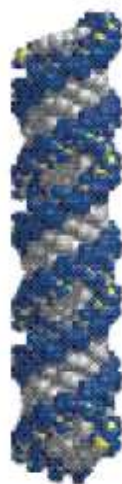
Structure of DNA obtained from Lehninger's's Principles of Biochemistry

3.1 DIFFERENT FORMS OF DNA

Structurally, there are 3 different forms of DNA: the A form, B and Z forms.

3.1.1 A DNA

The A form of DNA is favoured in a right handed helix with a diameter approximately 26Å. It has 11 base pairs per helical turns and rise per base pair is 2.6Å.



A form

The A form of DNA obtained from Lehninger's's Principles of Biochemistry.

3.1.2 B DNA

The B DNA is also referred to as the Watson-Crick DNA structure. The DNA is arranged as a right handed helix with approximate diameters of 20Å. The base pairs per helical turns are 10.5 and base turns rise of helix 3.4Å.

*B form of DNA was obtained from
Lehninger's's principles of
Biochemistry*



B form

3.1.3 Z-DNA

The Z-DNA is a more radical departure from B-DNA with left handed helical rotation. There are 12 base pairs per helical turn, and its structures appears to be more slender and elongated.

*The Z form of DNA was obtained from
Lehninger's's principles of Biochemistry.*



Z form

3.2 STRUCTURE OF RNA

Primary structure

The RNA molecule is usually an unbranched linear polymer containing nucleotides as its monomers which are usually joined by phosphodiester linkage. Modification of the bases of RNA occurs usually after polymerization and adds to some structural features of the RNA molecule e.g. the 5' terminus 7 methyl cap in eukaryotic mRNA which you will come across later.

The linkage of the ribonucleotides in RNA is 3'5' phosphodiester link involving 3'-OH group of ribose and 5'-phosphate group of another ribonucleotide. This linkage forms the backbone from which the chains are extended. The length of RNA molecule in eukaryotes is from 65 nucleotides to 6000 nucleotides.

Secondary structure

RNA in solution exhibits greater varieties of structures. In low ionic strength solutions, the molecules appear as extended polyelectrolyte chains while in high ionic strength solutions they contract.

A single strand of RNA may have double helical regions formed by hydrogen bonding between complimentary base sequences within the RNA molecule. These double helical regions may or may not have large unpaired loops at the end as demonstrated in tRNA.

Tertiary structure

RNA in solution are dynamic molecules in solution. They undergo changes in conformation during synthesis, processing and functioning. The association of RNA with proteins enables the RNA molecule to be stable and also fold into specific conformations e.g. the "L shaped" conformation of the tRNA. The arms and the loops of tRNA are folded in specific conformations held in position not only by the base pairing interactions but also other interactions. This folding that occurs in the tRNA molecule apparently occurs during its functioning eg. during transcription

3.3 STRUCTURE OF DIFFERENT TYPES OF RNA

Although different types of RNA do exist, this section of the unit is going to describe the structures of the 3 major types of RNA namely: mRNA, tRNA and rRNA.

3.3.1 MESSENGER RNA (mRNA)

Messenger RNA (mRNA) especially the eukaryotic mRNA has some unique structures not found in rRNA or tRNA. Structurally, the 5' terminus mRNA is "capped" i.e its 5' end being covered with a methylated base especially (Guanosine 5' triphosphate)

The methylation is on the 2'-hydroxyl group of the ribose sugar. The capping is followed by a non translated or "leader" sequence. Following the leader sequence is an initiation codon or sequence, most often AUG. The coding region follows the non-translated region of the mRNA molecule. At the end of the coding sequence, a termination sequence is found. A second non translated sequence follows, which is terminated by a series of adenylic acids called poly A tail which makes up 3' terminus of the mRNA molecule.

3.3.2 TRANSFER RNA (tRNA)

Transfer RNAs range in length from 65-110 nucleotides which corresponds to molecular weight of 22, 000-37500 Daltons. The sedimentation coefficient for tRNAs as a group is 4S. The letter, S (Svedberg) in 4S is often used to designate the unit of tRNA. Structurally, tRNAs contain high proportion of modified nucleotides and bases involved in secondary conformation, helices and tertiary folding that makes them to conform to the general 2 dimensional "cloverleaf" structure or three dimensional 'L-form" as determined by x-ray crystallography. The tRNA is a single stranded 5' to 3' nucleotide stretch folded into a conformation with different loops as a result of intramolecular hydrogen bonding of base pairs within the molecule. The various loops are: the D-loop, anticodon loop, variable loop or arm, TψC loop and the acceptor system, each having its own function.

3.3.3 STRUCTURE OF RIBOSOMAL RNA(rRNA).

Structurally the rRNA has a helical structure resulting from the folding back of single stranded polymer but may exist in several conformations.

3.3 SELF ASSESSMENT EXERCISES(SMA).

- 1(a) Briefly distinguish between the primary, secondary and tertiary structures of RNA.
- (b). Write short notes on the different forms of DNA.

4.0 CONCLUSION

In conclusion, it is now clear that nucleic acids DNA and RNA have their respective structures which are basically derived from its components. The forms of DNA namely: A form, B form and Z form each has its own independent structure. In addition, each of the type of RNA: tRNA, mRNA and rRNA have structures differing from one another derived from their components.

5.0 SUMMARY

- In this unit we have learnt that:
- DNA has a structure different from RNA
- Structurally there are 3 forms of DNA.
- Structures of mRNA, rRNA and rRNA have been described
- RNA have primary, secondary and tertiary level structural organization.

6.0 TUTOR MARKED ASSIGNMENT (TMA)

- 1(a) Describe the structure of DNA
- (b) Write short notes on the following:
 - i) mRNA structure
 - ii) tRNA structure
- 2 Discuss the structural hierarchy of RNA.

7.0 REFERENCES AND FURTHER READING.

- Elegbede J.A.(1990) Introductory Biochemistry (Chemistry of Macromolecules) .Institute of Education Press.
- Nelson L.,D., and Cox M.,M (2000) Lehninger's Principles of Biochemistry. New York. Worth Publishers.
- White A.,Handler P.,Smith E.,L., Hill R.,L., Lehman R.I.(1978). Principles of Biochemistry (6th.edition)Mc Graw Hill, Kogakusha.
- Devlin, T. (1986). Textbook of Biochemistry with Clinical Correlations.(2nd Edition) John Wiley and sons New York

MODULE 3: NUCLEIC ACIDS**UNIT 5: ROLES OF DNA AND RNA**

- 1.0 Introduction.
- 2.0 Objectives.
- 3.0 Differences between Deoxyribonucleic Acid (DNA) and Ribonucleic Acid (RNA)
 - 3.0.1 Structural and Chemical Differences between DNA and RNA.
 - 3.0.2 Similarities between DNA and RNA.
- 3.1 Functions / roles of DNA
- 3.2 Function / Roles of RNA.
- 3.3 Self Assessment Exercises.
- 4.0 Conclusion.
- 5.0 Summary.
- 6.0 Tutor Marked Assignment (TMA).
- 7.0 References and Further Reading.

1.0 INTRODUCTION

Like any other macromolecule found in living systems, nucleic acid have their roles and functions anywhere they are found. Aside from the fact that nucleic acids differ from one another structurally and chemically, they also have different functions and roles which is very much reflected in their chemistry. In this unit you will study the roles of nucleic acids and the differences between them.

2.0 OBJECTIVES

The objectives of this unit is to teach you;

- Differences between DNA and RNA;
- Similarities between DNA and RNA;
- The functions/roles of DNA;
- The function/roles of RNA;
- The function/roles of the different types of RNA.

3.0 DIFFERENT BETWEEN DNA AND RNA

Although both deoxyribonucleic acid (DNA) and ribonucleic acid (RNA) are nucleic acids, they however have some differences chemically and structurally which will now be described.

3.0.1 CHEMICAL AND STRUCTURAL DIFFERENCES BETWEEN DNA AND RNA

DNA	RNA
Contains deoxyribose sugar	Contains ribose sugar
Contains the bases: Adenine, Thymine, Cytosine and Guanine.	Contains the bases: Adenine, Guanine, Cytosine and Uracil. RNA does not contain Thymine.
Can only be hydrolysed by deoxyribonucleases (DNAses).	Can only be hydrolysed by ribonucleases (RNAses).
DNA is synthesized in 5'-3' direction.	RNA is synthesized in 3'-5' direction.
DNA is synthesized by DNA polymerase enzyme.	RNA is synthesized by RNA polymerase enzyme.
DNA is double stranded.	RNA is single stranded.

3.0.2 SIMILARITIES BETWEEN DNA AND RNA

- DNA and RNA contain three major components: nucleotide, nitrogenous base and phosphoric acid.
- DNA and RNA both contains Adenine, Guanine and Cytosine nitrogenous bases.
- Both DNA and RNA carry genetic information.
- DNA and RNA are both polymers of nucleotides
- Both DNA and RNA can be found in the cell.

3.1 FUNCTION AND ROLES OF DNA.

Having discovered that DNA is a genetic material. It is worthwhile emphasizing that the main role of the DNA is storage and transmission of genetic information from parents to offsprings or from one generation to another. DNA is capable of undergoing replication (synthesis of another copy of DNA) and being transcribed into RNA (transcription). These two processes enables the genetic information encoded in the DNA found in the nucleus to be transformed into a functional biological material e.g protein in the cytoplasm.

3.2 FUNCTION AND ROLES OF RNA

RNA, like DNA has shown to be a general constituent of prokaryotic and eukaryotic cells. Although RNA molecules are not as stable as DNA, they also serve as genetic information carrier in some organisms e.g some viruses where RNA is their genetic material.

The main functions of tRNA include:

Transportation of specific amino acids to the ribosome's (site for protein synthesis) decoding the genetic information in the messenger RNA in terms of the proper amino acid to be inserted in the sequence of protein/polypeptide synthesised. Each tRNA carries one amino acid and also possess an anticodon by which it recognizes the message on the mRNA template during protein synthesis. Transfer RNAs have two primary active sites, the 3'hydroxyl terminus to which specific aminoacid are attached covalently and the anticodon triplet.

Ribosomal RNAs (rRNA) serve as a structural framework for the ribosomes. The hinging mechanism between the two ribosomal subunits enable translocation and mRNA movement.

Messenger RNA (mRNA) are direct carriers of genetic information from the nucleus to the cytoplasmic ribosomes. Each eukaryotic mRNA contain information for only one polypeptide and is therefore monocistronic whereas prokaryotic mRNA can contain information for more than one polypeptide chain and therefore designated polycistronic.

3.4 SELF ASSESSMENT EXERCISES(SMA)

- 1.(a) Define the terms polycistronic and monocistronic.
(b) Outline the similarities between DNA and RNA.

4.0 CONCLUSION

Conclusively, there are different types of nucleic acids, each having its own characteristic function. These nucleic acids differ structurally and chemically although they do have some similarities.

5.0 SUMMARY

In this unit we have learnt that:

- DNA and RNA have differences and similarities
- DNA serves in storage and transmission of genetic material from one generation to another or from parents to offsprings.
- Messenger RNA carries genetic information from nucleus to the cytoplasm.
- Transfer RNA carries amino acids to the site of protein synthesis.
- Ribosomal rRNA serves as the structural framework of the ribosome.

6.0 TUTOR MARKED ASSIGNMENT (TMA)

1. Compare and contrast DNA and RNA.
2. Describe the functions of the following.
 - (a) mRNA
 - (b) tRNA
 - (c) rRNA.

7.0 REFERENCES AND FURTHER READING.

- Elegbede J.A.(1990) Introductory Biochemistry (Chemistry of Macromolecules) .Institute of Education Press.
- Nelson L.,D., and Cox M.,M (2000) Lehninger's Principles of Biochemistry. New York. Worth Publishers.
- White A.,Handler P.,Smith E.,L., Hill R.,L., Lehman R.I.(1978). Principles of Biochemistry (6th.edition)Mc Graw Hill, Kogakusha.
- Devlin, T. (1986). Textbook of Biochemistry with Clinical Correlations.(2nd Edition) John Wiley and sons New York