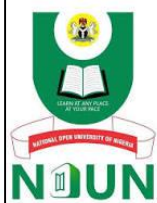


**COURSE
GUIDE**

**BIO216
General Biochemistry II**

Course Team:

Mr. Timothy Bulus (Writer) –
KSU
Prof. Friday E.Uboh (Course
Reviewer)



NATIONAL OPEN UNIVERSITY OF NIGERIA

© 2023 by NOUN Press
National Open University of Nigeria
Headquarters University Village
Plot 91, Cadastral Zone Nnamdi Azikiwe
Expressway Jabi, Abuja

Lagos Office
National Open University of Nigeria
14/16 Ahmadu Bello Way Victoria Island
Lagos

E-mail: centrainfo@nou.edu.ng
URL: www.nou.edu.ng

Published By:
National Open University of Nigeria First Printed 2011
Reviewed 2023

ISBN: 978-058-285-1

All Rights Received

COURSE GUIDE

Introduction

Biology is the science of living things. The functions of various cells are only possible because of molecular interaction among several biosubstances that exist in these cells. The major classes of these biosubstances/biomolecules (also called macromolecules because of their sizes) include: proteins, carbohydrates, fats and oil, and nucleic acids. The understanding of their structures will aid you to understand their functions.

This course, General Biochemistry II, covers carbohydrates, lipids and nucleic acids. In this course you will study these three macromolecules. You will learn their structures, roles in living organisms, the both their physical and chemical properties.

Course Competencies

This course is to provide a comprehensive study on the three macromolecules (carbohydrates, lipids and nucleic acids. A study of the chemical structures and properties as it relates to their functions in the biological system

Course Objectives

In addition to the aim of this course, the course sets an overall objective which must be achieved. In addition to the course objectives, each of the units has its own specific objectives. You are advised to read properly the specific objectives for each unit at the beginning of that unit. This will help you to ensure that you achieve the objectives.

As you go through each unit, you should from time to time go back to these objectives to ascertain the level at which you have progressed. By the time you have gone through this course, you should be able to:

- Explain what carbohydrates are;
- Discuss the chemistry, properties and functions of carbohydrates
- Discuss the chemistry, properties and functions of lipids
- Discuss the components and properties of membranes
- Discuss the chemistry, properties and functions of Nucleic Acids

Working through this Course

Spend time studying through this material. You are required to do all that

has been stipulated in the course: study the course units, read the recommended reference textbooks and do all the unit(s) self-assessment exercise (s) at the stipulated time, attempt and submit your assignment (TMAs) for assessment. Please avail yourself of the opportunity of being present during the facilitation sessions so that you can ask questions on difficult areas and also interact with your colleagues.

Study Units

This course is divided into 3 modules with a total of fifteen units which are divided as follows:

Module 1: Carbohydrates

- Unit 1: Carbohydrates: physical properties and functions.
- Unit 2: Monosaccharides
- Unit 3: Structure of other monosaccharides and properties
- Unit 4: Disaccharides
- Unit 5: Oligosaccharides
- Unit 6: Polysaccharides

Module 2: Lipids

- Unit 1: Chemistry of lipids
- Unit 2: Classification of lipids
- Unit 3: Properties & method of analysis of lipids
- Unit 4: Lipoproteins lipoproteins
- Unit 5: Membranes and membrane

Module 3: Nucleic Acids

- Unit 1: Chemistry of nucleosides
- Unit 2: Chemistry of nucleotides
- Unit 3: Chemistry of nucleic acids
- Unit 4: Structure of nucleic acids
- Unit 5: Roles of DNA and RNA

References and Further Readings

You would be required to do all that has been stipulated in the course: study the course units and read the recommended reference textbooks in each unit of the course material.

Presentation Schedule

Presentation schedule for this course will be uploaded on the online course page.

Assessment

You are required to attempt and submit your assignment (TMAs) online on your course page.

How to get the Most from the Course

The course comes with a list of recommended textbooks. These textbooks are supplement to the course materials so that you can avail yourself of reading further. Therefore, it is advisable you acquire some of these textbooks and read them to broaden your scope of understanding.

Online Facilitation

Online facilitation for this course will hold once in a week for the period of eight weeks. The time and day for the online facilitation will be one hour between 6-7pm, every Thursdays in a week for the period of eight weeks.

Course Information

Course Code:	BIO216
Course Title:	GENERAL BIOCHEMISTRY II
Credit Unit:	Two (2)
Semester:	Second Semester
Course Duration:	Eight weeks
Required Hours for Study:	One hour

Presentation Schedule

Presentation schedule for this course will be uploaded on the online course page.

Assessment

There are three aspects to the assessment of the course. The first is made up of Self-Assessment Exercises, the second consists of the Tutor-Marked Assignments and the third is the end of course examination.

You are advised to practise the exercises. In tackling the assignments, you are expected to apply information, knowledge and techniques you gathered during the course. Your TMA will account for 30% of your total course work. At the end of the course you will be required to sit for end of course examination. The examination will account for 70% of your total course mark.

Tutor-Marked Assignment

The TMA is a continuous assessment component of your course. As earlier noted it accounts for 30% of the total score. Your TMA questions will be uploaded on your course page. Please make sure you answer the questions and submit before the due date.

Final Examination and Grading

The end of course examination for this course has a value of 70% of the total course work. The examination will consist of questions, which will reflect the type of self-testing, practice exercise and tutor-marked assignment problems you have previously encountered. All areas of the course will be assessed. Please do not wait for the examination time table before starting your studies.

You should use the interval between completing the last unit and sitting for the examination to revise the whole course. You will find it useful to review your self- assessment test, TMAs and comments on them before the examination. The end of course examination covers information from all parts of the course.

Facilitators/Tutors and Tutorials

There will be 8 weeks of online facilitation for this course. Please join the online facilitation classes. Go through the unit before the class. If there are areas which are not clear to you bring such to the class so that you can discuss with your colleagues and facilitator

Finally, best wishes in the course and trust you will give it your best.

Module 1: CARBOHYDRATES.

Module Introduction

Unit 1:	CARBOHYDRATES: PHYSICAL PROPERTIES AND FUNCTIONS.
Unit 2:	MONOSACCHARIDES
Unit 3:	STRUCTURE OF OTHER MONOSACCHARIDES AND PROPERTIES
Unit 4:	DISACCHARIDES
Unit 5:	OLIGOSACCHARIDES
Unit 6:	POLYSACCHARIDES

Unit 1: CARBOHYDRATES: PHYSICAL PROPERTIES AND FUNCTIONS

Contents

- 1.1 Introduction
- 1.2 Intended Learning Outcomes (ILOs)
- 1.3 Main Content
 - 1.3.1 Definition of Carbohydrates
 - 1.3.2 Classification of Carbohydrates.
 - 1.3.3 Function/Role of Carbohydrates
 - 1.3.4 Physical property of Carbohydrates
 - 1.3.5 Stereochemistry of Carbohydrates.
- 1.4 Summary
- 1.5 References/Further Readings/Web Sources
- 1.6 Possible answers to Self-Assessment Exercises

1.1 Introduction

The term ‘Carbohydrates’ describes a group of organic compounds, ranging from simple sugars through polysacchacharides, 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, learners are going to study the physical properties, classification, functions and stereochemistry of carbohydrates.

1.2 Intended Learning Outcomes (ILOs)

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

- Understand what carbohydrates are;
- Describe the various classes of carbohydrates, and the basis of their classification;
- List any three physical properties of carbohydrates;
- Mention any four functional roles of carbohydrates in living system;
- Understand the stereochemistry of carbohydrates.

1.3 Main Contents

1.3.1 Definition of Carbohydrates

Carbohydrates can be defined as polyhydroxy aldehydes or ketones, or as substances that yield one of these compounds on hydrolysis. They are one of the four major important biological molecules required by living organisms. Most of carbohydrates, but not all, have the empirical formula $(CH_2O)_n$, where n in most cases is three (3), or greater than three. However, this formula does not is not applicable for all carbohydrates because some carbohydrates have been found to contain nitrogen, phosphorus or sulfur, while some are deoxysugars (eg deoxyribose). That in most cases the formula of water has 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 presence of nitrogen, phosphorus or sulfur in some carbohydrate molecules as earlier mentioned.

1.3.2 Classification of Carbohydrates

Based on the chemical constituents and degree of structural polymerization, carbohydrates are classified into four (4) classes, including Monosaccharaides, Disaccharides, Oligosaccharides and Polysaccharides. The word “saccharide” is derived from the Greek word “sackaron” meaning sugar.

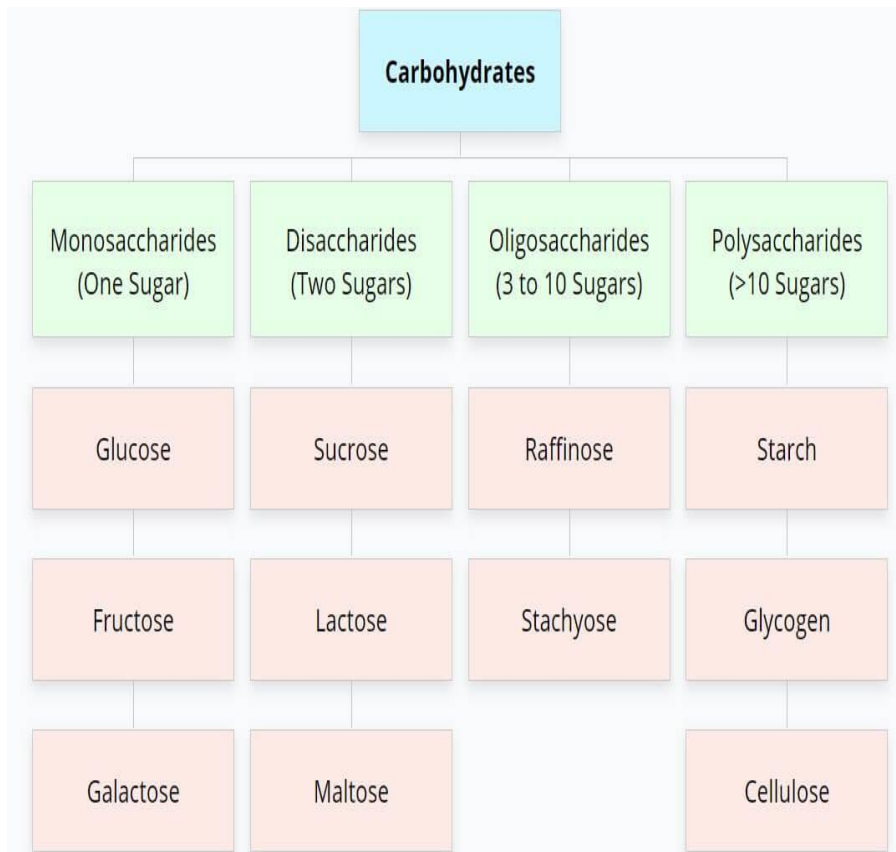
Monosaccharaides refers to the single sugar unit. They are simple sugars with single polyhydroxy aldehyde or ketone unit. The most abundant monosaccharide in nature is the six-carbon sugar D-glucose. Other monosaccharaides include: Mannose, Galactose, Fructose, Ribose etc. Disaccharides are carbohydrates with two sugar units. They are formed by the condensation of two molecules of monosaccharides. To form a disaccharide, the hydroxyl group of one monosaccharide combines with the hydrogen of another monosaccharide through a covalent bond, releasing a molecule of water. The covalent bond so formed between the two sugar molecules is referred to as **glycosidic bond**. The most abundant, and common examples of disaccharides include Maltose

(consisting of two molecules of glucose), Lactose (consisting of glucose and galactose) and Sucrose (consisting of glucose and fructose).

Oligosaccharides are carbohydrates with three to ten molecules of same or different monosaccharides, joined by glycosidic bonds. On the basis of the number of the constituent monosaccharide units, oligosaccharides are classified as trisaccharides, tetrasaccharides, pentasaccharides, etc. Generally, most oligosaccharides are normally present as glycans, linked to either amino acid side chains in proteins or lipids by N- or O-glycosidic bonds to form glycoproteins or glycolipids, respectively.

Polysaccharides are a chain of sugar polymers that contain more than ten monosaccharide units in a continuous range of sizes. Generally, they may contain hundreds to thousands of similar or different monosaccharaides units, joined together by glycosidic bonds. Basically, they are ubiquitous and mainly involved in the structural or storage functions in living organisms. Also, their physical and biological properties depend on the constituent molecules, the architecture of their binding or reacting molecules and their interaction with the enzymatic machinery. Polysaccharides are generally classified based on their functions, the type of monosaccharide units they contain, or their origin. And based on the type of the constituent monosaccharides in the polysaccharide structures, they are classified into two groups main classes, namely homopolysaccharides and heteropolysaccharides. Homopolysaccharides are those polysaccharides with repeating units of same monosaccharide molecules, while heteropolysaccharides are polysaccharides with two or more types of repeating units of different monosaccharide molecules. Typical examples of homopolysaccharides include starch, glycogen, cellulose; examples of heteropolysaccharides include glycosaminoglycans, agarose, and peptidoglycans, linked to proteins, lipids and peptides.

Some examples of the different classes of carbohydrates are presented below:



1.3.3 Functions / Roles of Carbohydrates

The functional roles of carbohydrates in living organisms are as follow:

1. Carbohydrates generally serve as the major source of energy-nutrients to the cells of living organisms. Particularly, glycogen serve as the storage form of energy in animal cells, while starch serve at the storage form of energy in plant cells.
2. Carbohydrates serve as structural components of cells and tissue in living organisms. Typically, cellulose provides structural support to plant cells, while chitin provides structural support in insects.
3. Carbohydrates like peptidoglycans, a major supportive component of the most bacterial cell walls, also serve as 'ground substance' in connective tissues (a gelly-like material) that is very important to the proper functioning of the tissue.
4. Carbohydrates, particularly hyaluronic acid is a major constituent of synovial fluid; hence serve as lubricants due to their viscosity in the joints.
5. Carbohydrates, in complex with proteins form glycoproteins which are involved cellular/molecular recognition, and perform antigenic function in some animal cells. Generally, glycoproteins are relevant as cell-surface receptors, cell-adhesion molecules, immunoglobulins, and tumor antigens. Specifically, galactose and fucose function as antigenic determinant of blood group (ABO) system.

6. Glycolipids also play important role in cell recognition and modulation of membrane proteins that act as receptors. Typically, glycolipids serve as recognition site by toxins such as cholera and pertussis toxins, hence they play a role in infection in that they.
 7. Some carbohydrates (typically sialic acid) serve protecting roles by shielding oligosaccharides of glycoconjugates from the action of hydrolytic enzymes.
 8. Hyaluronic acids are an essential component of the vitreous humor in the eye and synovial fluid (a lubricant fluid present in the body's joints). It's also involved in other developmental processes like tumor metastasis, angiogenesis, and blood coagulation.
 9. Heparin, an example of polysaccharides, acts as a natural anticoagulant that helps in preventing circulating blood from clotting.
 10. A typical polysaccharide, keratan sulfate, is found in the cornea, cartilage, and bone joints where it acts as a cushion that absorbs mechanical shocks.
 11. Chondroitin is a polysaccharide that forms important component of cartilage which provides resistance against compression.
 12. Dermatan sulfate is also a polysaccharide forms an essential component of the dermal tissue. It is known to play an important role in wound repair, blood clotting regulation, infection responses, and cardiovascular diseases.
 13. Carbohydrates provide precursors for the synthesis of other biological molecules. For instance, ribose sugar forms the structural framework of ribonucleic acid and deoxyribonucleic acid (RNA and DNA).
- Define carbohydrates. List the classes of carbohydrates you know.

1.3.4 Physical Properties of Carbohydrates

- **Solubility:** Most carbohydrate (particularly monosaccharaides, diasacchareides, and some polysaccharides) are soluble in water but insoluble in such organic solvents as chloroform. Also, such polysaccharides as cellulose are insoluble in water, but soluble in ammoniacal solution of cupric salts.
- **Temperature Stability:** Most carbohydrates (including monosaccharaides, oligosaccharides and polysaccharides) are normally solid at room temperature.
- **Taste:** Most monosaccharaides and some disaccharides e.g. sucrose are sweet to taste.
- **Colour:** Most carbohydrates (including such monosaccharaides as glucose, disaccharides as sucrose, and polysaccharides as starch) are colourless crystalline solids inn nature.
- **Odour:** Most carbohydrates (including monosaccharaides, disaccharides and polysaccharides) are naturally odourless.

1.3.5 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. For instance, enantiomers are stereoisomers that are non-super imposable 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:



The structure of D and L Glyceraldehyde Enantiomers (from Lehninger's Principles of Biochemistry).

Enantiomers are distinguished from each other by designations D for dextrorotatory and L for levorotatory. The maximum numbers of stereoisomers possible is 2^n , where n is the number of chiral carbon atoms. In sugars, what determines whether a molecule is a D or L form 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 image 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. eg. of epimers include: glucose, galactose and mannose. Epimers therefore exhibit the concept of epimerism (differing around only one chiral carbon atom).

Anomers are special form of carbohydrate stereoisomers in which the difference is specifically about the anomeric carbon. Carbohydrates that exhibit difference around anomeric carbon atom are said to undergo anomerism eg. 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 (eg. α – D glucose); while when $-\text{OH}$ group is up or above the plane, it is a beta (β) anomer (eg. β – D glucose).

Self-Assessment Exercise(s)

1. List three most common disaccharides in nature
2. What are enantiomers?
3. Define glycosidic bond
4. State the functions of carbohydrates in the biological systems.

1.4 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 exhibits stereoisomerism, including anomerism, epimerism, enantiomerism and diastereoisomerism.

1.5 References/Further Readings/Web Sources

- Aryal, S. (2023). Introduction to Carbohydrates
- BeMiller, J. N. (2019). Monosaccharides. *Carbohydrate Chemistry for Food Scientists*, 1–23. doi:10.1016/b978-0-12-812069-9.00001-7.
- Devlin, T. (1986). *Textbook of Biochemistry with Clinical Correlations*. (2nd Edition) John Wiley and sons New York.
- 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.
- Sharon, N. (1980). Carbohydrates. *Scientific American*, 243(5), 90–117.
- White A.,Handler P.,Smith E.,L., Hill R.,L., Lehman R.I.(1978). *Principles of Biochemistry* (6th.edition)Mc Graw Hill, Kogakusha
- <https://microbenotes.com/carbohydrates-structure-properties-classification-and-functions/>
- <http://www.jstor.org/stable/24966460>
- <https://study.com/learn/lesson/chemical-structure-of-carbohydrates-types-properties.html>

1.6 Possible answers to Self-Assessment Exercis

1. Sucrose, Maltose and Lactose
2. Enantiomers are stereoisomers that are non-super impossible mirror images of each other
3. Glycosidic bond is the covalent bond so formed between the two sugar molecules
 - 4a). Carbohydrates generally serve as the major source of energy-nutrients to the cells of living organisms. Particularly, glycogen serve as the storage form of energy in animal cells, while starch serve at the storage form of energy in plant cells.
 - b). Carbohydrates serve as structural components of cells and tissue in living organisms. Typically, cellulose provides structural support to plant cells, while chitin provides structural support in insects.
 - c). Carbohydrates like peptidoglycans, a major supportive component of the most bacterial cell walls, also serve as 'ground substance' in connective tissues (a gelly-like material) that is very important to the proper functioning of the tissue.
 - d). Carbohydrates, particularly hyaluronic acid is a major constituent of synovial fluid; hence serve as lubricants due to their viscosity in the joints.
 - e). Carbohydrates, in complex with proteins form glycoproteins which are involved cellular/molecular recognition, and perform antigenic function in some animal cells.
 - f). Glycolipids also play important role in cell recognition and modulation of membrane proteins that act as receptors. Typically, glycolipids serve as recognition site by toxins such as cholera and pertussis toxins, hence they play a role in infection in that they.
 - g). Some carbohydrates (typically. sialic acid) serve protecting roles by shielding oligosaccharides of glycoconjugates from the action of hydrolytic enzymes.
 - h). Hyaluronic acids are an essential component of the vitreous humor in the eye and synovial fluid (a lubricant fluid present in the body's joints).
 - i). Heparin, an example of polysaccharides, acts as a natural anticoagulant that helps in preventing circulating blood from clotting.
 - j). A typical polysaccharide, keratan sulfate, is found in the cornea, cartilage, and bone joints where it acts as a cushion that absorbs mechanical shocks.
 - k). Chondroitin is a polysaccharide that forms important component of cartilage which provides resistance against compression.
 - l). Dermatan sulfate is also a polysaccharide forms an essential component of the dermal tissue. It is known to play an important role in wound repair, blood clotting regulation, infection responses, and cardiovascular diseases.

m). Carbohydrates provide precursors for the synthesis of other biological molecules. For instance, ribose sugar forms the structural framework of ribonucleic acid and deoxyribonucleic acid (RNA and DNA).

Unit 2: MONOSACCHARIDES

Contents

- 2.1.1 Introduction
 - 2.1.1 Classification of Monosaccharides
- 2.2 Intended Learning Outcomes (ILOs)
- 2.3 Main Contents
 - 2.3.1 Structure of Glucose.
 - 2.3.2 Projection and Perspective Formula.
 - 2.3.3 Fischer's Projection Formula.
 - 2.3.4 Cyclisation of Fischer Projection Formula in Monosaccharides.
 - 2.3.5 Optical activity in Monosaccharides.
- 3.6 Measurement of Optical Activity.
- 3.7 Haworth Projection Formula
- 2.4 Summary
- 2.5 References/Further Readings/Web Sources
- 2.6 Possible answers to Self-Assessment Exercises

2.1 Introduction

Monosaccharides are simple sugars that constitute the building blocks of oligosaccharides and polysaccharides, which are more complex carbohydrates. They are the simplest carbohydrates that are also referred to as simple sugars. They are the first of the major general classes of carbohydrates characterized by being products of hydrolysis of non-simpler sugars (disaccharides, oligosaccharides and polysaccharides). Monosaccharides consist of a single polyhydroxy aldehyde or ketone unit. The most abundant monosaccharides in nature is the six carbon sugar D-glucose, which is sometimes referred to as dextrose. Monosaccharides are generally categorized into two classes, based on the identifying functional group, namely aldoses (those containing aldehyde functional group) and ketoses (those with ketonic group), each having its own characteristic structure. This unit is going to elaborate on some aspects of monosaccharide (glucose) chemistry.

2.1.2 Classification of Monosaccharides

Generally, monosaccharides are classified into two broad classes on the basis of the functional group that they possess, as earlier stated. While those that contain an aldehyde group are known as “**aldose**”, those that contain a keto group are referred to as “**ketose**”. Monosaccharides can also be classified on the basis of the combination of the number of carbon atoms and the functional group they possess as follows:

Number of Carbon Atoms	Aldoses	Ketoses
3	Aldotriose (eg. Glyceraldehyde)	Ketotriose (eg. Dihydroacetone)
4	Aldotetrose (eg. Erythrose)	Ketotetrose (eg. Erythrulose)
5	Aldopentose (eg. Ribose)	Ketopentose (eg. Ribulose)
6	Aldohexose (eg. Glucose)	Ketohexose (Fructose)
7	Aldoheptose	Ketoheptose

2.2 Intended Learning Outcomes (ILOs)

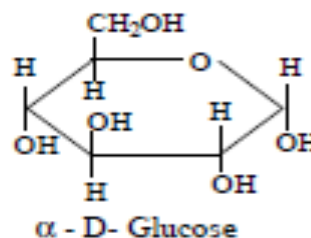
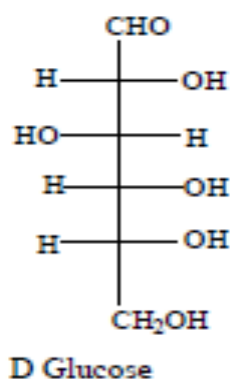
By the end of this unit, you should be able to:

- Draw the structure of glucose;
- Describe the perspective and projection formula of glucose;
- Explain the Fisher and Haworth projection of glucose

2.3 Main Contents

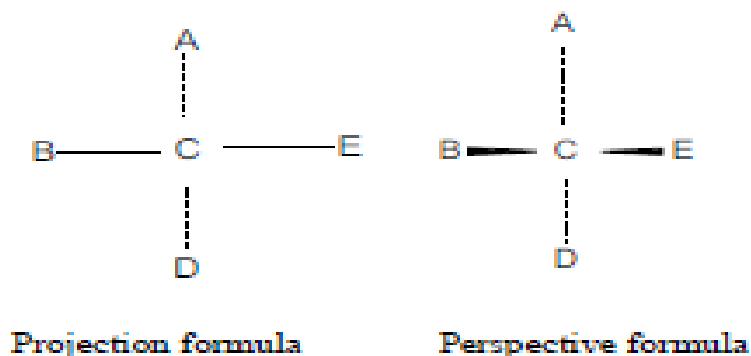
2.3.1 Structure of Glucose

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



2.3.2 Projection and Perspective Formulas

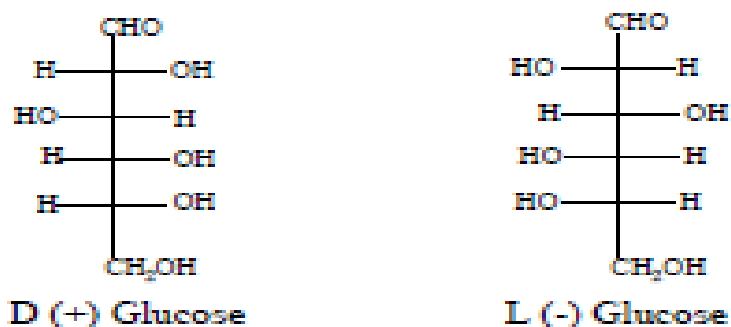
The tetrahedral nature of carbon compounds presents a unique problem in writing the three dimensional structure of a compound on a two dimensional surface such as paper. This difficulty persisted until Emil Fischer introduced the projection formula in which 4 groups attached to a carbon atom are projected 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:



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.

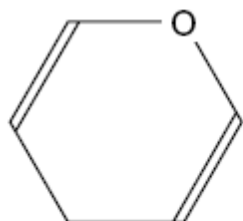
2.3.3 Fischer's Projection

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.

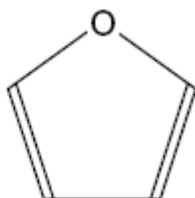


2.3.4 Cyclisation of the Fischer's Projection Formula in Monosaccharides.

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 aldehyde and alcohol while hemiketals are formed between ketones and alcohols. In glucose, the hemiacetal reaction occurs between 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

Source: 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.

Monosaccharides may be classified as aldose and ketose. Differentiate between the two classes. Draw the Fischer's structure of D – and L – Glucose. What do you understand by the term, “anomer”?

2.3.5 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.

2.3.6 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:

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

Where dm = decimeter (0-1m)

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

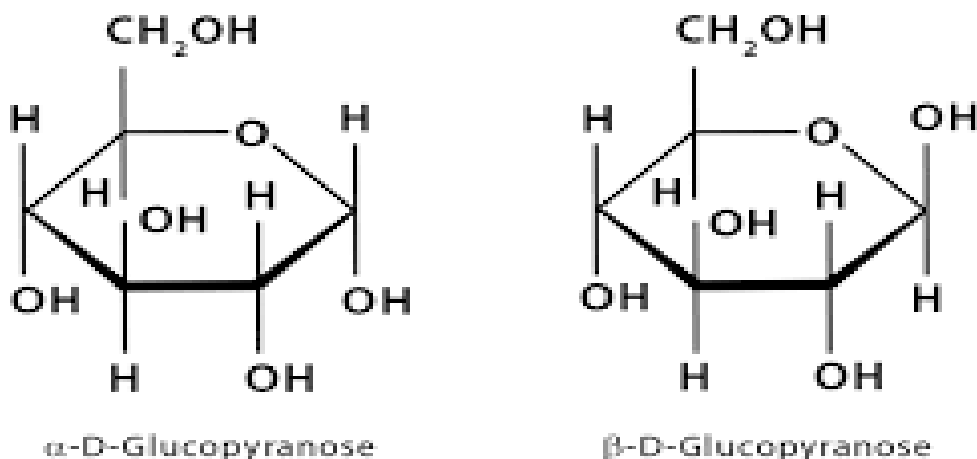
25° C = Temperature of measurement

(α) = Specific Rotation

2.3.7 Haworth's Projection Formula

Haworth projections formula are used to present sugars in their cyclic forms. The formula is attributed to the English chemist, W.H. Haworth, who 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

confirmation. Generally, Haworth's formula provides important information about the arrangement of atoms and functional groups within the molecule. The Haworth's projection structure of α - and β -D-Glucopyranose are presented below.



Self-Assessment Exercise(s)

1. On the basis of the functional group and number of carbon atoms, classify monosaccharides
2. Draw the structure of α - and β -D-Glucopyranose

2.4 Summary

- Straight chain structure of glucose can cyclise into the pyranose and furanose rings.
- The Fischer's projection formula of glucose is 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.

2.5 References/Further Readings/Web Sources

- 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.

<https://byjus.com/jee/glucose-structure/>

<https://www.ncbi.nlm.nih.gov/books/NBK545201/>

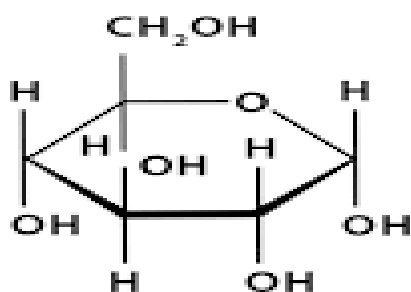
[https://chem.libretexts.org/Bookshelves/Organic_Chemistry/Basic_Principles_of_Organic_Chemistry_\(Roberts_and_Caserio\)](https://chem.libretexts.org/Bookshelves/Organic_Chemistry/Basic_Principles_of_Organic_Chemistry_(Roberts_and_Caserio))

2.6 Possible answers to Self-Assessment Exercises

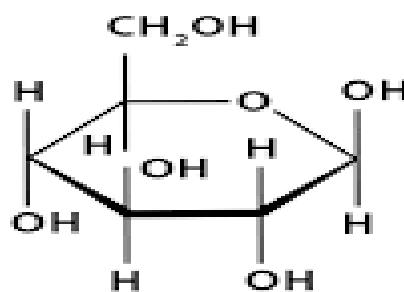
1. On the basis of the functional group and number of carbon atoms, monosaccharides can be classified as follow:

Number of Carbon Atoms	Aldoses	Ketoses
3	Aldotriose (eg, Glyceraldehyde)	Ketotriose (eg. Dihydroacetone)
4	Aldotetrose (eg. Erythrose)	Ketotetrose (eg. Erythrulose)
5	Aldopentose (eg. Ribose)	Ketopentose (eg. Ribulose)
6	Aldohexose (eg. Glucose)	Ketohexose (Fructose)
7	Aldoheptose	Ketoheptose

2.



α -D-Glucopyranose



β -D-Glucopyranose

Unit3: STRUCTURE AND PROPERTIES OF OTHER MONOSACCHARIDES

Contents

- 3.1 Introduction
- 3.2 Intended Learning Outcomes (ILOs)
- 3.3 Main Contents
 - 3.3.1 Structure of Monosaccharides with 3 and 4 carbon atoms (Trioses, Tetroses)
 - 3.3.2 Structure of monosaccharides with more than 4 carbon atoms.
 - 3.3.3 Structure of Derived Monosaccharides.
 - 3.3.3.1 Sugar Acids.
 - 3.3.3.2 Deoxy Sugars.
 - 3.3.3.3 Amino Sugars.
 - 3.3.4 Properties of Monosaccharides.
 - 3.3.4.1 Mutarotation.
 - 3.3.4.2 Reducing Property.
 - 3.3.4.3 Glycoside Formation.
 - 3.3.4.4 Ester Formation.
 - 3.3.4.5 Dehydration.
 - 3.3.4.6 Rearrangement in Alkaline Solution.
 - 3.3.4.7 Reduction of Monosaccharides.
- 3.4 Summary
- 3.5 References/Further Readings/Web Sources
- 3.6 Possible answers to Self-Assessment Exercises

3.1 Introduction

Apart from glucose, there are many other monosaccharides units in nature. 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.

3.2 Intended Learning Outcomes (ILOs)

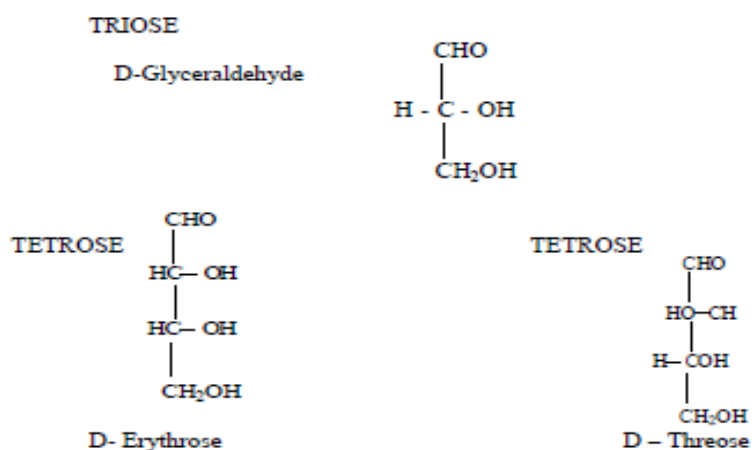
By the end of this unit, you should be able to:

- Describe the structure of other monosaccharides units with 3 and 4 carbon atoms.
- Draw the structure of monosaccharides with more than 5 carbon atoms.
- List any three properties of monosaccharides.

3.3 Main Contents

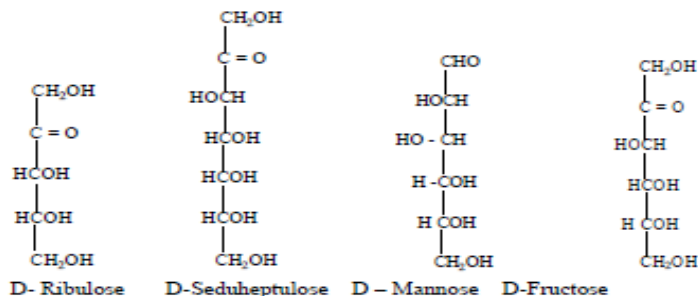
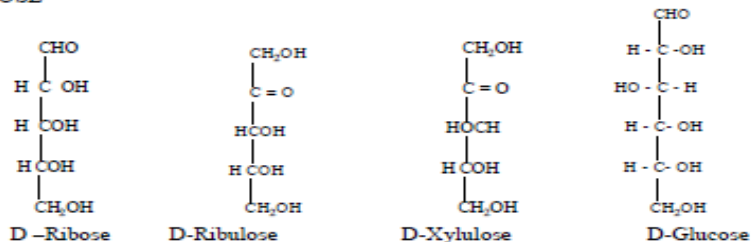
3.3.1 Structure of Monosaccharides with three (3) Carbon and four (4) Carbon atoms (trioses and tetroses)

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.



3.3.2 Structure of Monosaccharides with more than four (4) Carbon atoms

PENTOSE

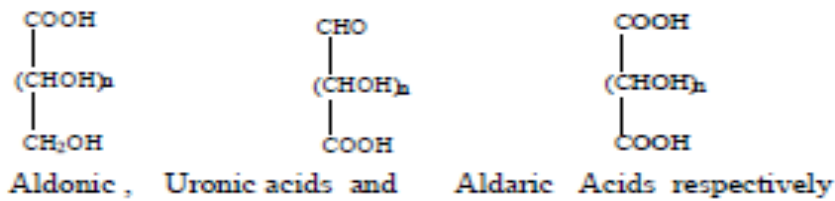


3.3.3 Structure of derived Monosaccharides

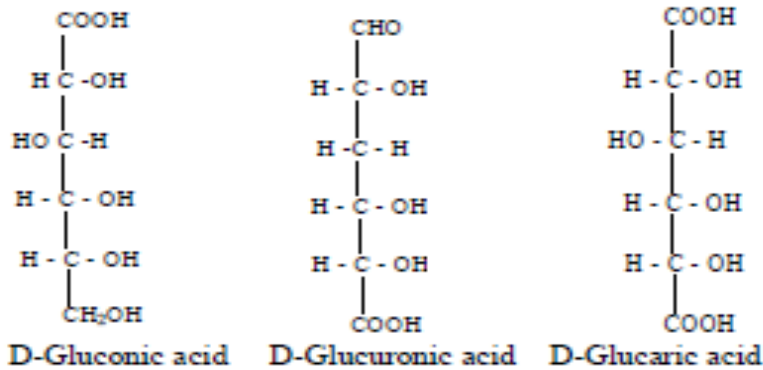
Many derivatives of monosaccharides are constituents of living things. Among the more important are the sugar acids, the amino sugars and the deoxy sugars.

3.3.3.1 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.

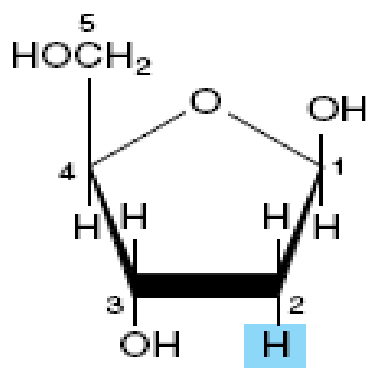


Oxidation of glucose gives rise to the following acids



3.3.3.2 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).



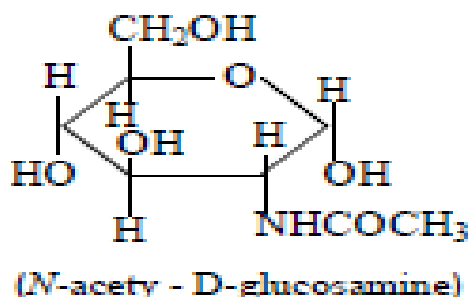
The structure of 2-deoxy ribose

Source: Harper's Review of Biochemistry

3.3.3.3 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

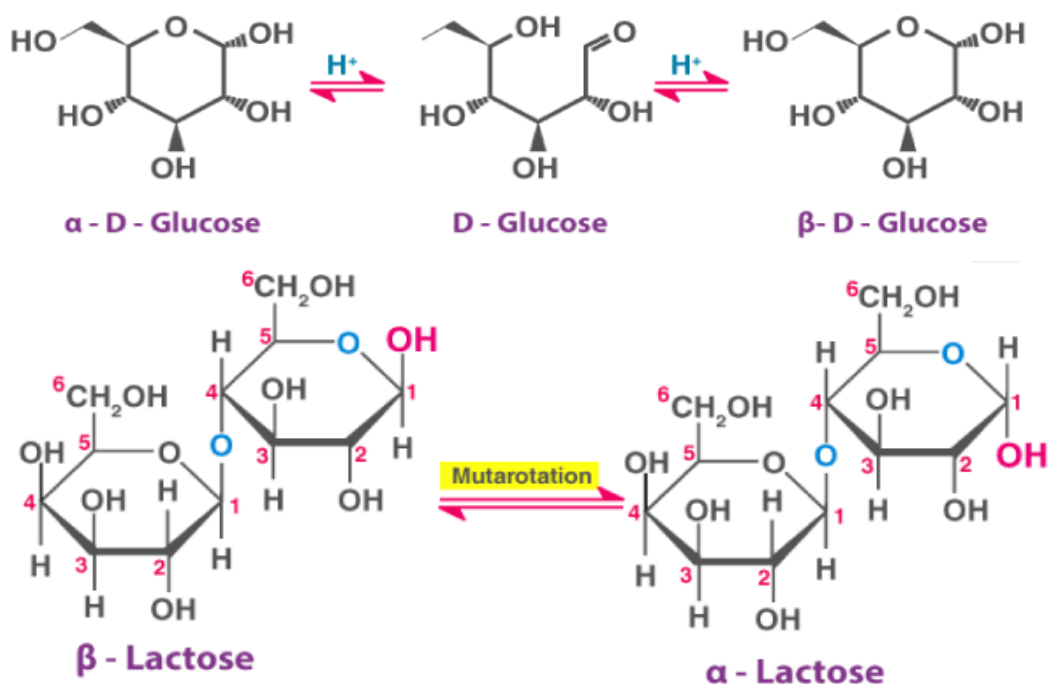
and animals. Example of amino sugars are acetyl D-glucosamine and acetyl D-galactosamine.



3.3.4 Properties of Monosaccharides.

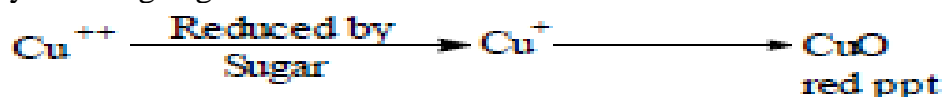
3.3.4.1 Mutarotation

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 Dglucose interconvert in aqueous solution. In an aqueous solution, D-Glucose exists as 36% α -D glucose and 64% of β -D glucose. When β -D-glucopyranose is dissolved in water, it rotates a plane-polarized light by $+18.7^\circ$. Some amount of β -D-glucopyranose undergoes mutarotation to give α -D-glucopyranose, and it turns a plane-polarized light by $+112.2^\circ$. The equilibrium mixture of the solution contains about 36% of α -D-glucopyranose and 64% of β -D-glucopyranose. Mutarotation of glucose and lactose is presented below:



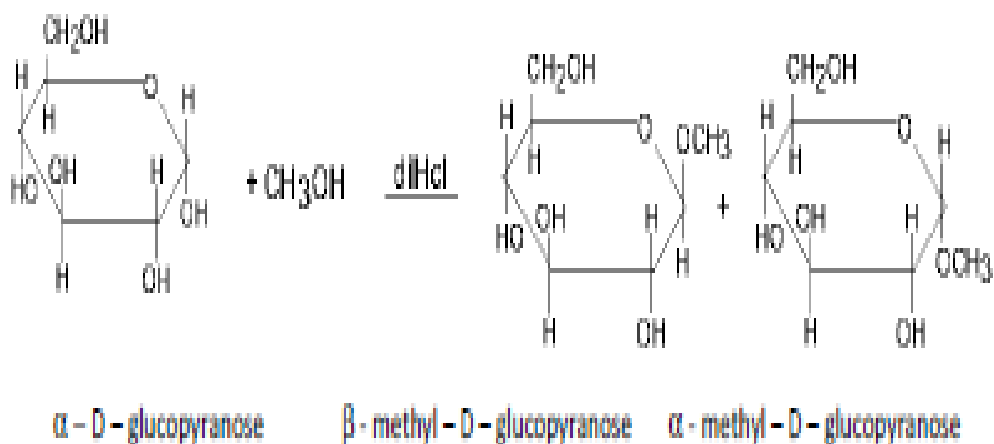
3.3.4.2 Reducing Property

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.



3.3.4.3 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, α -methyl - D- glucopyranoside and β -methyl-D-glucopyranoside (Glycosides). Glycosides are not reducing sugars and does not show the phenomenon of mutarotation.

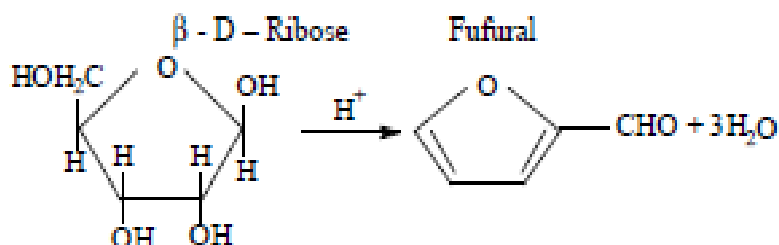


3.3.4.4 Ester formation

Another important property of monosaccharides is their ability to form esters. Typically, if D-glucopyranose. is treated with acetic anhydride, all the $-\text{OH}$ 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.

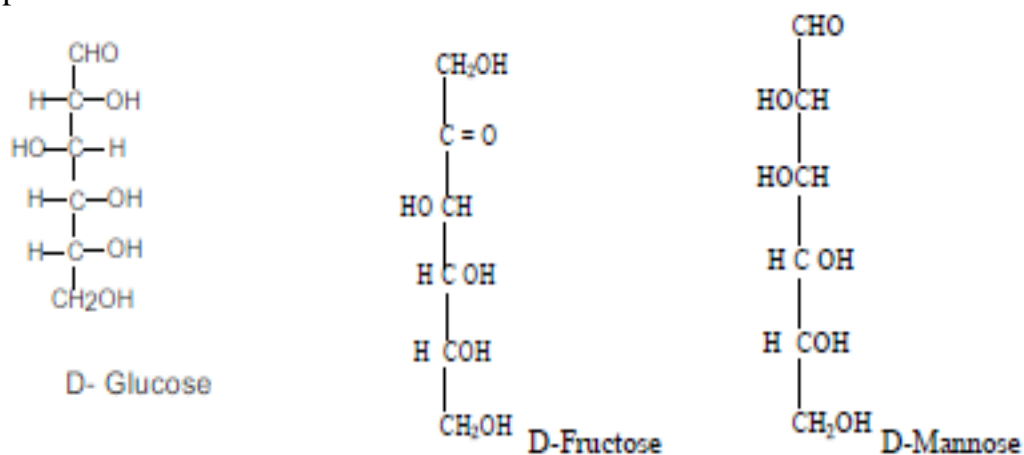
1.3.4.5 Dehydration

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



3.3.4.6 Rearrangement in Alkaline Solution

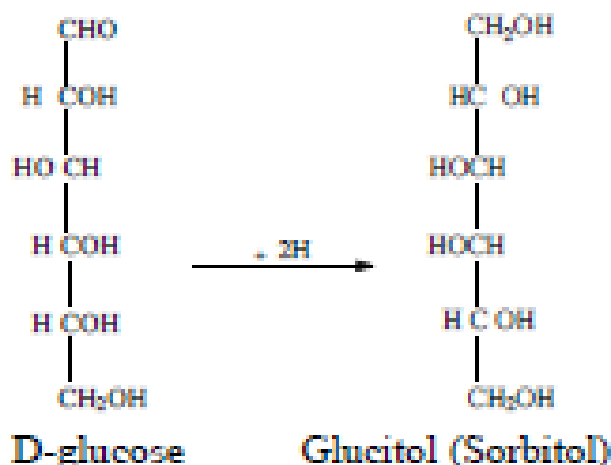
In cold, dilute alkaline solution, glucose forms both mannose and fructose. This interconversion is attributable to enolisation reaction that involves removal of hydrogen from carbon atom adjacent to the carbonyl group.



Source: Harper's Review of Biochemistry

3.3.4.7 Reduction of Monosaccharides

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



Draw the structure of the sugar molecule that is present in DNA. Define mutarotation of monosaccharide. Draw the structure of a named three carbon atom monosaccharide

Self-Assessment Exercise(s)

1. Describe any five properties of monosaccharides
2. Does sucrose undergo mutarotation? Justify your answer.

3.4 Summary

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

3.5 References/Further Readings/Web Sources

- Egbede 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

[https://chem.libretexts.org/Bookshelves/Organic_Chemistry/Organic_Chemistry_\(Morsch_et_al.\)/25%3A_Biomolecules-](https://chem.libretexts.org/Bookshelves/Organic_Chemistry/Organic_Chemistry_(Morsch_et_al.)/25%3A_Biomolecules-)
[https://chem.libretexts.org/Courses/Georgia_Southern_University/CHEM_1152%3A_Survey_of_Chemistry_II_\(GSU_-_Dr._Osborne\)](https://chem.libretexts.org/Courses/Georgia_Southern_University/CHEM_1152%3A_Survey_of_Chemistry_II_(GSU_-_Dr._Osborne))
<https://byjus.com/chemistry/monosaccharides/#>:

3.6 Possible answers to Self-Assessment Exercises

1.

- (i) Mutarotation: In aqueous solution, monosaccharides interconvert between α and β anomers
- (ii) Reducing property: Monosaccharides readily reduce oxidizing agents such as (Cu^{2+}) cupric ions and hydrogen peroxide (H_2O_2).
- (iii) Glycoside formation: Monosaccharides have the capacity to form acetals or glycosides when in solution are exposed to methanol in the presence of dilute HCl.
- (iv) Ester formation: Monosaccharides form esters when treated with acetic anhydride. For example, if D-glucopyranose. is treated with acetic anhydride, all the $-\text{OH}$ groups become acetylated to yield an ester, penta – O- acetyl glucose.
- (v) Dehydration: Monosaccharides are usually dehydrated in strong mineral acids. For instance, pentoses and hexoses in strong mineral acid, like HCl, are dehydrated to form fufurals and hydroxymethylfurfural compounds respectively.

2. No.

An ordinary table sugar (Sucrose) is an example of a disaccharide, having α -D-glucopyranose and β -D-fructofuranose linked by a glycosidic bond at their anomeric carbons. Sucrose is not a reducing sugar, and because of the absence of the hemiacetals, it does not undergo mutarotation.

Unit 4: DISACCHARIDES

Contents

- 4.1 Introduction
- 4.2 Intended Learning Outcomes (ILOs)
- 4.3 Main Contents
 - 4.3.1 Chemistry of Disaccharides
 - 4.3.2 Types of Disaccharides.
 - 4.3.3 Maltose.
 - 4.3.4 Lactose.
 - 4.3.5 Sucrose.
 - 4.3.6 Trehalose
 - 4.3.7 Properties of Disaccharides.
- Self-Assessment Exercise(s)
- 4.4 Summary
- 4.5 References/Further Readings/Web Sources
- 4.6 Possible answers to Self-Assessment Exercises

4.1 Introduction

Disaccharides represent the second class of carbohydrates which consists of two (2) monosaccharide units linked by characteristics covalent bond referred to as glycosidic bond. Generally, the two monosaccharide units can be the same or different. The most common disaccharides in nature include sucrose, maltose, and lactose. In this unit you are going to study the various types of disaccharides.

4.2 Intended Learning Outcomes (ILOs)

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

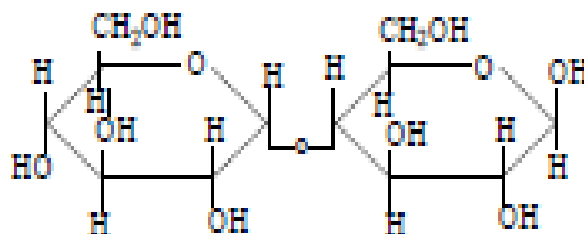
- Understand the chemistry of disaccharides
- Identify the different types of important disaccharides
- Draw the structure of different types of disaccharides

4.3 Main Contents

4.3.1 CHEMISTRY OF OLIGOSACCHARIDES

All common disaccharides have names ending with suffix – ose. Generally, the glycosidic bonds that link the monosaccharide units of disaccharides are usually the O-glycosidic bonds, which can either be an alpha (α) or beta (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 a disaccharides, 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 →4) shows that C – 1 of the first named sugar residue is joined to C – 4 of the second.



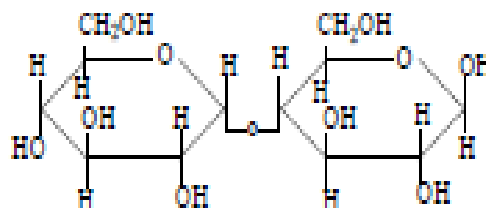
Example of *O*-glycosidic linkage holding the two glucose molecules in Maltose

4.3.2 TYPES OF DISACCHARIDES

Different types of disaccharides do exist and the differences in these disaccharides are based upon the type of monosaccharides units contained in them. In addition, the orientation of the component monosaccharides units determines whether the disaccharide is a reducing or a non-reducing one.

4.3.3 MALTOSE

The disaccharide 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 disaccharide. The configuration of the anomeric carbon atom in maltose and its systematic naming are presented below:



Maltose. α , α - D Glucopyranosyl (1→4) D-glucopyranose.

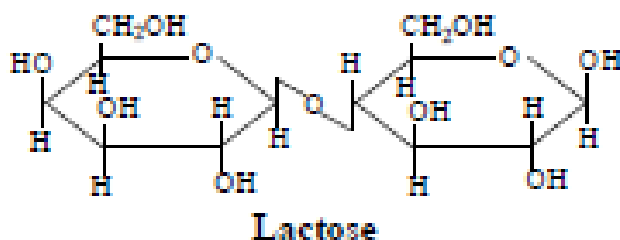
The above indicate that maltose is formed when – OH group of one glucose molecule (right) condenses with intermolecular hemiacetal of the

other glucose molecule (left) with the elimination of water and formation of *O*-glycosidic bond (linkage)

4.3.4 LACTOSE

Lactose contains D – galactose and D – glucose units. Lactose occurs in abundance naturally in milk and other dairy products, hence referred to as “milk sugar”. It is among the most commonly known sugars, although unlike other disaccharides, it does not have a sweet taste.

The constituent monosaccharide units of lactose include β -D-glucose and β -D-galactose, bound together by a 1 \rightarrow 4 glycosidic bond. It is abbreviated as Gal (β -1, α - 4) Glc. The anomeric carbon of glucose is available for oxidation and thus lactose is a reducing disaccharide. The presence of a free hemiacetal hydroxide in the structure of lactose is the reason behind its reactive nature. Lactose gives monocarboxylic acid when treated with bromine water.



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

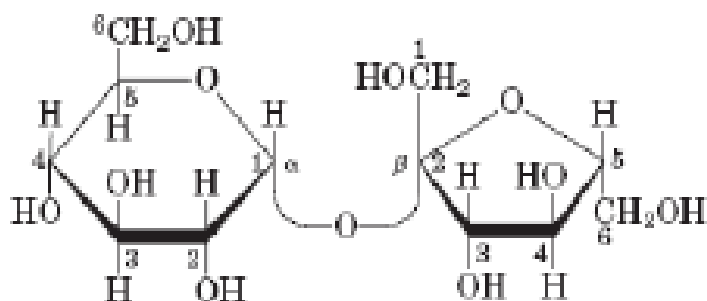
4.3.5 SUCROSE

Sucrose is common known as table sugar is sucrose and is a diasaccharides of glucose and fructose. It is formed by plants but not by higher animals. It is a white crystalline solid compound that is highly soluble in water. Its solubility is known to increase with increase in temperature. Also, sucrose has a melting point of 180°C, and it forms a dark viscous substance when heated above the melting point,

Moreover, sucrose is dextrorotatory in nature and exhibits a characteristic rotation of (+66.7°). Generally, the structure of sucrose molecules comprises of both- the α type of glucose and β type of fructose. And sucrose is unable to exhibit mutarotation (α to β change) due to the unavailability of free hemiacetal hydroxyl group; and it cannot form osazones based on same reason.

In contrast to maltose and lactose, sucrose contains no free anomeric carbon atom. The formula of sucrose is C₁₂H₂₂O₁₁. The anomeric units of both diasaccharides 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. When sucrose is subjected to catalytic hydrolysis, it gives one mole of D-Glucose and one mole of L-Fructose. And the overall mixture shows a levorotatory turn because the laevorotation of fructose (-92.4) is greater than the dextrorotation of glucose (+52.5).



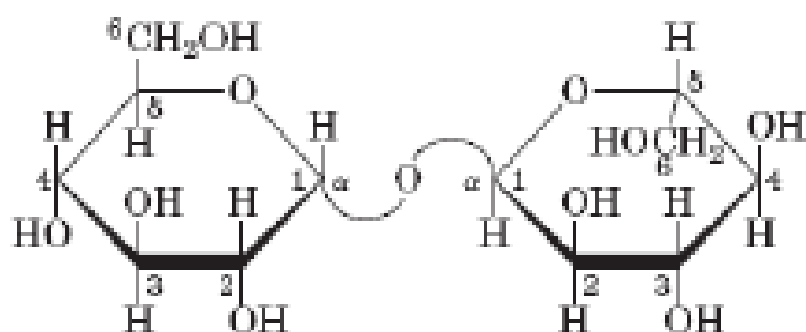
Sucrose

α - D – glucopyranosyl β - D –fructofuranoside
[Glc(α 1 \rightarrow 2 β)Fru]

Source: *Lehninger's Principles of Biochemistry*

4.3.6 TREHALOSE

Trehalose, Glc (α 1 \leftrightarrow 1 α) 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. Also, traces of trehalose are found in yeasts and different parasitic organisms.



Trehalose

α - D – glucopyranosyl α - D –glucopyranoside
[Glc(α 1 \rightarrow 1 α)Glc]

Source: *Lehninger's Principles of Biochemistry*

What are disaccharides? What monosaccharides are obtained by the hydrolysis of (a) sucrose, (b) maltose, (c) lactose. Identify the glycosidic bond in sucrose

4.3.7 PROPERTIES OF DISACCHARIDES (DISACCHARIDES)

- i. Disaccharides can be hydrolyzed by acids or other hydrolytic enzymes to their monomeric units.
- ii. Some disaccharides can undergo mutarotation because they have reducing properties eg. lactose.
- iii. Some disaccharides (e.g. maltose) are reducing sugars while some (e.g. sucrose) are not.
- iv. Disaccharides units are held together by glycosidic linkages
- v. Disaccharide molecules show high solubility in aqueous solutions due to the presence of a large number of hydroxyl groups which form hydrogen bonds with water molecules
- vi. Disaccharides are polar compounds due to the presence of hydroxyl groups bearing partial negative charge and hydrogen atoms linked to the carbon chain, which bears partial positive charge
- vii. Disaccharides have a characteristic sweet taste, hence are used as sweetening agents
- viii. Due to the large volume of the molecules, disaccharides almost do not show diffusion gradient, and are hence impermeable across cell membranes.

Self-Assessment Exercise(s)

1. Highlight the properties of disaccharides.
2. Draw the structure of the following: Maltose, Sucrose, Lactose and Trehalose.
3. Illustrate how maltose undergoes mutarotation

4.4 Summary

Disaccharides 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.

Disaccharides have *O*-glycosidic linkage joining their monosaccharide unit together

4.5 References/Further Readings/Web Sources

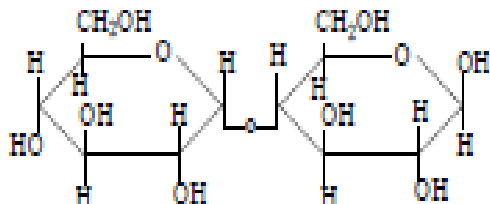
- Elegbede J.A.(1990) Introductory Biochemistry (Chemistry of Macromolecules) .Institute of Education Press.
- Nelson L.,D., and Cox M.,M (2000) Lehninger's Principles of Biochemistry. New York. Worth Publishers.
- White A.,Handler P.,Smith E.,L., Hill R.,L., Lehman R.I.(1978). Principles of Biochemistry (6th.edition)Mc Graw Hill, Kogakusha.
- Devlin, T. (1986). Textbook of Biochemistry with Clinical Correlations.(2nd Edition) John Wiley and sons New York
- <https://byjus.com/chemistry/disaccharides/>
- [https://chem.libretexts.org/Bookshelves/Introductory_Chemistry/Basics_of_General_Organic_and_Biological_Chemistry_\(Ball_et_al.\)/](https://chem.libretexts.org/Bookshelves/Introductory_Chemistry/Basics_of_General_Organic_and_Biological_Chemistry_(Ball_et_al.)/)

4.6 Possible answers to Self-Assessment Exercises

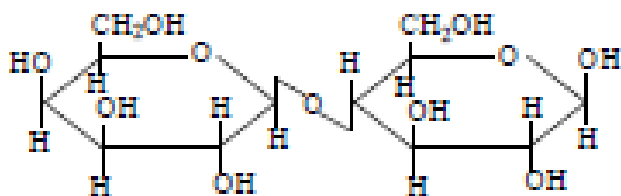
1.

- i. Disaccharides can be hydrolyzed by acids or other hydrolytic enzymes to their monomeric units.
- ii. Some disaccharides can undergo mutarotation because they have reducing properties eg. lactose.
- iii. Some disaccharides (e.g. maltose) are reducing sugars while some (e.g. sucrose) are not.
- iv. Disaccharides units are held together by glycosidic linkages
- v. Disaccharide molecules show high solubility in aqueous solutions due to the presence of a large number of hydroxyl groups which form hydrogen bonds with water molecules
- vi. Disaccharides are polar compounds due to the presence of hydroxyl groups bearing partial negative charge and hydrogen atoms linked to the carbon chain, which bears partial positive charge
- vii. Disaccharides have a characteristic sweet taste, hence are used as sweetening agents
- viii. Due to the large volume of the molecules, disaccharides almost do not show diffusion gradient, and are hence impermeable across cell membranes.

2.

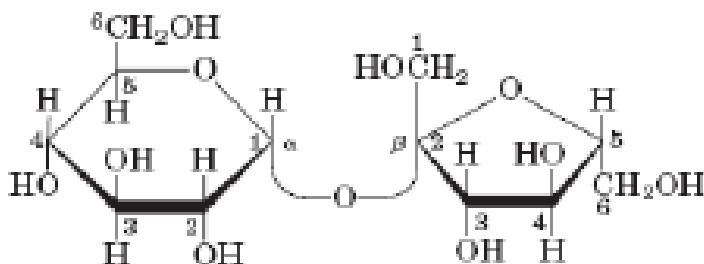


Maltose: α, α - D Glucopyranosyl (1 \rightarrow 4) D-glucopyranose.

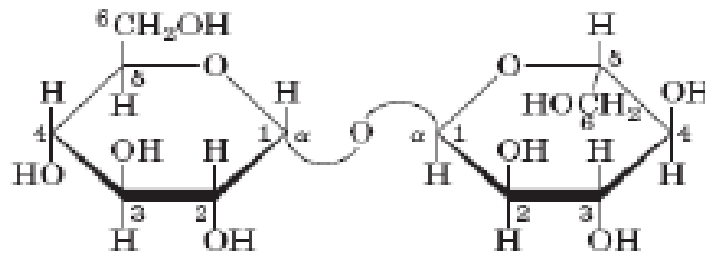


Lactose

Lactose: β - D - galactopyranosyl (1 \rightarrow 4) α - D - glucopyranose

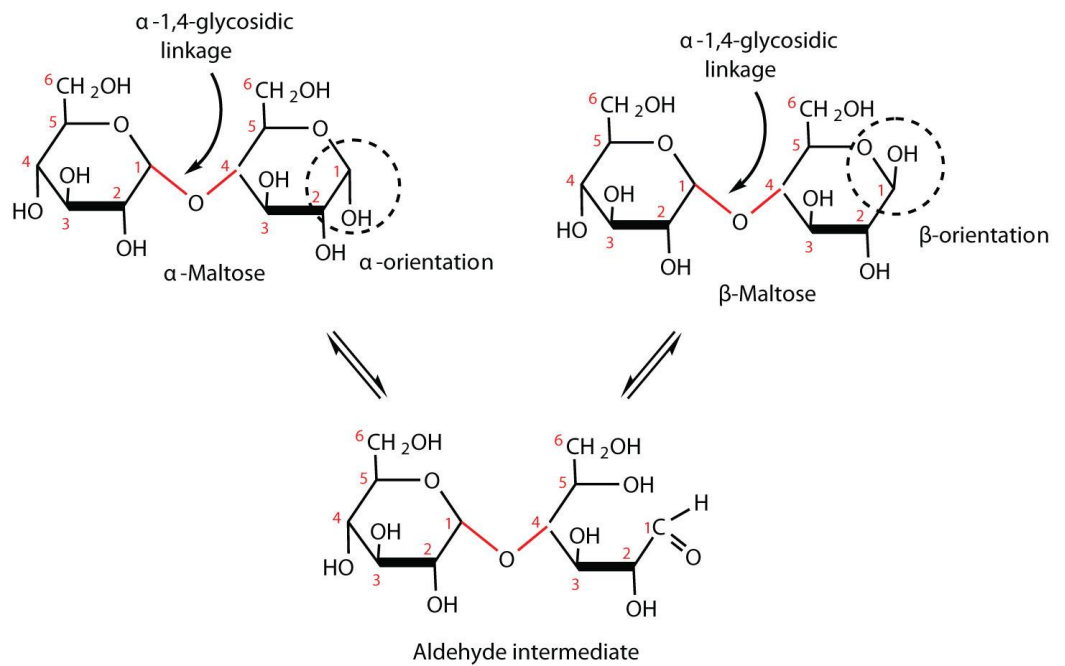


Sucrose: α - D - glucopyranosyl β - D -fructofuranoside



Trehalose: α - D – glucopyranosyl α - D –glucopyranoside

3.



Unit 5: OLIGOSACCHARIDES

Contents

- 5.1 Introduction
- 5.2 Intended Learning Outcomes (ILOs)
- 5.3 Main Contents
 - 5.3.1 Chemistry of Oligosaccharides
 - 5.3.2 Types of Oligosaccharides.
 - 5.3.3 Properties of Oligosaccharides.
 - 5.3.4 Functions of Oligosaccharides.
 - 5.3.5 Properties of Oligosaccharides (disaccharides)
- 5.4 Summary
- 5.5 References/Further Readings/Web Sources
- 5.6 Possible answers to Self-Assessment Exercises

5.1 Introduction

Oligosaccharides represent the third class of carbohydrates formed by the linkage of three to seven monosaccharide units joined by characteristics glycosidic bonds. Oligosaccharides therefore can be 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 molecular formula of an Oligosaccharide is $C_{37}H_{62}N_2O_{29}$. Oligosaccharides are commonly found in garlic, legumes, pear, white onion, and watermelon. For example, **Raffinose**, is a type of oligosaccharide that is formed by linkage of 3 molecules of monosaccharide, including fructose, gentianose, and melibiose.

5.2 Intended Learning Outcomes (ILOs)

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

- Understand the chemistry of Oligosaccharides
- Describe the different types of Oligosaccharides
- Draw the structure of different types of Oligosaccharides

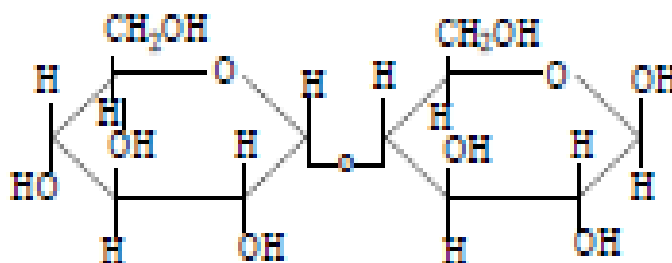
5.3 Main Contents

5.3.1 CHEMISTRY OF OLIGOSACCHARIDES

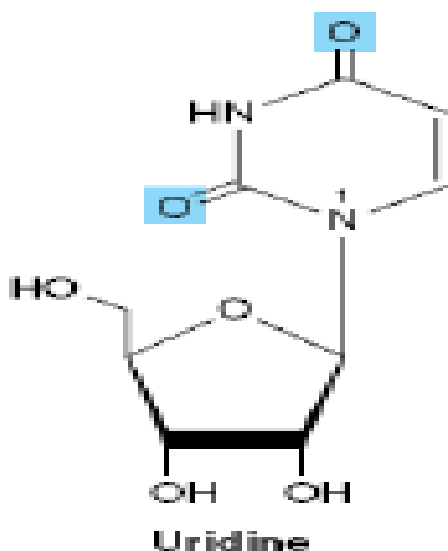
All common Oligosaccharides have their names ending with suffix – ose. In cells, most Oligosaccharides having three or more units do not occur as free entities but are joined to non-sugar molecules (lipids or protein) in

glycocojugates. Oligosaccharides are involved in different types of linkages, including *O* –glycosidic linkage and *N*-glycosidic linkage among others. The *O*-glycosidic linkage is more common in joining the monosaccharides unit together while *N*-glycosidic linkage usually links. Oligosaccharides therefore function as glycans that forms complexes with non-carbohydrate residues. There are two types of oligosaccharides: N-linked oligosaccharide, and O-linked oligosaccharide.

Oligosaccharides with non-carbohydrate residues like protein, lipid and nucleic acid, forming a glycoconjugates. 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. Examples of *O*–glycosidic and *N*-glycosidic linkages are presented below:



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



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.

5.3.2 TYPES OF OLIGOSACCHARIDES

Based on the number of monosaccharides present, oligosaccharides may be divided into following subclasses, among others:

Trisaccharides

Trisaccharides are a type of oligosaccharides formed by the three units of monosaccharides combined with two glycosidic linkages. Examples of Trisaccharides include raffinose, galactooligosaccharides, maltotriose, nigerotriose, melezitose, and maltotriose.

Raffinose is a trisaccharide that is made up of three monosaccharide units: glucose, fructose, and galactose. The chemical formula of Raffinose is $C_{18}H_{32}O_{16}$. Raffinose when hydrolyzed leads to the production of sucrose and D-galactose by the action of the galactosidase enzyme. Raffinose is usually found in whole grains, cabbage, legumes, broccoli, sprouts, beetroot molasses, asparagus, cottonseed, and many other foods.

Galactooligosaccharides are made up of galactose molecules. Typical example is the human milk oligosaccharides (HMOs). They are derived from lactose. 2'-fucosyllactose, i.e., a trisaccharide composed of fucose, galactose, and glucose accounts for 30% of all HMOs. They are particularly present in breast milk.

Tetrasaccharides

Tetrasaccharides are formed by linking four monosaccharides with each other. Some examples of tetrasaccharides are - maltotetraose, nigerotetraose, nystose, lychnose, and sesamose. Typically, Sesamose is made up of four monosaccharides; 2 galactose units, one fructose and one glucose unit.

Pentasaccharides

Polysaccharides are composed of five monosaccharides units. Most of the N-linked oligosaccharides are pentasaccharides. A typical example of pentasaccharides is verbascose, which is composed of three units of galactose, one unit of fructose and one unit of glucose.

Hexasaccharides: These are made up of six sugar units. What are Oligosaccharides? Highlight the subclasses of oligosaccharides

5.3.3 PROPERTIES OF OLIGOSACCHARIDES

- i. Like all other carbohydrates, oligosaccharides comprise hydrogen, carbon, and oxygen.
- ii. Since oligosaccharides contain carbon, C-C, and C-H bonds they are considered organic substances. Oligosaccharide consists of a long chain of saccharide units.

Glycosylation: A Glycosylation is a chemical reaction in which oligosaccharides, commonly referred to as glycans, gets combined with lipid, protein or with another molecule by the enzymatic action. There are two types of glycosylation processes: N-linked glycosylation and O-linked glycosylation. These two processes differ as per the type of atom attached with the glycan. For example, in the N-linked glycosylation process glycan makes a bond with nitrogen atoms in an arginine residue. While in the O-linked glycosylation process, O-linked glycans attach with hydroxyl oxygen of protein's serine, threonine, tyrosine, hydroxylysine, or hydroxyproline side chains. Other glycosylation processes include P-linked (where glycan connects with phosphorus), C-linked (where glycan connects with carbon), and S-linked (where glycan connects with sulphur). Particularly, the cell surface and extracellular proteins are most often O-glycosylated. In the N-linked oligosaccharides, the glycosylation site can be determined by secondary and tertiary structures of the protein molecules.

5.3.4 FUNCTIONS OF OLIGOSACCHARIDES

Among the various functions of oligosaccharides include the following:

Cell Recognition: Cells are either coated in glycoproteins or glycolipids. Both these help in determining the cell type. Oligosaccharides can be determined by the lectins or proteins which combine the carbohydrates. These proteins or lectins provide some information that can be used in cell recognition.

An example of an oligosaccharide when it acts as a cell recognition is blood type determining. All the types of blood are differentiated with the modification of glycan present on the blood cell surface. Blood types can be seen using mass spectrometry. There are three types of antigens in mass spectrometry - A, B, and H. The H antigen indicates an O blood type. All those oligosaccharides found on all three antigens (A, B, and H) take place on the non-reducing side of an oligosaccharide.

Cell Adhesion: Some cells produce carbohydrate-binding proteins known as lectins. These lectins mediate cell adhesion with oligosaccharides. Selectins (known as a family of lectins) mediate cell to cell adhesion. In the immune system, the endothelial cells can express some selections in response to the damage or injury to the cells.

Also, reciprocal selectin oligosaccharides interaction between the two molecules will take place that helps white blood cells to recover the infection or damage that happened. Also, Protein Carbohydrate bonding is arbitrated by hydrogen bonding and intermolecular force

5.3.5 PROPERTIES OF OLIGOSACCHARIDES (DISACCHARIDES)

- i. Oligosaccharides can be hydrolyzed by acids or other hydrolytic enzymes to their monomeric units.

- ii. Oligosaccharides units are held together by glycosidic linkages.
- iii. Oligosaccharides possess inherent cell recognition and cell-cell adhesion properties.

Self-Assessment Exercise(s)

1. List five examples each of (a) trisaccharides and (b) tetrasaccharides
2. What is the difference between the O-linked and N-linked glycosylation processes?
3. Why is blood type O known as a Universal donor?
4. Highlight some of the oligosaccharides that are found in our diet?

5.4 Summary

- Oligosaccharides represent the third class of carbohydrates.
- Oligosaccharides have *O*-glycosidic linkage joining their monosaccharide units together and *N* – glycosidic linkages links oligosaccharides to other glycoconjugates like proteins and nucleic acids.
- Oligosaccharides are polymers that contain very few numbers of monosaccharides units connected through glycosidic linkage.
- Most of the oligosaccharides are found in plants.
- Oligosaccharides can be divided into trisaccharides, tetrasaccharides and pentasaccharides.
- The main functions of oligosaccharides are cell recognition and cell adhesion.
- Among the examples of Oligosaccharides include Raffinose, Galactooligosaccharide and Fructooligosaccharide.

5.5 References/Further Readings/Web Sources

- 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
- <https://wou.edu/chemistry/files/2020/03/Carbohydrates-%E2%80%93-Part-4-Disaccharides-Oligosaccharides-and-Polysaccharides.pdf>
- <https://www.biologyonline.com/dictionary/oligosaccharide>

5.6 Possible answers to Self-Assessment Exercises

1.
 - (a) Examples of Trisaccharides: Raffinose, Galactooligosaccharides, Maltotriose, Migerotriose and Melezitose, and maltotriose
 - (b) Examples of tetrasaccharides; Maltotetraose, Nigerotetraose, Nystose, Lychnose, and Sesamose.

2. In the O-linked glycosylation process, O-linked glycans attach with hydroxyl oxygen of protein's serine, threonine, tyrosine, hydroxylysine, or hydroxyproline side chains. While in the N-linked glycosylation process, glycan makes a bond with nitrogen atoms in an arginine residue.

3. There are three types of antigens in mass spectrometry - A, B, and H. The presence of H-antigen indicates the blood type O in the human body. Thus the persons with any of the blood groups - A, B, AB, and O will have H-antigens. That is why blood type O is considered a universal donor.

4. Many oligosaccharides that have a high nutritional value are found in our diet. Some of them are:
 - (i) Fructo-oligosaccharides: This oligosaccharide is found in the fruits and vegetables of our daily diet.
 - (ii) Fructan-oligosaccharides: They are found in foods like banana, wheat, oats, garlic, onion, and many other foods.
 - (iii) Galacto-oligosaccharides: It is an important component of human milk important for infants' survival.
 - (iv)

Unit 6: POLYSACCHARIDES

Contents

- 6.1 Introduction
- 6.2 Intended Learning Outcomes (ILOs)
- 6.3 Types of Polysaccharides.
 - 6.3.1 Homopolysaccharides.
 - 6.3.1.1 Cellulose.
 - 6.3.1.2 Starch.
 - 6.3.2 Heteropolysaccharides.
 - 6.3.2.1 Pectin.
 - 6.3.2.2 Hyaluronic acid.
 - 6.3.2.3 Chondroitin
 - 6.3.3 Properties of Polysaccharide
- 6.4 Summary
- 6.5 References/Further Readings/Web Sources
- 6.6 Possible answers to Self-Assessment Exercises

6.1 Introduction

Most carbohydrates found in nature occur as polysaccharides. They represent the fourth class of carbohydrate types. 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 also in molecular weight and other structural features. Thus, while some polysaccharides are linear, some are highly branched. In this unit we are going to study the different types of polysaccharides, their chemical compositions and structures.

6.2 Intended Learning Outcomes (ILOs)

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

- Classification of polysaccharides into their various classes.
- Describe the chemical composition of each type of polysaccharide.
- Draw the structure of polysaccharides.

6.3 TYPES OF POLYSACCHARIDES

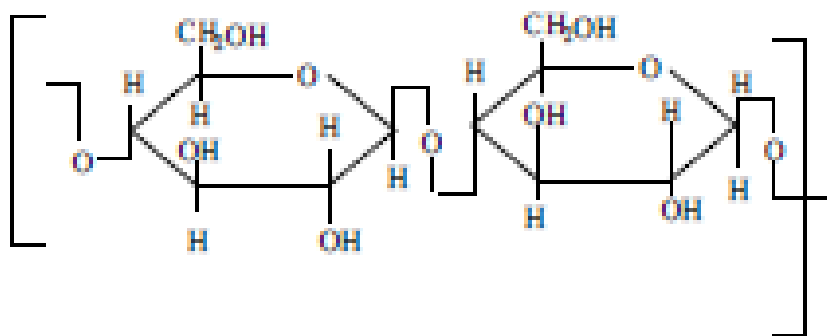
Although there are various indices that can be used in classifying polysaccharides, the most widely used index is the product of hydrolysis of the polysaccharides, whether they are similar in which case they are called homopolysaccharides or whether the products of hydrolysis are different in which case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

6.3.1 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.

6.3.1.1 CELLULOSE

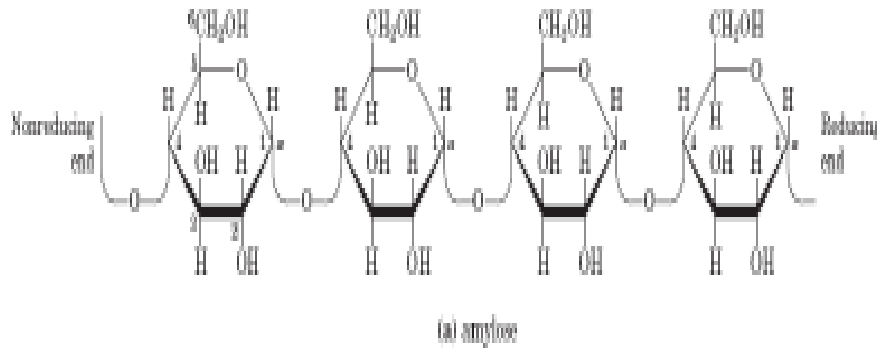
Cellulose is unquestionably the most abundant carbohydrate and the most abundant organic compound in the world, constituting 50% or more of all the carbon in vegetation. It is a linear homopolysaccharide composed of D-glucopyranose units linked by β (1-4) linkages. On partial hydrolysis of cellulose,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



Repeating cellobiose unit of cellulose

6.3.1.2 STARCH

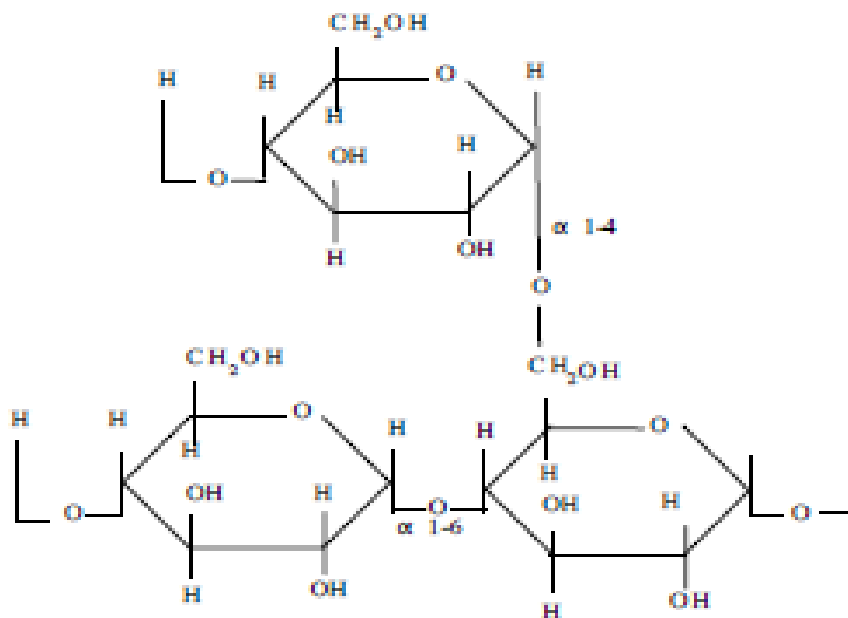
Starch is a polymer of glucose units linked in α 1 – 4 linkages. It serves as nutritional reservoir in plants. The repeating disaccharide unit in starch therefore is maltose.



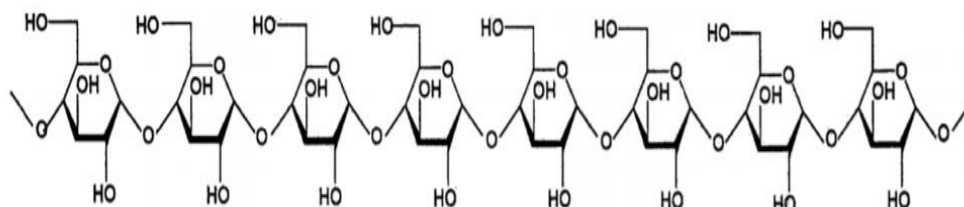
Repeating unit of Starch (Amylose Unit) containing two Maltose Units.

Source: *Lehninger's Principles of Biochemistry*.

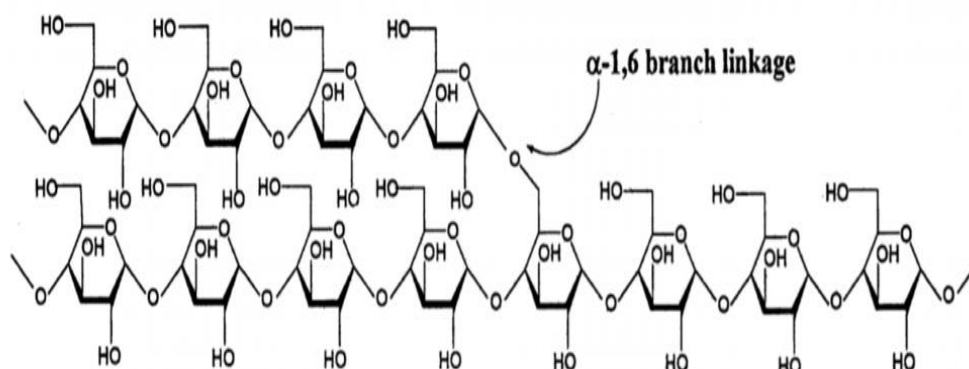
Native starches are a mixture of two compounds that are separable from each other, Amylose and Amylopectin. Amylose is a component that is believed to be a long unbranched chain of glucose joined together by α 1-4 bonds and amylopectin which is a branched chain polysaccharide. The glucose residue that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



Repeating Unit of Starch (Amylopectin Unit)



Segment of an amylose molecule



Segment of an amylopectin molecule, showing one α -1,6 branch linkage

Source: Singh A. (2021). Biomolecules, Science: Polysaccharides: Properties, Functions, and Application. <https://conductscience.com/polysaccharides-properties-functions-and-applications>

3.1.2 GLYCOGEN

Glycogen is another homopolysaccharide of glucose. It is also a storage polysaccharides 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 1- and α 6- amylases to yield glucose, maltose and limit dextrins. The homopolysaccharides are presented below

Homopolysaccharide	Sugar component	Linkage	Function	Sources
Cellulose	Glucose	β , 1 \rightarrow 4	structural	throughout kingdom
Amylose	Glucose	α , 1 \rightarrow 4	food storage	starches, e corn, potatoes, r

Chitin	N-acetylglucosamine	$\beta, 1 \rightarrow 4$	structural	insect and crustacean skeleton
Inulin	Fructose	$\beta, 2 \rightarrow 1$	food storage	artichokes, chicory
Xylan	Xylose	$\beta, 1 \rightarrow 4$	structural	all land plants
Glycogen	Glucose	$\alpha, 1 \rightarrow 4, 6 \leftarrow 1, \alpha$	food storage	liver and muscle cells of all animals
Amylopectin	Glucose	$\alpha, 1 \rightarrow 4, 6 \leftarrow 1, \alpha$	food storage	starches, especially corn, potatoes, rice
Dextran	Glucose	$\alpha, 1 \rightarrow 6, 4 \leftarrow 1, \alpha$	unknown	primarily bacterial

6.3.2 HETEROPOLYSACCHARIDES

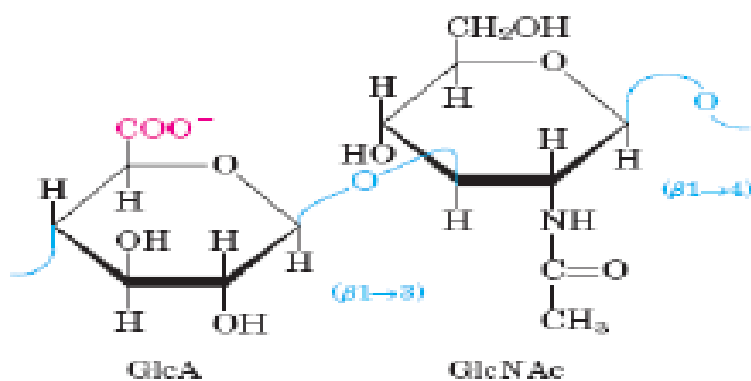
These are class of carbohydrate composed of repeating monomeric unit that are different. Many types of heteropolysaccharides do exist.

6.3.2.1 PECTINS

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

6.3.2.2 HYALURONIC ACID

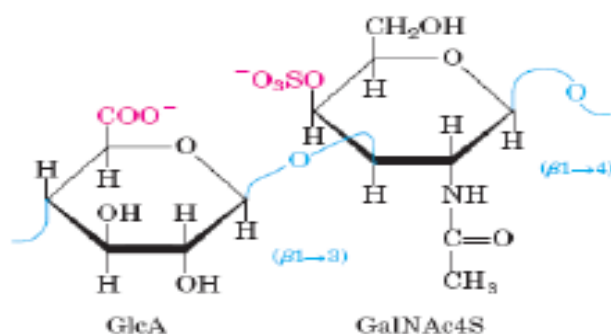
This is a heteropolysaccharide consisting of repeating units of D-glucuronic acid and N-acetyl D glucosamine. The monosaccharides are linked together by $\beta 1 - 3$) bonds to form a disaccharides which is linked by $\beta 1 - 4$) bond to the next repeating unit. It is soluble in water and form viscous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



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

6.3.2.3 CHONDROITIN

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

Examples of some heteropolysaccharides are listed below

Heteropolysaccharide	Component sugars	Functions	Distribution
hyaluronic acid	D-glucuronic acid and <i>N</i> -acetyl-D-glucosamine	lubricant, shock absorber, water binding	connective tissue, skin
chondroitin-4-sulfate	D-glucuronic acid and <i>N</i> -acetyl-D-galactosamine-4- <i>O</i> -sulfate	calcium accumulation, cartilage and bone formation	cartilage
Heparin	D-glucuronic acid, <i>L</i> -iduronic acid, <i>N</i> -sulfo-D-glucosamine	Anticoagulant	mast cells, blood
gamma globulin	<i>N</i> -acetyl-hexosamine, D-	Antibody	blood

blood substance	group	mannose, D- galactose	blood group specificity	cell surfaces, especially red blood cells
		D-glucosamine, D-galactosamine, L-fucose, D- galactose		

What are polysaccharides? How are polysaccharides classified?

Self-Assessment Exercise(s)

1. List the (a) properties (b) functions and (c) applications of starch
2. What are Glycosaminoglycans? Highlight the (a) properties, (b) functions, and (c) applications of Glycosaminoglycans
3. What is peptidoglycan? State the (a) properties and (b) functions of peptidoglycan

6.3.3 Properties of Polysaccharides

Among the properties of polysaccharides include the following:

1. They usually do not have sweet taste.
2. Most polysaccharides are insoluble in water.
3. They are usually hydrophobic in nature.
4. They do not form crystals on desiccation.
5. They can be extracted to form a white powder.
6. They are high molecular weight carbohydrates.
7. Within the cells, they are compact and osmotically inactive.
8. Chemically, they consist of hydrogen, carbon, and oxygen; and the hydrogen to oxygen ratio being 2:1

6.4 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, chondiotin sulfate e.,t.c.

6.5 References/Further Readings/Web Sources

- Devlin, T. (1986). Textbook of Biochemistry with Clinical Correlations.(2nd Edition) John Wiley and sons New York
- 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.
- Robyt, J. F. (2008). Starch: Structure, Properties, Chemistry, and Enzymology. Glycoscience, 1437–1472. doi:10.1007/978-3-540-30429-6_35
- Singh A. (2021). [Biomolecules](#), [Science](#): Polysaccharides: Properties, Functions, and Application.
- Yadav, H., & Karthikeyan, C. (2019). Natural polysaccharides: Structural features and properties. Polysaccharide Carriers for Drug Delivery, 1–17. doi:10.1016/b978-0-08-102553-6.00001-5
- White A.,Handler P.,Smith E.,L., Hill R.,L., Lehman R.I.(1978). Principles of Biochemistry (6th.edition)Mc Graw Hill, Kogakusha.
- <https://conductscience.com/polysaccharides-properties-functions-and-applications/>
- <https://biologydictionary.net/polysaccharide/>
- <https://www.biologyonline.com/dictionary/polysaccharide>

6.6 Possible answers to Self-Assessment Exercises

1.

(a) Properties

- i. Starch is a white tasteless powder that's insoluble in cold water, alcohol, or other solvents.
- ii. The basic formula to deduce starch is $(C_6H_{10}O_5)_n$, where n is the number of glucose molecules in the chain.
- iii. The breakdown of starch by dry heat forms pyrodextrins which are responsible for the browning of bread.

(b) Functions

- i. In plants, starch serves as a reserve for food supply.
- ii. In humans and animals, starch is broken down by amylase into its sugar molecules, which act as a reserve of energy supply.

(c) Applications

- i. Starch is used in paper industries for the strengthening and surface sizing of paper.
- ii. It's used in brewing industries.
- iii. Starch is used in kitchens for nutritional purposes or as thickening agents in baked foods.
- iv. Starch is used to manufacture paperboard, paper bags, paper boxes, gummed paper, and tape.
- v. Corn starch is used as a lubricant in surgical gloves.

2. Glycosaminoglycans, abbreviated GAGs, are negatively charged unbranched heteropolysaccharides, composed of repeating units of disaccharides that include acidic and amino sugars. The amino sugar in GAGs is either N-acetylglucosamine or N-acetylgalactosamine, and the acidic sugar is usually a uronic acid (like glucuronic acid). GAGs are found in animals and bacteria but are absent in plants.

(a) Properties

- i. It's composed of amino sugar and uronic acids.
- ii. Except for hyaluronic acids, all GAGs are sulfated, either as O-esters or N-sulfate.
- iii. Except for hyaluronic acids, all GAGs are covalently attached to some proteins forming proteoglycans.
- iv. The sulfate groups present on the surface of glycosaminoglycans make them negatively charged. The charged compound creates an osmotic pressure that causes the tissue to imbibe water and swell. This enhances the tissue's ability to bear the load.

(b) Functions

- i. Hyaluronic acids are an essential component of the vitreous humor in the eye and synovial fluid (a lubricant fluid, present in the joints of the body). It is also involved in other developmental processes like tumor metastasis, angiogenesis, and blood coagulation.

- ii. Heparin acts as a natural anticoagulant that prevents blood from clotting.
- iii. Keratan sulfate is present in the cornea, cartilage, and bones. In joints, it acts as a cushion to absorb mechanical shocks.
- iv. Chondroitin is an essential component of cartilage that provides resistance against compression.
- v. Dermatan sulfate is involved in wound repair, blood coagulation regulation, infection responses, and cardiovascular diseases.
- (c) **Applications**
 - i. Chondroitin sulfate is used in alternative medicine as dietary supplements to treat osteoarthritis.
 - ii. Heparin is a major drug to treat diseases like venous thromboembolism (VTE) and atherothrombotic syndromes.
 - iii. Hyaluronic acid has been shown to decrease the inflammation related to cystic fibrosis in mice models.
 - iv. Chondroitin sulfate and heparin are considered promising molecules in antitumor therapeutics.

3. Peptidoglycan is a heteropolymer of alternating units of N-acetylglucosamine (NAG) and N-acetylmuramic acids (NAM), linked together by beta-1,4-glycosidic linkage

(a) **Properties**

- i. It is degraded by an enzyme, lysozyme, that causes the hydrolysis of beta-1,4-linkage between N-acetylglucosamine (NAG) and N-acetylmuramic acids (NAM).
- ii. The production of peptidoglycans can be interfered with by using penicillin.
- iii. N-Acetylmuramoyl-L-alanine amidases are enzymes that cause the hydrolysis of peptidoglycans and the dissolution of their structure.

(b) **Functions**

- i. It is an essential component of bacterial cell walls. It provides strength to the cell wall and participates in binary fission during bacterial reproduction.
- ii. It also protects bacterial cells from bursting by counteracting the osmotic pressure of the cytoplasm.

GLOSSARY

Hemiacetal : an alcohol and ether attached to the same carbon.

C-4: Carbon number 4

D- Dextrorotary- rotating the plane of polarization of light to the right (turning toward the right or counterclockwise)

L-Levorotary - rotating the plane of polarization of light to the left (turning toward the left or counterclockwise)

End of module Questions

1. A phenomenon where α and β anomers of D-glucose interconvert in aqueous solution is known as _____
2. What is the name of the disaccharide formed due to the on partial hydrolysis of cellulose?
3. Give the name of the alcohol sugar formed when glucose is reduced by hydrogen in the presence of a metal catalyst

Module 2: LIPIDS **Module Title**

Module Introduction

Introduce the module and state the units under the module.

Unit 1:	CHEMISTRY OF LIPIDS
Unit 2:	CLASSIFICATION OF LIPIDS
Unit 3:	PROPERTIES & METHOD OF ANALYSIS OF LIPIDS
Unit 4:	LIPOPROTEINS LIPOPROTEINS
Unit 5:	MEMBRANES AND MEMBRANE

Unit 1: CHEMISTRY OF LIPIDS

Contents

- 1.1 Introduction
- 1.2 Intended Learning Outcomes (ILOs)
- 1.3 Main Content
 - 1.3.1 Classification of Fatty acids.
 - 1.3.2 Properties of fatty acids and lipids.
 - 1.3.2.1 Physical property of Fatty acids.
 - 1.3.2.2 Chemical property of Lipids.
 - 1.3.3 Nomenclature of fatty acids.
- 1.4 Summary
- 1.5 References/Further Readings/Web Sources
- 1.6 Possible answers to Self-Assessment Exercises

1.1 Introduction

Lipids can be defined as organic compounds that contain hydrogen, carbon, and oxygen atoms. They are a group of chemically heterogeneous compounds with a common property of insolubility in polar solvents such as water, but solubility in non-polar (organic) solvents such as chloroform, hydrocarbon or alcohols. Lipids are usually fatty, oily, waxy 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.

1.2 Intended Learning Outcomes (ILOs)

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

- 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.

1.3 Main Content

1.3.1 Chemical Composition of Lipids

Chemically, lipids are predominantly made up of glycerols and fatty acids; with fatty acids as their major building blocks. However, the proportion of glycerols and fatty acids, and the overall chemical composition of lipids differs with the type, nature and complexity of the lipids. Depending on the type and complexity, some lipids contain other non-polar compounds like cholesterol and its derivatives, and polar compounds like alcohols, nitrogenous bases and phosphate groups, among others.

1.3.2 Classification of Fatty Acids

Fatty acids, being the major chemical composition in most lipids, are long chain organic acids (carboxylic acids). Being monocarboxylic hydrocarbons, they contain 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. Basically, there are several ways of classifying fatty acids.

Based on the chemistry point of view, fatty acids are classified based on the characteristics of the carbon chains as follows:

- The presence or absence of double bonds within the hydrocarbon chain, as saturated and unsaturated fatty acids. **Saturated fatty acids** are those fatty acids without double bond within the hydrocarbon chains, example include palmitic acid. Examples of major saturated fatty acids are listed in the Table below:



A saturated fatty acid (palmitic acid, C16)

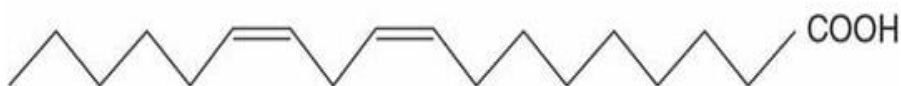
Major saturated fatty acids and their structures

S. No.	Name of fatty acids	Structure
1.	Butyric acid	$\text{CH}_3(\text{CH}_2)_2\text{COOH}$
2.	Caproic acid	$\text{CH}_3(\text{CH}_2)_4\text{COOH}$
3.	Caprylic acid	$\text{CH}_3(\text{CH}_2)_6\text{COOH}$
4.	Capric acid	$\text{CH}_3(\text{CH}_2)_8\text{COOH}$
5.	Lauric acid	$\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$
6.	Myristic acid	$\text{CH}_3(\text{CH}_2)_{12}\text{COOH}$
7.	Palmitic acid	$\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$
8.	Stearic acid	$\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$

Unsaturated fatty acids are those with double bonds within their hydrocarbon chains. Depending on the number of double bonds, the unsaturated fatty acids can further be classified into **monounsaturated fatty acids** (when there is only one double within the hydrocarbon chain, and **polyunsaturated fatty acids – PUFAs** (when there is more than one double within the hydrocarbon chain). Moreover, the unsaturated fatty acids can further be classified based on the position of the first double bond from the terminal methyl end of the chain into (a) **Omega-3 PUFAs** :- where the first double bond is three carbon atoms from the methyl end, including alpha-linolenic acid, stearidonic acid, eicosapentaenoic acid (EPA), and docosahexaenoic acid (DHA); (b) **Omega-6 PUFAs** :-, where the first double bond is six carbon atoms from the methyl end, including linoleic acid, gamma-linolenic acid, dihomo-gamma-linolenic acid, arachidonic acid (ARA), and adrenic acid; (c) **Omega-7 fatty acids** :- where the first double bond is seven carbon atoms from the methyl end (as in palmitoleic acid), and (d) **Omega-9 fatty acids** : - where the first double bond is nine carbon atoms from the methyl end (as in oleic acid, erucic acid, nervonic acid and mead acid); (e) **Omega-11 fatty acid** :- where the first double bond is eleven carbon atoms from the methyl end (as in gadoleic acid).



A monounsaturated fatty acid (oleic acid, C18:1)



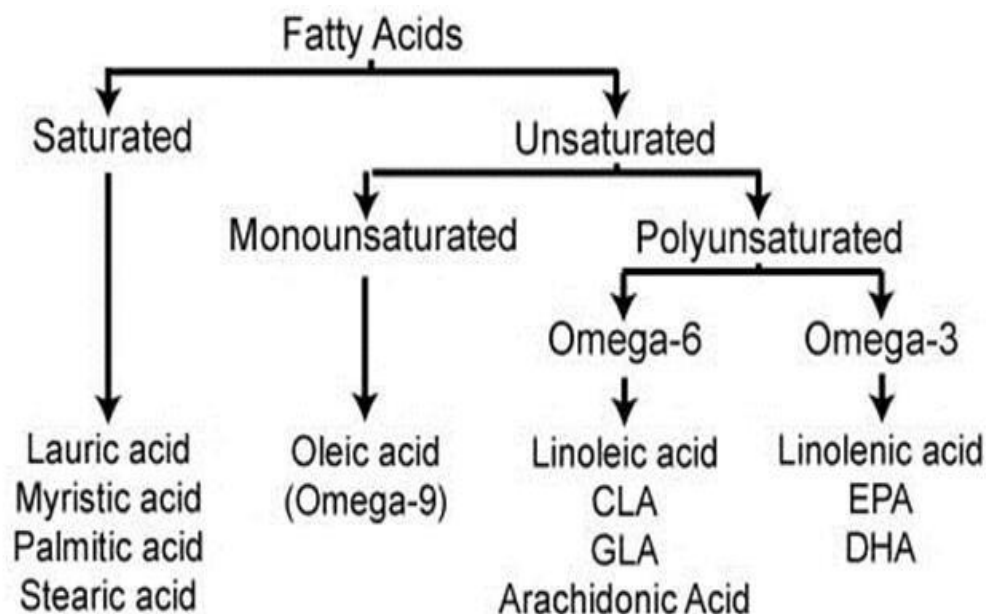
A polyunsaturated fatty acid (linoleic acid, C18:2)

(i) The length of the hydrocarbon chain as **short-chain fatty acids** (those with chain length of 2 to 5 carbons), **medium-chain fatty acids** (those with chain length of 6 to 12 carbons), **long-chain fatty acids** (those with chain length of 13 to 21 carbons) and **very long chain fatty acids** (those with chain length equal or greater than 22 carbons).

(ii) Nutritionally, fatty acids can be classified based on their essentiality of their requirement in humans' diet into Essential and Non-Essential fatty acids. **Essential fatty acids** are those that cannot be synthesized in the body to meet the biochemical and physiological requirements, and hence must of necessity be supplied through dietary source. Examples of essential fatty acids include linoleic and linolenic acids. While linoleic acid is a precursor of Omega-6 arachidonic acid, α -linolenic acid is a precursor of Omega-3 fatty acid. On the other hand, the **Non-Essential fatty acids** are those that can be synthesized in the body, and hence are not necessarily required in the diets.

(iii) Finally, fatty acids can also be classified based on the following criteria: (a) whether they contain even or odd number of carbon atoms, (b) the presence or absence of branches or cyclic structures.

The summary of the various classes of fatty acids are presented in the flow charts and Table below:



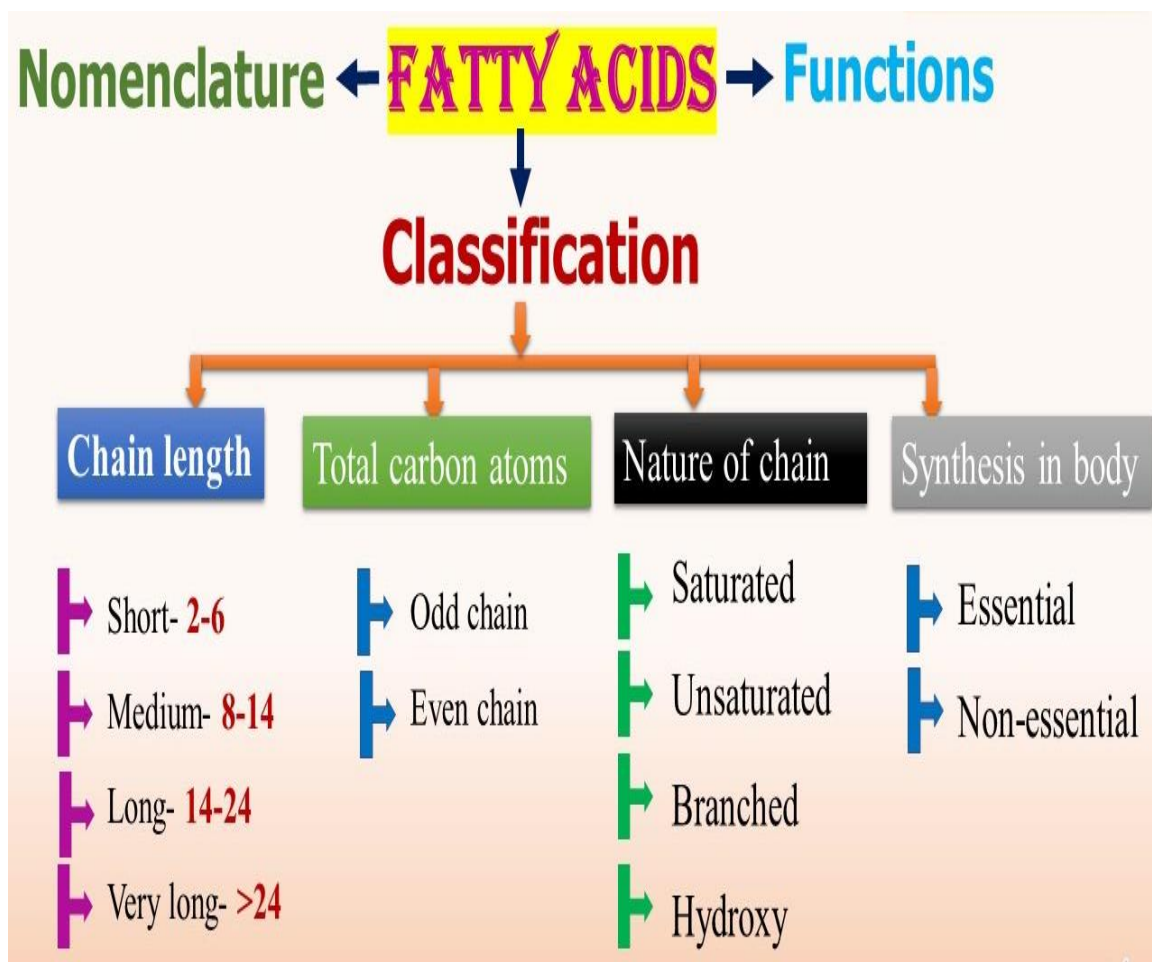


Table 1.0 shows some naturally occurring fatty acids

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		

Source: Lehninger's's Principles of Biochemistry.

1.3.3 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.

1.3.2.1 Physical Properties of Fatty Acids and Fats.

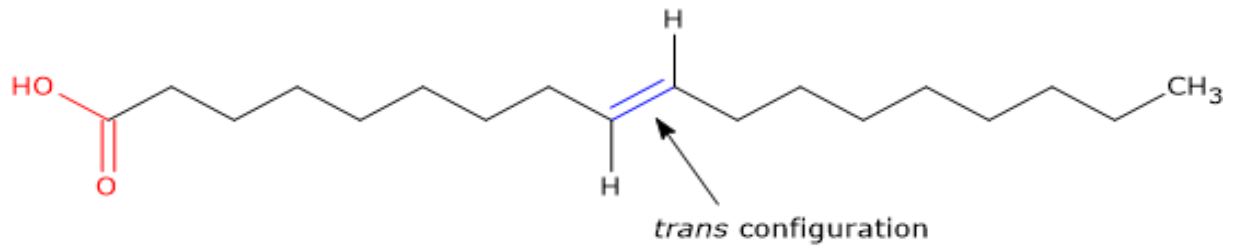
Physical properties of fatty acids are largely determined by the length of the fatty acid and the degree of unsaturation of the hydrocarbon chain.

1. Fats and fatty acids are soluble in organic solvents, such as petroleum ether, benzene and chloroform; and insoluble in water. 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.

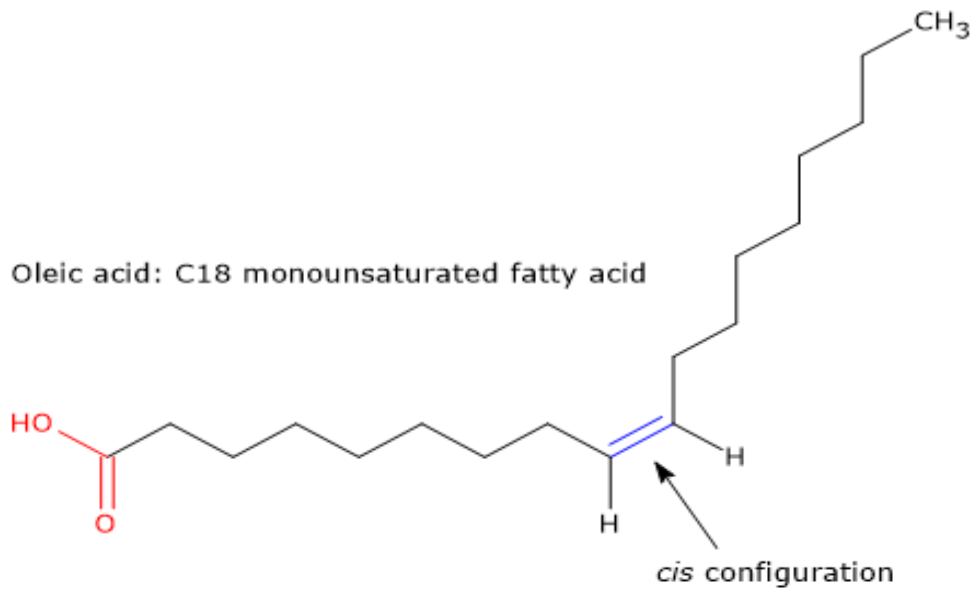
2. Fats and saturated fatty acids require high temperature for melting, whereas unsaturated fatty acids require relatively lower temperature for its melting. The melting points to a greater extent are influenced by the length and the degree of unsaturation of hydrocarbon chain. At room temperature (25°C), the saturated fatty acids from 12 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 deference 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. Isomerism- The presence of double bonds in the fatty acid chain results in the existence of isomers. Cis isomers are common in nature but unstable, while trans isomers are less common but more stable. Most fatty acids in our body are of the cis type. Trans fatty acids are common in the triglycerides of dairy and meat products, and in partially hydrogenated oils. Saturated fatty acids like stearic acid, and unsaturated fatty acids with trans bonds, have linear shapes but the presence of a cis double bond bends the shape of the molecule. The trans and cis configurations in fatty acids are illustrated below:

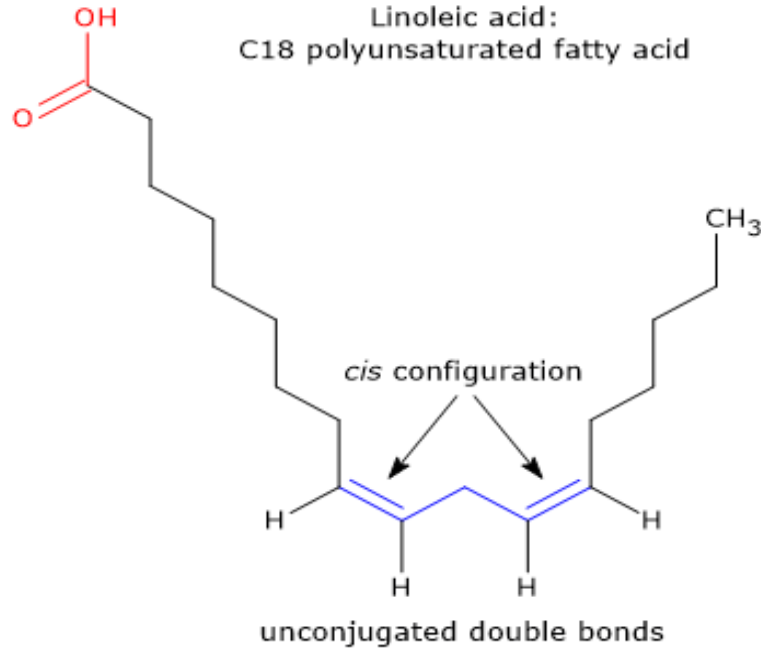
Elaidic acid: C18 monounsaturated fatty acid



Oleic acid: C18 monounsaturated fatty acid



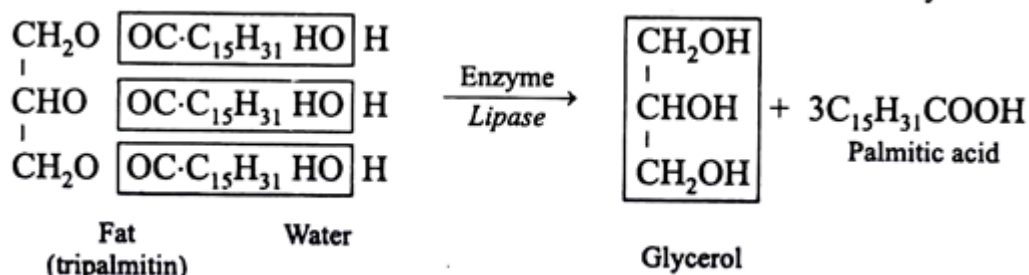
Linoleic acid:
C18 polyunsaturated fatty acid



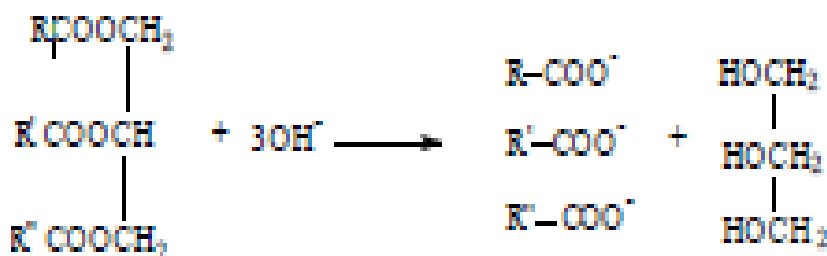
4. Fats and saturated fatty acids are solid at room temperature, while unsaturated fatty acids are liquid.
5. Fats and fatty acids are bad conductors of heat.

1.3.2.2 Chemical Properties of Fats.

1. Hydrolysis: Fats undergo hydrolysis when treated with mineral acids, the alkalis or fat splitting enzyme lipase or hydrolases to yield glycerol and the constituent fatty acids.

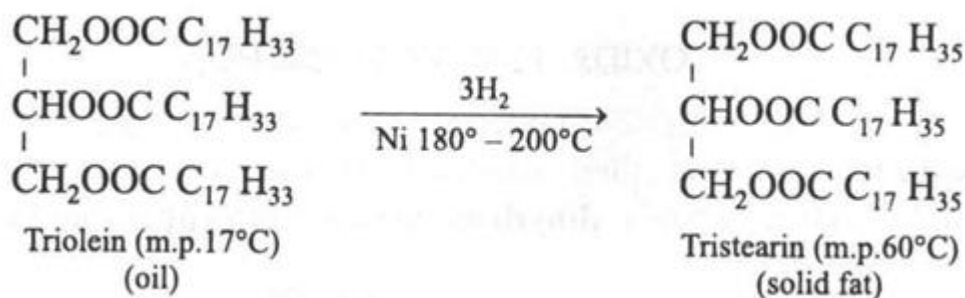


Alkaline (using NaOH or KOH) hydrolysis of lipids is called saponification. The reaction is irreversible and therefore the carboxylate ions combine with sodium (Na) or potassium (K) salt of the alkali to form soap. Saponification of lipids is measured by its saponification value which is the number of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

2. Hydrogenation: Oils containing unsaturated fatty acids can be hydrogenated in presence of high temperature, pressure and finely divided nickel. By this process the oils are converted into solid fats (glycerides of saturated fatty acids). This reaction forms the basis of the industrial production of hydrogenated oil (vegetable ghee).



3. Hydrogenolysis: Oils and fats are converted into glycerol and a long chain aliphatic alcohol when excess of hydrogen is passed through them under pressure and in presence of copper-chromium catalyst. This splitting of fat by hydrogen is called hydrogenolysis.

4. Halogenation: When unsaturated fatty acids are treated with halogens, such as iodine and chlorine, they take up iodine or other halogens at their double bond site. This process of taking of iodine is called halogenation which is an indication of unsaturation. Iodine number is the percentage of iodine absorbed by a fat.

5. Rancidity: Oils and fats on long storage in contact with heat, light, air and moisture, develop an unpleasant odour. Such oils and fats are known as rancid oils and fats. The rancidity develops due to certain chemical changes taking place in the fat. These changes include:

- (i) Enzymatic hydrolysis,
- (ii) Air oxidation of unsaturated fatty acids, and
- (iii) β - oxidation of saturated fatty acids.

To prevent rancidity, it is necessary to protect oils and fats from air, light and moisture during storage.

6. Emulsification: The process of breaking of large-sized fat molecules into smaller ones is called emulsification. In animals, this process is brought about by bile juice liberated from liver. Other emulsifying agents are water, soaps, proteins and gums.

7. 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.

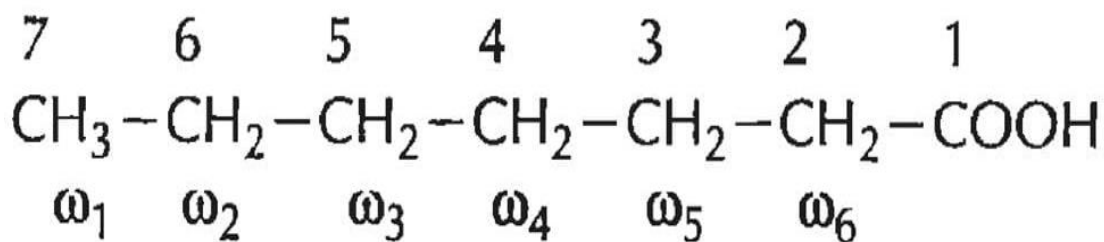
8. Iodine Value: Iodine value is another property of lipids which is defined as the number of grams of iodine absorbed by 100g of lipid. A molecule of iodine adds across each double bond of the unsaturated fatty acid. Iodine value gives a measure of the degree of unsaturation of a lipid.

1.3.3 Nomenclature of Fatty Acids

The general rule in the nomenclature of fatty acids considers the number of carbon atoms, then the number of double bonds if any and finally the position of the double bonds counting from -COOH carbon as carbon number 1. Below is a highlight of the summary of the general rules in the nomenclature of fatty acids:

- i. The systematic nomenclature of the fatty acid is based on the hydrocarbon it is derived from.
- ii. The names of the saturated fatty acids end with a suffix **-anoic** (e.g., octanoic acid), while the names of unsaturated fatty acids end with a suffix **-enoic** (e.g., octadecenoic acid).
- iii. The numbering of carbon atoms begins from its carboxyl carbon, hence the carboxy carbon is given the number 1. Adjacent carbon atoms are numbered 2, 3, 4 so on. The second, third, and fourth carbons are also referred to as α , β , and γ .

iv. The terminal carbon atom on the other end containing the methyl group is referred to as Omega (ω) carbon. Carbon atoms are alternatively numbered from the ω carbon side as ω_1 , ω_2 , ω_3 , ω_4 , etc.



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, $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$, a monounsaturated fatty acid is written as 18: 1 (9) which means the fatty acid has 18 carbon atoms and one double bond on carbon atom number 9. The notation () simple mean carbon atom number. For polyunsaturated fatty acid (PUFA) arachidonic acid, its nomenclature is written as 20:4 (5,8,11,14), meaning that it is 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. Define lipids. Highlight some important characteristics of Lipids.

Self-Assessment Exercise(s)

1. What are the major constituents of neutral fats?
2. Highlight any five biological importance of lipids
3. Highlight of the summary of the general rules in the nomenclature of fatty acids.
4. Discuss the chemical Properties of Fats
5. Draw the structure of any two (2) named unsaturated fatty acids.

1.4 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

1.5 References/Further Readings/Web Sources

- 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
- <https://conductscience.com/classification-and-biological-functions-of-lipids/>
- <https://byjus.com/biology/lipids/>
- <https://microbenotes.com/lipids-properties-structure-classification-and-functions/>

1.6 Possible answers to Self-Assessment Exercises

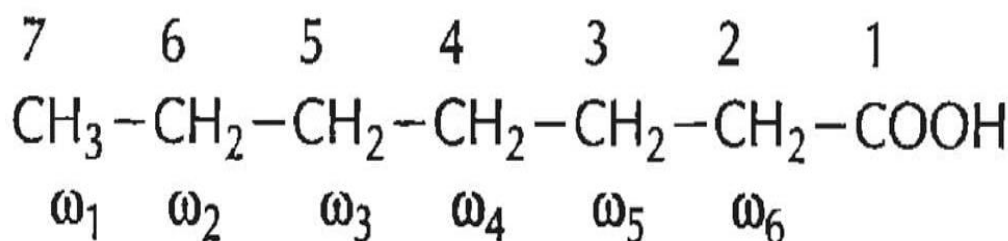
1. Neutral fats are made up of a glycerol molecule attached to three fatty acid molecules, and they are referred to as triacylglycerols.

2.

- i. Lipids serve as a source of energy in the body, producing twice the amount of energy generated by same weight of carbohydrates and proteins.
- ii. Lipids serve as natural solvent for fat soluble vitamins.
- iii. Lipids serve as pads, providing protection and shock absorbing functions to the internal organs such as kidneys.
- iv. Lipids serve as thermal insulators under the skin
- v. Lipids in the myelin sheath of the nerve fibers serve as electrical insulator.

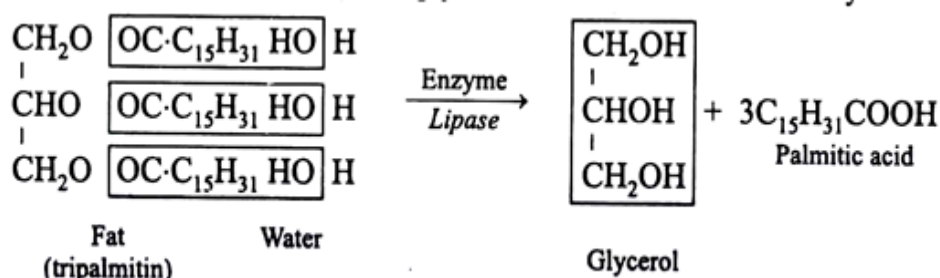
3.

- i. The systematic nomenclature of the fatty acid is based on the hydrocarbon it is derived from.
- ii. The names of the saturated fatty acids end with a suffix **-anoic** (e.g., octanoic acid), while the names of unsaturated fatty acids end with a suffix **-enoic** (e.g., octadecenoic acid).
- iii. The numbering of carbon atoms begins from its carboxyl carbon, hence the carboxy carbon is given the number 1. Adjacent carbon atoms are numbered 2, 3, 4 so on. The second, third, and fourth carbons are also referred to as α , β , and γ .
- iv. The terminal carbon atom on the other end containing the methyl group is referred to as Omega (ω) carbon. Carbon atoms are alternatively numbered from the ω carbon side as ω_1 , ω_2 , ω_3 , ω_4 , etc.

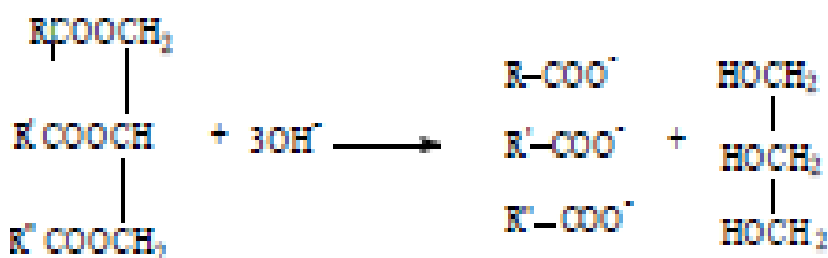


4.

a. Hydrolysis: Fats undergo hydrolysis when treated with mineral acids, the alkalies or fat splitting enzyme lipase or hydrolases to yield glycerol and the constituent fatty acids.

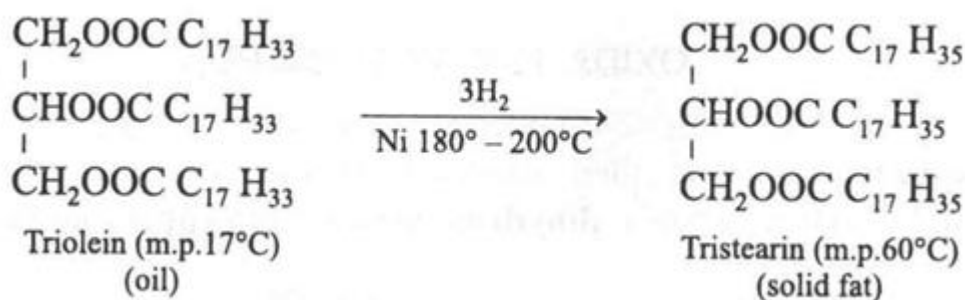


Alkaline (using NaOH or KOH) hydrolysis of lipids is called saponification. The reaction is irreversible and therefore the carboxylate ions combine with sodium (Na) or potassium (K) salt of the alkali to form soap. Saponification of lipids is measured by its saponification value which is the number of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

b. Hydrogenation: Oils containing unsaturated fatty acids can be hydrogenated in presence of high temperature, pressure and finely divided nickel. By this process the oils are converted into solid fats (glycerides of saturated fatty acids). This reaction forms the basis of the industrial production of hydrogenated oil (vegetable ghee).



c. Hydrogenolysis: Oils and fats are converted into glycerol and a long chain aliphatic alcohol when excess of hydrogen is passed through them under pressure and in presence of copper-chromium catalyst. This splitting of fat by hydrogen is called hydrogenolysis.

d. Halogenation: When unsaturated fatty acids are treated with halogens, such as iodine and chlorine, they take up iodine or other halogens at their double bond site. This process of taking of iodine is called halogenation which is an indication of unsaturation. Iodine number is the percentage of iodine absorbed by a fat.

e. Rancidity: Oils and fats on long storage in contact with heat, light, air and moisture, develop an unpleasant odour. Such oils and fats are known as rancid oils and fats. The rancidity develops due to certain chemical changes taking place in the fat. These changes include:

- (i) Enzymatic hydrolysis,
- (ii) Air oxidation of unsaturated fatty acids, and
- (iii) β - oxidation of saturated fatty acids.

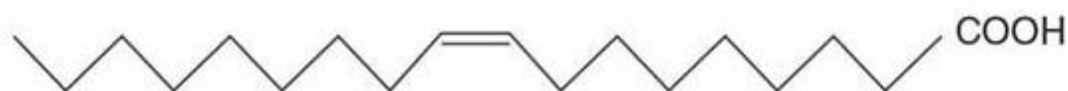
To prevent rancidity, it is necessary to protect oils and fats from air, light and moisture during storage.

f. Emulsification: The process of breaking of large-sized fat molecules into smaller ones is called emulsification. In animals, this process is brought about by bile juice liberated from liver. Other emulsifying agents are water, soaps, proteins and gums.

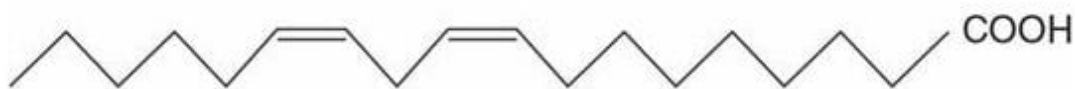
g. Acid Value: The acid value of fat can be defined as the number of milligram of KOH required to neutralize the free fatty acids present in 1 gram of fat. Each lipid sample has a characteristic acid value which is defined by the number of and type of fatty acid contained in it.

h. 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.

5.



A monounsaturated fatty acid (oleic acid, C18:1)



A polyunsaturated fatty acid (linoleic acid, C18:2)

Unit 2: CLASSIFICATION OF LIPIDS

Contents

- 2.1 Introduction
- 2.2 Intended Learning Outcomes (ILOs)
- 2.3 Classification of lipids.
 - 2.3.1 Acylglycerols .
 - 2.3.2 Phosphoacylglycerols.
 - 2.3.3 Sphingolipids.
 - 2.3.4 Sphingomyelins.
 - 2.3.5 Glycosphingolipids.
 - 2.3.6 Gangliosides.
 - 2.3.7 Waxes.
 - 2.3.8 Steroids.
 - 2.3.9 Terpenes
- 2.4 Summary
- 2.5 References/Further Readings/Web Sources
- 2.6 Possible answers to Self-Assessment Exercises

2.1 Introduction

Lipids have been classified and sub classified 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.

2.2 Intended Learning Outcomes (ILOs)

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

- Describe the various classes of lipids.
- Draw the structures of lipids of various classes.

2.3 CLASSIFICATION OF LIPIDS

Lipids are classified based on different criteria, including their chemistry and chemical reaction. On the basis of chemistry or chemical composition, lipids are broadly classified into three classes: simple, compound or complex, and derived lipids. Whereas, lipids are classified into saponifiable and non-saponifiable lipids.

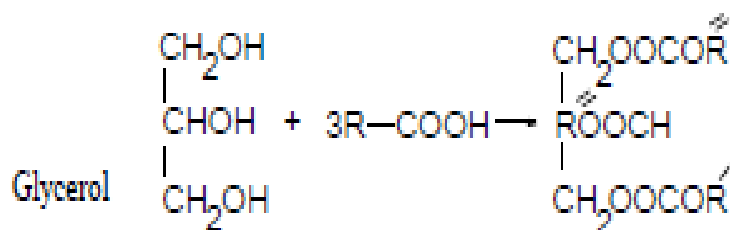
Lipids have been broadly classified into saponifiable and non saponifiable lipids. Saponifiable lipids are those lipids that yield salt of fatty acids upon alkaline hydrolysis while non saponifiable lipids are not usually subjected

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.

2.3.1 Simple Lipids

These are esters of fatty acids with glycerol or higher alcohols, with Acylglycerols (fats) and Waxes as typical examples.

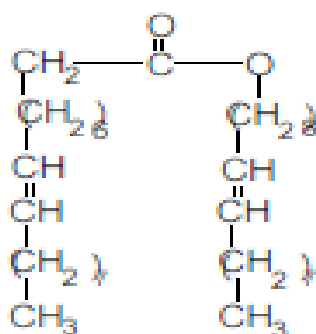
Acylglycerols: These are the most abundant and widespread of all lipids, they are also called neutral lipids. Acylglycerols are compounds in which one or more of the three hydroxyl groups (OH) is esterified to fatty acids. Acylglycerols can either be mono when only one –OH group is esterified, diacylglycerol 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 those fatty acids contained in it.

Waxes: These are esters of long chain alcohols with long-chain fatty acids. They can also be defined as a class of saponifiable lipids with esters of long chain fatty acids (14 – 36 Carbon atoms) and long chain monohydric alcohols (16 – 22 atoms). Basically, the molecule of wax has a weakly polar head (the ester moiety itself) and a long, non-polar tail (the hydrocarbon chain). The fatty acids found in waxes are usually saturated, while the alcohols found in waxes may be saturated or unsaturated and may include sterols. Generally, waxes are water insoluble and chemically. This property confer water repellent character to animal skin, leaves of certain plants and bird feathers where waxes are commonly found. Typical examples of waxes include Carnuba wax, Beeswax and Lanolin. The chemical structure of a typical biological wax is shown below:

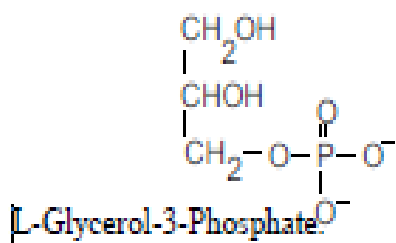


Structure of Biological wax

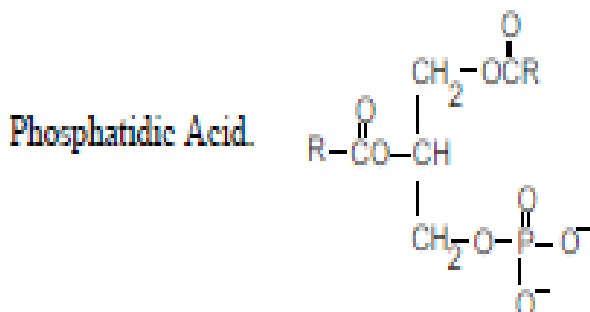
2.3.2 Compound / Complex Lipids

These are esters of fatty acid with one of the various alcohols in addition, and other groups (which are usually non-lipid component). The compound lipids are made up of different subclasses, including phosphoacylglycerols or phospholipids and sphingolipids.

Phosphoacylglycerols: These are compound/complex lipids containing alcohol, phosphoric acid and a nitrogenous base or other alcoholic group. Phosphoacylglycerols are derivatives of (L – Glycerol – 3 – phosphate)

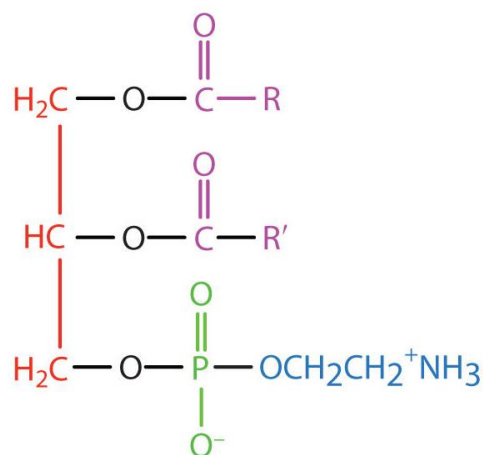


The parent compound of phosphoacylglycerols, (phosphatidic acid) is derived from L-glycerol – 3- phosphate by esterification of its two –OH groups.

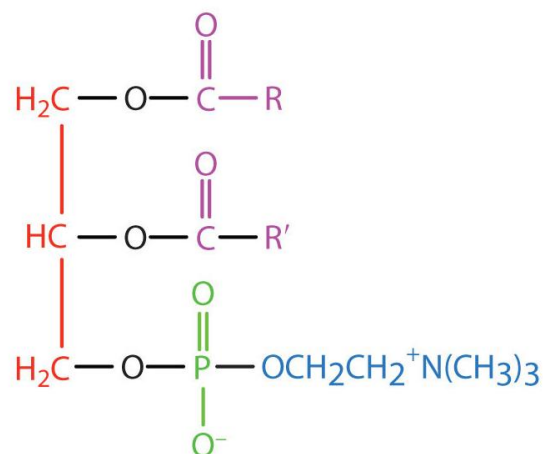


All phosphoacylglycerols (phosphoglycerides) or phospholipids have negative charge around pH 7. They are amphipathic (possessing a polar head group and non-polar hydrophobic tails). These lipids form one of the largest classes of natural lipids and one of the most important and essential components of cell membranes. In these compounds, a variety of polar groups are esterified to the phosphoric acid moiety of the molecule. The

phosphate, together with such esterified entities, is referred to as a “head” group. The common head groups found in phosphatides include choline, ethanolamine, glycerol, serine and inositol. Hence, examples of phosphoacylglycerols include phosphatidylcholine (lecithine), phosphatidylethanolamine (cephalin), phosphatidylinositol and phosphatidylserine



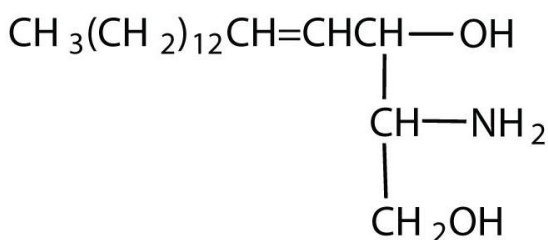
Phosphatidylethanolamine
(cephalin)



Phosphatidylcholine
(lecithin)

Also, 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.

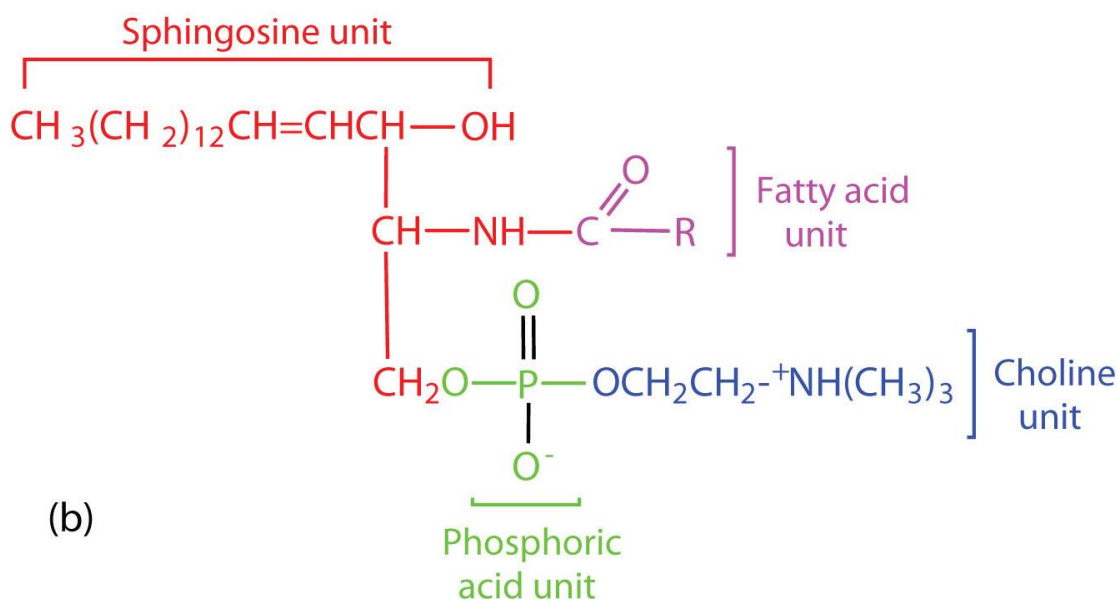
Sphingolipids: Sphingolipids are the second largest class of lipids found frequently in biological membranes. They are a complex lipids composed of long chain fatty acids, one molecule of long chain (18 carbon) amino alcohol (sphingosine) or its derivative and a polar head alcohol. In sphingolipids, sphingosine forms the backbone of these lipids rather than glycerol. Hence, sphingolipids contain no glycerol backbone and are of 3 types. Typically, a fatty acid is joined to a sphingosine via an amide linkage to form a ceramide. Sphingomyelins represent a phosphorous-containing subclass of sphingolipids and are especially important in the nervous tissue of higher animals.



(a) Sphingosine

(a) Structure of Sphingosine (Parent compound of Sphingolipids). In ceramides, a long chain fatty acid in amide linkage to sphingosine

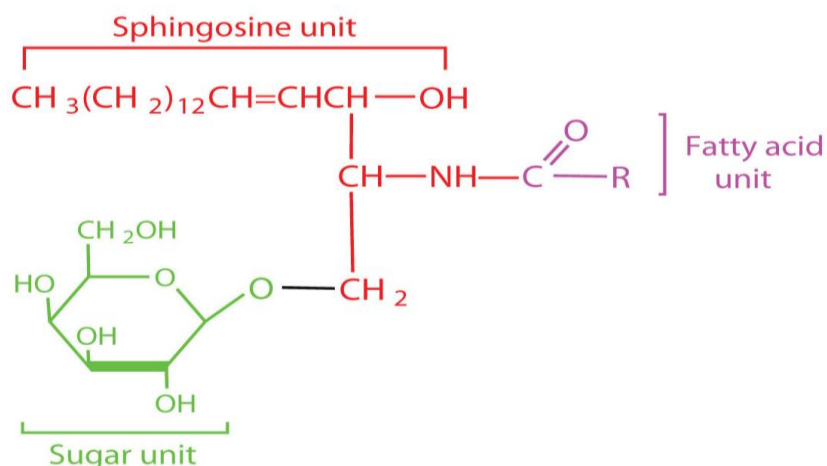
Sphingomyelins: These are the most common class of sphingolipids. In sphingomyelins the $-\text{OH}$ group at C-1 of sphingosine is esterified to phosphocholine or phosphoethanolamine while one of the H atoms of the $-\text{NH}_2$ group attached to C - 2 of sphingosine is linked to a fatty acid. Sphingomyelins resemble phosphatidylcholines in general properties and three dimensional structures.



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

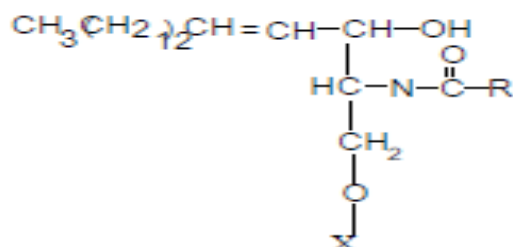
Glycosphingolipids: These are type of sphingolipids that occur largely on the outer surface of plasma membranes. They have head groups with one or more sugars attached directly to the $-\text{OH}$ at C - 1 of the sphingosine moiety. They do not contain phosphate. Cerebrosides are example of Glycosphingolipids 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)

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.

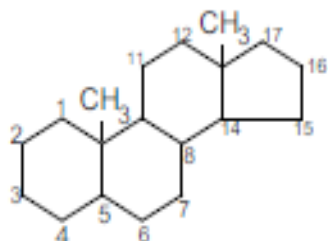


X is oligosaccharide containing sialic acid

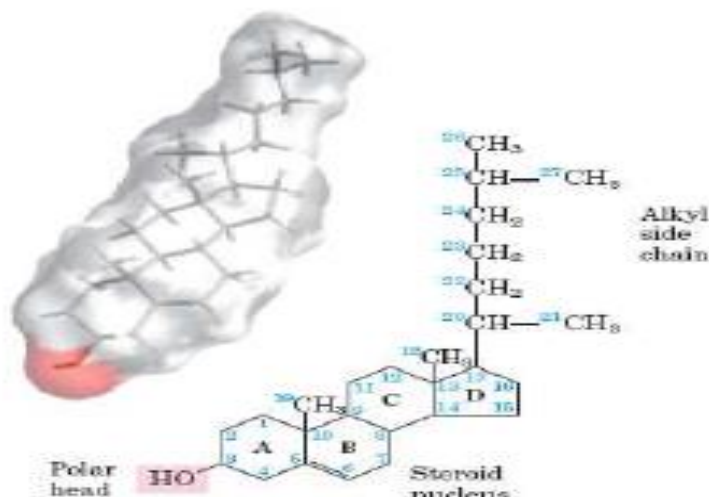
2.3.3 Derived Lipids

These are substances derived from simple and compounds lipids by hydrolysis. Typical examples include steroids, terpenoids and carotenoids

Steroids: These are non-saponifiable lipids that are derivatives of a fused and fully saturated ring system called cyclopentanoperhydrophenanthrene (steroid nucleus). The steroid nucleus is essentially planar, rigid consisting of four (4) faced rings (3 cyclohexane rings fused in nonlinear or phenanthrene manner to a terminal cyclopentane ring). Most steroids in humans have methyl groups at position 10 and 13 and frequently a side chain at position.

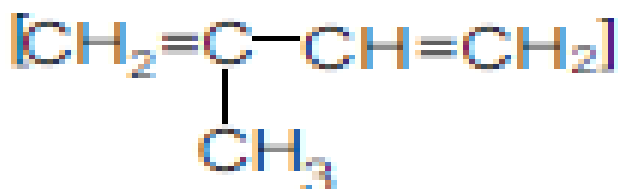


Sterols contain steroid nucleus with one or more (-OH) groups free or esterified to fatty acids. The most abundant sterols in animal tissue is the cholesterol which has the structure.



Structure of Cholesterol. Source: *Lehninger's Principles of Biochemistry*

Terpenes: Terpenes are a class of lipids formed from the combination of two or more molecules of 2 methyl 1,3-butadiene (otherwise known as isoprene). Isoprene is a 5 five carbon compound with the structure



Structure of Isoprene unit

Terpenes are other examples of non-saponifiable lipids; and the simplest terpenes are called monoterpenes ($\text{C}_{10}\text{H}_{16}$), followed by sesquiterpenes ($\text{C}_{15}\text{H}_{24}$), diterpenes ($\text{C}_{20}\text{H}_{32}$) and triterpenes ($\text{C}_{30}\text{H}_{48}$).

Carotenoids: Carotenoids are tetraterpenes that are widely distributed in both the plant and animal kingdoms, though exclusively of plant origin. They are isoprene derivatives with high degree of unsaturation. And because of the many conjugated double bonds, they are reddish or yellowish in colour. Some examples of carotenoids include lycopene (in tomato), α - and β -carotene (in carrot) and xanthophyll.

What are the main types of lipids?

Differentiate between saponifiable and non-saponifiable lipids, giving at least two examples each.

Self-Assessment Exercise(s)

1. Define simple lipids, and two examples of simple lipids.
2. What are compound lipids? State the two major subclasses of compound lipids.

3. Draw the structures of phosphatidylethanolamine and phosphatidylcholine
4. Draw the structure of the parent compound of sphingolipids.

2.4 Summary

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

2.5 References/Further Readings/Web Sources

- 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
- <https://byjus.com/biology/phospholipid/>
- <https://byjus.com/biology/lipids/>
- <http://www.chem.latech.edu/~deddy/chem121/Lipids.htm>

2.6 Possible answers to Self-Assessment Exercises

Unit 3: FUNCTIONS AND METHOD OF ANALYSIS OF LIPIDS

Contents

- 3.1 Introduction
- 3.2 Intended Learning Outcomes (ILOs)
- 3.3 Main Contents
 - 3.3.1 Functions of lipids.
 - 3.3.2 Analysis of Lipids
 - 3.3.3.1 Extraction of lipids.
 - 3.3.3.2 Quantitative/Qualitative Analysis of Lipids.
- 3.4 Summary
- 3.5 References/Further Readings/Web Sources
- 3.6 Possible answers to Self-Assessment Exercises

3.1 Introduction

Like other macromolecules, lipids can be analysed qualitatively or quantitatively. 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 functions and methods of analysis of lipids.

3.2 Intended Learning Outcomes (ILOs)

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

- Explain the various functions performed by lipids in the biological systems
- Understand how to extract and analyse lipids.

3.3 Main Contents

3.3.1 Functions of Lipids

1. Lipids are stored in tissues largely in a water free state and therefore serve as reservoirs of energy.
2. Some lipids serve as structural components of membranes e.g. phospholipids.
3. Some lipids act as intracellular signals e.g. (phosphatidylinositols).
4. 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
5. Lipids e.g. gangliosides form a very important components of specific receptor sites on the surfaces of cell membranes.

6. Lipids (phospholipids) play significant roles in the architectures of membranes.
7. Lipids serve as good sources of fat soluble vitamins: A, D, E and K.

3.3.2 Extraction 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. Neutral lipids (triacylglycerols, waxes, pigments) are readily extracted from tissues with ethyl ether, 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.

3.3.3 Analyses of Lipids

3.3.3.1 Qualitative Analyses of Lipids

The qualitative analysis of lipids helps us determine the presence or absence of lipid, depending upon the colour change. The different qualitative methods for the analysis of lipids are described in this section. The qualitative analysis of lipid involves some preliminary tests and specific tests to detect lipids' presence or absence. Depending upon lipids' reactivity with the chemical reagents, we can also classify the different groups of lipids based. Thus, the qualitative analysis of lipid is an analytical method that detects lipids by the characteristic change in the sample's colour. There are several methods used for the qualitative analysis of lipids and their components.

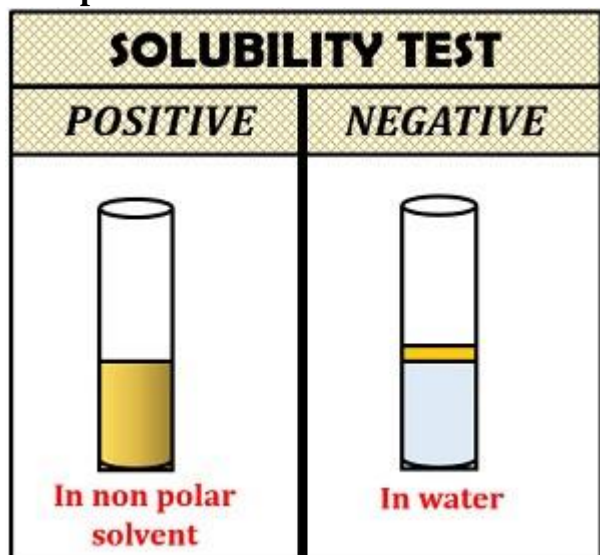
A. Solubility Test; It is the preliminary test that detects the presence of all lipids. Solubility test detects lipid solubility in various solvents to check whether it is miscible or immiscible in polar or non-polar solvents. Thus, it is based on the property of lipid solubility in different solvents. Lipids are readily miscible in non-polar solvents like chloroform, partially soluble in a polar solvent like ethanol and immiscible in a polar solvent like water.

Method:

1. Take the lipid sample in three different test tubes by labelling it as A, B and C.
2. Then, add different solvents like water, ethanol and chloroform in each test tubes A, B and C.
3. Shake the tubes and allow it to stand for 1 minute.

4. Check the solution for whether lipid is soluble or insoluble.

Interpretation of result:



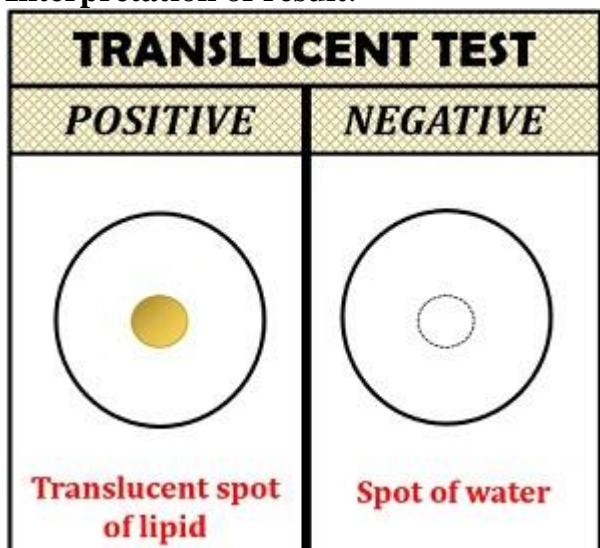
- **Positive result:** Lipids are soluble in a non-polar solvent, i.e. chloroform and partially soluble in ethanol which can solubilize upon heating.
- **Negative result:** Lipids are insoluble in a polar solvent, i.e. water.

B. Translucent Spot Test: A translucent spot test is also a preliminary test for the lipids, which is characterized by a translucent and greasy spot. The lipid will not wet the filter paper, unlike water. The lipids will form a greasy or translucent spot due to their greasy texture, and penetrate the filter paper. Unlike lipids, the spot of water will disappear from the paper.

Method:

1. Take a filter paper.
2. Add one drop of water at one end and a drop of oil or lipid at the other end.
3. Observe the appearance of a translucent spot on the filter paper.

Interpretation of result:



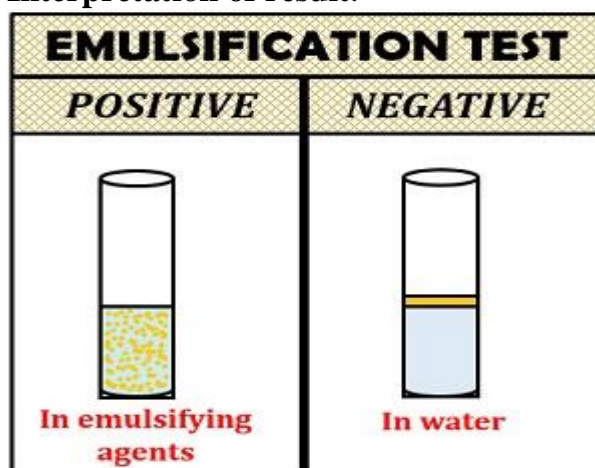
- **Positive result:** Translucent spot will appear on the filter paper.
- **Negative result:** Translucent spot will not appear on the filter paper.

C. Emulsification Test: Emulsification test is used to detect the presence of lipids. It is the process that stabilizes the water and oil emulsion by using the emulsifying agents. The lipid or oil in water will appear as the supernatant. The high surface tension of water develops a separate layer by adding emulsifying agents like bile salts, soap etc. Emulsifying agents emulsify the lipid, after which the lipids appear as the tiny droplets suspended in the solution.

Method:

1. Take two test tubes and label it as test tube A and test tube B.
2. Add oil to each of the test tubes.
3. Shake the test tube and allow it to stand for about two minutes.
4. Observe the test tube for the appearance of tiny droplets in the suspension of liquid.

Interpretation of result:



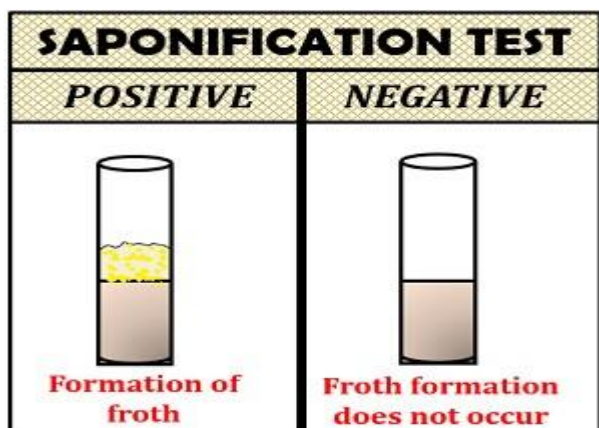
- **Positive result:** It gives a permanent or stable emulsion of lipid and water.
- **Negative result:** Oil in water emulsion will form at the top, due to the high surface tension of water.

D. Saponification Test: It is based on the saponification reaction, in which the triglycerides of lipid react with an alkali NaOH to produce soap and glycerol in the presence of ethanol. This reaction is also known as alkaline hydrolysis of esters.

Method:

1. Take a sample of lipid in a test tube.
2. Then, add strong alkali NaOH.
3. Then, boil the solution in a water bath for 5 minutes.
4. At last, add ethanol.
5. Observe the test tube for the appearance of froth.

Interpretation of result:



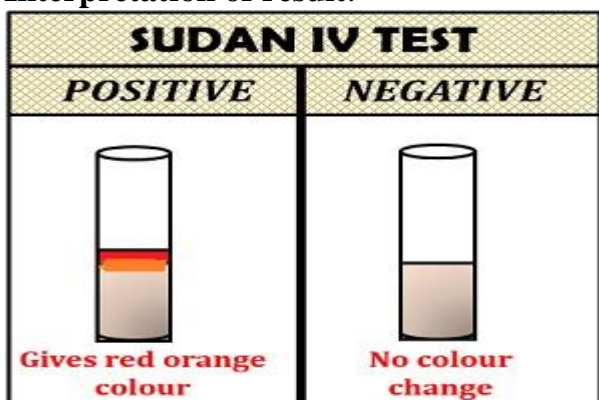
- **Positive result:** Froth appears in the test tube.
- **Negative result:** Froth does not appear in the test tube.

E. Sudan IV Test: Sudan IV test is used to detect the presence of lipid in a solution. This test is based upon the principle of binding and solubility of lipid in non-polar compounds. As Sudan IV is a non-polar stain, the lipid will bind with it and retain the stain's colour by giving a red-orange colour. Sudan IV does not stain or bind to the polar compounds.

Method:

1. Take 1 ml of the lipid sample in a test tube.
2. Then add 1-2 drops of Sudan IV to the solution.
3. Observe the tubes for the appearance of red-orange colour in the solution.

Interpretation of result:



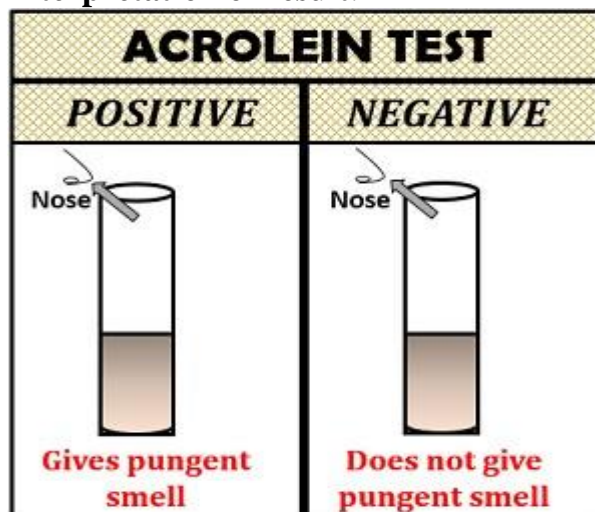
- **Positive result:** Gives red-orange colour to the solution.
- **Negative result:** The solution of the colour will remain unchanged.

F. Acrolein Test: Acrolein test is used to detect the presence of glycerol and fat. This test is based on the dehydration reaction, in which the water molecules are removed from the glycerol by adding reagent potassium hydrogen sulphate. The reaction between glycerol and potassium hydrogen sulphate results in acrolein formation, which is characterized physically by the release of the pungent smell.

Method:

1. Take 1 ml of the lipid sample in a test tube.
2. Add crystals of potassium hydrogen sulphate.
3. Heat the solution for a few minutes.
4. Smell the test tube for the pungent smell.

Interpretation of result:





- **Positive result:** If glycerol present in the sample, it will give a pungent smell.
- **Negative result:** If glycerol is absent in a sample, it will not produce a pungent smell.

G. Dichromate Test: Dichromate test is also used to detect the presence of glycerol. It is based on the principle of an oxidation reaction. In this, glycerol and dichromate ions react to give a brown colour to the solution. Then, the chromic ions oxidize the glycerol and reduce into chromous ions by giving a blue colour to the solution in the presence of nitric acid.

Method:

1. Take 2-3 ml of a sample in a test tube.
2. Then, add a few drops of 5% potassium dichromate solution.
3. After that, add 5 ml of concentrated nitric acid.
4. Observe the test tube for the appearance of a blue colour.

Interpretation of result:

DICHROMATE TEST	
POSITIVE	NEGATIVE
 <p>Gives blue colour</p>	 <p>Gives brown colour</p>

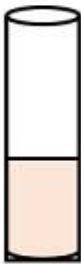

- **Positive result:** If the colour of the solution changes from brown to blue, it indicates glycerol.
- **Negative result:** In this, the brown colour will not change into blue.

H. Tests for the Free Fatty Acids: This is based on the neutralization reaction where the alkali neutralizes by adding free fatty acids into the lipids.

Method:

1. Add phenolphthalein solution in a test tube.
2. Then, add dilute alkali to the above solution (gives a pink colour).
3. At last, add a lipid sample.
4. Observe the tube for the disappearance of the pink colour after the addition of lipid.

Interpretation of result:

FREE FATTY ACID TEST	
<i>POSITIVE</i>	<i>NEGATIVE</i>
 <p>Pink colour disappears</p>	 <p>Gives pink colour</p>


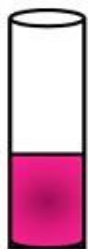
- **Positive result:** If the pink colour disappears by adding the lipid sample, it indicates free fatty acids in the sample.
- **Negative test:** The pink colour will not disappear.

I. Unsaturation Test: Unsaturation test is used to detect the unsaturated fatty acids or double bond in a lipid sample. All the neutral fat contains glycerides of fatty acids. Double bonds are found in the structure of unsaturated fatty acids, which becomes saturated by taking up either bromine or iodine. If the lipid contains more unsaturated fatty acids or more double bonds, it will take more iodine.

Method:

1. Take 5 ml of chloroform and 5 ml of Hubble's iodine reagent in a beaker, giving pink colour to the solution.
2. Add lipid sample drop by drop and shake vigorously, until pink colour disappears.
3. Count the number of drops added to chloroform and Hubble's iodine solution until pink colour disappears. The number of drops determines the taking up of iodine by the unsaturated fatty acid of lipids.

Interpretation of result:

UNSATURATION TEST	
POSITIVE	NEGATIVE
 <p>Pink colour disappears</p>	 <p>Pink colour appears</p>



- **Positive result:** Pink colour will disappear by the addition of unsaturated fatty acids.
- **Negative result:** Pink colour will not disappear.

J. Burchard Test: Burchard test was first given by the scientist Liebmann to detect the presence of cholesterol. Cholesterol reacts with the strong concentrated acid, i.e. sulphuric acid and acetic anhydride. Sulphuric acid and acetic anhydride act as a dehydrating and oxidizing agent.

Method:

1. Take crystals of cholesterol in a test tube.
2. Then, add 2 ml of chloroform to dissolve the cholesterol.
3. Add 10 drops of acetic anhydride in a solution and 2-3 drops of concentrated sulphuric acid.
4. Observe the test tube for the appearance of a bluish-green colour.

Interpretation of result:

BURCHARD TEST	
POSITIVE	NEGATIVE
 <p>Gives bluish green colour</p>	 <p>No colour change</p>

- **Positive result:** It indicates cholesterol in a sample by giving bluish-green colour to the solution.
- **Negative result:** The colour of the solution will not change.

K. Test for Cholesterol:

1. Salkowski's Test (H_2SO_4 Test): Dissolve cholesterol in 2 ml of chloroform in dry test tube. Add equal amount of con. H_2SO_4 . Shake gently. The upper layer turns red and the sulphuric acid layer shows a yellow colour with a green fluorescence.

2. Formaldehyde- H_2SO_4 Test: Add 2 ml of formaldehyde-sulphuric acid solution (1 part of 40% formaldehyde to 50 parts of the acid) to 2 ml of chloroform solution in a dry test tube. The cherry colour is developed in the chloroform. Pour off the chloroform in another test tube and add 2-3 drops of acid anhydride. The blue colour develops.

3.3.3.2 Quantitative analyses of Lipids.

Determination of Iodine Number: The iodine number of a fat is the amount in gm. of iodine taken up by 100 gm. of fat. Not only iodine but also equivalent amounts of other halogens will add at double bonds; so bromine is often used instead of iodine because it is more reactive. The halogenating reagent used in this method is pyridine sulphate di-bromide. This reagent can be prepared by adding carefully 8.1 ml pyridine in 20 ml glacial acetic acid and making the volume up to 1 litre with glacial acetic acid.

Weigh the bottle containing sample of oil plus a medicine dropper and then transfer about 0.1 to 0.3 gm. of oil to a flask. Reweigh the bottle containing oil and dropper to find out the exact quantity of the sample transferred. Add 10 ml of chloroform and then 25 ml of the pyridine sulphate di-bromide reagent.

Shake thoroughly; allow standing for 5 minutes and then determining the residual bromine. To do this, add 10 ml of 10% KI and titrate the equivalent amount of iodine liberated by the residual bromine with the help of 0.1 (N) $\text{Na}_2\text{S}_2\text{O}_3$ (sodium thiosulphate). The titration can be done by adding sodium thiosulphate solution through a burette to the flask.

When the colour of the solution in flask becomes light yellow add 1 ml of starch solution. It will become blue. Slowly add the thiosulphate solution again till it becomes colourless. Note the total volume of thiosulphate used.

The total amount of bromine originally added is found by titrating 25 ml of the pyridine sulphate di-bromide reagent with thiosulphate after adding KI as in the previous case. The amount of bromine taken up by the fat sample can be determined by the difference between the two titers and then the iodine number can be calculated.

Chromatographic Technique: 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. State the usefulness of Acrolein test. Phenolphthalein solution is to test the presence of ----- in a lipid. Mention any two tests for cholesterol

Self-Assessment Exercise(s)

1. State the functions of lipids.
2. Mention some techniques that can be used in qualitative and quantitative analysis of lipids

3.4 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.
- i. Lipids can be analyzed by chromatographic techniques and colorimetric procedures can be used to quantitatively analyze lipids

3.5 References/Further Readings/Web Sources

- 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

Supriya, N. (2019). Qualitative Analysis of Lipids. *Biology Reader*;
Retrieved on the 24th of September, 2023.
<https://people.umass.edu/~mcclemen/581Lipids.html>
<https://biologyreader.com/qualitative-analysis-of-lipids.html>

3.6 Possible answers to Self-Assessment Exercises

1. Some of the functions of lipids are listed below:
 - i. Lipids are stored in tissues largely in a water free state and therefore serve as reservoirs of energy.
 - ii. Some lipids serve as structural components of membranes e.g. phospholipids.
 - iii. Some lipids act as intracellular signals e.g. (phosphatidylinositols).
 - iv. 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
 - v. Lipids e.g. gangliosides form a very important components of specific receptor sites on the surfaces of cell membranes.
 - vi. Lipids (phospholipids) play significant roles in the architectures of membranes.
 - vii. Lipids serve as good sources of fat soluble vitamins: A, D, E and K.
2. Thin layer Chromatography (TLC), High Performance Liquid Chromatography (HPLC), Gas Liquid Chromatography (GLC) and Colorimetric techniques.

Unit 4: LIPOPROTEINS

Contents

- 4.1 Introduction
- 4.2 Intended Learning Outcomes (ILOs)
- 4.3 Main Content.
 - 4.3.1 Types/Classification of Lipoproteins.
 - 4.3.2 Function of Lipoproteins.
- 4.4 Summary
- 4.5 References/Further Readings/Web Sources
- 4.6 Possible answers to Self-Assessment Exercises

4.1 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.

A lipoprotein is therefore 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.

4.2 Intended Learning Outcomes (ILOs)

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

- Understand what lipoprotein are;
- List the chemical composition of different types/classes of lipoproteins;
- Explain the functions of lipoproteins;

4.3 Main Contents

4.3.1 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 known widely in humans. They include 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.

The densities of the four different classes of lipoproteins

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

Source: Text book of Biochemistry with Clinical Correlations by Thomas Devlin.

4.3.2 Composition of Lipoproteins (Plasma)

The lipid fraction of the plasma lipoproteins contains significant amount of triacylglycerols, phospholipids, free cholesterol, 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., 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 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 predominatly in VLDL. Other chemically distinct apolipoprotein are the apolipoproteins D & E (ApoD) and (ApoE). ApoD is found in HDLare described in the table below.

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

Source: Text book of Biochemistry with Clinical correlations by Thomas Devlin.

Some properties of apolipoproteins in human plasma is described in the Table 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	-

Source: Text book of Biochemistry with Clinical Correlations by Thomas Devlin.

4.3.3 Structure of Lipoproteins

The structure of lipoprotein molecules has 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

4.3.4 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 cholesterol 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.

What are the components of the lipid fractions of plasma lipoproteins? What are apolipoproteins, and how can they be obtained State the functional difference between LDL and HDL

Self-Assessment Exercise(s)

1. State the components of lipoproteins.
2. Identify the sources of the following apolipoproteins: apolipoprotein A (ApoA), Apolipoprotein B (ApoB), Apolipoprotein C (Apo C), Apolipoproteins D & E (ApoD) and (ApoE).

4.4 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.

4.5 References/Further Readings/Web Sources

- 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
- <https://my.clevelandclinic.org/health/articles/23229-lipoprotein#>:
- <https://www.ncbi.nlm.nih.gov/books/NBK305896/#>:
- <https://www.news-medical.net/life-sciences/Lipoprotein-Classification.aspx>

4.6 Possible answers to Self-Assessment Exercises

1. Lipoproteins include (i) high density lipoproteins (HDL), (ii) low density lipoproteins (LDL), (iii) very low density lipoproteins (VLDL) and (iv) chylomicrons. The LDL is further classified into LDL1 and LDL2 or Intermediate density lipoproteins (IDL) and the chylomicrons.

2.

Apolipoprotein	Source
apolipoprotein A (ApoA)	HDL
Apolipoprotein B (ApoB)	LDL
Apolipoprotein C (Apo C)	VLDL
Apolipoproteins D (ApoD)	HDL
Apolipoproteins E (ApoE)	HDL

Unit 5: MEMBRANES AND MEMBRANE STRUCTURE

Contents

- 5.1 Introduction
- 5.2 Intended Learning Outcomes (ILOs)
- 5.3 Main Contents
 - 5.3.1 Chemical Composition of Membranes.
 - 5.3.1.1 Lipids of membrane.
 - 5.3.1.2 Membrane Proteins.
 - 5.3.1.3 Carbohydrate of Membranes.
 - 5.3.2 Molecular Structure of Membranes.
 - 5.3.3 Properties of Biological Membranes.
 - 5.3.4 Function of Membranes.
- 5.4 Summary
- 5.5 References/Further Readings/Web Sources
- 5.6 Possible answers to Self-Assessment Exercises

5.1 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.

5.2 Intended Learning Outcomes (ILOs)

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

- Explain the chemical composition of membranes.
- Draw the structure of biological membranes.
- List the properties of biological membranes.
- Describe the function of biological membranes

5.3 Main Contents

5.3.1 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.

5.3.1.1 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.

5.3.1.2 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, whereas peripheral proteins can be removed with little or no change in the integrity of the membrane.

5.3.1.3 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-acethylglucosamine, N-acetylgalactosamine and Sialic acid.

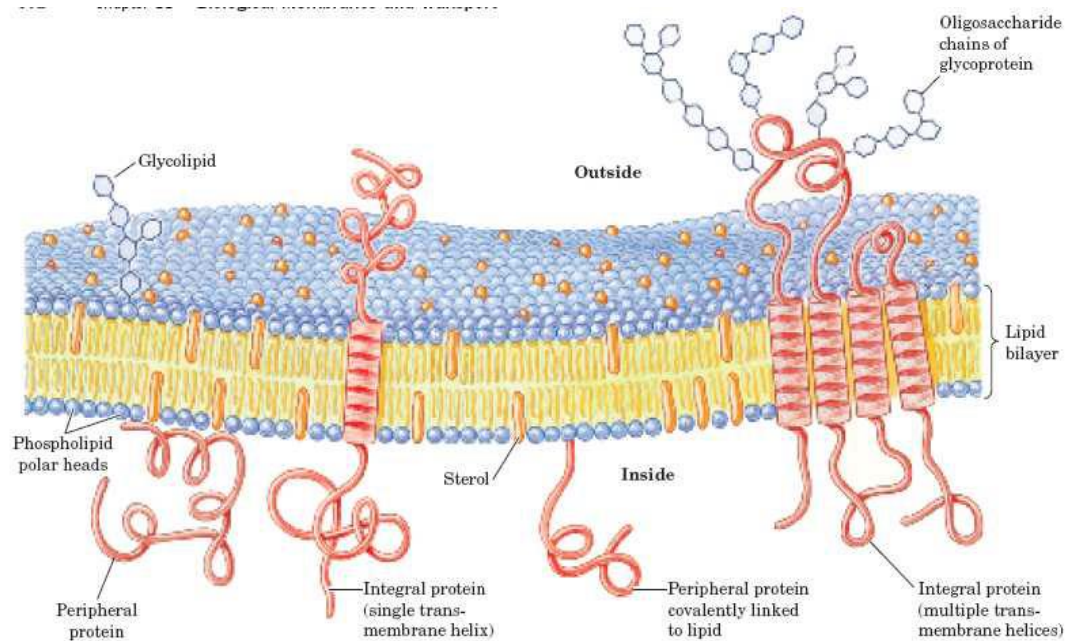
5.3.2 Molecular Structure of Membranes

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 vesicles 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 of 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. Nicolson 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

Source: Lehninger's Principles of Biochemistry

5.3.3 Properties of Biological Membranes

1. 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.
2. They possess specific recognition sites e.g receptors.
3. 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.
4. 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.
5. They contain electrically charged surface groups which support a different electrical potential across membrane structure.
6. Biological membranes allow diffusion of solute molecules through them.

5.3.4 Function of Membranes

1. Recognition of certain molecular signals.
2. They serve as components of nerve cells.
3. They control movement or translocation of molecules in and out of the cell.

4. They serve as receptors for hormones.
 5. Protect the intracellular components of the cell.
- Mention the two major components of biological membranes.
In what form do carbohydrates exist in biological membranes

Self-Assessment Exercise(s)

1. What are the functions of membranes?
2. Outline the properties of membranes.

5.4 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.

5.5 References/Further Readings/Web Sources

- 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
- <https://www.britannica.com/science/membrane-biology>
- <https://www.ncbi.nlm.nih.gov/books/NBK9898/>
- <https://byjus.com/biology/cell-wall-and-cell-membrane/#>:

5.6 Possible answers to Self-Assessment Exercises

1.
 - i. Recognition of certain molecular signals.
 - ii. They serve as components of nerve cells.
 - iii. They control movement or translocation of molecules in and out of the cell.
 - iv. They serve as receptors for hormones.
 - v. Protect the intracellular components of the cell.

2. Among the numerous properties of biological membranes include the following:
 - i. 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.
 - ii. They possess specific recognition sites e.g receptors.
 - iii. 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.
 - iv. 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.
 - v. They contain electrically charged surface groups which support a different electrical potential across membrane structure.
 - vi. Biological membranes allow diffusion of solute molecules through them.

Glossary

KOH: Potassium hydroxide

KI: Potassium Iodide

NaOH: Sodium Hydroxide

H₂SO₄: Tetraoxosulphate (VI) acid

End of the module Questions

1. The two major components of all membranes are protein and _____
2. Lipids are transported in the blood bound with protein as _____
3. Another name for phosphoglycerides is _____
4. Alkaline hydrolysis of lipids is called _____.

Module 3: NUCLEIC ACID

Module Introduction

Introduce the module and state the units under the module.

Unit 1:	CHEMISTRY OF NUCLEOSIDES
Unit 2:	CHEMISTRY OF NUCLEOTIDES
Unit 3:	CHEMISTRY OF NUCLEIC ACIDS
Unit 4:	STRUCTURE OF NUCLEIC ACIDS
Unit 5:	ROLES OF DNA AND RNA

Unit 1: CHEMISTRY OF NUCLEOSIDES

Contents

- 1.1 Introduction
- 1.2 Intended Learning Outcomes (ILOs)
- 1.3 Main Contents
 - 1.3.1 Components of Nucleosides.
 - 1.3.1.1 Nitrogenous Bases and Their Structures.
 - 1.3.1.2 Pentose Sugars and Their Structures.
 - 1.3.1.3 Linkages between Pentose Sugars and Nitrogenous Bases.
 - 1.3.2 Some Common Purines and Pyrimidine Bases and their Structures.
 - 1.3.3 Nomenclature of Nucleosides.
- 1.4 Summary
- 1.5 References/Further Readings/Web Sources

1.1 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. Nucleosides are therefore 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.

1.2 Intended Learning Outcomes (ILOs)

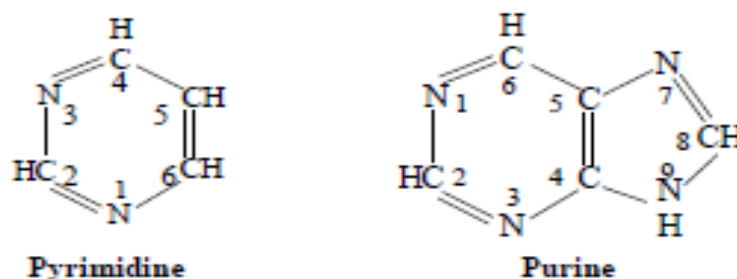
At the end of this Unit, the students should be able to;

- Define nucleosides are;
- Describe the different components that are present in nucleosides;
- Draw the structure of different types of nucleosides;

1.3 Main Contents

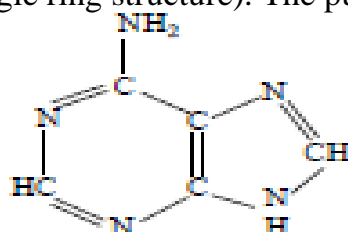
1.3.1 Components of Nucleoside.

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

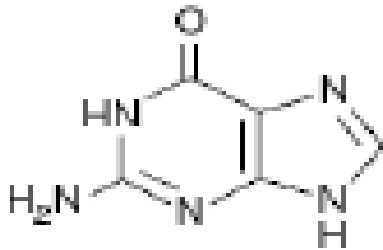


1.3.1.1 Nitrogenous Bases and their Structures

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:

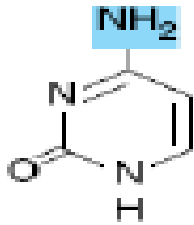


Adenine denoted by A and has the structure:



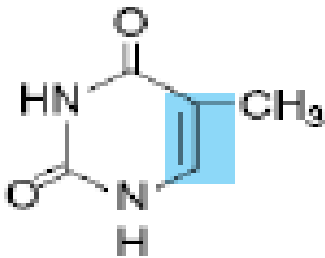
Guanine denoted by G and has the following structure:

The pyrimidine bases include cytosine, thymine and uracil, and their structures are presented below:



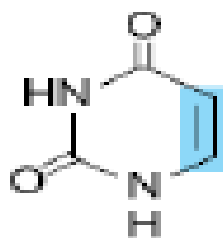
Structure of Cytosine (cytosine is denoted by C)

Source: Harper's Review of Biochemistry



Structure of Thymine (thymine is denoted by T)

Source: Harper's Review of Biochemistry



Structure of Uracil (uracil is denoted by U)

Source: Harper's Review of Biochemistry

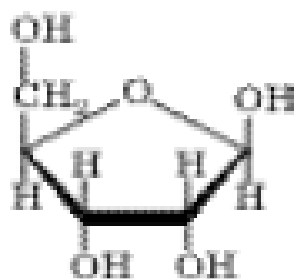
In addition to the purine bases A and G other unusual purine bases do exist and

they include: hypoxanthine, 1 methylguanine, 1 methylhypoxanthine etc. Also, unusual pyrimidine bases derived from the cytosine, thymine and uracil exist. These include: 5-methylcytosine, thiouracil etc.

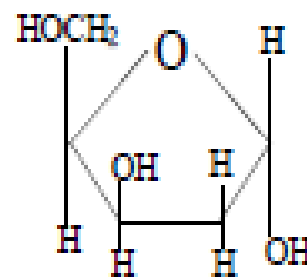
1.3.1.2 Pentose Sugars and their Structures

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).



β - D - Ribofuranose
(Ribose sugar)



2 - Deoxy - α - D-
ribose sugar structure)

Source: Lehninger's Principles of Biochemistry

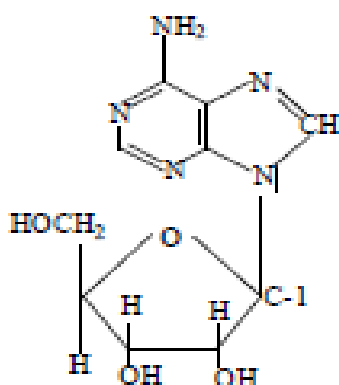
1.3.1.3 Linkages Between Pentose Sugars and Nitrogenous

Bases in Nucleosides

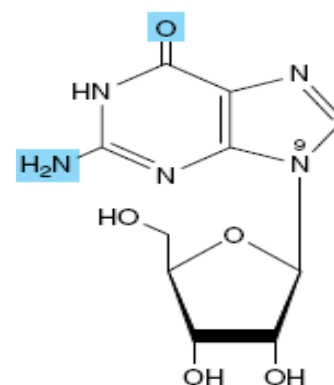
In nucleosides, nitrogenous bases are joined to pentose sugar through the hemiacetal hydroxyl group on the C-1 (first carbon atom of the sugar). Generally, the purines are attached to the sugar through the N-9 nitrogen atom while pyrimidines are attached through the N-1 nitrogen atom.

1.3.2 Common Purine and Pyrimidine Nucleosides and their Structures

1.3.2.1 Purine Nucleosides.



(a) Adenosine

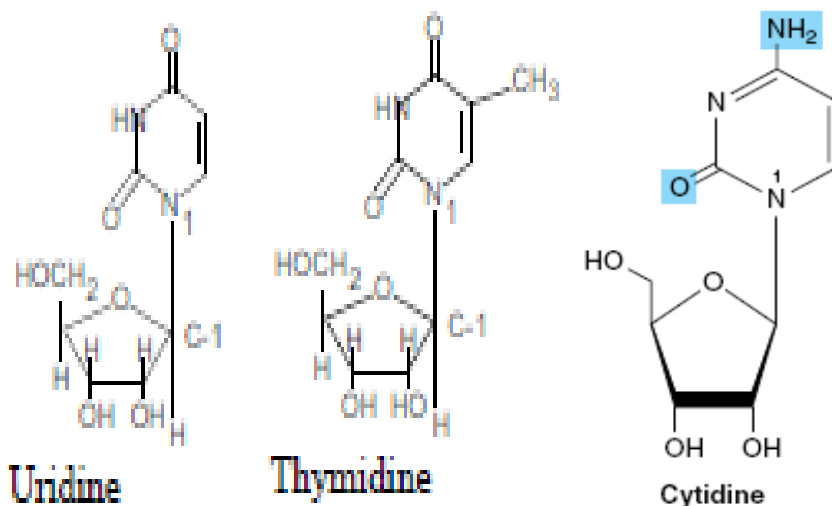


(b) Guanosine

Structure of Adenosine and Guanosine

Source: Lehninger's Principles of Biochemistry

1.3.2.1 Pyrimidine Nucleosides



Source: Harper's Review of Biochemistry.

1.3.3 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 (-acyl) 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.

What are nucleosides? Mention the type of sugars found in RNA and DNA

Self-Assessment Exercise(s)

1. Draw the structures of the major nitrogenous bases in nucleic acids.
2. State how purine and pyrimidine nucleosides are named.
3. Draw the structure of two named purine and pyrimidine nucleosides

1.4 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.

1.5 References/Further Readings/Web Sources

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.

<https://www.cliffsnotes.com/study-guides/biology/biochemistry-ii/dna-structure-replication-and-repair/dna-and-rna-structures>.

<https://www.slideshare.net/RajwantiSaran/secondary-and-tertiary-structure-of-rna>

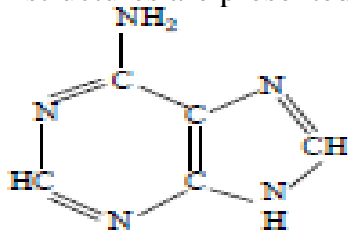
<https://www.genome.gov/genetics-glossary/Nucleic-Acids#>

<https://www.britannica.com/science/nucleic-acid>

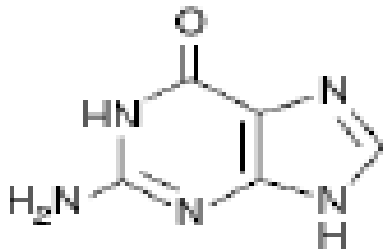
1.6 Possible answers to Self-Assessment Exercises

1. The nitrogenous bases in nucleic acids are classified into purines and pyrimidines. The major purines include adenine and guanine; while the major pyrimidines include cytosine, thymine and uracil, depending on the type of nucleic acid.

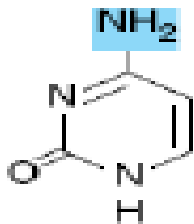
Their structures are presented below:



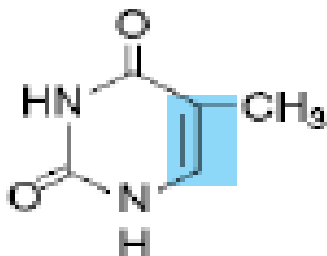
Structure of Adenine (A)



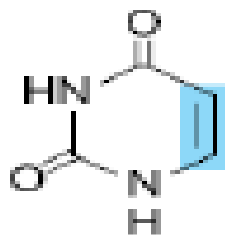
Structure of Guanine (G)



Structure of Cytosine (C)

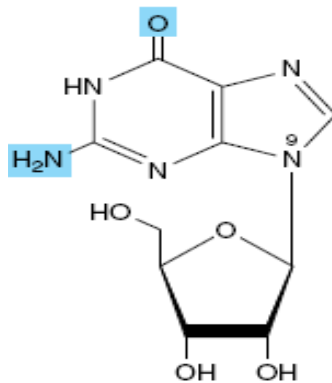
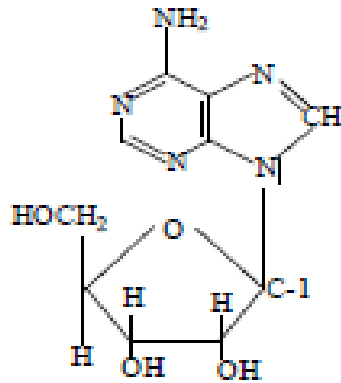


Structure of Thymine (T), present only in DNA



Structure of Uracil (U), present only in RNA

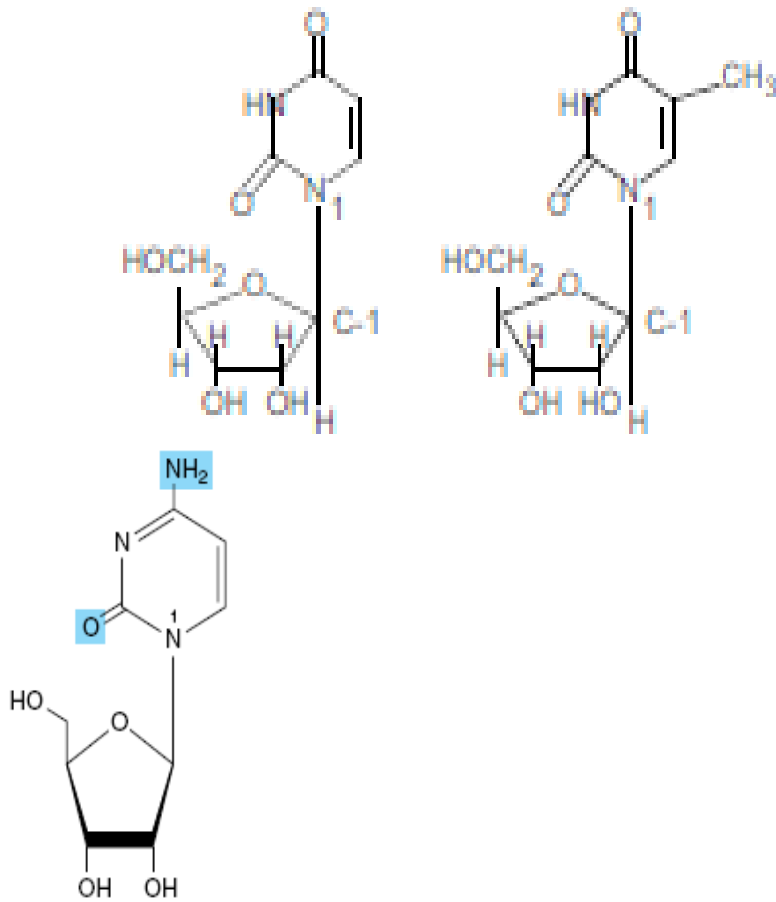
1. Purine nucleosides are: Adenosine, guanosine, deoxynadenosine and deoxyguanosine.
Pyrimidine nucleosides are: 2'- deoxythymididine, 2' - deoxycytidine, 2'- deoxyadenosine, 2'- deoxyguanosine and 2'- deoxyuridine.
- 2.



(a)

(b)

Purine Nucleosides: (a) Adenosine and (b) Guanosine



(a) Uridine

(b) Thymidine

(c) Cytidine

Structure of pyrimidine nucleosides

Unit 2: CHEMISTRY OF NUCLEOTIDES

Contents

- 2.1 Introduction
- 2.2 Intended Learning Outcomes (ILOs)
- 2.3 Main Contents.
 - 2.3.1 Components of Nucleotides.
 - 2.3.2 Nomenclature of Nucleotides.
 - 2.3.3 Structures of Some Common Nucleosides.
 - 2.3.4 Derivatives of Nucleotides.
 - 2.3.5 Functions/Roles of Nucleotides and Their Derivatives
- 2.4 Summary
- 2.5 References/Further Readings/Web Sources
- 2.6 Possible answers to Self-Assessment Exercises

2.1 Introduction

Nucleotides are phosphoric acid esters of nucleosides. They are the monomeric units of nucleic acids (RNA & DNA), and are of different types and structures. 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. Nucleotides 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.

2.2 Intended Learning Outcomes (ILOs)

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

- Describe what a nucleotide is and its components;
- Draw the structures of different nucleotide types;
- List four roles and functions of nucleotides;

2.3 Main Contents

2.3.1. 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.

2.3.2. 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.

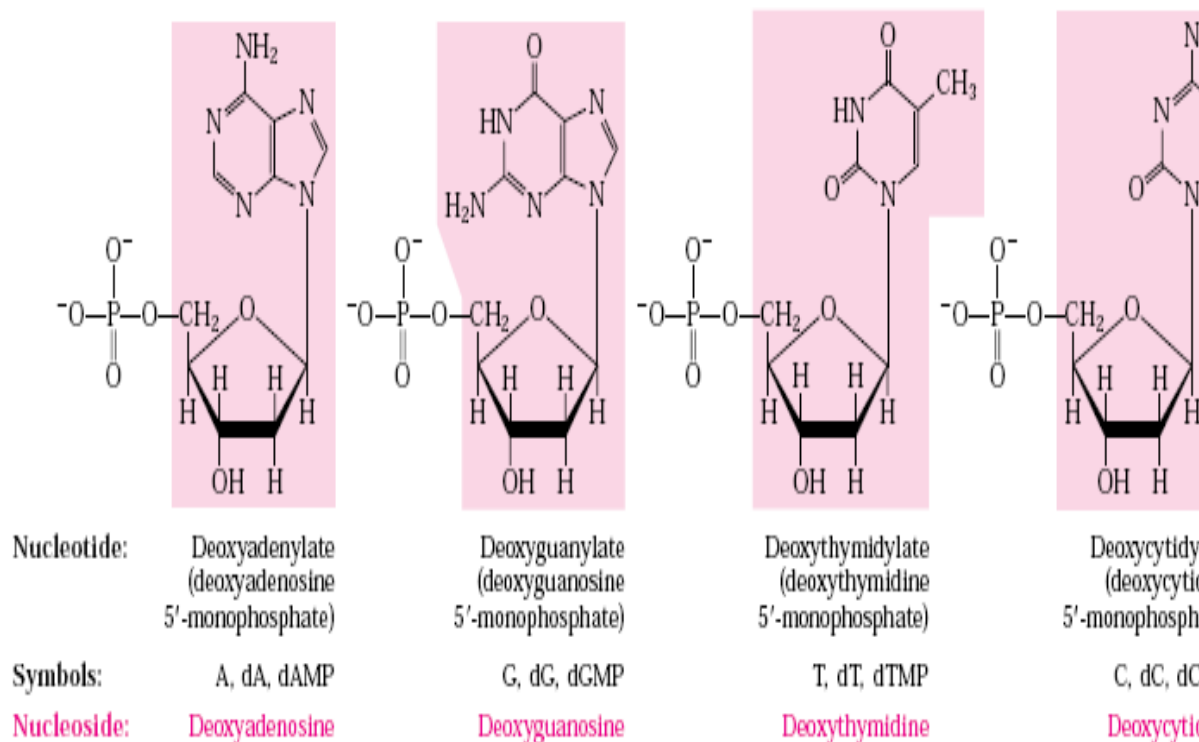
Adenylic acid (Adenylate)	Adenosine 5'-monophosphate
Guanylic acid (Guanylate)	Guanosine-5'-monophosphate
Thymidylic acid (Thymidylate)	Thymidine-5'-monophosphate
Cytidylic acid (Cytidylate)	Cytidine-5'-monophosphate
Uridylic acid (Uridylate)	Uridine-5'-monophosphate

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.

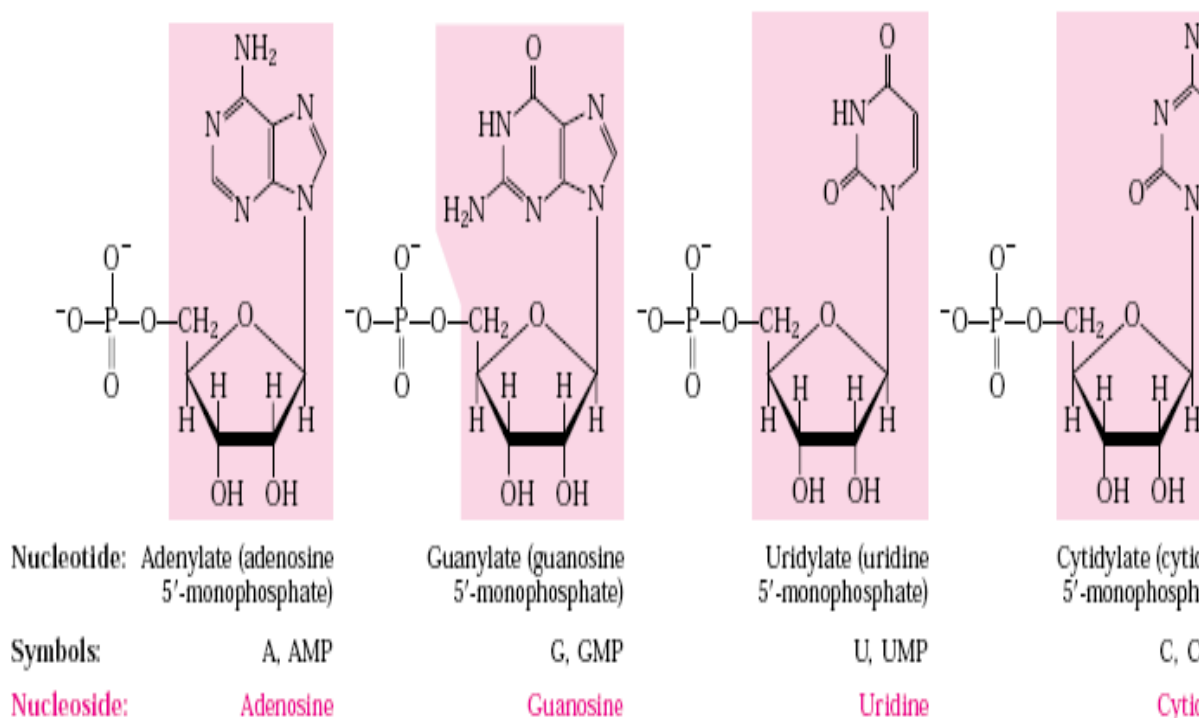
When the phosphate is on position 2, the nucleotide is named ribo nucleoside 2' monophosphate e.g. adenosine 2' monophosphate. When the phosphate is on position 3, the nucleoside is called ribo nucleoside 3' the monophosphate. The ribonucleoside could be a cyclic monophosphate where a single phosphate 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).

2.3.3. Structures of Some Common Nucleotides



(a) Deoxyribonucleotides



(b) Ribonucleotides

The structures of Nucleotides.

Source: Lehninger's's Principles of Biochemistry.

2.3.4. 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.

2.3.5. Importance / Role of Nucleotides/Nucleotide Derivatives

1. 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.
2. 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.
3. Nucleotide have also been found to play role in metabolic regulation. A derivative of AMP, cyclic AMP (cAMP) is directly involved in this process.
4. Nucleotides also serve as source of electrons (H^+) in reductive biosynthetic pathways e.g. synthesis of cholesterol, NADP is very relevant in this process

How are nucleotides different from nucleoside?

State the possible positions of esterification for the phosphate groups in nucleotides.

Self-Assessment Exercise(s)

1. Highlight the biological importance of nucleotides
2. Highlight how purine and pyrimidine nucleotides are named

2.4 Summary

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

2.5 References/Further Readings/Web Sources

- 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
- <https://www.cliffsnotes.com/study-guides/biology/biochemistry-ii/dna-structure-replication-and-repair/dna-and-rna-structures>.
- <https://www.slideshare.net/RajwantiSaran/secondary-and-tertiary-structure-of-rna>
- <https://www.genome.gov/genetics-glossary/Nucleic-Acids#>
- <https://www.britannica.com/science/nucleic-acid>

2.6 Possible answers to Self-Assessment Exercises

1.
 - i. 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.
 - ii. 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.
 - iii. Nucleotide have also been found to play role in metabolic regulation. A derivative of AMP, cyclic AMP (cAMP) is directly involved in this process.
 - iii. Nucleotides also serve as source of electrons (H^+) in reductive biosynthetic pathways e.g. synthesis of cholesterol, NADP is very relevant in this process.

2.

:Acidic name	Sytematic name
Adenylic acid (Adenylate)	Adenosine 5'monophosphate
Guanylic scid (Guanylate)	Guanosine-5'-monophosphate
Thymidylic acid (Thymidylate)	Thymidine-5'-monophosphate
Cytidylic acid (Cytidylate)	Cytidine-5'-monophosphate
Uridylic acid (Uridylate)	Uridine-5'-monophosphate

Unit 3: CHEMISTRY OF NUCLEIC ACIDS

Contents

- 3.1 Introduction
- 3.2 Intended Learning Outcomes (ILOs)
- 3.3 Main Contents.
 - 3.3.1 Characteristics of Nucleic Acids.
 - 3.3.2 Types of Nucleic Acids.
 - 3.3.2.1 mRNA
 - 3.3.2.2 rRNA
 - 3.3.2.3 tRNA
- 3.4 Summary
- 3.5 References/Further Readings
- 3.6 Possible answers to Self-Assessment Exercises

3.1 Introduction

Nucleic acids are macromolecules that are found in the cells and are responsible for storage and transmission of genetic information. The Chemistry of nucleic acids basically refers to the chemical compositions of nucleic acids. These include the chemical groups that constitute them, the bonding / linkages in their molecules and their chemical characteristics (including their nomenclature and their structures). Chemically, nucleic acids are polymers of nucleotides joined together by phosphodiester linkages (bonds). Nucleic acids are generally 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. In this unit, you will study the basics about nucleic acids.

3.2 Intended Learning Outcomes (ILOs)

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.

3.3 Main Contents

3.3.1 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 (25°C). When such solution is subjected to extreme pH or temperature above 80°C, 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 (10⁻⁴cm) 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 (5x10⁻⁴cm) 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.

3.3.2 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.

3.3.2.1 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.

3.3.2.2 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.

3.3.2.3 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. What do you understand by

denaturation of DNA. State the three criteria for determining the size of nucleic acids.

Self-Assessment Exercise(s)

1. Highlight the any three differences between DNA and RNA

3.4 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.

3.5 References/Further Readings/Web Sources

- 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
- <https://www.cliffsnotes.com/study-guides/biology/biochemistry-ii/dna-structure-replication-and-repair/dna-and-rna-structures>.

<https://www.slideshare.net/RajwantiSaran/secondary-and-tertiary-structure-of-rna>

<https://www.genome.gov/genetics-glossary/Nucleic-Acids#>
<https://www.britannica.com/science/nucleic-acid>

3.6 Possible answers to Self-Assessment Exercise

1.

Property	RNA	DNA
Nitrogenous base	Contain uracil, and lacks thymine	Contain thymine and lack uracil
Sugar residue	Ribose	Deoxyribose

Strand	Generally stranded	single	Generally stranded	double
--------	-----------------------	--------	-----------------------	--------

Unit 4: STRUCTURE OF NUCLEIC ACIDS

Contents

- 4.1 Introduction
- 4.2 Intended Learning Outcomes (ILOs)
- 4.3 Main Contents
 - 4.3.1 Structure of DNA
 - 4.3.2 Different forms of DNA
 - 4.3.2.1 A DNA
 - 4.3.2.2 B DNA
 - 4.3.2.3 Z DNA
 - 4.3.3 Organizational levels of RNA Structure
 - 4.3.4 Structure of Different forms of RNA
 - 4.3.4.1 Messenger RNA (mRNA)
 - 4.3.4.2 Transfer RNA (tRNA)
 - 4.3.4.3 Ribosomal RNA (rRNA) Main Content
- 4.4 Summary
- 4.5 References/Further Readings/Web Sources
- 4.6 Possible answers to Self-Assessment Exercises

4.1 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 is 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.

4.2 Intended Learning Outcomes (ILOs)

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

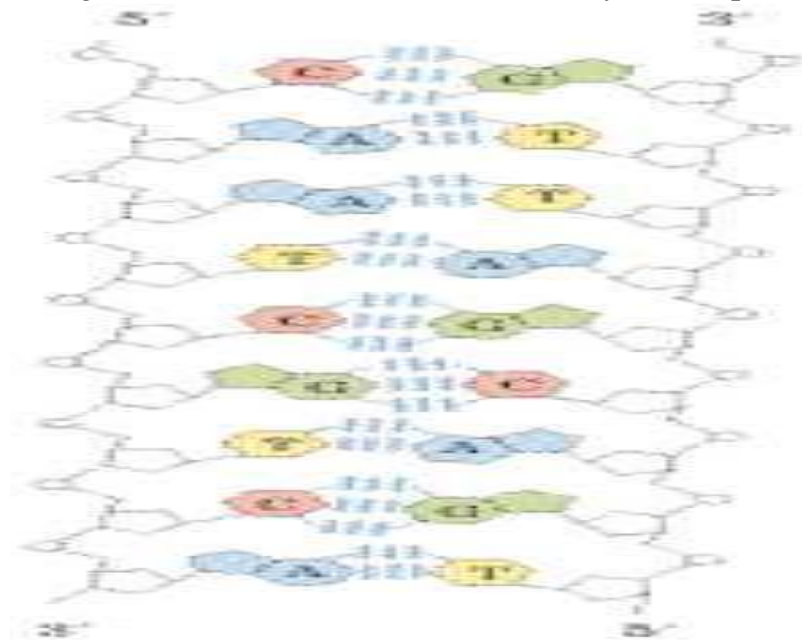
- Describe the structure of nucleic acids;
- Draw the structure of DNA;
- Describe the structure of RNA;
- Explain the structure and properties of different types of RNA

4.3 Main Contents

4.3.1 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.

- i. 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.
- ii. 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.
- iii. 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; Source: Lehninger's's Principles of Biochemistry

4.3.2 Different Forms of DNA

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

4.3.2.1 A DNA

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



A form

The structure of A form of DNA

Source: Lehninger's Principles of Biochemistry

4.3.2.2 B DNA

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



B form

The structure of B form of DNA

Source: Lehninger's principles of *Biochemistry*

4.3.2.3 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 slenderer and elongated.



The structure of Z form of DNA

Source: Lehninger's principles of *Biochemistry*

4.3.3 Organizational levels of RNA Structure

RNA exist at different structural organizational levels, including primary, secondary and tertiary structural levels

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, 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

4.3.4. 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.

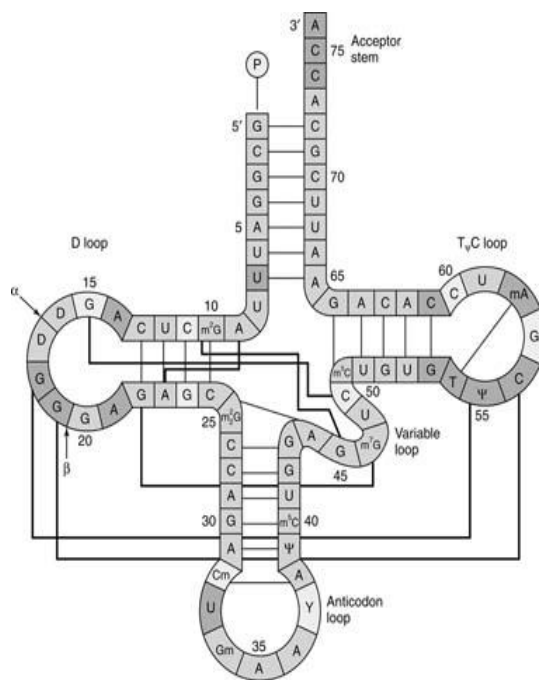
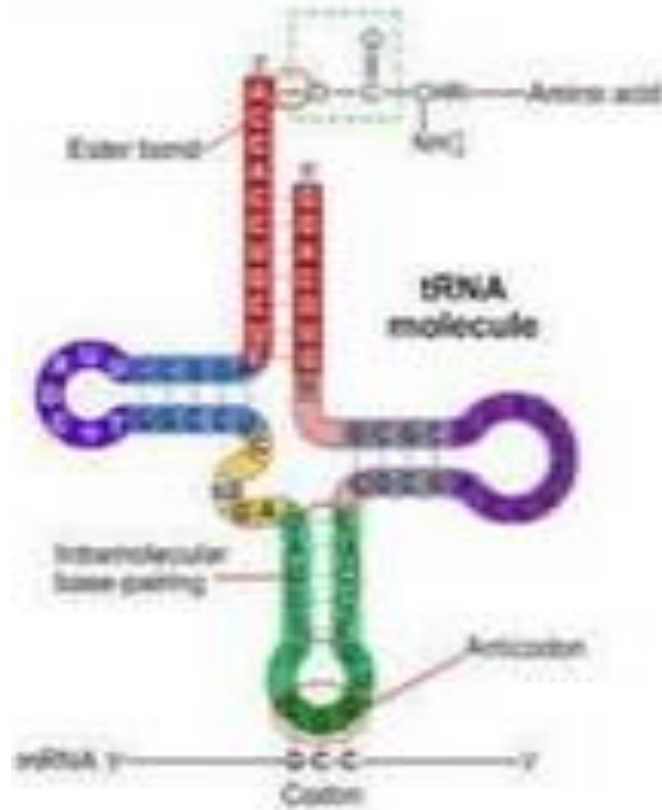
4.3.4.1 Messenger RNA (mRNA)

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.

4.3.4.2 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, T Ψ C loop and the acceptor system, each having its own function.



Secondary = Base pairs

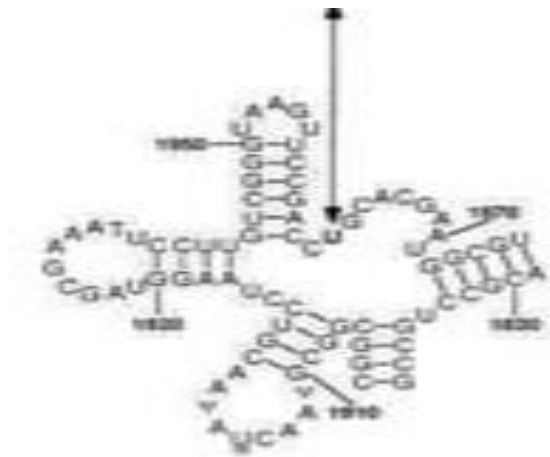
(a)

Structure of tRNA

4.3.3.3 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. rRNAs are found in the ribosomes and account for 80% of the total RNA present in the cell. Ribosomes are composed of a large subunit called the 50S and a small subunit called the 30S, each of which is made up of its own specific rRNA molecules. Different rRNAs present in the ribosomes include small rRNAs and large rRNAs, which belong to the small and large subunits of the ribosome, respectively. rRNAs combine with proteins and enzymes in the cytoplasm to form ribosomes, which act as the site of protein synthesis. These complex structures travel along the mRNA molecule during translation and facilitate the assembly of amino acids to form a polypeptide chain. They interact with tRNAs and other molecules that are crucial to protein synthesis.

In bacteria, the small and large rRNAs contain about 1500 and 3000 nucleotides, respectively, whereas in humans, they have about 1800 and 5000 nucleotides, respectively. However, the structure and function of ribosomes is largely similar across all species



4.4 Summary

- 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.

4.5 References/Further Readings/Web Sources

- Devlin, T. (1986). Textbook of Biochemistry with Clinical Correlations.(2nd Edition) John Wiley and sons New York
- 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.
- Rajwanti, S. and Rari, D. J.(2013). Secondary and Tertiary structures of RNA
- White A.,Handler P.,Smith E.,L., Hill R.,L., Lehman R.I.(1978). Principles of Biochemistry (6th.edition)Mc Graw Hill, Kogakusha.
- <https://www.slideshare.net/RajwantiSaran/secondary-and-tertiary-structure-of-rna>
- <https://www.genome.gov/genetics-glossary/Nucleic-Acids#>
- <https://www.britannica.com/science/nucleic-acid>

4.6 Possible answers to Self-Assessment Exercises

1. Messenger RNA (mRNA), transfer RNA (tRNA) and ribosomal RNA (rRNA)

2. 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’.. 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, T ψ C loop and the acceptor system, each having its own function.

Unit 5: ROLES OF DNA AND RNA

Contents

- 5.1 Introduction
- 5.2 Intended Learning Outcomes (ILOs)
- 5.3 Main Contents
 - 5.3.1 Differences between Deoxyribonucleic Acid (DNA) and Ribonucleic Acid (RNA)
 - 5.3.1 Structural and Chemical Differences between DNA and RNA.
 - 5.3.2 Similarities between DNA and RNA.
 - 5.3.3 Functions / roles of DNA
 - 5.3.4 Function / Roles of RNA
- 5.4 Summary
- 5.5 References/Further Readings
- 5.6 Possible answers to Self-Assessment Exercises

5.1 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.

5.2 Intended Learning Outcomes (ILOs)

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

- List three differences between DNA and RNA;
- Give three similarities between DNA and RNA;
- Explain the functions/roles of DNA;
- Describe the functions/roles of RNA;
- Explain the functions/roles of the different types of RNA.

5.3 Main Contents

5.3.1 Difference 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.

5.3.1.1 Differences between DNA and RNA

S/N	RNA	DNA
1	Mainly single stranded, except where they form double strand with self-complementary sequences (hairpin structure in tRNA)	Mostly double stranded, except for certain viral DNA which are single stranded)
2	The main sugar moiety is ribose	he main sugar moiety is deoxyribose
3	Lacks Thymine pyrimidine base in the structure, except in tRNA,	DNA has Thymine pyrimidine base in its structure.
4	RNA has Uracil pyrimidine base in its structure	Lacks Uracil pyrimidine base in the structure.
5	RNA does not follow Chargaf's rule being a single-stranded structure	DNA follows Chargaf's rule being a double-stranded structure, with total purine and pyrimidine contents being equal in its double strand
6	RNA can easily be destroyed by alkaline solutions to cyclic diesters of mono nucleotides.	DNA has the ability to resist the action of alkaline solutions due to the absence of free OH group at 2' position.
7	RNA is a relatively labile molecule that undergoes spontaneous degradation easily.	DNA is relatively stable molecule, with very slow spontaneous degradation.
8	RNA is mainly presence in the cytoplasm, although primary transcript and small nuclear RNA are found in the nucleus.	DNA are found mainly in nucleus, although extra nuclear DNA is found in the mitochondria and plasmids
9	The base content of RNA molecule varies from 100 to 5000	DNA molecules contain millions of base pairs depending on the species of organisms.
10	There are different types of RNA (mRNA, rRNA, tRNA, etc), each performing different functions.	There is only one type of DNA that performs the function of storage and transfer of genetic information.

5.3.1.2 Similarities between DNA and RNA

1. DNA and RNA contain three major components: nucleotide, nitrogenous base and phosphoric acid.

2. DNA and RNA both contains Adenine, Guanine and Cytosine nitrogenous bases.
3. Both DNA and RNA carry genetic information.
4. DNA and RNA are both polymers of nucleotides
5. Both DNA and RNA can be found in the cell.

5.3.2 Functions 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 enable 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.

5.3.3 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 contains 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.

Highlight the similarities between RNA and DNA

Briefly describe the roles of tRNA, mRNA and rRNA in the biological systems

Self-Assessment Exercise(s)

1. Highlight the differences between RNA and DNA

5.4 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.

5.4 References/Further Readings/Web sources

Biochemistry II. in *Cliff's Note*. Retrieved on 25th September, 2023.
 Devlin, T. (1986). Textbook of Biochemistry with Clinical Correlations. (2nd Edition) John Wiley and sons New York
 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.
 Rajwanti, S. and Rari, D. J. (2013). Secondary and Tertiary structures of RNA White A., Handler P., Smith E., L., Hill R., L., Lehman R. I. (1978). Principles of Biochemistry (6th. edition) Mc Graw Hill, Kogakusha.s

Links for reading materials

<https://www.cliffsnotes.com/study-guides/biology/biochemistry-ii/dna-structure-replication-and-repair/dna-and-rna-structures>.

<https://www.slideshare.net/RajwantiSaran/secondary-and-tertiary-structure-of-rna>

<https://www.genome.gov/genetics-glossary/Nucleic-Acids#>

<https://www.britannica.com/science/nucleic-acid>

5.6 Possible answers to Self-Assessment Exercises

1. Differences between DNA and RNA

S/N	RNA	DNA
1	Mainly single stranded, except where they form double strand with self-complementary sequences (hairpin structure in tRNA)	Mostly double stranded, except certain viral DNA which are stranded
2	The main sugar moiety is ribose	The main sugar moiety is deoxyribose
3	Lacks Thymine pyrimidine base in the structure, except in tRNA,	DNA has Thymine pyrimidine base in its structure.
4	RNA has Uracil pyrimidine base in its structure	Lacks Uracil pyrimidine base in its structure.
5	RNA does not follow Chargaf's rule being a single-stranded structure	DNA follows Chargaf's rule being a double-stranded structure, with purine and pyrimidine contents equal in its double strand
6	RNA can easily be destroyed by alkaline solutions to cyclic diesters of mono nucleotides.	DNA has the ability to resist the action of alkaline solutions due to the absence of free OH group at 2' position.
7	RNA is a relatively labile molecule that undergoes spontaneous degradation easily.	DNA is relatively stable molecule with very slow spontaneous degradation
8	RNA is mainly present in the cytoplasm, although primary transcript and small nuclear RNA are found in the nucleus.	DNA are found mainly in the nucleus, although extra nuclear DNA is found in the mitochondria and plasmids
9	The base content of RNA molecule varies from 100 to 5000	DNA molecules contain millions of base pairs depending on the species of organisms.
10	There are different types of RNA (mRNA, rRNA, tRNA, etc), each performing different functions.	There is only one type of DNA which performs the function of storage and transfer of genetic information.

,

Glossary

cAMP: Cyclic adenosine monophosphate, is a cyclic form of adenosine monophosphate where a single phosphate is attached to both the 3rd and 5th carbon of the ribose sugar linked to adenosine

dA: Deoxyadenosine

dAMP: Deoxyadenosine monophosphate

dGMP: Deoxyguanosine

NAD: Nicotinamide adenine dinucleotide

End of the module Questions

1. In nucleotides, nitrogen bases are joined to the sugar through the hemiacetal group on _____
2. Phosphoric acids esters of nucleosides are called _____
3. Macromolecules responsible for storage and transmission of genetic materials in cell are called _____
4. _____ is ultimately involved in transcription and translation of information coded by DNA for protein synthesis.